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Organometallic Chemistry

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Foreword

This Volume of the Specialist Periodical Reports 'Organometallic Chemistry' surveys the literature for the calendar year 1984. The organization is similar to that employed in previous Volumes of this Series. In Chapters 1 through 15 reference is made to approximately 3000 articles. Moreover, the rapidly expanding use of *X*-ray diffraction methods in organometallic chemistry leads to 1209 literature citations in Chapter 16. It will thus be evident to the reader that our Reporters face a formidable task in surveying in a comprehensive manner developments in organometallic chemistry which have occurred during the course of a year. A necessary consequence is the presentation of the material in a somewhat terse manner.

E.W. Abel

F.G.A. Stone

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Abbreviations

Ac	acetate ($MeCOO^-$)
acac	acetylacetonate
acacen	*NN'*-ethylenebis(acetylacetone iminate)
Ad	adamantyl
AIBN	azoisobutyronitrile
Ar	Aryl
arphos	1-(diphenylphosphinio)-2-(diphenylarsino)ethane
ATP	adenosine triphosphate
Azb	azobenzene
9-BBN	9-borabicyclo[3.3.1]nonane
bipy	2,2'-bipyridyl
Bz	benzyl
Bzac	benzoylacetonate
cbd	cyclobutadiene
1,5,9-cdt	cyclododeca-1,5,9-triene
chd	cyclohexadiene
chpt	cycloheptatriene
[Co]	cobalamin
(Co)	cobaloxime [$Co(dmg)_2$ derivative]
cod	cyclo-octa-1,5-diene
cot	cyclo-octatraene
Cp	η^5-cyclopentadienyl
CTTM	charge transfer to metal
Cy	cyclohexyl
dab	1,4-diazabutadiene
dba	dibenzylideneacetone
DCA	9,10-dicyanoanthracene
depe	1,2-bis(diethylphosphino)ethane
depm	1,2-bis(diethylphosphino)methane
diars	*o*-phenylenebis(dimethyl)arsine
diarsop	{[2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene)] bis-(diphenylarsine)}
dien	diethylenetriamine
diop	{[2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene)] bis-(diphenylphosphine)}
diphos	1,2-bis(diphenylphosphino)ethane
DME	dimethoxyethane
DMF	*NN*-dimethylformamide
dmg	dimethylglyoximate
$dmgH_2$	dimethylglyoxime
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
DMSO	dimethyl sulphoxide
dpa	di(2-pyridyl)amine
dpae	1,2-bis(diphenylarsino)ethane
dpam	bis(diphenylarsino)methane
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
en	ethylene-1,2-diamine
EXAFS	extended X-ray absorption fine structure
F_6acac	hexafluoroacetylacetonate
Fc	ferrocenyl

Fp	$Fe(CO)_2Cp$
glyme	ethyleneglycol dimethyl ether
GVB	generalized valence band
HDPG	diphenylglyoximato
hfa	hexafluoroacetone
hfacac	hexafluoroacetylacetonato
hfb	hexafluorobutyne
HMPA	hexamethyl phosphoric triamide
LDA	lithium diisopropylamide
LiDBB	lithium di-t-butylbiphenyl
$Me_6[14]dieneN_4$	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene
$Me_6[14]N_4$	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane
4,7-Me_2phen	4,7-dimethyl-1,10-phenanthroline
3,4,7,8-Me_4phen	3,4,7,8-tetramethyl-1,10-phenanthroline
Mes	mesityl
mcpba	metachloroperbenzoic acid
nap	1-naphthyl
nbd	norbornadiene
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
OEP	octaethylporphyrin
Pc	phthalocyanin
PMDT	pentamethylenediethylenetetramine
PMHS	polymethylhydrosiloxane
pd	pentane-2,4-dionate
phen	1,10-phenanthroline
$[PPN]^+$	$[(Ph_3P)_2N]^+$
py	pyridine
pz	pyrazolyl
sal	salicylaldehyde
salen	*NN'*-bis-(salicylaldehydo)ethylenediamine
saloph	*NN*-bisalicylidene-*o*-phenylenediamine
SCF	self consistent field
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
terpy	2,2',2"-terpyridyl
TFA	trifluoroacetic acid
tfacac	trifluoroacetylacetonato
tfo	triflate, trifluoromethylsulphonate
THF	tetrahydrofuran
tht	tetrahydrothiophen
TMBD	*NNN'N'*-tetramethyl-2-butene-1,4-diamine
TMED	tetramethylethylenediamine
tmen	tetramethylethylenediamine
TMS	tetramethylsilane
tol	tolyl
TPP	*meso*-tetraphenylporphyrin
triphos	*1,1,1-tris(diphenylphosphinomethyl)ethane*

1

Group I: The Alkali and Coinage Metals

BY J. L. WARDELL

1 Alkali-metal Compounds

1.1 General. Reviews have been published on structures of organolithiums[1] and on Cu(I) catalysed reactions[2] of organolithiums.

The degree of aggregation of various RLi in THF has been determined by cryoscopy;[3] 2-R-2-Li-1,3-dithiane (1, R=Me), PhLi and PhC≡CLi all exist as monomers and dimers. The ^{13}C n.m.r. spectral data for (1; R=Me, Ph or p-PhC_6H_4), 9-R-9-LiFl (R=H, Me or Ph) and (p-$PhC_6H_4)_nCH_{3-n}Li$ (n=1 or 2) in THF have been discussed in terms of structures and charge densities;[4] (1) was considered to be a sp^3 hybridised and delocalised carbanion.

The LICKOR reagents - BuLi.KOR - exhibit different reactivity than does BuK (obtained from Bu_2Hg and K), for example towards $PhCHMe_2$[5a] and THF.[5b] While BuLi.$KOBu^t$ (2) is stable in THF for hours at -50°C, BuK immediately metallates THF at -75°C, to give the unstable 2-K-THF. An earlier report that BuK metallates such hydrocarbons as hexane and cyclopentane was found to be incorrect. The e.s.r. spectrum of the cycloheptatrienyl radical dianion, a product of metallation of cycloheptene by (2), clearly indicates[6] the counterions are K^+. Phenyl substituted 1,6,6a-R^4-trithiapentalenes, 3H-1,2-dithiole-3-thiones, 2-(4-phenyl-3H-dithiol-3-ylidine)-acetophenone and $PhCOCH_2COCH_2COPh$ form[7] polylithium compounds on reaction with 7-10 Li atoms in THF at 0°C. Direct lithiation of imines, e.g. $Me_2C{=}NPr^i$, and RC≡CH results[8] using Li in presence of phenanthrene in THF.

1.2 Alkyl-lithiums. Ions detected in the e.i.m.s. of halide-free $(MeLi)_4$ included[9] $Me_{n-1}Li_n^+$ (n=2-4) and $CH_mLi_n^+$ (m=0-2; n=2 or 3). The 6.95 and 8.58 ev ionizations in the p.e.s. of $(Bu^sLi)_4$ have been interpreted[10] as transitions of the ^2T and ^2A states.[10] As deduced from the ^{13}C, ^6Li n.m.r. spectra, Bu^sLi exists in hydrocarbons as dimers (minor), tetramers and hexamers, which undergo fast intra- and inter-aggregate C_α-Li bond exchanges and much slower inversion at C_2Li;[11] the value of the equilibrium constant

[For References see page 9

for hexamer ⇌ tetramer at -15°C was 2.3M with ΔH = 7 Kcal and ΔS = 28 e.u. 7-Norbornadienyl-lithium (RLi), obtained from Li and RCl or R_2Hg, exists in Me_2O as monomers and dimers ($K_{-140°C}$ = $2x10^{-3}$ M).[12]

Crystal structures have been determined for monomeric[13] 1-Li-2-Me-1,2-dicarba-closo-dodecaborane. PMDET [Li-C 2.176(8) Å] and hexameric ether-free 2,2,3,3-tetramethylcyclopropyl-lithium (R Li), produced[14] from reaction of Li with R_2Hg,RCl or $H_2C{=}CHCMe_2CMe_2Cl$ in Et_2O [Li-C 2.123(8), 2.159(8) and 2.297(8)].

1.3 Substituted Alkyl Compounds. An ab-initio study of XCH_2M (M= Li or Na; X=Me, NH_2, OH, F, SiH_3, PH_2, SH or Cl) has been conducted[15] using 3-21G, 6-31G basis sets with correlation energies at the MP2 level with further optimisation with diffuse functions (3-21+G); stability orders calculated were for $LiCH_2X$: X=Cl > F > SiH_3 > OH > SH > NH_2 > PH_2 > H > Me and for $NaCH_2X$: X=Cl > SiH_3 > F > SH > OH > PH_2 > H > NH_2 > Me. Optimized geometries of $LiCH_2S(O)H$ (3), $LiCH_2S(O)_2H$ (4) and $LiCH_2\overset{+}{S}H_2$ have been obtained[16] at the 3-21G level. The most stable structures of (3) and (4) have intramolecular Li-O bonds; however with Li^+ present, intermolecular Li-O bonding results in (4) with the C-Li bond antiperiplanar to C-O. The p.e. surface of FCH_2Li has been examined by an ab-initio method, including electron correlation and zero-point energy corrections; the lowest energied species is fluorine bridged.[17]

α-Lithioalkylamines have been prepared[18] via reaction of Bu^sLi-$KOBu^t$ with $MeNR_2$ [R_2=Me_2; $(CH_2)_n$, n = 4 or 5].[18a] in isopentane at 0°C and BuLi with $Bu_3SnCH_2NR_2$[18b] (both providing $LiCH_2NR_2$) as well as from RLi with 1-Bu^t-N=CH- derivatives of piperidines, pyrolidines, hexahydroazepines.[18c] The α-lithio products of the latter reactions can be alkylated, the N-protecting group removed, to provide good yields of α-alkylated heterocycles.

The crystal structures of $(Me_2PCH_2Li.TMED)_2$ (5)[19a] and $[(Me_2P)_3CLi.THF]_2$ (6)[19b] have been determined; in (5) there[19a] is a 6-membered heterocycle ring in which the Me_2PCH_2 units bridge TMED chelated Li atoms via C and P. In (6), Li is co-ordinated to O, 2P [of a $(Me_2P)_3C$ group] and has a c.i.p. type interaction with the C centre of the other anion[19b] in the dimer. Methylation of $(Me_2P)_3CLi$ by MeI in TMED/pentane provides $Me_3P{=}C(PMe_2)_2$ but in THF, $(Me_2P)_3CMe$ is formed.

2-Lithiocyclohexanone dimethylhydrazone (7) is polymeric in the solid state, with Li^+ and the carbanions forming an extended

array; the stereoselectivities in alkylations of substituted derivatives of (7) have been investigated.[20] Use has been made of organomercurial-alkali metal transmetallations to provide $MYCH_2CH(NMPh)CH_2M$, $PhNMCH_2CHMCHMeNMPh$, $M'CH_2CH(NMPh)CH_2M'$ and $LiCH_2CH(NLiPh)CH(NLiPh)CH_2Li$ (Y=NPh or O; M,M'=Li, Na or K).[21] Alkoxyalkyl-lithiums, e.g. (S)-$MeCH(OLi)CH_2Li$, have been generated from the corresponding hydroxyalkyl chlorides on successive treatments with BuLi and $Naph^{-\cdot},Li^+$ (or Li powder).[22]

A new route[23] to α-lithiated 5- and 6-membered cyclic ethers involves conversion of lactones to α-PhS -substituted cyclic ethers and then treatment with $1\text{-}Me_2N\text{-}Naph^{-\cdot},Li^+$. Other routes to α-metallated ethers include metallations of Me_2O or THF by BuK[5b] and Sn-Li transmetallations,[24] equation (1). The stability of organolithiums, based on values of the equilibrium constants at -60°C in

$$Bu_3SnCR^1R^2OR + BuLi \rightleftharpoons Bu_4Li + LiCR^1R^2OR \qquad (1)$$

DME,[24] has been established as $ROCH_2Li$ > $ROCHR^1Li$ > (MeLi) > $ROCRR^1Li$ > BuLi > cyclo-$C_6H_{11}Li$.

The compounds $(PhSCH_2Li.TMED)_2$ (7) and $(MeSCH_2Li.TMED)_2$(8) have different crystal structures; (7) is a 6-membered heterocycle with TMED chelated Li atoms bonded to C of one $PhSCH_2$ and S of another (Ph-S bonds are antiperiplanar to C-Li bonds) while in (8), there is a non-planar LiCLiC ring (Li....Li 2.46 Å).[25] A low temperature ^{13}C n.m.r. study has been reported of ^6Li, ^{13}C labelled organolithiums derived from methyl or phenyl thio-ethers, thioacetals, trithio-orthoesters and their selenium analogues in THF or 2-MeTHF.[26] For many of the compounds, the H-decoupled ^{13}C n.m.r. signals, observed below -80°C, were triplets, indicating that the C_α atom is bonded to a single ^6Li atom either in a momomer or a heteroatom bridged dimer. The tentative structure, proposed[27] for PhS(O)-$^{13}CH^6LiF$ from its ^{13}C n.m.r. spectrum, was $Ph(LiO)S^+$ $\bar{C}HF$.

1.4 Di- and Poly-lithioalkanes. A double lithium bridged structure was calculated (ab-initio, 3-21G basis set) to be the lowest energy geometry of 1,3-dilithiopropane.[28] A further theoretical treatment of CH_2Li_2 (at the 6-31^{XX} level) was undertaken.[29] The synthesis and solid state ^{13}C n.m.r. spectrum of $CH_2{}^6Li_2$ have been reported; a highly symmetric structure was deduced from the sharp singlet in the ^1H, ^6Li decoupled spectrum.[30] Reaction of Li vapour with $(Me_3Si)_nCH_{2-n}Cl_2$ (n=1 or 2) in a Knudsen cell gave $(Me_3Si)_nCH_{2-n}Li_2$ (9); flash vapourisation m.s. of (9)

indicated positive ions due to monomeric and dimeric species.[31] Ions, $CH_nLi_{5-n}^+$ (n=0, 1 or 2), have been observed[32] in a related study of CH_nLi_{4-n}. A new synthesis of CLi_4, a red-brown, highly pyrophoric solid,[33] is the reaction between $C(HgCl)_4$ and excess Bu^tLi.

1.5 Aryl-lithiums. Tetrameric phenyl-lithium has a similar structure in cyclohexane:Et_2O (2:1) as in the solid state; the internuclear distances in $(PhLi)_4$ in this solution have been calculated from the contribution of ^7Li to the spin-lattice relaxation times using an isotopic substitution method.[34] Insoluble ArM (M=Li, K) can be solubilized in PhH or PhMe on complexation[35] with $(EtOCH_2CH_2O)_2Mg$. The anion in $[Li_4Cl_2(Et_2O)_{10}][Li_2Cu_3Ph_6]_2$, prepared[36] in Et_2O from PhLi and CuCN, contaminated with CuCl, is made up of a trigonal bipyramid of apical Li and equatorial Cu, with each Li-Cu vector bridged by Ph. 2,2'-Dilithio-1,1'-binaphthyl, obtained from chiral 2,2'-Br_2-1,1'-binaphthyl, completely retains its optical activity in Me_2O solution up to at least -45°C,[37] and hence cannot have a symmetrical structure as previously calculated for $(\underline{o}\text{-}LiC_6H_4)_2$ (10) and determined for the TMED adduct of (10) in the solid state. In contrast to the monolithiation of PhOMe or $\underline{m}\text{-}(MeO)_2C_6H_4$ using 2-5 equivalents of BuLi.TMED, dilithiation occurs[38] with $\underline{o}\text{-}(MeO)_2C_6H_4$ (at C_3 and C_6), $\underline{p}\text{-}(MeO)_2C_6H_4$ (C_2 and C_5), 1,3,5-$(MeO)_3C_6H_3$ and 1,2,4-$(MeO)_3C_6H_3$ (C_3 and C_6). Pyridine has been kalliated[39] by $BuLi.KOBu^t$; in Et_2O, the major product is 2-KC_5H_4N (>85%), while in THF.HMPT, 4-KC_5H_4N predominates (90%).

1.6 Benzylic and Related Compounds. The variety of bonding interactions available to benzyl derivatives are well illustrated by the following compounds:- (i) $[LiTMED]_2$ $[\underline{o}\text{-}PhCHC_6H_4CHPh\text{-}\underline{o}]$ {Li atoms are in different locations: in agreement with a theoretical study on the TMED-free species};[40] (ii) $[LiTMED]_2[\underline{p}\text{-}Me_3SiCHC_6H_4CHSiMe_3]$ {there is a dominant p-quinodimethanide bonding contribution; Li interacts with C_α and the adjacent ring carbon}[41] (iii) $[LiTMED]_2[\underline{o}\text{-}CH_2C_6H_4C_6H_4CH_2\text{-}\underline{o}]$ {polymeric with a 'metallacycle' Li and a Li bridging methylene groups of metallacycles};[42] (iv) $[LiTMED]_2$ $[\underline{o}\text{-}Me_3SiCHC_6H_4CHSiMe_3]$ {c.i.p. structure};[42] (v) $[LiTMED]_2[\overline{CHSiMe_2C(SiMe_3)C_{10}H_6}]$ {two polymorphs differing both in modes of interaction of LiTMED units with anion and in the conformation of the heterocycle};[43] (vi) $[2\text{-}(Me_3Si)_2CMC_5H_4N]_2$ (11, M=Li) {8-membered cycle;dimeric with Li bond to C_α of one

ligand and to N of another};[44] (vii) 2-$(Me_3Si)_2CLiC_5H_4N$.TMED, [2-$(Me_3Si)_2CLiC_5H_4N$. 2-$(Me_3Si)_2CHC_5H_4N$] and 2-$Me_3SiCHLiC_5H_4N.Et_2O$ {all contain a Li-η^3-aza-allyl ligand interaction}[44] and (vii) [$Li(TMED_2)$ [TMEDLi$(PhCH_2)_2Mg(CH_2Ph)_2$] {distorted tetrahedral Mg in anion with TMED-chelated Li bridging two benzyl groups}.[45]

The structures of $PhCH_2Li$, indenyl-Li and Ph_3CLi as well as allyl-Li have been accounted for using a simple electrostatic model.[46] There is greater restriction to rotation of the methylene group in 2-$LiCH_2$-3-R-pyridine (R=H or Me) than in phenylmethanides.[47] The ^{13}C n.m.r. spectra of 9-Li-10-R-9,10-dihydroanthracenes (R=H or Bu^t) indicate sp^2 hybridised anions with flattened geometries.[48] U.v. and circular dichroism spectra were measured[49] for solutions containing 9-LiFl, $Ph_nCH_{3-n}Li$ (n=1-3) and $Me(CH_2)_4CPh_2Li$ and chiral diamines, e.g. (-)-sparteine and (+)- or (-)-$[Me_2NCH_2CH(OMe)]_2$.

Syntheses, ^1H and ^{13}C n.m.r. spectra as well as MNDO calculations have been reported for the Y-shaped dianions $[(PhCH{=}{)}_3{=}C]^{2-}$,$2Li^+$ (12) and $[PhCH{-}{)}_2{-}C{-}O]^{2-}$,$2Li^+$ (13); in related studies, ab-initio calculations have been performed on $LiCH_2COCH_2Li$, and crystal structures have been determined for the bis(TMED) adducts of (12) and (13). In contrast to the MNDO conclusions for (12), there was no 3-fold symmetry in its bis-(TMED) complex.[50]

1.7 Alkenyl and Other Unsaturated Compounds. The configurational stabilities of CHD=CLiX (X=CN or CO_2Me) and RCH=CLiY (Y=OR' or Me_3Si) have been investigated;[51] thermodynamic data for the equilibriation of $MeCH{=}CLiSiMe_3$ were calculated. Compounds, $Li_2C{=}\dot{C}(CH_2)_2CHRCH_2\dot{C}H_2$ (R=H or Bu^t) have been produced from the corresponding bis(halomercuri) compounds and either Li in Et_2O or Bu^tLi in cyclopentane.[52] Heteroatom directed lithiation of $MeOCH_2OCPh{=}CH_2$ by Bu^sLi at -78°C gave (Z)-LiCH=CPhOCH_2OMe, with no ring metallation[53] occurring. The crystal structure of dimeric 1-Li-2-$Me_2NCH_2CH_2CH_2NMe$-1-cyclohexane has been determined;[54] Li is coordinated to 2C and 2N, in addition there is a short Li....Li interaction (2.34 Å).

Ab initio SCF-MO and SCF-X scattered wave calculations have been carried out[55] on CpLi. A double pentahapto structure was predicted for dilithium pentalenide (14); u.v. irradiation of (14) provided the corresponding radical anion.[56] The Li in solid [(η-$C_5H_4SiMe_3$)Li.TMED] is essentially trigonal bipyramidal, with

coordination to 2N and to the centroid of the Cp ring.[57]

2 Copper, Silver and Gold

2.1 Interaction with π-ligands. E.s.r. spectra have been obtained[58] for paramagnetic species produced from metal atoms and propene, alkynes or HCN. Among the carbene complexes studied[59] were (i) $ClAu[C(Ph)NH(CH_2)_nNHC(Ph)]AuCl$ (n = 2 or 6) (prepared[59a] from the bis-$(CO)_5W$ analogues), (ii) $\{[trans,trans\text{-}(p\text{-}MeC_6H_4)_2C]Au\}^+ BF_4^-$ (cation contains linear C-Au-C portion),[59b] (iii) $\{Au(C_6F_5)_2[C(NHR)NPh]_2\}ClO_4$ (15), a chelated bis-carbene, prepared[59c] from cis-$[Au(C_6F_5)_2(CNR)_2]ClO_4$ (16, R=Ph or p-MeC_6H_4) and PhNHNHPh and (iv) $\{Au[C(NHR)NR'N{=}C(NHR)](C_6F_5)_2\}$(17, R=Ph or p-$MeC_6H_4$; R'=H or Ph), a square-planar chelated mono-carbene, obtained from (16) and H_2NNHR'. Treatment of (15) with OH^- gave another carbene complex,[59c] $\{Au[C(NHR)NPhNPhC(=NR)](C_6F_5)_2\}$.

2.2 σ-Bonded Compounds. 1-Norbornylcopper (RCu), from $Cu(acac)_2$ and RLi, is tetrameric in PhH or cyclohexane;[60] it is stable to 80°C. The ylide complex, $[AuCH_2P(S)Ph_2]_2$, obtained from $LiCH_2P(S)Ph_2$ and $Ph_3AsAuCl$ in Et_2O, contains a 8-membered ring, PCAuSPCAuS [intra- and inter-molecular Au....Au contacts 3.040(1) and 3.223(1) Å respectively]; oxidative addition of I_2 in $ClCH_2CH_2Cl$ provided $[(I)Au^{II}CH_2P(S)Ph_2]_2$, with a similar ring system [Au-Au 2.609(1) Å] while in CH_2I_2-$ClCH_2CH_2Cl$ a mixed Au^I-Au^{III} complex, $Ph_2PCH_2Au^{III}(I)_2CH_2PPh_2SAu^IS$ (Au....Au 3.05 Å), is formed.[61] Further reports by Fackler and coworkers[62] on the dinuclear, 8-membered cycles, $R_2PCH_2AuPR_2CH_2AuCH_2$, included catalysis of halogen exchange among alkyl halides as well as formation and structures of Au^{II} and Au^{III} oxidative addition products with CH_2XY (X,Y=Cl,I) and $MeNO_2$.

The reaction[63] of $[Au(C_6F_5)_2CH_2(PPh_2)_2]ClO_4$ with NaH provided the neutral ylide complex $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]$ (18); (18) reacted with Ag or Au salts to form such di- and tri-nuclear complexes as $Au(C_6F_5)_2(Ph_2PCHPPh_2)AuC_6F_5$ and $Au(C_6F_5)_2(Ph_2PCHPh_2)Au(Ph_2PCHPPh_2)Au(C_6F_5)_2ClO_4$. Other ylide complexes generated included $[(Me_2N)_3PCH_2MCH_2P(NMe_2)_3]Cl$ (19, M=Cu, Ag or Au), $(Me_2N)_3PCH_2AgCl$,[64a] Ph_3PCH_2AuCN and trans-$Ph_3PCH_2Au(X)_2CN$ (X=Cl or I).[64b]

Syntheses and spectra were reported[65] for Ph_3PAuCR_2CN (19, R= Cl) [obtained from $HCCl_2CN$ and $(Ph_3PAu)_3O^+$, BF_4^-] (19, R=H) (from

$LiCH_2CN$ and Ph_3PAuCl) and $(Ph_3PAu)_2CH_2CN$ [from (19, R=H) and Ph_3PAu^+,BF_4^-]. Auration[66] of $RR'CCH_2CHCOCH_2M$ (20, M=H) by $(Ph_3PAu)_3O^+$, BF_4^- gave (20, M=$AuPPh_3$).

Copper has a pseudotetrahedral geometry[67] in monomeric $PhCu(Ph_2PCH_2)_3CMe$ [Cu-C 2.020(4) Å]. Crystal structures have also been reported[68] for cis-{[o-(PhN=N)C_6H_4]$_2$Au}[$AuCl_4$] (square planar Au in cation)[68a] and $Au_2Li_2(C_6H_4CH_2NMe_2\text{-}o)_4$ (asymmetric bridging aryl groups; two Ar_2Au anionic units and two cationic N_2Li sites; square planar core of Au_2Li_2).[68b] The o-$Me_2NCH_2C_6H_4$ ligand has also been used in Au^{III} complexes.[69] Light sensitive (11, M=Ag) is not isostructural[70] with the corresponding Cu or Li compounds;[44] all are 8-membered cycles with M bound to C_α of one ligand and to N of the other ligand in the dimer. Series of $(C_6F_5)_2Au^{III}$, 4,4'-octafluorobiphenyl-Au^I, $C_6Cl_5Au^I$ and $C_6Cl_5Au^{III}$ complexes have been investigated.[71]

Compounds, $CpM.PR_3$ (21, M=Cu or Au) and $C_5Me_5Au.PR_3$ have been produced;[72] the Au species are fluxional in solution. In the solid state, at -120°C, Au is primarily σ-bonded to Cp in $CpAuPPr^i_3$ with a slight distortion towards a η^3 coordination. Alkynyl derivatives, $RC{\equiv}CM.PR_3$ have been obtained from (21);[72] see also ref. 73. Other alkynyl species produced include;[74] (i) $[RC{\equiv}C(AuPPh_3)_2]BF_4$ (R=Ph or Pr), from[74a] $RC{\equiv}CAuPPh_3$ and Ph_3PAu^+,BF_4^- (ii) $[RC{\equiv}CAuC{\equiv}CR]^-$, (iii) $[(Ph_3P)_2N][PhC{\equiv}CAuC{\equiv}CPh]$ $[MC{\equiv}CR]$ (M = Ag or Au; R=Ph or p-MeC_6H_4)[74b] and (iv) $R_3PAuC{\equiv}CAuPR_3$.[74c] The crystal structure of linear $PhC{\equiv}CAu.PPh_3$ was reported.[74a]

The series of ate complexes, $[Li(THF)_4]\{M[C(SiMe_3)_3]_2\}$ (21, M=Li, Cu or Ag) are isomorphous[75] [linear CMC in the anions; Cu-C 2.027(7) and 2.070(9) Å; Ag-C 2.162(7) and 2.198(7) Å]; the solid state structure is maintained in solution. Initial formation of a π-complex was indicated by the ^{13}C n.m.r. spectrum in the Me_2CuLi-$PhCH{=}CHCO_2Bu^t$ reaction.[76] Uses of the higher order organocuprates, $R_2CuCNLi_2$, have been further indicated.[77]

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2

Group II: The Alkaline Earths and Zinc and its Congeners

BY J. L. WARDELL

1 Beryllium

In the crystal structure of CpBeX (1, X=Cp) at 128 K, Be is disordered between two equivalent sites; in each site Be is centrally bonded to one ring and peripherically bonded to the other, via a largely sp^2 hybridised carbon.[1] SCF-X_α scattered wave calculations[2] on 1 (X=H or Cl) and i.r. spectra of 1 (X=Cl, Br or Cp) were reported.[3] The reaction of $Ph_3As{=}CH_2$ and MCl_2 gave[4] the chlorine bridged dimers, $[Ph_3AsMCl_2MAsPh_3]Cl_2$ (M=Be or Mg). In the solid state structure[5] of $[(MeC{\equiv}C)_2BeNMe_3]_2$, there are two modes of interaction of MeC≡C groups with Be. In one dimer, bridging alkynyl groups act as 1 electron donors to provide a predominantly electron deficient Be_2C_2 ring [Be...Be 2.319(6) Å]; in the other the Be_2C_2 ring is effectively electron precise with MeC≡C acting as a 3e(σ,π) donor [Be...Be 2.549(6) Å].

2 Magnesium

N.m.r. spectra of the magnesium anthracene solvate, [Anth.Mg.3THF] (2), obtained as orange needles from Mg and anthracene in THF, suggest[6] that Mg interacts most strongly with C_9 and C_{10}. The reaction of (2) with R_2AlH in THF gave magnesium-μ-(9,10-dihydro-9,10-anthrylene)dialkylhydridoaluminate (3); in (3, R=Et), Al and Mg occupy axial positions (magnesium interacts with the hydride of the aluminate anion).[7] The use of (2)- or of Mg in the presence of anthracene has been claimed as superior to that of Mg in the syntheses of benzylic or allylic-Gringards from halides.[8] So-called magnesium cluster Grignard reagents, $R(Mg)_xBr$, have been generated from Mg clusters and RX in inert matrices.[9]

Carbometallation of alkenes and alkynes has attracted attention. The product of reaction of $Me_3SiC{\equiv}CCHR(CH_2)_nBr$ (4, R=H, n=3) with Mg in THF was $Me_3SiC{\equiv}C(CH_2)_4MgBr$ (5) at r.t.; on refluxing in THF (5) cyclises[10] in an exo-dig, suprafacial manner to $Me_3Si(BrMg)C{=}$

[For References see page 21

$\overline{C(CH_2)_3CH_2}$ (6). Compound (6) is obtained from (4, R=H, n=3) and Mg in refluxing Et_2O. Cyclisation of other (4) was studied. Also reported were the intermolecular additions of RMgX to (i) $HOCH_2C{\equiv}CCH_2OH$ (trans-addition),[11] (ii) spiro[2.4]hept-1-ene (syn-addition);[12] (iii) cyclopropenes,[13] (iv) $XMe_2SiCH{=}CH_2$ (X=Me, OR' or NR'_2) [the predominant products are $\equiv SiCH(MgX)CH_2R$; with allylic rearrangement occurring with allyl-Grignards],[14] and (v) $PhCH{=}C_\alpha[P(O)(OEt)_2]CO_2Et$ (addition of Mg to C_α).[15] The complex, Cp_2TiCl_2, effectively catalyses[16] the hydromagnesiation of alkenes by MgH_2 {e.g. $PhCH{=}CH_2$ provided $[(PhCHMe_2)Mg]:[(PhCH_2CH_2)_2Mg] = 95:5$, while isoprene gave a mixture of 2,3- and 3,3-dimethylallyl magnesiums} and by Et_2NMgH. Reactions of Me_2Mg with $LiAlH_4$ in ethers provide[17] MeMgH, $MeMg_2H_3$ or MgH_2, depending on the mole ratio of reagents. The combination, RMgX-$LiBH_4$ (4:1), reduces 2-equivalents of esters to secondary alcohols.[18]

Enthalpies of formation of RMgBr were calculated[19] from enthalpies of reaction of RH with $Me(CH_2)_4MgBr$ in Et_2O (RH=CH_4, PhH, $\overline{CH_2(CH_2)_nCH_2}$ (n=1, 3 or 4). The structure of EtMg[(+)-6-benzylsparteine]Br involves tetrahedral Mg with the chiral ligand in an all chair conformation.[20] The reaction of p-$(ClCH_2)_2C_6F_4$ with Mg in THF provided oligomeric $[Mg_{1.5}Cl(THF)_2C_8H_8]_n$, which formed[21] p-$(Me_3SiCH_2)_2C_6H_4$ on reaction with Me_3SiCl. The lithium magnesiates $Li_2[(PhC{\equiv}C)_3MgTMED]_2$, (7), $[Li(TMED)_2][TMEDLi(PhCH_2)_2$-$Mg(CH_2Ph)_2]$ (8), $[LiTMED]_2[Mg(C{\equiv}CPh)_4]$ and $[Li_2Me_2N(CH_2)_6NMe_2]$ $[Mg(C{\equiv}CPh)_4]$ have been prepared; Mg in (7) has a trigonal bipyramidal geometry, while in (8) it is tetrahedral.[22]

The ^{25}Mg n.m.r. spectra have been obtained for R_2Mg and R_2MgX (R=Me, Et, Cp, $CH_2{=}CHCH_2$ or $CH_2{=}CMeCH_2$) in solvents such as THF, dioxan, DME, PhMe or PMe_3; the n.m.r. parameters suggest that the Cp-Mg bond in Cp_2Mg has a largely covalent character.[23] Thermodynamic parameters for the Schlenk equilibrium[24] for the Bu^t-Grignard reagent were calculated using n.m.r. data.

Complete retention of configuration at the benzylic site occurs on formation of 2-PhCRH-pyridine from 2-PhCRHSO-pyridine and Grignard reagents.[25] An electron transfer (from R_2Mg) is the principal initial step leading to the formation of ethers and reduction products in reactions of Grignard reagents with o-quinol acetates;[26] normal or conjugated addition products arise from non-electron transfer mechanisms. Electron transfer processes were also implicated in the reactions of $PhC{\equiv}CSO_2Ph$ and o-$\overline{C_6H_4N{=}CPh{-}C}{=}NPh$ with $CH_2{=}CH(CH_2)_4MgBr$, from formation of cyclo-

pentylmethyl products.[27]

3 Zinc and Cadmium

Ylide complexes, $[Ph_3AsCH_2MCH_2AsPh_3]Cl_2$ (9, M=Zn),[4] $(Me_2N)_3PCH_2ZnCl_2$[28] and $[(Me_2N)_3PCH_2MCH_2P(NMe_2)_3]Cl_2$ (10, M=Zn or Cd)[28] have been prepared from the appropriate ylide and $ZnCl_2$; all have limited stability in chlorocarbon solvents. Gas phase electron diffraction[29a] studies of the chelates, $Zn[(CH_2)_nOMe]_2$ (n=3 and 4), revealed Z-O distances of 2.37(3) and 2.38(5) Å. The transmetallation reaction,[29b] between $(PhSCH_2)_2Hg$ and Zn provided $(PhSCH_2)_2Zn$.

Reduction of chloro-capped, (hexa-azabicyclo[6.6.6]icosane)-cobalt(III) complexes by Zn dust in H_2O provides[30] exceptionally stable organozincs; the crystal structure of one product, $(CoC_{15}H_{33}N_6ZnCl_4.2H_2O)$, isolated from 6M HCl, contained tetrahedral Zn [3Cl and 1C]. The Reformatsky reagents (11), obtained from Zn and $BrCH_2CO_2R$ (R=Et or Bu^t) are dimeric in all but the most polar solvents; in the solid state, $[BrZnCH_2CO_2Bu^t.THF]_2$ has tetra-coordinate Zn (2 O, C and Br) and a eight-membered heterocycle,[31] ^{13}C n.m.r. Spectra have been reported for (11) and $Bu^tO_2CCMeRZnBr$ (R=H or Me). The preparation of $(R_F)_2Zn$ (R_F=CF_3 or C_6F_5) and adducts with Lewis bases (B) has been achieved from R_FI and R_2Zn in the presence of B; an <u>in-situ</u> synthesis of R_FZnI [R_F=C_nF_{2n+1} (n= 4, 6 or 8)] using a Zn-Cu couple has been described.[32] An n.m.r. study of the reaction of CH_2Br_2 with Zn in THF indicated the formation of $BrCH_2ZnBr$ (12) as well as Me_2Zn, $(BrCH_2)_2Zn$ and a di- or tri-zinc species; (12) gave moderate to good yields of cyclo-propanes with alkenes.[33] The chelates, R_2M (13) and RMCl (M=Zn or Cd; R=<u>o</u>-$Me_2NCH_2C_6H_4$) have been obtained from RLi and MCl_2; in addition, RMgBr was produced electrochemically from Cd and RBr. The H n.m.r. spectra of (13) indicated rapid intramolecular chelate bond fissions and formations.[34]

From the p.e. spectra [He(I) and He(II)] of the free radicals, RZnL· (R=Me or Et; L=Bu^tN=CHCH=NBu^t), it was concluded that the unpaired electron is in an orbital, mainly π^* in character but with some delocalisation into the R groups.[35] There are four independent Zn atoms in solid $[MeZnON{=}CMe_2]_4$, sited at the corners of a distorted tetrahedron. The Me_2C=NO groups, above each tetrahedral face,[36] are coordinated to two Zn atoms, <u>via</u> O, and to a third Zn, <u>via</u> N. The compound, $EtZnN(SiMe_3)_2$, is dimeric[37] in PhH. Hydrolysis of Et_2Zn

in dioxan provides sequentially $(EtZnOH)_2$ and $EtZn(OZn)_3OH$; an S_E1 mechanism has been proposed for the reaction of Et_2Zn with ArOH in dioxan.[38]

The values of ν(C=C) stretch (1655-1606 cm^{-1}) in the solution i.r. and Raman spectra of diallylzincs are those expected for isolated C=C bonds in η'-allyl-metal compounds; in the solid state spectra of $(CH_2{=}CRCH_2)_2Zn$ (R=H or Me) and allyl zinc chlorides, values of ν(C=C) stretch are 1550-1480 cm^{-1}, indicating the presence of delocalised allyl groups.[39] The fluxional character of diallylzincs was investigated by n.m.r. spectroscopy.[39] It was concluded from a gas phase electron diffraction study that 80% of $(CH_2{=}CHCH_2{-}CH_2)_2Zn$ were in a coiled back gauche,syn-conformation [Zn....C_4 3.15(6) Å]; a value of 4.5 $kJmol^{-1}$ was calculated[40] for the zinc-alkene interaction energy ($-\Delta G_o$). For $(CH_2{=}CHCH_2CH_2CH_2)_2Zn$, it was found that greater than 80% is in one of two coiled back conformations (gauche+,gauche-,anticlinal+, or gauche+,gauche-,syn) [Zn...C_4 3.00(8) Å, $-\Delta G_o$ 6 $kJmol^{-1}$].

The electronic and structural properties of MeZnCp were obtained[41] using a tight binding method of band structure calculation. The preparation {from Cp_2Zn and $Zn[N(SiMe_3)_2]_2$} and crystal structure of $\{Cp[\mu\text{-}N(SiMe_3)_2](ZnCp)_2\}$ have been reported;[37] also reported were zinc-transition metal bonded complexes produced[42] by reaction of Cp_2Zn with $(MeC_5H_4)_2TaH_3$ or Cp_2NbH_3. Syntheses of $(ICdC_5H_4)M(CO)_3$ (RCdI, M=Mn or Re) and R_2Cd (14) have been obtained from RLi and CdI_2; (14) exists in cis- and trans-forms.[43]

4 Mercury

4.1 Methylmercury compounds. It was concluded that LCAO-MO (HFS) calculations on Me_2Hg and MeHgCN, as well as $(MeC{\equiv}C)_2Hg$, that at least 80% of Hg-C bonding is due to the Hg 2S orbital and that the bonding is best described in terms of a 3c-2e bond.[44] The mechanism of methylation of Hg^{2+} in aqueous media by methylcobalamins (e.g. $^{13}CH_3\text{-}E_{12}$) involves an electron transfer from an initial complex formed from the reactants and a subsequent Me· transfer.[45] The syntheses and ^1H and ^{199}Hg n.m.r. spectra of MeHgSeR (R=Me or Ph) were reported;[46] ligand exchanges were also studied. Theophylline, $R\overset{3}{N}C(O)\overset{1}{N}RC(O)\underbrace{C{=}C}_{9}N{=}CHNH$ (15, R=Me) forms various complexes with $MeHg^{II}$, depending on the pH and the mole ratio of reagents;[47a] {a mono $MeOCH_2CH_2Hg^{II}$ complex [bonding to N_7; Hg-C 2.13(2), Hg-N 2.08(1) Å; C-HgN 173.3(6)°], m.p.

439-439.5° has a 3-D structure in the solid, with intermolecular interactions Hg...O($MeOCH_2CH_2$) and Hg...N_9 2.81(1) and 2.91(1) Å respectively.[47b] Solid complexes isolated from interactions of $MeHg^{II}$ and xanthine (15, R=H) in aqueous media include; μ-(xanthinato-N_3,N_7,N_9)-tris(methylmercury)nitrate.H_2O [linear coordination of MeHg to N_3, N_7 and N_9 of a dianionic xanthine moiety retaining its proton at N_1] and μ-(xanthinato-N_1,N_3,N_7,N_9)tetrakis(methylmercury)nitrate [two independent cations: linear coordination of MeHg to all four nitrogens of a xanthine trianion].[48]

The coordination chemistry of $MeHg^{II}$ with flexible tripod ligands, containing pyridyl (py) and N-Me-imidazolyl (N-MeIm) groups has been investigated;[49] in the crystal structure of MeHg {(2-py)[2-(N-MeIm)]$_2$COH}NO_3, there is one strong Hg-N [to a N-MeIm group; C-Hg-N 170.5(7)°, Hg-N 2.12(1) Å] and two weaker Hg-N interactions {Hg-N Å [C-Hg-N°] 2.58(1)[114.2(6)] and 2.89(1) [110.3(6)]}

Various n.m.r. spectra, including ^{14}N n.m.r., have been reported[50] for RHgCNO (16, R=Me or Ph); (16) reacts with MeOCC≡CR' (R'=Ph or MeO_2C) to give instable 3-R-Hg-isooxazoles, which ring open to $MeO_2CC(CN)=CR'(OHgMe)$.

4.2 Other Alkyl- and Aryl-Mercurials. The complex (10, M=Hg) has been prepared.[28] Series of $(Me_{3-n}X_nSiCH_2)_2Hg$ (17, R_2Hg; n=0-3, X=Cl or MeO),[51] $(Me_3MCH_2)_2Hg$ (M=C, Si, Ge or Sn)[52] and $Bu^iHgCH_2NMe_3$[52] have been synthesised and characterized by n.m.r. spectroscopy (^1H, ^{13}C, ^{29}Si, ^{119}Sn and ^{199}Hg); the synthesis of (17) involved photochemical reaction of $(Et_3M)_2Hg$ (M=Si or Ge) with RCl. The preparation of $C(HgX)_4$ (18, X=F, Cl, Br or I)[53a] and force field calculations[53b] for (18, X=Cl, F, Br, I, Me or CN) and $CH_2(HgCl)_2$ have been published. Zinc porphyrins can be mercurated at unsubstituted β-positions and at adjacent meso-sites.[54] High-melting, trimeric substituted phenylene- and -biphenylene-mercurials have been synthesised from 1,2-dihaloarenes and Na/Hg(or Hg); there is m.s. evidence for trace quantities of a tetramer in the bulk sample of perfluorobiphenylenemercury.[55] The complex, $\{[Me_2NFcHg]_2\}^{2+}$ $2[Ph_3BCN]^-$ contains[56] a centrosymmetric 4-nuclear dication with mean Hg-C 2.06(1), Hg...N 2.83(1) Å and CHgC 179.5(6)°. Crystal structures have also been determined for $PhHgN(SO_2Ph)C_6H_4NO_2$-o [Hg-C 1.99(1), Hg-N 2.12(1), Hg...O(NO_2) 3.00(1), Hg...O(SO_2) 2.87(1) Å][57] PhHg quinoline-8-thiolate [two independent moles, mean Hg-C 2.08(3), Hg-S 2.401(7), Hg...N

2.46(2) Å; CHgC 160.9(8) and 162.3(7) Å],[58] $(ClHg)_3CCO_2H.DMSO$ [mean Hg-C 2.06 Å, Hg-Cl 2.33(3) Å][59] and $PhHgOCOCF_3$ [Hg-C 2.05(1), Hg-O 2.121 Å and two Hg...O interactions 2.819, 2.952 Å][60] as well as PhHgOAc (a refinement).[60] Mercuretin, the compound formed from $Hg(OAc)_2$ either on melting or on heating in Ac_2O, is a condensation polymer[59] of $(AcOHg)_3C.CO_2H$, namely, $AcO[HgC(HgOAc)_2-CO_2]_nH$ ($n \sim 10$).

$^{199}Hg-^{199}Hg$ Coupling (^4J 2163 Hz) was detected[61] in the ^{199}Hg n.m.r. spectrum of $2-MeO-3,5-(CF_3CO_2Hg)_2C_6H_2NO_2$.

4.3 Alkenyl and Other Unsaturated Mercurials. The stereospecificity in reactions of vinylboron derivatives with Hg^{2+} salts has been studied. The best reagent (for retention of configuration) appear to be $Hg(OAc)_2$ and vinylcatecholboranes in the presence of NaOAc in THF;[52] equally as good are the more difficult to prepare $RCH=CHB(OH)_2$ (19).[62,63] The latter reagents were used to prepare (E)-RCH=CHHgX [20; $R=Me(CH_2)_7$, $Y(CH_2)_3$ (Y=Cl, I or PhO) or $MeO_2C(CH_2)_8$]. Bisvinylmercurials have also been obtained from (20) either using alkaline stannite or (19). The ^{19}F n.m.r. spectrum and synthesis of $(C_3F_7CF=CF)_2Hg$, from the thermolysis of $(C_3F_7CF=CFCO_2)_2Hg$ in presence of K_2CO_3 have been reported.[64] Propargylic bromides and iodides and mercury in sunlight provide either an allenic or a propargylic mercurial, e.g. $ICH_2C{\equiv}CH$ gave $CH_2=C=CHHgI$ [ν(C=C=C) 1926 cm^{-1}; δ ^1H 4.26 and 5.20]. As mixtures of allenic and propargylic mercurials were never obtained, it appears that these compounds do not exist in equilibrium.[65] Photoelectron spectra and i.r. intensity measurements provided[66] evidence for $d_\pi-p_\pi$ interaction between the Hg 5d orbital and the C≡C π bonds in compounds such as $(RC{\equiv}C)_2Hg$ and $PhHgC{\equiv}CH$.

4.4 Solvomercuration. The effectiveness of HgX_2 (X=OAc, $OCOCF_3$, NO_3 or SO_3Me) in oxymercuration reactions of alkenes in alcohols (ROH, R=Me, Et, Pr^i or Bu^t) has been studied;[67] $Hg(OCOCF_3)_2$ is effective in all four alcohols whereas $Hg(OMe)_2$ is only effective in MeOH or EtOH. Oxymercuration of $CH_2=CMeCH=CH_2$ by $Hg(OAc)_2$ in MeOH at r.t. gave after ½ h, the 1,2-adduct, $AcOHgCH_2C(OMe)MeCH=CH_2$; which on prolonged standing in solution rearranged to $CH_2=CMeCHOMeCH_2HgOAc$ (21). Other salts, HgX_2, also gave both products with the rate of formation of (21) depending[68] on the acidity of HX. Both 1,2-[trans-MeCH=CHCH(OMe)CH_2HgX] and 1,4-[(22), MeCHOMeCH=CHCH_2HgX] adducts are obtained from trans-

$MeCH{=}CHCH{=}CH_2$; the allylic products (22) are very easily solvolysed. Reactions of $PhNHCH_2CH{=}CH_2$ and $HYCH_2CH{=}CHMe$ (Y=O or PhN) with $Hg(OAc)_2$ and H_2O or $PhNH_2(YH_2)$ in THF provides such compounds[69] as $PhNHCH_2CH(YH)CH_2HgOAc$ and $HYCH_2CH(HgOAc)CHNHPhMe$. Oxymercuration of cis,cis-COD, using HgX_2, is reversible unless a base (e.g. NaOAc) is also present; in contrast aminomercuration is only reversible if HX is a strong acid.[70] Hence aminomercuration using $Hg(OAc)_2$ is irreversible and provides the kinetic controlled product. The nature of the mercurating species in aminomercurations has also been investigated.[71] N-Substituted heterocycles have been produced[72] by sulphonamidomercuration of dienes, using p-$MeC_6H_4SO_2NH_2$ and $Hg(NO_3)_2$, and by intramolecular amidomercuration, e.g. of $CH_2{=}CH(CH_2)_3CHMeNHCO_2Me$; in both cases demercuration of the adducts was achieved using $NaBH_4$. A variety of heterocycles, e.g. benzofurans, benzothiophenes, isocoumarins and chromones have been synthesised, via intermolecular solvomercuration by $Hg(OAc)_2$ in AcOH of o-$MeXC_6H_4Y$ [X=O,S or CO_2; Y= $C(O)C{\equiv}CR$ or $C{\equiv}CR$] or m-$XC_6H_4YCH_2C{\equiv}CR$ (X=H, Y=O, R=Me; X=MeO, Y= CH_2, R=Pr^i).[73]

4.5 Cleavage of Mercury-Carbon Bonds. Cleavage of Ar-Hg has been reported by AcOF and CF_3OF.[74] The reaction of ArHgR (R=Me or Et; Ar=di- or poly-chlorophenyl) with $Pt(PPh_3)_3$ in PhH provided air-stable, light-sensitive $[(PPh_3)_2Pt(R)HgAr]$; ^{31}P and ^1H n.m.r. were reported.[75] Further synthetic use has been made of the additions to alkenes of free radicals, generated from organomercurials by reaction with metal hydrides; some examples include radicals derived from oxymercurated sugars, oxymercurated alkenes and cyclic alkenes (including dihydro-furan and -pyran) and amidomercurated alkenes.[76]

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3
Boron with the Exception of the Carbaboranes

BY J. W. WILSON

1 Introduction

This chapter is an attempt to give a balanced report on the significant chemistry of organoboron compounds containing at least one boron-carbon bond. As such it is not a comprehensive review of the chemistry of organic compounds of boron.

2 Books and Reviews

An English translation from Russian of a book on the use of organoboron compounds in organic synthesis is now available.[1] The most recent volume of Inorganic Synthesis contains a chapter on methods of preparation of a range of organoboranes and carboranes.[2] Reviews have appeared on the following topics: stereoselection by allylboronates,[3] thermochemistry of organoboron compounds,[4] the kinetics and mechanism of hydroboration,[5] the chemistry of di and tricoordinate boron cations[6] and the chemistry of 1-boraadamantane.[7,8]

3 Uses of Organoboranes and Organoborates in Organic Syntheses

Studies on the rate of hydroboration of 1-octene by several borane-Lewis base adducts indicate that the mechanism proceeds *via* prior dissociation of the adduct which is contrary to the direct attack mechanism proposed on the basis of *ab initio* calculations.[9] Hydroboration of representative alkenes by borinane dimer in n-heptane proceeds through dissociation of the dimer followed by reaction of the monomer and alkene. Borinane shows similar behaviour to 9-BBN, both molecules differing markedly from other common monofunctional reagents.[10] The factors that affect the stereoselectivities achieved by various hydroborating reagents have been investigated theoretically and the analysis developed into a predictive tool.[11] The reduction of ketones and hydroboration of alkenes by catecholborane is catalysed by lithium bromide.[12]

9-BBN is proving to be a very useful reagent. Hydroboration of

[For References see page 37

α,ω-dienes followed by redistribution of the trialkyborane products with $Me_2S \cdot BH_3$ produces six and seven membered boracyclanes in excellent yields[13] whereas dimethyldivinyl silane with the same reagents followed by methanolysis gives (1) in 80% isomerically pure yield.[14] Vinyl cuprates react with 9-BBN to give α,β-unsaturated organoboranes and thus provide a new route to aldehydes and ketones.[15] Carbonylation of alkyl-9BBN derivatives using ^{13}C enriched carbon monoxide gives an effective method for synthesising labelled aldehydes, alcohols and carboxylic acids.[16]

The dimethylsulphide adduct of thexylchloroborane reduces aliphatic carboxylic acids to aldehydes in 93-99% yields at 25°C.[17] Investigations of the relative merits of dimethyl and diphenylbromoborane as reagents for the cleavage of acetals and ketals have been reported[18] as has a new method for the regioselective introduction of the oxycarbonyl or thioacetal functionalities into alkenes.[19]

Alpine-borane (B-3-pinanyl-9BBN) reduces prochiral α-keto esters[20] and ketones[21] very efficiently with 100% optical purity in selected cases. Elevated pressures significantly accelerate the rate of reduction, at the same time suppressing the competing dehydroboration and reduction brought about by dissociation of the reagent into α-pinene and 9-BBN.[21] Asymmetric reduction of propargyl ketones[22] and α-chiral alkynyl ketones[23] is readily achieved by the same reagent. The latter study involves a steroid precursor in which the α chiral centre is observed to influence the enantioselectivity. Cram selectivity is remarkably enhanced in the reaction of certain imines with allyl-9-BBN and the work provides further insight into the Cram/anti-Cram problem.[24] Prochiral ketones of moderate steric bulk are reduced by B-(<u>cis</u>-10-pinanyl)-9-BBN in modest to good enantiomeric excesses of the S alcohols. This is the opposite stereochemistry to that obtained with a similar organoaluminium reagent.[25]

$IpcBH_2$, which can now be made with high optical purity,[26] hydroborates suitable alkenes in diethyl ether and selective crystallisation of the corresponding alkylboranes gives essentially 100% optically pure products that are readily converted to the corresponding boronic acids and esters.[27] Both mono and diisopinocampheylboranes asymmetrically hydroborate appropriate alkenes to give intermediates that readily eliminate α-pinene on treatment with acetaldehyde providing a direct route to chiral boronic and borinic esters of high enantiomeric purities. The

latter have been used to make chiral acyclic ketones via carbenoidation.[28] $IpcBH_2$ reduces ketones most effectively when used in a 1:1 ratio to give alcohols consistently enriched (14-46% ee) in the S enantiomer[29] whereas tert-butoxyisopinocampheylborane produces alcohols enriched (4.9-23% ee) in the R enantiomer.[30] Aldehydes condense with methallyldiisopinocampheylborane to give 2-methyl-1--alken-4-ols in ≥ 90% enantiomeric purities. This reaction provides an alternative to Hoffmann's route based on boronates.[31] A series of chiral B-allyldilkylboranes have been prepared from readily available terpenes. The isocaranyl derivative proved the most effective and with selected aldehydes gave homoallylic alcohols with 86-99% enantiomeric purities.[32] Reaction of α-chloroallylboronic esters with aldehydes gives ≥ 90% transfer of chirality to the corresponding homoallylic alcohols.[33] This procedure is based on a new chiral directing group, R,R-2,3-butanediol, for the synthesis of (S)-α-chloroboronic esters developed by Matteson's group.[34] It has been demonstrated that α-amino boronic acids or esters have limited stability but α-amido derivatives are much more resilient and that the boron analogue of N-acetylphenylalanine can be prepared.[35] A Japanese patent reports the use of allenylboronic esters with optically active dialkyl tatrates in the synthesis of prostaglandin derivatives.[36]

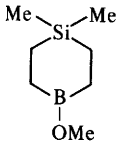
A new reducing agent, potassium 9-(2,3-dimethyl-2-butoxy)--9-boratabicyclo(3.3.1)nonane achieves highly stereoselective reduction of cyclic ketones with very simple recovery of the product.[37] Systematic exploration of the reaction of representative organic functional groups with Li9-BBNH in tetrahydrofuran has shown that the reagent exhibits a wide range of reactivity and is recommended as the reagent of choice for the selective reduction of esters and lactones in the presence of many functional groups such as carboxylic acids and amides.[38] Alkenes and alkynes which are normally inert to lithium borohydride are readily hydroborated by this reagent in diethyl ether in the presence of ethyl acetate at 25°C. The intermediates can be changed into other derivatives which makes the procedure a useful route in organic syntheses.[39] A study of the reaction of lithium borohydride with a range of functional groups in the presence of boron Lewis acids has been made and a simple method for the catalysed selective reduction of esters discovered.[40] Lithium monoorganyl borohydrides can now be made in near quantitative yields by the reaction of boronic acids or esters with LAH.[41] Borinic

esters react rapidly with lithium monoethoxyaluminium hydride to give the corresponding dialkyborohydrides. These systems are stable compounds and provide a means of storing dialkylboranes which are quantitatively released on treatment with methyliodide or hydrochloric acid.[42] Hydroboration of substituted styrenes with lithium triethylborohydride goes smoothly to give the Markovnikov product as an ate complex, protonolysis of which yields mixed trialkylboranes by selective removal of an ethyl group.[43] Evidence to show that hydride induced carbonylation of organoboranes proceeds via alkali metal trialkylborohydride intermediates has been published.[44] Reaction of carbon dioxide with trialkylalkynylborates gives high yields of (Z)α,β-unsaturated acids[45] and α,β-alkynyl ketones are produced by the reaction of alkynyltrifluoroborates with acid anhydrides.[46] Boron ate compounds of heterosubstituted allylic carbanions direct carbonyl and reactive halide substrates to the α position with high regioselectivity.[47]

Routes to 1-iodo-4-hydroxymethyl-1,6-heptadienes and 1-iodo-1,4-pentadienes from boracyclohexenes have been optimised.[48,49] Trialkylboranes react efficiently with N-chloroalkylamines to produce functionally substituted dialkylamines[50] and tri-n-butylborane forms chelate ate complexes with β-hydroxyketones which can then be reduced in a highly selective way to 1,3-diols.[51]

4 Preparations and Reactions of Organoboranes

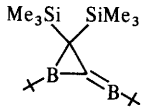
The chemistry of 1-boraadamantane has been explored further. Triphenylphosphorus ylides react with the tetrahydrofuran adduct to give a stable compound which can be thermally rearranged to 4-alkyl-3-borahomoadamantanes.[52] Adducts of benzonitriles are formed in a similar way and these rearrange at 200° to the dimeric 3-bora-4-aza-1,1-bihomoadamant-4-enes.[53] The antiviral activity of amine complexes of 1-boraadamantane has been investigated[54] and silicon and sulphur containing derivatives reported.[55,56] Ate complexes of 3,8-dimethyl, 3,4,8-trimethyl and 3,4,4,8-tetramethyl-3-borabicyclo[4.3.1]decanes react with acetyl chloride to produce the corresponding 2-(3-methylene-5-methylcyclohex-1-yl)alkyl(dimethyl)boranes.[57] 3-Borabicyclo[3.3.1]nonane and non-6-ene derivatives are homologated by α-haloalkyl lithium compounds[58] and 7-methyl-3-borabicyclo[3.3.1]nonane dimer hydroborates dialkylalkynes to give the corresponding B-alkenyl compounds which rearrange to 3-borabicyclo[4.3.1]decanes in the


Me
Me
Si
B
OMe

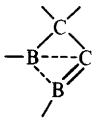
(1)

B

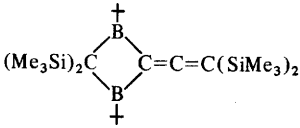
(2)


Me3Si
SiMe3
B
B

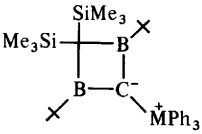
(3)


C
B
C
B

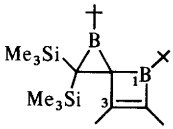
(4)


B
(Me3Si)2C
C=C=C(SiMe3)2
B

(5)


SiMe3
Me3Si
B
B
C
MPh3

(6)


B
Me3Si
B
1
Me3Si
3

(7)

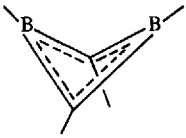
presence of catalytic amounts of hydrochloric or hydrobromic acid.[59]

The chemistry of boron containing small rings is expanding due almost entirely to work carried out in West Germany. Three very different routes for the synthesis of borirene (2) derivatives have been described.[60,61,62] Theoretical studies on the structure of "2,4-diboramethylenecyclopropane" (borandiylborirane) the only known derivative of which is (3) conclude that the structure may correspond to the non-classical (4) arrangement, furthermore the mechanism of topomerisation of (3) may include a carbene intermediate.[63,64] Such an intermediate has been considered in explaining some of the reactions of (3) in that bis(trimethylsilyl)-acetylene and (3) give the first characterised 1,3-diboretane (5). With MPh_3 (M = P,As) the ylides (6) are obtained.[65] With other alkynes cyclisation takes place to give spiro 1,2-dihydroboretene derivatives (7) in which a strong 1,3 interaction is indicated from the pronounced shielding of the B-1 and a broadening of C-3 carbon n.m.r. signal.[66] Such an interaction justifies the description of these systems as homoborirenes with a bent structure as indicated by ab inito calculations.[67] Two groups have synthesised derivatives of 1,3-dihydro-1,3-diboretenes (8). These molecules can be reduced to the radical anion.[68] A crystal structure determination[69] confirms the puckered structure indicated by past and more recent calculations[70] for parent molecules which can be considered as non planar 2π Hueckel aromatic molecules. Methylborolene, generated from $MeBBr_2$ and C_8K, reacts with various alkynes to give borirenes which dimerise to give diboracyclohexadienes (9). With di-tert-butylacetylene the actual borinene is isolated in conjunction with the corresponding 1,3-diboretene.[71]

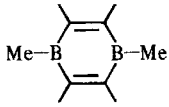
Treatment of 1-(diisopropylamino)-3-borolene with Me_3CLi gives the borole dianion (10) which reacts with chlorotrimethylsilane to give the disubstituted 2-borolene.[72] It should be possible to make a similar pentaalkyl dianion from a 2,5-distannyl-3-borolene since at room temperature both trimethylstannyl groups migrate around the ring.[73]

Amino substituents have made it possible to isolate a less energetically favourable isomer of $C_4B_2H_6$ with the classical structure (11) which dynamic n.m.r. measurements show to be in equilibrium with structure (12) in solution.[74]

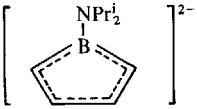
The redox behaviour of p-$(R_2B)_2C_6H_4$ (R = mesityl) indicates that such systems behave as mirror images of p-phenylenediamines.[75]


B
B

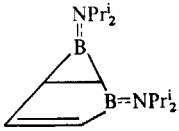
(8)


Me—B
B—Me

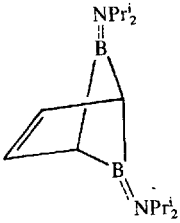
(9)


NPr$^i_2$
B
2−

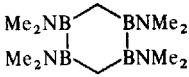
(10)


NPr$^i_2$
B
B=NPr$^i_2$

(11)


NPr$^i_2$
B
B
NPr$^i_2$

(12)


Me$_2$NB
BNMe$_2$
Me$_2$NB
BNMe$_2$

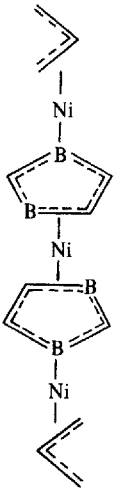
(13)

A 1,2,4,5-tetraborinane (13) has been synthesised and its crystal structure determined showing that the molecule prefers the chair conformation.[76]

Reaction of diborane and tetraarylstannanes brings about transmetallation in which one or more aryl group is transferred to boron.[77] The course of the reaction between dimethylbis(phenylethynyl)stannane and trialkylboranes can be followed by ^{119}Sn n.m.r. spectroscopy which is also useful in observing the distribution of products in the final mixture.[78] 1,2-Di-tert-butyl-1,2-dichlorodiborane (4) and 1,2-dichloro-1,2-bis(dimethylamino)diborane (4) add to 1-trimethylsilylalkynes to give 1,1-disubstituted boryl alkenes. The former compound reacts with other alkynes to give the 1,2-bis(tertbutylchloroboryl)alkene or no reaction takes place.[79] A method for the synthesis of (Z)-1-alkenylboronic esters in high yields and excellent stereochemical purities has been published which complements an earlier procedure for the synthesis of (E) isomers.[80] The reaction of 1-halo-1-alkenyldialkylboranes with Grignard reagents is not clean and mixtures of (E) $(R_2BC(R')=CHR''$ and the transfer product (E) $RR'BC(R)=CHR''$ are obtained.[81]

Bis(allyl)nickel complexes react with alkyl derivatives of 2,3-dihydro-1,3-diborole to give the first η^3-allyl tetradecker complexes (14) to be isolated.[82]

Several new azaborolinyl complexes have been reported. 1,2-Azaborolinyl lithium derivatives react with ruthenium dichloride to give sandwich complexes which exist as two isomers one of which has had its X-ray crystal structure determined.[83] 1-Tert-butyl-2-methyl-1,2-azaborolinyl lithium reacts with $[(CH_3CN)_3Mn(CO)_3]PF_6$ to give the half sandwich complex (15) whereas an X-ray structure of the product shows that the neutral ligand reacts with hexacarbonylmolybdenum (O) to form π-allyl(1-tert-butyl-2-methyl-η-1,2-azaborolinyl)dicarbonyl molybdenum (O). The allyl fragment resulting from decomposition of the ligand under the reaction conditions used.[84] Crystal structure determination of bis(1-tert-butyl-2-methyl-η^3-1,2-azaborolinyl)nickel shows that the ligands are bonded through the three carbon fragment only. The first example of such behaviour to be observed.[85] Six bis(borabenzene)vanadium complexes have been reported together with the crystal structure of the half sandwich compound $C_5H_5BCH_3V(CO)_4$.[86] The X-ray structure of $Co(PMe_3)_2BPh_4$ shows that one of the phenyl groups of the anion is π bonded to the cobalt



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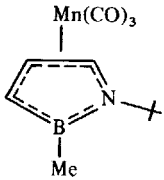

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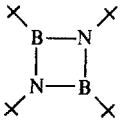

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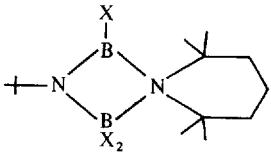

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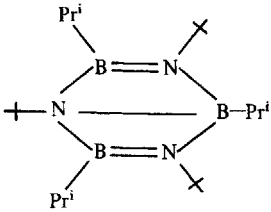


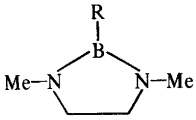
(18)

atom. The first example of the tetraphenylborate anion being coordinated to a first row transition metal ion.[87]

Protic reagents such as HCl, Bu^tOH and $HNBu^t_2$ give cis addition products with iminoboranes.[88] Bu^tNBBu^t behaves as a typical iminoborane and slowly dimerises to the diazadiboretidine (16). The structural properties of the two molecules are similar to their isoelectronic hydrocarbon analogues.[89] Diazadiboretidines (17) have been made from the corresponding aminoiminoborane and BX_3(X = Cl,Br). The crystal structure for X = Br shows a planar B_2N_2 ring with four significantly different B-N bonds.[90] Addition of bromodimethylborane to the same aminoiminoborane produces a compound which has been formulated as a 1,3,2,4-diazadiboretidinium salt.[91] The iminoborane $Me_2CHBNBu^t$ which is metastable at -78°C trimerises to give (18) at elevated temperatures. The X-ray structure of (18) shows it to be the first example of a Dewar borazine with two short BN double bonds and a long (175.2 pm) BN single bond.[92]

Diazaborolidines (19) form 1:1 adducts with gallium and aluminium halides in which one of the ring nitrogens is coordinated to the Lewis acid.[93] Similar behaviour is observed with alkylhaloboranes irrespective of the boron substituents.[94] Aluminium and gallium halides also form simple 1:1 adducts with the dimethylaminoboranes Me_2BNMe_2 and $RB(NMe_2)_2$ (R = Me,Ph).[95] Simple complexes of boranes have also been reported with benzimidazole[96] malonamides and malonimidines.[97] The reactions of symmetrically substituted ethanediamides with bromodimethylborane have been investigated[98] and the reaction of lithiopyridines with dialkylmethoxyborane gives reasonable yields of dialkylpyridylboranes.[99] Thermally stable nitrogen-silicon-boron heterocycles containing an ethylperoxy substituent on the boron atom are obtained from the oxidation of 1,2,5-azasilaboroles (20)[100] and cyclisation of 3,5-disubstituted 1,2,4-trithia-3,5-borolanes with RN=S=NR gives dithiadiazadiborinanes (21).[101]

Several organoborane molecules containing phosphorus have been reported. Reaction of R_2BCl (R = n-pentyl, cyclopentyl and cyclohexyl) with $R'CH{=}PPh_3$ (R' = Me,Et,Ph) leads to the corresponding dialkylboryl containing ylides $R_2BCR'{=}PPh_3$.[102] Dimeric diorgano(organophosphinoyloxy)boranes $R_2BOP(O)C_6H_5R'$ have been shown by n.m.r. to exhibit monomer-dimer equilibria in solution.[103] Several organophosphorus acids containing the $-OBR_2$ group have been characterised.[104] Reaction of $MePhPCH_2OH$ with



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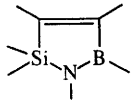

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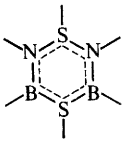

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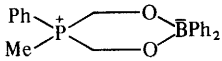

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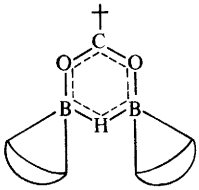


(23)

$Ph_2BOCH_2CHMe_2$ gives a 47% yield of the diphenylborylphosphine (22).[105]

Cyclisation of Me_3CCOOH with 9BBN dimer gives a quantitative yield of (23) the crystal structure of which has been determined.[106] The adducts formed by (ethylcarbamoyl)borane with ammonia and the methylamines, which are boron analogues of amino acids, have had their structure-activity behaviour investigated.[107] Although not possessing boron-carbon bonds some significant compounds containing hypervalent boron atoms have been made and characterised by spectroscopic means. The ^{11}B chemical shifts reported include the highly shielded six coordinate atom ($\delta^{11}B$ = -122.9) in (24).[108]

5 Physical Data

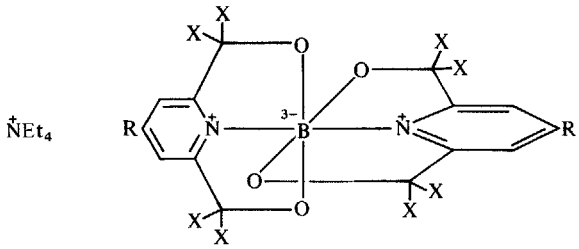
Rate constants for the reaction of phenylisocyanate and a series of aminoboranes have been determined using an infra-red spectroscopic technique[109] and the fragmentation patterns of some 2-phenyl--1,3,2-diazoboracycloalkanes have been assigned.[110] Rotational barriers about the B-NMe_2 bonds in a series of alkyldimethylamino[bis(trimethysilyl)amino]boranes have been determined from dynamic n.m.r. measurements and the results discussed in terms of steric interactions.[111] Infra-red spectra of gaseous and solid divinylfluoroborane and the Raman spectra of the liquid and solid phases have been recorded and all the normal modes assigned.[112]

Gas chromatography over optically active metal chelates permits analytical separation of the enantiomers of optically active diols as their n-butylboronate esters.[113]

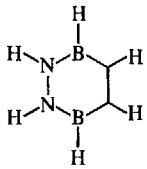
Photolysis of trinaphthylborane does not provide evidence for the formation of naphthylborene[114] in contrast to the findings of an earlier investigation. Anodic oxidation of organoboranes is more readily achieved if the molecules are converted into ate complexes with nucleophiles such as hydroxide, amine or pseudohalide. The oxidation produces dimerisation of the alkyl groups and the yields vary with substituents on the group.[115] Molecular orbital calculations predict that 1,4 dibora-2,3-diazarine (25) is 48 kJ mol^{-1} more stable than its 2,5-diazarine isomer (26)[116] and that borepin is approximately 150 kJ mol^{-1} more stable than the boranorcaradiene isomer.[117] Very good agreement is observed between the experimental frequencies for MeB_2H_5 and those calculated from scaled and refine 4-21 ab initio force constants.[118]

Several X-ray structures have been reported including tris(Z trimethylsilylprop-1-enyl)borane,[119] [tris(trimethylsilyl)-

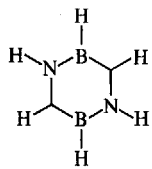
methyl]diphenylborane[120] and a series of nitrogen-oxygen-boron heterocycles.[121,122,123] One of the latter (27) contains the longest $B(sp^3)$-$N(sp^3)$ bond (175.9 pm) recorded to date.[123]



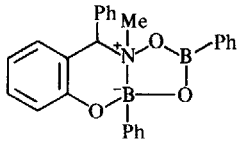
(24) X = CF_3



(25)



(26)



(27)

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4

Carbaboranes, including their Metal Complexes

BY T. R. SPALDING

1 Introduction, Reviews and theoretical aspects

This Chapter concerns the synthesis, characterisation, reactions, and properties of carbaboranes and their σ- and cage-bonded metal derivatives.

Two extensive reviews of carbaboranes and their metal derivatives have appeared during 1984.[1a,b] Other reviews concerned σ-bonded metallocarbaboranes,[2a] and recent work on carbaborane based polymers.[2b] Related articles discussed metallaboranes,[3a,b] compounds of carbon containing multicentre bonds,[3c] the thermochemistry of organoboron compounds,[3d] and main group III chemistry in general.[3e] Reference must also be made to volumes of the "Comprehensive Organometallic Chemistry" series which deal with carbaborane and organoboron chemistry (Vol. 1) and with transition metal derivatives (Vol. 6).[3f]

Dissertations on carbaborane and borane salts,[4a] routes to organoboranes and metallaboranes,[4b] and icosahedral metallaheteroboranes have appeared.[4c] Aspects of catalysis by metallacarbaboranes were reported.[5a,b]

A paper concerning the development of unique descriptor systems for *conjuncto* - structures involving carbaboranes, boranes, and metal derivatives has been published.[6]

1.1. Theoretical Aspects. - Relatively few articles of an original nature have been published. Instead, most concerned the extension of previous work such as Wade's approach to cluster bonding,[7a-c] or the suitability of BH or CH units to cap four-, five-, or six-membered rings.[8] A hypothetical "B_4H_4(H)CH" model was used to analyse the observed C-H bond weakening in the isolobal analogue $[Fe_4(H)(CO)_{12}CH]$.[9]

The feasibility of devising localised bond schemes for n-atom borane clusters with *closo*-structures and n, (n+1), or (n+2) skeletal electron pairs was examined and compared with results from MO treatments.[10]

[For References see page 55

2 Carbaborane Synthesis, Characterisation, and Reactions

Possibly some of the most interesting work in synthesis presently concerns carbon rich C_4-carbaboranes. Three isomers of $C_4B_2H_6$-compounds have now been reported. The parent compound and some alkyl derivatives take structure (1), whilst others (e.g. R^1, R^2 = Ph) take (2), an organoborane form. A compound with the third structure (3, R = NPr_2^i) has been obtained from reaction of the dilithium salt of the B-substituted di*iso*propylaminoborole (4) with $(Pr_2^iN)BCl_2$, Scheme 1.[11] Reaction with $MeBBr_2$ gave the carbaborane [5≡1, R^1 = Me R^2 = NPr_2^i)].

The effect of R in $R^1C{\equiv}CR^2$ on the products of the reaction between acetylenes and methylborylene (generated from $MeBBr_2$ and C_8K) has been studied.[12] For R = Me, only the carbaborane (1) is formed, but for R = Et, both (1) and (2) are observed. When R is a primary alkyl group (>Et), only type (2) compounds are found. For R = Bu^t, both borirene and 1,3-diboretane products were identified.

The first C_4B_6-carbaborane, $Et_4C_4B_6Et_6$, was synthesised by reaction of the dipotassium salt of 1,5-$C_2B_3Et_5$ with I_2.[13a] A *nido* decaborane-type structure was suggested on evidence from ($^{11}B^{11}B$) and ($^{13}C^{11}B$) - correlated n.m.r. spectroscopy but the molecule appeared to be fluxional at room temperature and above. Previously only adamantane type derivatives of C_4B_6-systems had been reported.[13b]

The formation of *nido* $(Me_3Si)_2C_4B_8H_{10}$ was achieved by elimination of Me_3SiH molecules from two $(Me_3Si)_2C_2B_4H_6$ molecules "fusing" at 210°C.[14] The reaction was one-step, high yield, and non metal-catalysed. The product was non-fluxional in either solution or the liquid state, unlike the alkyl derivative $R_4C_4B_8H_8$.

This section on C_4-compounds cannot be concluded without reference to recent experimental and theoretical studies of borirene(R_3C_2B),[12,15] 1,3-diborete ($R_2^1C_2B_2R_2^2$),[16] and 1,3-diboretane ($R_4^1C_2B_2R_2^2$) derivatives,[17] since related species clearly play important roles in the chemistry of carbaboranes and isomeric organoboranes. Recently characterised compounds include 1-*tert*butylborirenes,[15a] and 1,3-dihydro-1,3-diboretes and their radical anions.[16a,b] High level (6-31G*) MO calculations were performed on a number of these and related species.[15b,16c,d]

The ability of R_2N-substituents to facilitate unusual structures, see Scheme 1, was used to produce a novel C_2B_4-derivative.[18] Whereas the parent $C_2B_4H_8$ has the expected *nido*

structure, an *X*-ray diffraction study of $(H_2C)_2(BNMe_2)_4$ revealed a *cyclo*hexane like chair conformation. The C_2B_4-product was obtained from reaction of potassium and $H_2C[B(NMe_2)Cl]_2$.

Both 5-perfluoropropanol and 5-perfluoropinacol derivatives of 2,4-$C_2B_5H_7$ were synthesised in the gas phase photolysis of hexafluoroacetone and the carbaborane.[19] The 5-position substitution was expected on the basis of calculated electron densities but the O-B bonded pinacol derivative was unexpected.

Platinum bromide catalysed the formation of B-B linked *conjuncto*-bis-carbaboranes from 1,5-$C_2B_3H_5$ or 1,6-$C_2B_4H_6$.[20] The reactions were highly selective, giving only 2,2'-isomer products.

A revised structure, $[6,9\text{-}C_2B_8H_{10}]^{2-}$, for the product of the pyrolysis of $[5,6\text{-}C_2B_8H_{11}]^-$ has been suggested based on n.m.r. spectroscopic evidence.[21]

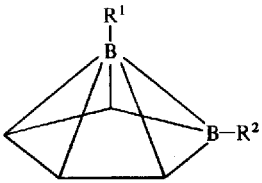
Reaction of $[7,9\text{-}C_2B_9H_{12}]^-$ with $NaNO_2$ in dilute hydrochloric acid afforded the known compound 6,8-$C_2B_7H_{13}$.[22] With Na_2SO_3, a new thiacarbaborane, $SC_2B_6H_{10}$, was obtained. From spectroscopic evidence it was suggested that either the 4,6,8-(^1H and ^{11}B n.m.r.) or perhaps 7,6,8-(Raman)-isomer had been isolated.

In refluxing ethanol $[NH_4]_2[1,2\text{-}(SC)_2B_{10}H_{10}]$ forms $[NH_4][7,8\text{-}(HSC)_2B_9H_{10}]$.[23] Oxidation of this salt with $[I_3]^-$ in water afforded $[\overline{SCB_9H_{10}CS\text{-}SCB_9H_{10}CS}]^{2-}$. An *X*-ray diffraction study established that the two C_2B_9-cages bonded in an anti-conformation across the two bridging S-S bonds. Reaction of 1,2- or 1,7-$C_2B_{10}H_{12}$ with E_2Cl_2 (E = S or Se) in the presence of $AlCl_3$ followed by protonation gave 9,12- and 9,10-$(HE)_2C_2B_{10}H_{10}$ products.[24a] A number of RE-, and cyclic thia- and selena-acetals and - ketals were characterised.[24a] Related tellurium derivatives have been prepared.[24b] Reactions of 3-[1',2'-$C_2B_{10}H_{11}$] -1,2-epithio- and -1,2-dimercaptopropanes have been studied.[25]

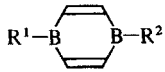
Derivatives of $C_2B_{10}H_{12}$ with C-bonded allyl,[26a] hydroxy-methyl,[26b] *iso*cyanato,[26c] sila*cyclo*butyl,[26d] and $Me_2(Cl)SiCH_2$-groups[26e] have been reported as well as some related carboxylic acids[26f] and methyl sulphonates.[26g]

Phenyl-2-[1',12'-$C_2B_{10}H_{11}$] iodonium tetrafluroborate has been characterised.[27a] Reaction with DMSO afforded 5(6)-dimethyl-sulphoxonium-7,8-dicarba-*nido*-undecaborate whose structure was established by *X*-ray crystallography.[27b]

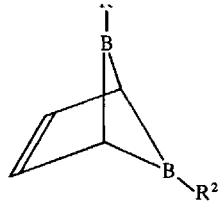
A number of transition metal complexes with P, N, or As donor ligands attached to 1,2-$C_2B_{10}H_{12}$ residues have been reported.



(1)



(2)



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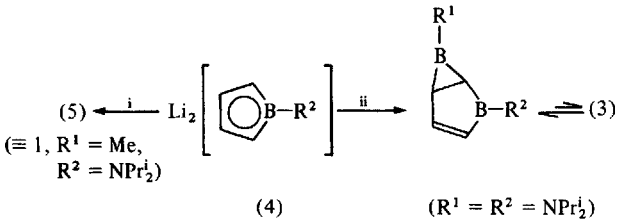
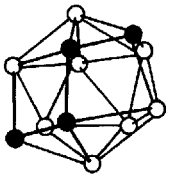


Reagents: i, $MeBBr_2$; ii, $Pr^i_2NBCl_2$

Scheme 1



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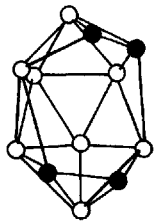


(7)

Scheme 2

These include ($Ph_2PCB_{10}H_{10}CCH_2PPh_2$) complexes of Cr, Mo, W, Fe, and Ni carbonyls,[28a] [$(Me_2N)_2PCB_{10}H_{10}CPR_2$] complexes of Co,[28b] Ni,[28c] and Pt,[28d] ($Ph_2PCB_{10}H_{10}CPPh_2$) complexes of η^5-CpMn(CO)$_n$,[28e] and Pt,[28d] ($Ph_2PCB_{10}H_{10}CH$) complexes of Co,[28b] and Ni,[28c] and ($Ph_2PCH_2CB_{10}H_{10}CH$) complexes of Pt and Pd.[28f] The last mentioned compounds gave intramolecularly metallated (M-B bonded) products on heating in toluene. A related Pd-B bonded complex with the ($R_2NCH_2CB_{10}H_9CR$)-ligand was reported.[28g]

The synthesis and properties of carbaborane containing polymers continue to be studied especially in the USSR.[26] Polymers based on various organic groups such as acrylacetylenes,[29a-d] methacryloyl derivatives,[29e] cellulose esters,[29f] acetals,[29g] epithiopropanes,[29h] amides,[29i-m] and siloxanes have been reported.[29-n-p] Polyamides containing dicarbaundecaborate units have been characterised.[30]

Work on monocarbon carbaboranes has mainly concerned derivatives of $[CB_{11}H_{12}]^-$. Reaction of *nido* 7-Me_3N-7-$CB_{10}H_{12}$ with Et_3NBH_3 yields *closo* 1-Me_2NH-1-$CB_{11}H_{11}$.[31a] This could be methylated[31a] or demethylated[31b] to give Me_3N- or $MeNH_2$-products. The parent $[1\text{-}CB_{11}H_{11}]^-$ could be obtained from the Me_3N-derivative.[31a] Reaction of the $MeNH_2$-compound with formaldehyde and I_2 gave 1-[(HO)CH=NMe]-1-$CB_{11}H_{11}$.[31b] The synthesis and properties of Li, Na, K, Rb, and Cs salts of $[CB_{11}H_{11}]^-$,[32a] and $[CB_9H_9]^-$ have been studied.[32b]

A full report has been published of the application of *J*-correlated two-dimensional ^{11}B-^{11}B n.m.r. spectroscopy to determine B-B connectivities.[33] This important technique was used successfully for a variety of carbaboranes, metallacarbaboranes, and related boranes. Generally, mutual coupling is observed for directly bonded B atoms but not for H-bridged B atoms. A stepwise procedure for deducing structures from 2D-spectra was presented.

Previously unobserved long- and short-range spin couplings have been reported for 2,4-$C_2B_5H_7$ and some derivatives thereof.[34] Using resolution enhanced $^1H\{^{10}B,^{11}B\}$ data, more accurate *J* and δ values were obtained. Boron coupled *conjuncto*-carbaboranes were studied with ^{10}B and ^{11}B n.m.r. spectroscopy.[35] Values of $J^{11}_B{}^{11}_B$ were reported (between ~79 to 151Hz) and used to estimate the sp-hybridisation at the *conjuncto* B atoms. Intracage B-B spin coupling was also discussed. The ^{11}B quadrupole coupling constants for 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ have been measured.[36] An attempt to calculate these and related assymmetry parameters

using an X_α-SCF procedure was unsuccessful.

Reversible cage rearrangements of $R_4C_4B_8H_8$ (R = Me, Et, Pr^n) have been studied by ^1H, ^{11}B, and ^{13}C n.m.r. spectroscopy.[37] Each compound exists in solution as a mixture of isomers (6) and (7), Scheme 2. Values of ΔH and ΔS were calculated for the rearrangements from variable temperature experiments. In the solid state compound R=Me exists as (6), whilst R=Et is (7). The propyl compound apparently takes both (6) and (7) forms in the solid. The *X*-ray diffraction study of R=Et was reported.

An *X*-ray diffraction analysis of $Li[1\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}][MeN(CH_2CH_2NMe_2)_2]$ revealed a tetracoordinated lithium atom with a formal single Li-C bond.[38] The crystallographic study of $8\text{-}(Me_2S)\text{-}7,9\text{-}C_2B_9H_{11}$ has been reported.[39]

Raman spectra of 1,2-, 1,12-$C_2B_{10}H_{12}$ and 1,10-$C_2B_8H_{10}$ were studied.[40]

The use of carbaboranes to form B-containing epitaxial films,[41] or as ion conductors for transportation of large ions across lipid membranes was noted.[42]

The application of chromatographic techniques (t.l.c., m.p.l.c.) for separation of carbaborane monoanions was described.[43] Several of the ions studied were suitable for attachment to monoclonal antibodies for subsequent use in ^{10}B neutron capture therapy. A number of reports have dealt with aspects of this therapy.[44]

3 σ-Bonded Metallacarbaboranes

Work in this area has again mainly concerned the preparation and reactions of B- and C- mercurated $C_2B_{10}H_{12}$ derivatives. Reaction of $[HgBr_4]^{2-}$ with $1\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11}$ gave C-bonded. bis(carbaboranyl) compounds.[45] The synthesis of 9-B-bonded compounds from $9\text{-}Tl(CO_2CF_3)_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ and Hg,[46] and a 9-HgCl derivative of $[3\text{-}(\eta^5\text{-}Cp)\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$ were reported.[47] Reactions of B-bonded Hg derivatives with tin(II)bisacetylacetonate ,[48a] and digermanium reagents[48b] afforded compounds with B-Hg-Sn-B, B-Hg-Ge, and Ge-Hg-B-B-Hg-Ge bonds. Insertion of $(Ph_3P)_2Pt$-units into the Hg-Ge bonds was reported.[48b] Mercury reagents were used to prepare B- and C- bonded derivatives of the lanthanides Sm, Tm, Yb,[49a,b] and La.[49a] Other C-bonded lanthanide (Sm, Eu, Yb) derivatives RLnI were prepared from C-lithium carbaboranes and LnI_2, or C-iodocarbaboranes and Ln.[50a] Divalent Yb compounds were formed by reaction of $1\text{-}PhC_2B_{10}H_{11}$ and organoytterbium iodides.[50b]

The synthesis of σ B-Fe bonded 9-[(η^5-Cp)Fe(CO)$_2$]-1,2-$C_2B_{10}H_{11}$ and a corresponding 1,7-derivative were reported.[51] Reaction with Br_2 converted these into compounds with a (η^5-C_5H_4)FeBr(CO)$_2$-unit attached to the carbaborane (σ-B-C) via the cyclopentadienyl ring.

Reaction of [6,9-$C_2B_6H_{10}$]$^{2-}$ with the Pt or Ni complexes [MCl_2L_2] affords [μ-6,9-(ML_2)-6,9,-$C_2B_8H_{10}$].[21] The ML_2-group was considered to be a bridging rather than cluster unit on the evidence of an *X*-ray diffraction study.

A kinetic and mechanistic study of the reductive elimination of carbaborane from [Ir(H)Cl(7-Ph-1,7-$C_2B_{10}H_{10}$)(CO)(Ph_3P)$_2$] implied a preliminary dissociation of Ph_3P to give a five coordinate intermediate.[52a] This reacted by either direct elimination, or phosphine induced isomerisation then elimination. A similar study of the elimination of succinic anhydride from a related compound was reported.[52b]

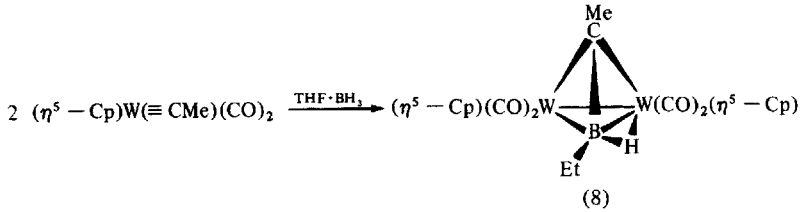
4 Cage Metallacarbaboranes

Discussion of these compounds in two sections. The first deals with reports emphasising synthesis and characterisation of novel compounds, the second concerns compounds of special interest in catalysis.

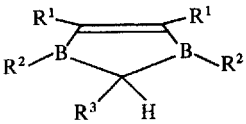
4.1. Compounds in this section are discussed in order of increasing complexity of the carbaborane unit.

The simplest "metallacarbaborane" reported was obtained from reaction of a BH_3 fragment with two[(η^5-Cp)W(≡CMe)(CO)$_2$] molecules.[53] The structure as established by an *X*-ray diffraction study contained a tetrahedral W_2CB-core, (8), (Scheme 3).

C-Trimethylsilylstannacarbaboranes, 2-(Me_3Si)-3-R-1,2,3-$SnC_2B_4H_4$ (R = H or Me_3Si,[54a] and Me[54]), were prepared by reaction of $SnCl_2$ with Na[(Me_3Si)R$C_2B_4H_5$]. Characterisation included ^1H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn n.m.r., and ^{119m}Sn Mossbauer spectra .[54] An *X*-ray crystallographic study of the 3-Me compound confirmed the stereochemistry. Other C_2B_4-compounds included *closo* [1,1,1-(CO)$_3$-2,3-(Me_3Si)$_2$-1,2,3-$OsC_2B_4H_4$], produced by reaction of either 2,3-(Me_3Si)$_2$-1,2,3-$SnC_2B_4H_4$ or 2,3-(Me_3Si)$_2$-2,3-$C_2B_4H_6$ with [Os_3(CO)$_{12}$],[55] and η^8-C_8H_8M (M = Ti or V), or η^7-C_7H_7Cr derivatives of $Et_2C_2B_4H_4$.[56] The latter compounds were all prepared by reaction of MCl_3 with K_2[C_8H_8] and Na[$Et_2C_2B_4H_5$] in THF.[56] *X*-ray crystallographic studies of the Ti, V, and Cr compounds showed *closo* MC_2B_4 pentagonal bipyramidal cages and planar C_nH_n ligands.

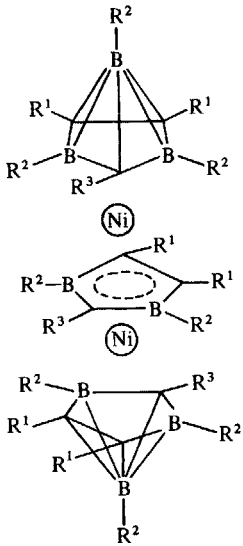


Scheme 3



(9)

	R^1	R^2	R^3
(i)	Et	Et	Me
(ii)	Et	Me	H
(iii)	Me	Me	H



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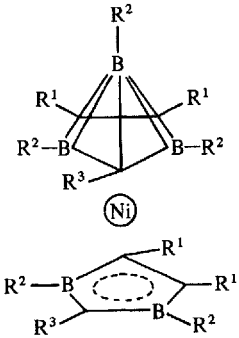

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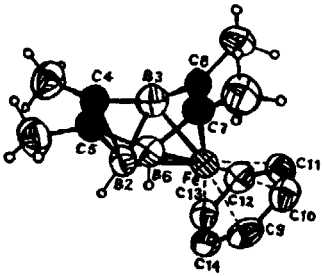


(13)

Figure 1. [1-(η^6-C_6Me_6)-4,5,7,8-Me_4-1,4,5,7,8-$FeC_4B_3H_3$] showing the cage structure and Fe-C_6 fragment. (Reproduced with permission from *Organometallics*, 1984, 3, 1396).

The air-stable, paramagnetic, chromium compound was the first reported (tropylium)-metal(carbaborane) sandwich complex.

Both C_3B_2- and C_3B_3-based systems have been used to construct multidecker sandwich compounds.[57] Reaction of bis(allyl) nickel and (9) unexpectedly produced (10), (11), and [Ni(11)$_2$]. One of the paramagnetic compounds (10), (R^1 = Et, R^2 = Me, R^3 = H), was structurally characterised by an *X*-ray diffraction study.

Thermally generated iron atoms reacted with B_5H_9, but-2-yne, and toluene to give [1-(η^6-C_6Me_6)-2,3-Me_2-1,2,3,-$FeC_2B_4H_4$] (12) as the major product and smaller amounts of carbon rich C_4-species [1-(η^6-arene)-4,5,7,8-Me_4-1,4,5,7,8-$FeC_4B_3H_3$] (arene = C_6Me_6 (13) or toluene), and *nido* - [2-(η^6-PhMe)-6,7,9,10-Me_4-2,6,7,9,10-$FeC_4B_5H_5$] (14).[58] Ethylcarbaborane analogues of (12) had been previously prepared from $Et_2C_2B_4H_4$. *X*-ray diffraction studies showed that (14) was an analogue of decaborane and (13) contained an *arachno*-cage with Fe bonded to two C and three B atoms, (Figure 1). The bond between the remaining two C atoms was remarkably short (1.392Å) implying some multiple bond character.

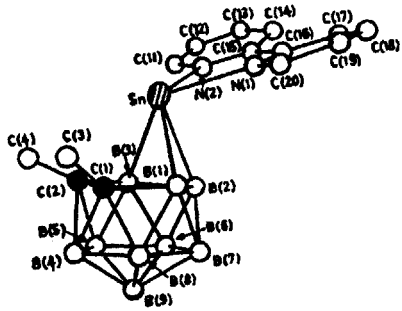
An *X*-ray diffraction study of [6,7-(η^5-Cp)$_2$-1,6,7-$CNi_2B_7H_8$], a minor paramagnetic product from the reaction of nickelocene and Na[CB_8H_{13}], has confirmed its bicapped square antiprism structure.[59]

A crystallographic analysis of [9,9-$(Ph_3P)_2$-7,8,9-$C_2RhB_8H_{11}$] has shown the $(Ph_3P)_2$Rh-unit to be part of an open $\overline{RhC_2}BB$ face containing a B-H-B bridge.[60]

The stannacarbaborane $Sn(Me)_2C_2B_9H_9$, obtained from $SnCl_2$ and $Na_2[(Me)_2C_2B_9H_9]$, was reacted with 2,2'-bipyridine to give the compound (15), (Figure 2), in which the Sn atom bonds exclusively to the three B atoms of the open face.[54b]

Reaction of Na_2[7,8-$(Me)_2C_2B_9H_9$ with [W(≡CR)Br$(CO)_4$] (R = 4-Me C_6H_4) produced the carbyne complex [W(≡CR)$(CO)_2$(η^5-1,2-$(Me)_2C_2B_9H_9$)]. Further reaction with [RhCl$(Ph_3P)_3$], [Rh$(Ph_3P)_2$(diene)] BF_4 (diene = cod or norbornadiene, nbd) or [AuCl(Ph_3P)] afforded μ-CR-bridged complexes with tungsten-rhodium or tungsten-gold bonds.[61] The W-carbaborane cage bonding remained essentially unaffected in all compounds. However the Rh-(nbd)-complex had reacted unexpectedly in that the product was a B-bonded nortricyclane derivative, (Figure 3). Presumably addition of the diene across a B-H bond had occured with concomitant C-C bond formation.

Reactions of a vinyl carbocation stabilised by bonding to the 1-C atom of a [3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{10}$]$^-$-unit have been reported.[62] The zwitterion was prepared by protonation of the



(15)

Figure 2. Structure of [{bipy)Sn]$C_2Me_2B_9H_9$]

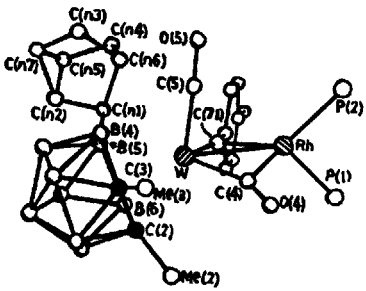


Figure 3. Structure of B-nortricyclane derivative produced in reaction of [W(≡CR)(CO)$_2$(η^5-1,2-(Me)$_2$C$_2$B$_9$H$_9$)] and [Rh(Ph$_3$P)$_2$(nbd)]BF$_4$.

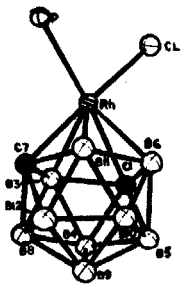


Figure 4. Cage structure of *closo*-[2-(Ph$_3$P)-2-Cl-2,1,7-RhC$_2$B$_9$H$_{11}$] (Reproduced with permission from *J. Am. Chem. Soc.*, 1984, 106, 2965).

corresponding acetylenic derivative. Reaction with MeLi, $NaBH_4$, or pyridine generated acetylene derivatives.

Synthesis of $[Fe(III)(C_2B_9H_{11})_2]^-$ salts by electrolysis of alkaline $[C_2B_9H_{11}]^-$ solutions at an iron anode has been studied.[63] The use of such anions for analysis and characterisation of large cations has been investigated.[64]

An iodonium cage bridged *commo*-complex $[8,8'-\mu-I-3,3'-Co(1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{10})]$ was obtained by reacting $[(8-I-1,2-C_2B_9H_{10})Co(1',2'-C_2B_9H_{11})]^-$ and $AlCl_3$ in benzene.[65] Reaction with Lewis bases cleaved one bridging B-I bond giving $[(8-I-1,2-C_2B_9H_{10})Co(8'-L-1',2'-C_2B_9H_{10})]$. Related complexes were obtained from bromonium analogues generated *in situ*.

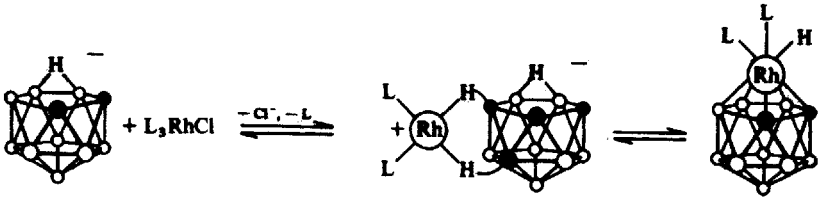
Specific rearrangements of $[3,3-(Ph_3P)_2-3-H-1-(R)-3,1,2-IrC_2B_9H_{10}]$ in refluxing toluene to $[2,2-(Ph_3P)_2-2-H-8-(R)-2,1,8-IrC_2B_9H_{10}]$ isomers (R = Me, Ph) have been reported.[66] The (R=H) complex apparently did not rearrange under these conditions. The structure of the phenyl derivative was established by an *X*-ray crystallographic analysis. Reaction of $[Ir(Ph_3P)_2(cod)][7:1'-(1',2'-C_2B_{10}H_{11})-7,8-C_2B_9H_{11}]$ in refluxing *cyclo*hexane gave the corresponding (R = $C_2B_{10}H_{11}$) 2,1,8-$IrC_2B_9H_{10}$-isomer directly. Technical reports concerning this work,[67a] previous work on a dimeric rhodacarbaborane derived from $B_{10}H_{12}CNH_3$,[67b] and rearrangement reactions of some nickelacarbaboranes have been published.[67c]

4.2. Studies of Catalytically Active Compounds. - Almost all the work discussed below is due to the group directed by M.F. Hawthorne and concerns rhodacarbaboranes.[68-74] In an extensive series of papers this group has described the synthesis, characterisation, and reactions of catalyst precursors and examined the kinetics and proposed mechanisms for some alkene isomerisations and hydrogenations. Initial work began with the reaction of $[RhCl(Ph_3P)_3]$ and various isomeric *nido* $[R^1R^2C_2B_9H_{10}]^-$ anions affording a large variety of R^1,R^2-substituted isomeric, *closo*-$\{[Rh(H)(Ph_3P)_2](R^1,R^2)C_2B_9H_9\}$ complexes.[68] Numerous 3,1,2-, 2,1,7-, and 2,1,12-RhC_2-isomers were prepared. Deuterium labelling of the bridging B-H-B in the carbaborane anion established that the H transfer to Rh was regiospecific. Displacement of Ph_3P ligands by more basic Et_3P or Me_2PhP occured in the unsubstituted (R^1=R^2=H) 3,1,2- and 2,1,7-isomers. Replacement of Rh(H) by Rh(Cl) in the unsubstituted 3,1,2-isomer was achieved by reaction with $HCl/CHCl_3$ (L = Ph_3P) or CH_2Cl_2 (L = Me_2PhP). For the 2,1,7-isomer (L = Ph_3P),

reaction with $HCl/CHCl_3$ produced the unusual 16-electron species *closo* [2-(Ph_3P)-2-Cl-2,1,7-$RhC_2B_9H_{11}$] which was characterised by an *X*-ray diffraction study, (**Figure** 4). The metallocarbaborane cage appeared relatively unaffected suggesting that the electron deficiency was metal and not cluster centred. This complex readily added a variety of $2e^-$ donor ligands and some reactions, e.g. with CO, were reversible. The chiral compound *d-closo* [3,3-$(Ph_3P)_2$-3-H-1-Me-3,1,2-$RhC_2B_9H_{10}$] reacted with certain acrylic esters to displace Ph_3P and H ligands and afford chelated Rh systems with [$(Ph_3P)RhCH_2CH_2C(OR')O$]-units. The n-butyl acrylate derivative was characterised crystallographically. In the single case of the 1-Bu^n substituted - 3,1,2-complex a polytopal rearrangement (in refluxing THF) to the 8-Bu^n-2,1,8-isomer was reported. All the above *closo* compounds were catalytically active in alkene isomerisation and hydrogenation reactions.[68]

The existence of a *closo—exo-nido* equilibrium in solution (Scheme 4) was observed for a number of compounds including [3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_9R^1R^2$] for R^1R^2 = Me_2 (16) or μ-1',2'-$CH_2C_6H_4CH_2$ (17).[69] *Exo-nido* complexes could be regarded as $[L_2Rh]^+$ units and carbaborane ions interacting *via* two *exo*-polyhedral Rh-H-B bonds. N.m.r. spectroscopic evidence showed that in some cases the rhodium unit could apparently migrate to other positions on the polyhedral cage. Reaction of *exo-nido* $(Ph_3P)_2Rh$-compounds with strong σ-donors or CO gave ionic species containing four coordinate $[L_4Rh]^+$, or five coordinate $[L_2Rh(CO)_3]^+$ units. Refluxing $[(Et_3P)_4Rh]^+$ complexes in benzene generated *closo* [$(Et_3P)_2Rh(H)C_2B_9H_9R^1R^2$] compounds. Both 3,1,2- and 2,1,8-products were obtained depending on the R^1 and R^2 substituents. Oxidative addition of H_2 to *exo-nido* compounds gave complexes with $[L_2Rh(H)_2]^+$-units still bonded *via* two Rh-H-B bonds to the carbaborane anion.[69] Not surprisingly, the *exo-nido* complexes were precursors to catalytically active species.

X-ray diffraction studies established the molecular structures of *closo* [3,3-$(Ph_3P)_2$-3-H-1,2-μ-(1',2'-$CH_2C_6H_4CH_2$-)-3,1,2-$RhC_2B_9H_9$] (18, Figure 5), the related *exo-nido* derivative {[6,10-(Ph_3P)-$(R_3P)Rh$]-6,10-μ-$(H)_2$-7,8-μ-(1',2'-$CH_2C_6H_4CH_2$-)-10,11-μ-H-7,8-$C_2B_9H_7$} (Figure 6, R = *cyclo*hexyl) formed from (18) by replacement of one Ph_3P ligand by R_3P, *exo-nido* {4,9-[$(Ph_3P)_2Rh$]-4,9-μ-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$} (19), and *closo* [2,2-$(Et_3P)_2$-2-H-1-Me-8-Ph-2,1,8-$RhC_2B_9H_9$], formed by rearrangement of (19) in refluxing THF in



Scheme 4

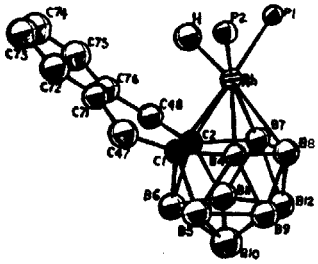


Figure 5. Cage structure of *closo*-[3,3-$(Ph_3P)_2$-3-H-1,2-μ-(1',2'-$CH_2C_6H_4CH_2$-)-3,1,2-$RhC_2B_9H_9$]. (Reproduced with permission from *J. Am. Chem. Soc.*, 1984, 106, 2990).

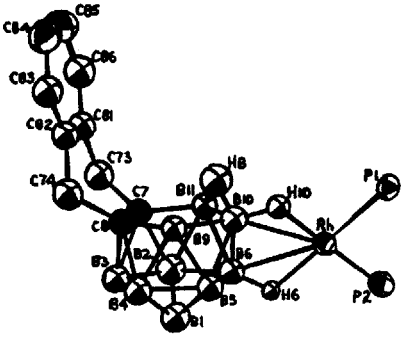
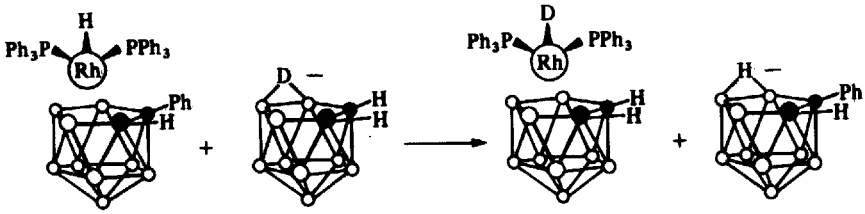


Figure 6. Cage structure of *exo-nido* {[6,10-$(Ph_3P)(R_3P)Rh$]-6,10-μ$(H)_2$-7,8-μ-(1',2'-$CH_2C_6H_4CH_2$-)-10,11-μ-H-7,8-$C_2B_9H_7$}, (R = *cyclo*hexyl). (Reproduced with permission from *J. Chem. Soc.*, 1984, 106, 2990).



Scheme 5

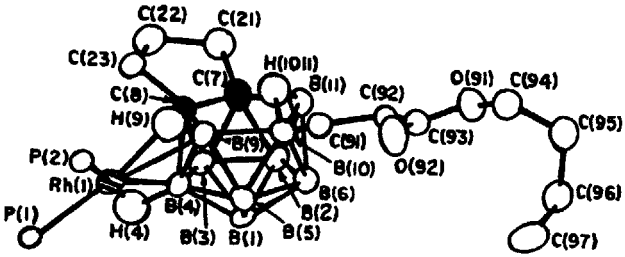


Figure 7. Cage structure of *exo-nido* {[4,9-$(Ph_3P)_2Rh$]-4,9-μ$(H)_2$-7,8-μ-$(CH_2)_3$-10,11-μ-H-10-[$CH_2CH_2C(OBu)O$]-7,8-$C_2B_9H_6$}. (Reproduced with permission from *J. Am. Chem. Soc.*, 1984, 106, 5757).

the presence of excess Et_3P.[70] The molecular structure of the salt $[Rh(Ph_3P)_3][nido\text{-}7\text{-}R\text{-}7,8\text{-}C_2B_9H_{11}]$, {R = 1'-{1',2'-$C_2B_{10}H_{11}$)} was also analysed. In general the overall geometries of the cage systems were not unusual. The *closo* compound (18, Figure 5) showed a P_2RhH-carbaborane conformation which was determined by steric interactions between the *exo*-σ-xylyene group and the $(Ph_3P)_2$ Rh-unit. Relief of this interaction in the *exo-nido* complex (Figure 6) led to a significant change in the orientation of the *exo*-σ-xylylene group with respect to the C_2B_3 face.[70]

An unusual property of *closo—exo-nido* complexes was their ability to exchange carbaborane units (Scheme 5).[71] The ease of displacement of the *nido*-carbaborane anions from *closo*-Rh-complexes was 7,8-R^1R^2 > 7,8-R,H > 7,8-$(H)_2$ > 7,9-$(H)_2$ ~ 2,9-$(H)_2$. A similar R^1,R^2 > $(H)_2$ sequence was observed with *exo-nido*-complexes. Kinetic studies showed the latter reactions to be much faster. A mechanism was suggested which involved an unobserved, possibly singly RH-H-B bridged, *exo-nido* intermediate.[71]

The kinetics and mechanisms of the catalytic hydrogenations of hex-1-ene, 3-methyl-3-phenylbut-1-ene,[72] and 1-butyl acrylate,[73] and the isomerisations of the alkenes have been studied.[72] The 3,1,2-, 2,1,7-, and 2,1,12-isomers of *closo* $\{[(Ph_3P)_2Rh(H)]C_2B_9H_{11}\}$ and *exo-nido* $[(Ph_3P)_2Rh\text{-}\mu\text{-}7,8\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$ complexes were used as catalyst precursors.[72,73] Rate laws were established for the alkene reactions. The use of deuterium labelled reagents proved that the Rh-hydride ligand was not directly involved in reactions with the *closo*-complexes. A comparison of results from *closo* and *exo-nido* precursors led to the suggestion that a common *exo-nido* (R_3P) Rh(alkene)-intermediate was involved. Isomerisation reactions were thought to proceed *via* further η^3-allylic-Rh intermediates whereas hydrogenation appeared to involve addition of H_2 followed by a rate determining decomposition of an (H)Rh (alkyl)-species.[72] The kinetics of the hydrogenation of 1-butyl acrylate were studied in detail for catalysts derived from 3,1,2- and 2,1,12-*closo* isomers.[73] Results were in general similar, with respect to non-involvement of Rh-H and the rate law, to those from the hydrogenation of 3-methyl-3-phenylbut-1-ene and an *exo-nido* (H)Rh(alkyl)-intermediate was suggested.[73]

The reaction of 1-butyl acrylate with *exo-nido*-$[(Ph_3P)_2Rh\text{-}\mu\text{-}7,8\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$ produced a (10)B-$CH_2CH_2C(OBu)O$-containing complex which was characterised by an *X*-ray diffraction study, (Figure 7).[74]

The participation of the Rh atom was proposed since the carbaborane anion did not react with the ester itself, but the B[10] substitution reaction was catalysed by addition of the Rh complex.

Activation of CO *via closo* [3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$] has been reported.[75] Reaction with $[OH]^-$ gave a $[Ru(H)(CO)_2]$-containing complex with loss of CO_2. Acidification with CF_3CO_2H produced a $[Ru(CF_3CO_2)(CO)_2]$-species which further reacted with CO to afford the original complex. Reactions of the $[Ru(CO)_3]$-complex with other nucleophiles (KOH/MeOH, MeLi, $K[BBu^s{}_3H]$) were studied.[75]

The hydrogenation and isomerisation of unsaturated hydrocarbons by rhodium complexes of phosphinocarbaboranes attached to polymers has been reported.[76]

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5

Group III: Aluminium, Gallium, Indium and Thallium

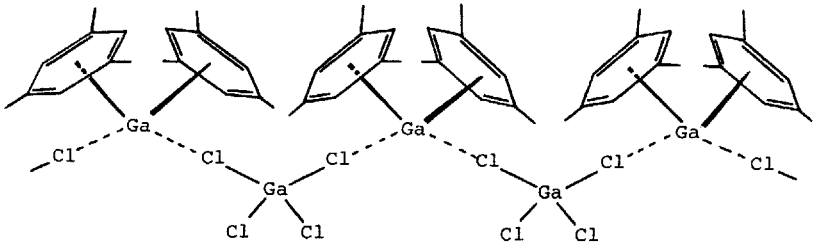
BY P. G. HARRISON

1 Synthesis, Structure and Bonding

Aluminium dicarbonyl, $Al(CO)_2$, has been generated in an argon matrix by co-condensation of aluminium atoms and carbon monoxide. The molecule has a bent OC-Al-CO structure with a semifilled orbital representing the back-donation from the aluminium p_π orbital into the antibonding π^* orbitals of the CO moiety.[1]

Solutions of $Ga[GaCl_4]$ in hot 1,3,5-trimethylbenzene yield crystals of the bis-arene complex, $[C_6H_3Me_3]_2Ga^+GaCl_4^-$, on cooling. In the solid, the material possesses a chain-like coordination polymer in which the $Ge^{III}Cl_4^-$ tetrahedra are linked via one chlorine atom to the Ga^+ centres of two $[C_6H_3Me_3]_2Ga^+$ moieties as in **I**. The Ga^I cation is situated above the centres of both mesitylene rings, which are mutually inclined at an angle of 39.7°. The metal-centre of ring distance is 2.673Å for each. In solution, the dinuclear species **II** is formed.[2] Similarly, suspensions of Ga_2X_4 (X = Cl,Br) in anhydrous toluene become clear upon addition of excess hexamethylbenzene and heating to 80-90°C, and afford colourless crystals of the mono-arene complexes **III**. X-ray analysis of **III** (X = Br) show it to comprise a three-dimensional, polycoordinated network composed of $Me_6C_6Ga^+$ cations and $GaBr_4^-$ anions. In the cation, the Ga^I is situated 2.552Å vertically above the centroid of the $[C_6]$ ring. Additional coordination arises from five bromine atoms originating from three different $GaBr_4$ tetrahedra. The arene ligand is distinctly non-planar.[3] Analogous procedures have also been employed to synthesise the first such arene-indium complex, **IV**, which is susceptible to loss of part of its arene content, particularly on reducing the pressure. In the crystal, this compound is a helical chain coordination polymer, with the tetrabromoindate(III) anions functioning as a unidentate bridge to a bis(arene)indium(I) unit on one side and a chelating group on the other. The two mesitylene rings are mutually inclined at an angle of 47.3°, and again the

[For References see page 77


Ga
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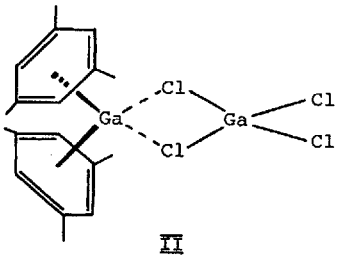
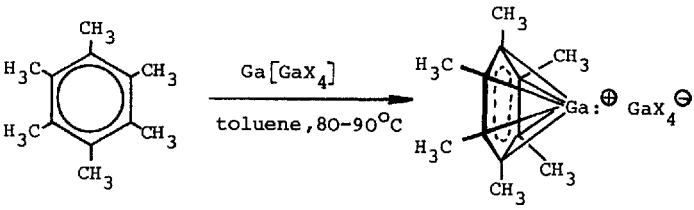
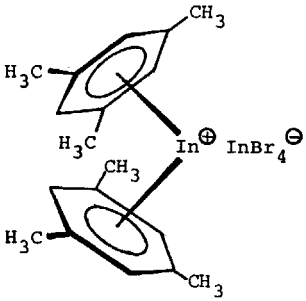
I


Ga
Cl
Cl
Ga
Cl
Cl

II


CH3
H3C
CH3
H3C
CH3
CH3
Ga[GaX4]
toluene, 80-90°C
CH3
H3C
CH3
Ga:⊕ GaX4⊖
H3C
CH3
CH3

III


CH3
H3C
H3C
In⊕ InBr4⊖
CH3
H3C
CH3

IV

metal lies above the centroid of each ring at about the same distance. The complexes, $[1,3,5\text{-}C_6H_3Me_3]_2In^+AlBr_4^-$ and $[C_6Me_6]In^+InBr_4^-$, were also reported to have been obtained, but no adducts with benzene (cf. $[(C_6H_6)_2Ga]GaCl_4$ [2]) could be isolated.[4] The structures of monomeric C_5H_5M (M = In, Tl) have been optimized with an SCF pseudopotential method with a double-ζ basis set, giving good agreement with experimental data. The bonding between the metal and the cyclopentadienyl ring has a large covalent component, although the influence of d orbitals on thallium is negligible. The zig-zag structure of the polymer is due to a minimization of repulsive factors, and can also be explained by polyhedral skeletal electron pair counting rules.[5]

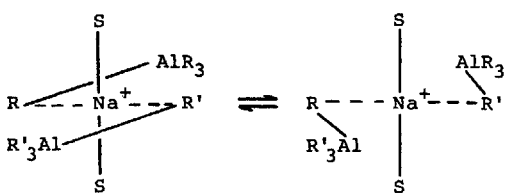
Monomeric Me_3Al has been isolated in an argon matrix by the Knudsen effusion technique.[6] The effect of ultrasonic irradiation on the synthesis of organoaluminium compounds has been examined. Reaction of aluminium with mono- and polyhaloalkanes, -alkenes, and cycloalkynes only occurs if the aluminium has been previously irradiated ultrasonically. Thus, treating aluminium so activated with $MeCH{=}CHCH_2Br$ in dioxane affords $(CH_2{=}CHCHMe)_3Al_2Br_3$ in 73% yield.[7] Me_2ClAl and $EtCl_2Al$ may be manufactured simultaneously by reacting MeCl, EtCl and aluminium (or its alloy) in a 2:1:2 molar ratio at $\leqslant 60^\circ$ in the presence of 2% iodine as catalyst. The resulting $Me_2Al_2Cl_3$-$Et_3Al_2Cl_3$ mixture was obtained in 95% yield, which could then be distilled *in vacuo* to afford the two separate products.[8] Available vapour pressure data for trialkylaluminium and alkylaluminium chloride compounds have been employed to determine the constants for the Antoine equation relating vapour pressure and temperature for each compound. From these, quatities such as cohesion energies, solubility parameters, Van der Waal's constants, and effective molecular radii have been calculated, leading to estimates of the extent of molecular association in the liquid and vapour phases.[9] A Japanese paper reports the influence of ethereal solvents on the formation of trimethylgallium from gallium metal, methylmagnesium iodide, and methyl iodide.[10] Tris(trifluoromethyl)-thallium, $Tl(CF_3)_3$, as well as other less well defined trifluoromethyl-Group III compounds such as $Tl(CF_3)(C_2F_5)_2$, $Tl(CF_3)_2(C_2F_5)$ and $Tl(CF_3)(C_2F_5)(C_3F_7)$, have been prepared by condensing metal atoms with trifluoromethyl radicals on a cryogenic surface.[11] Evidence for a "through-space" coupling between thallium and hydrogen in some *o*-alkylphenylthallium compounds has been reported. The effect is greatest for tert-butylphenyl derivatives.[12]

Several papers report the preparation and structural characterisation of neutral and ionic adduct species. The electrolysis of dimethylmagnesium in tetrahydrofuran with a gallium electrode gives the adduct $GaMe_3$.thf directly, whereas the trialkylamine and trialkylphosphine adducts $GaMe_3$.L (L = NEt_3, PMe_3 or PEt_3) may be obtained by the addition of an excess of the Group V donor to $GaMe_3$.thf. Reaction of a Ga-Mg alloy with methyl iodide in an ether solvent yields free $GaMe_3$.[13] Similarly, electrolysis of methylmagnesium chloride or dimethylmagnesium in tetrahydrofuran using an indium anode affords the adduct $InMe_3$.thf (characterised spectroscopically), which may be converted to the adducts $InMe_3$.L in the same way.[14] The complexes, $[TlR_3(diox)]$ (diox = 1,4-dioxan), have been prepared by the reaction of thallium(III) chloride with LiR (R = 2,4,6-$C_6F_3H_2$), or of $[NBu_4][TlR_4]$ with HBF_4 (R = C_6F_5) and subsequent addition of dioxan. The displacement of dioxane takes place readily with other neutral and anionic ligands to give the complexes TlR_3.L (L = $OPPh_3$, pyridine, PPh_3, $Ph_2PCH_2PPh_2$) or salts $\phi[TlR_3X]$ {ϕ = $[NBu_4]^+$ or $[N(PPh_3)_2]^+$; X = Cl^-, CN^-, NO_3^-, or $CF_3CO_2^-$, and with metal carbonylates affording $\phi[TlR_3M^*]$ M* = $[Mo(Cp)(CO)_3]^-$, $[W(Cp)(CO)_3]^-$, $[Co(CO)_4]^-$ or $[Mn(CO)_5]^-$} species.[15] The structure of the gaseous trimethylamine-gallane molecule, $Me_3N.GaH_3$, has been determined by electron diffraction (Ga-N = 2.124(7)Å).[16]

Triethyl-, triisobutyl-, and tri-n-hexylaluminium form complexes with monoglyme, diglyme, and triglyme in which the alkylaluminium compounds are involved in rapid chemical exchange. The monoglyme complexes undergo little, or no, measurable dissociation, whereas in those of diglyme and triglyme dissociation is more extensive. Low temperature studies of the triethylaluminium-diglyme complex in cyclopentane in the presence of excess triethylaluminium yield a value of 6.1 kcal. mol^{-1} for the activation energy for the exchange of complexed and free triethylaluminium, the low value suggesting a bimolecular displacement mechanism rather than a simple bond-breaking dissociation process.[17] The trimethylaluminium-crown complexes, (dibenzo-18-crown-6)tris(trimethylaluminium) and (18-crown-6)tetrakis(trimethylaluminium) have been prepared by adding trimethylaluminium to a suspension of the appropriate crown in toluene. The materials are extremely air-sensitive.[18] KCl does not react with trimethylaluminium in benzene in the absence of a crown ether, but upon addition of dibenzo-18-crown-6 a normal liquid clathrate ensues, from which the crystalline salt, [K(dibenzo-18-

crown-6)] $[Al_2Me_5Cl].2C_6H_6$, was isolated.[19] The analogous nitrate salt, [K(dibenzo-18-crown-6)] $[AlMe_3NO_3].0{\cdot}5C_6H_6$, was obtained analogously.[20] Crystal structures of all four complexes have been reported. The $[Al_2Me_5Cl]^-$ and $[AlMe_3NO_3]^-$ anions have the expected geometries.

The stable cationic iron(II) complex, $[Fe(dmpe)_2(acac)]^+[AlMe_4]^-$ (dmpe = 1,2-bis(dimethylphosphinoethane; acac = 2,4-pentanedionato ligand) has been prepared by the reaction of $Fe^{III}(acac)_3$ with trimethylaluminium in the presence of the phosphine. The tetramethylaluminate anion was considered to be formed by a methyl back-transfer reaction from iron to aluminium.[21] Alkyl exchange takes place when $NaAlMe_4$ and $NaAlEt_4$ are mixed in benzene solution containing hexamethylphosphotriamide resulting in a statistical distribution of alkylaluminate anions. Pseudo first-order rate constants for the exchange are a function of the HMPA/Na^+ mole ratio, decreasing essentially to zero in pure HMPA. The reactions are interpreted as occurring in contact ion pairs in which two aluminate anions occupy coordination sites on the same Na^+ cation, viz:

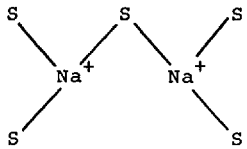


S = HMPA

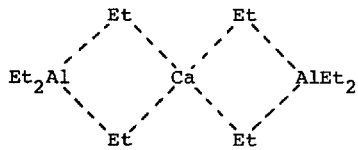
The large decrease in exchange rate occurring at an HMPA/Na^+ of 2.5 is proposed to be due to the formation of a solvent-bridged species **V** of stoichiometry $[2Na.5HMPA]^{2+}$.[22]

Calcium bis(tetramethylalanate) exists as an equilibrium of the ionic form, $Ca^{2+}[AlEt_4]_2^-$, and the trinuclear form, **VI**. Mixtures of dibutylmagnesium and triethylaluminium contain the alkyl-bridged species, **VII** and **VIII**, where R = Et or Bu.[23]

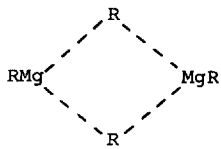
Anionic aluminates of the type $[Me_xAl(CHPMe_2)_{4-x}]^-$ have been synthesised according to scheme 1. The reaction of **IX** with MeLi does not yield the expected aluminate, but rather **X** and **XI** are formed via a disproportionation reaction. Complex **XII** is also unstable with respect to disproportionation, solutions decomposing to **X** and $[(tmeda)_2Li]^+[AlMe_4]^-$ over a few days. Complexes **X** and **XII** may be isolated as colourless, crystalline solids from donor solvents such



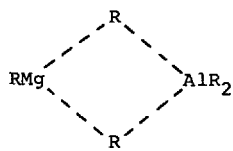
V



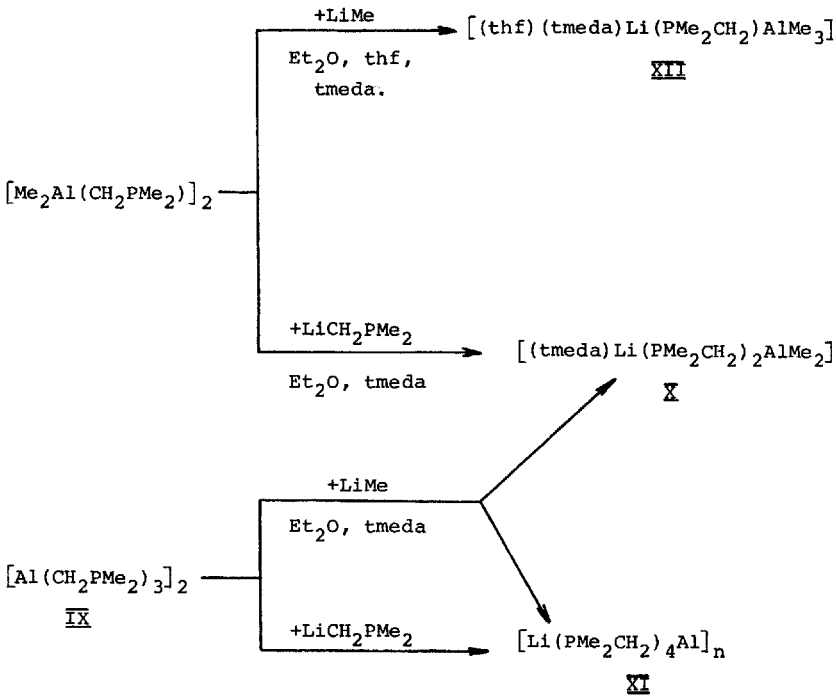
VI



VII



VIII



Scheme 1

as thf or tmeda, whereas XI is a sparingly soluble white powder. Coordination modes XIII, XIV and XV were proposed for XII, X, and XI, respectively, the structure of X being determined crystallographically (Fig. 1).[24]

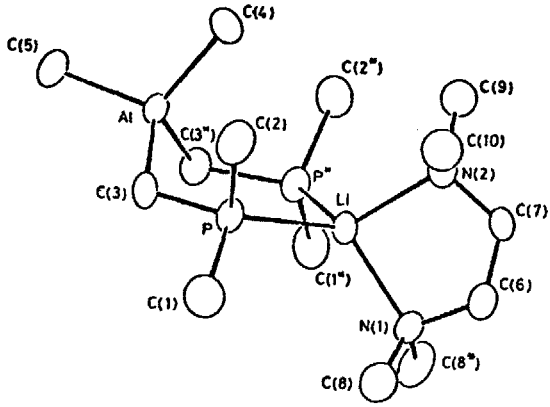
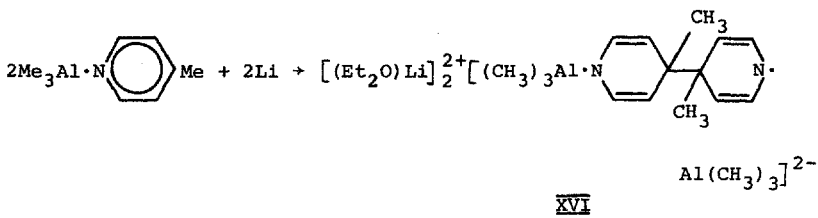


Figure 1. Molecular structure of $[(tmeda)Li(PMe_2CH_2)_2AlMe_2]$ (reproduced from ref. 24)

Treatment of $Ga(CH_2SiMe_3)_2Br$ with excess KH in dimethoxyethane affords $KGa(CH_2SiMe_3)_2H_2$ (XVI), which, when pure, is thermally stable below 200°. Further reaction of XVI with $Ga(CH_2SiMe_3)_2Br$ in benzene leads to the formation of $Ga(CH_2SiMe_3)_2H$, which readily decomposes at room temperature to gallium metal, hydrogen, and $Ga(CH_2SiMe_3)_3$. The mechanism of the decomposition appears to involve an exchange process leading to $Ga(CH_2SiMe_3)_3$ and unstable GaH_3.[25] Reduction of the trimethylaluminium-γ-picoline complex with two equivalents of lithium affords XVI:

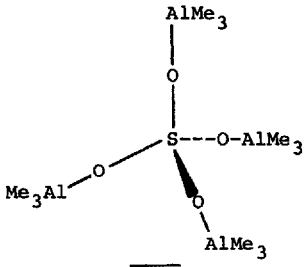


XVI

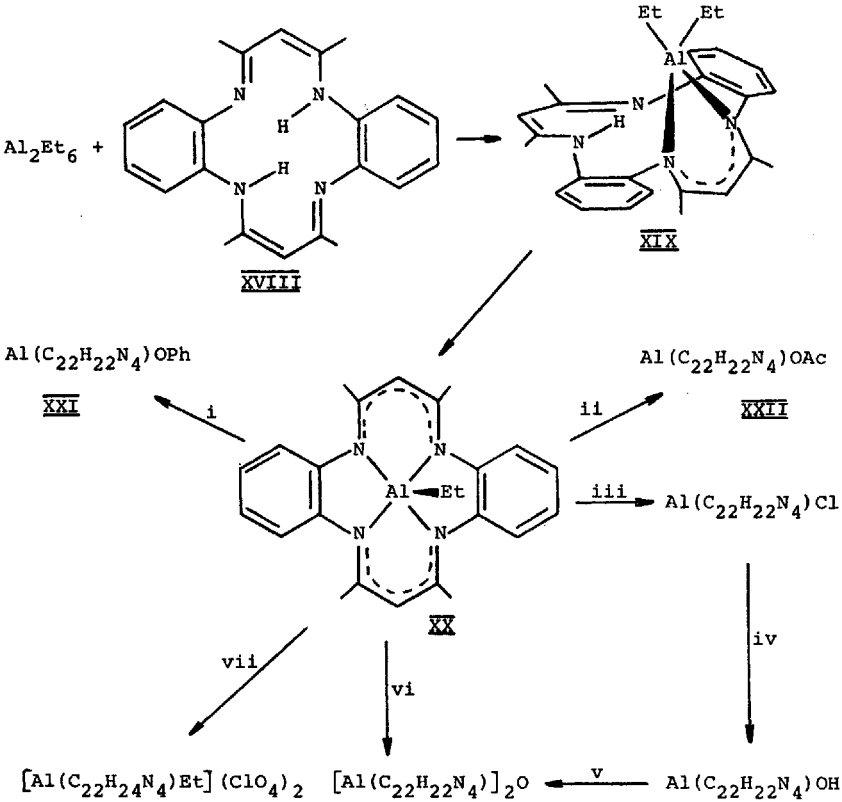
On acid hydrolysis, XVI gives methane and Al(III), but the fate of the organic amine residue was not investigated.[26] Trimethylaluminium reacts with stoichiometric quantities of potassium

sulphate in aromatic solvents to form a liquid clathrate of composition, $K_2[Al_4Me_{12}SO_4]$.n aromatic. With toluene, the value of n = 0, whilst for p-xylene, n = 0.5. In both cases the four $AlMe_3$ units are bonded to separate oxygen atoms of the SO_4^{2-} group as in XVII.[27]

Reaction of Al_2Et_6 with the $C_{22}H_{24}N_4$ macrocycle XVIII in hexane solution results in a two-step insertion reaction, initially producing the partially inserted species XIX. Upon heating to 100°C in the solid state, XIX yields XX and ethane quantitatively. XX is remarkably stable to Al-Et dissociation and resistant to demetallation. No decomposition was observed up to 300°C, or on attempted recrystallisation from hydroxylic or water-containing solvents. Al-C bond cleavage does occur in acidic media, the course of the reaction being dependent on the nature of the acid. Heating XX with phenol or acetic acid produces the corresponding phenolato- or acetato-derivatives, XXI and XXII, respectively. Reaction with HCl instantly produces the de-ethylated and protonated macrocycle complex, $[Al(C_{22}H_{24}N_4)Cl(H_2O)]Cl_2$. Other reactions with light, oxygen, H_2O, and $HClO_4$ are shown in scheme 2. The crystal structure of XIX (Fig. 2) shows it to exhibit a five-coordinate square pyramidal geometry and the usual saddle shape for the macrocyclic ligand. The stability of the Al-C bond appears to be due to kinetic factors.[28] Very similar geometries have also been observed for chlorophthalocyaninato)aluminium(III) and -gallium(III).[29] Crystals of the adduct $MeInCl_2 \cdot H_2NBu^t$ are formed when dimethylbis(t-butylamino)silane is allowed to hydrolyze in the presence of methylindium dichloride. In the solid state, the adduct has a one-dimensional chain structure in which adjacent molecules are held together by N-H---Cl interactions. The indium atom enjoys tetrahedral coordination in which the In-N distance is unusually short (2.21Å).[30] ESCA data has been presented for a large number of organogallium-azole derivatives. No correlations could be found between the ionisation potentials for Ga and N and the structure in the solid state, although the ionicity of the Ga-N bond appears to remain essentially invariant.[31] Bis(tropolonatodimethylgallium), $[(C_7H_5O_2)GaMe_2]_2$, has been synthesised by photolysis of trimethylgallium by tropolone in tetrahydrofuran. In the solid, the compound has a centrosymmetric binuclear structure with five-coordinated gallium atoms in an irregular trigonal bipyramidal coordination and a planar four-membered $[Ga_2O_2]$ ring.[32]



XVII



Scheme 2. Reagents and conditions: i, PhOH; ii, AcOH; iii, hν, $CHCl_3$; iv, H_2O; v, heat, C_6H_6 or PhMe; vi, O_2, 300°C; vii, $HClO_4$

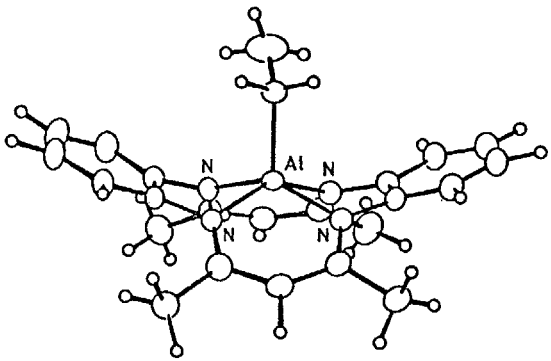
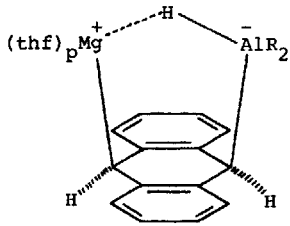


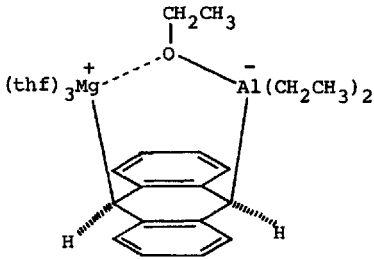
Figure 2 Molecular structure of $Al(C_{22}H_{22}N_4)Et$ (reproduced from ref. 28)

The reactions between $LiAlH_4$ and dimethylmagnesium in diethyl ether and tetrahydrofuran have been studied in detail. In the former solvent, insoluble magnesium hydride is formed over a wide molar ratio of reactants. The soluble products, $LiAlH_nMe_{4-n}$ (n = 0-4), were characterised spectroscopically by comparison with similar products formed by redistribution between $LiAlH_4$ and $LiAlMe_4$. In thf, MeMgH and $LiAlMe_4$ are formed by reaction of Me_2Mg and $LiAlH_4$ in a 4:1 molar ratio, but when a 2:1 ratio was employed, a mixture of $MeMg_2H_3$ and $LiAlMe_3$ was produced. Further addition of $LiAlH_4$ to Me_2Mg in thf produced insoluble MgH_2.[33] The relatively insoluble anthracenemagnesium-thf solvate reacts with dialkylaluminium hydrides or AlH_3 in thf to give magnesium-μ-(9,10-dihydro-9,10-anthrylene)-dialkylhydroaluminates XXIII. The values of the solvation number, p, varies with the alkyl group R from 2.67 to 5. Ethoxydiethylaluminium affords the analogous -ethoxydiethylaluminate derivative XXIV. Crystallographic studies of XXIII (R = Et) show that the aluminium and magnesium atoms occupy axial positions in the 9,10-dihydro-9,10-anthrylene system. The cationic magnesium interacts with the hydride of the aluminate anion. Similar complexes, XXV, with aluminium trialkyls can only be obtained if the anthracenemagnesium·nthf solvate is reacted with (n+1) moles of aluminium trialkyls in a non-Lewis base solvent.[34]

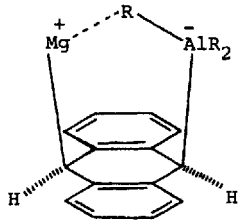
Bimetallic compounds containing aluminium and a transition metal are of interest because of their potential as catalysts, and several novel systems have been investigated. The reaction of trimethylaluminium with a number of bis(cyclopentadienyl)titanium



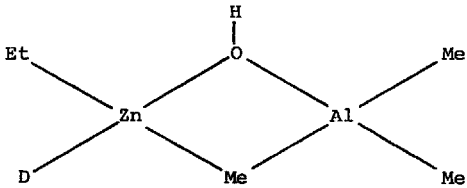
XXIII



XXIV

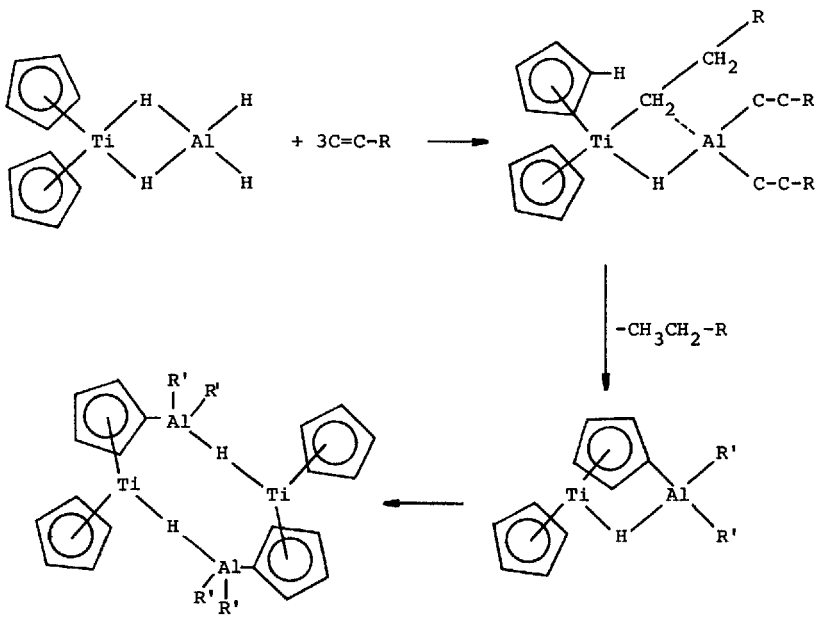


XXV

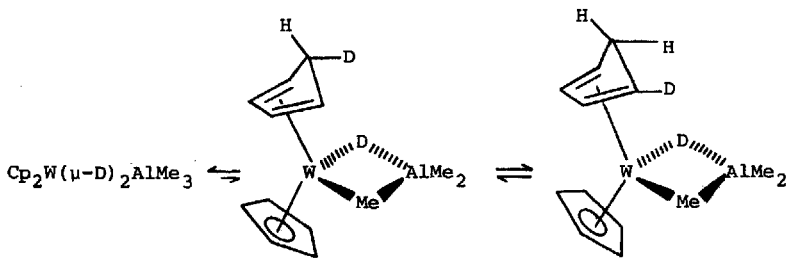


XXVII

dichlorides and related molecules produces complexes of the type $Cp_2TiMeCl \cdot AlMe_2Cl$, which can react with a second mole of trimethylaluminium to yield a $Cp_2Ti(CH_2)AlMe_2Cl$ derivative. Substituents on the cyclopentadienyl ring slow down the rate of methylene formation. The mechanism proposed for α-hydrogen abstraction from the Ti-(Me)Cl unit by the aluminium alkyl involves activation of the titanium methyl group by complexation of the chlorine by the Lewis-acidic aluminium alkyl.[35] The reaction pathway between the components of the Cp_2TiCl_2-$LiAlH_4$-unsaturated hydrocarbon catalytic system is considerably dependent on the nature of the reaction medium. For dienes which are able to form stable η^3-allyltitanocene derivatives, these represent the main product, and are catalytically active in double-bond shift processes. Those dienes which do not form stable η^3-allyltitanocene derivatives and in α-alkenes, the catalytically-active η^1-alkenyl and alkyl-titanocene derivatives are formed transiently, deactivating rapidly to give $[(C_5H_5)(C_5H_4)TiHAlR_2]_2$ complexes and minor amounts of η^3-allyltitanocene derivatives in a side reaction involving intermolecular hydrogen transfer:[36]



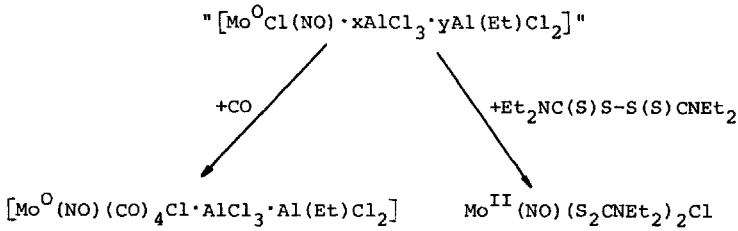
The structures of two binuclear Al/Ti complexes, though not strictly organometallic in nature, are worthy of mention. Crystals of the complex $[(C_5H_5)_2TiAlH_4]_2 \cdot Me_2NC_2H_4NMe_2 \cdot C_6H_6$ are composed of centrosymmetric $[(C_5H_5)_2TiAlH_4]_2 \cdot$tmeda molecules in which the two $[(C_5H_5)_2TiH_2AlH_2]$ moieties are linked by the diamine. The aluminium atom is bonded to the titanium by a double bridge and has trigonal bipyramidal stereochemistry.[37] A very similar bonding arrangement is also present in the dichloro complex, $(C_5H_5)_2Ti(\mu\text{-}H)_2AlCl_2 \cdot OEt_2$,[38] the tungsten complex $(C_5H_5)W(\mu\text{-}H)_2AlMe_3$.[39] Adduct formation between the deuterium isotopomer, $(C_5H_5)WD_2$, and Al_2Me_6 is complete in the time of mixing at -78°C in toluene with exclusive formation of $(C_5H_5)_2W(\mu\text{-}D)_2AlMe_3$. However, on warming to 20°C, a unimolecular H/D scrambling process takes place, which is thought to occur via the mechanism:[39]



The yttrium-aluminium hydride complexes, $\{[(C_5H_5)_2Y(\mu_3\text{-}H)][(\mu_2\text{-}H)AlH_2 \cdot thf]\}_2$,[40] $\{[(C_5H_5)_2Y(\mu_3\text{-}H)][(\mu_2\text{-}H)AlH_2 \cdot NEt_3]\}_2$[41] and $\{[(C_5H_5)_2Y]_2(\mu_3\text{-}H)\}[(\mu_2\text{-}H)_2AlH_2][(\mu_2\text{-}H)_2AlHOEt]$,[41] are somewhat different, exhibiting both doubly-bridging and triply-bridging hydride centres.

The two component Ziegler catalyst system of $[Rh(acac)_3]$-$AlEt_3$ has been investigated for potential as an alkyne- and alkene-hydrosilation catalyst. Terminal alkynes do not yield adducts, but internal alkynes, RC≡CR', afford the products of <u>cis</u>-addition with $SiHEt_2Me$, but not with $SiH(OEt)_3$, without regiospecificity for when R≠R'. Acyclic dienes give 1:1 adducts with $SiHX_3$ (X = Me, Et, OEt, or $OSiMe_3$; but not Ph), predominantly the products of 1,4-addition (exclusive in the case of penta-1,3-diene). Only cyclohexa-1,3- and -1,4-dienes of the cyclic dienes studied were hydrosilylated with $SiHEt_3$ to yield cyclohex-2-enyltriethylsilane.

Cycloocta-1,3-diene merely rearranges to the 1,5-isomer, norbornadiene is polymerised, and no reaction occurs with 2,5-dimethylhexa-2,4-diene. Disubstituted alkenes, RCH=CHR', afford isomerised terminal 1:1 adducts. Similarly, terminal alkenes $RCH{=}CH_2$ gave $RCH_2CH_2SiX_3$ (X = Ph, OEt) or a mixture of isomeric 1:1 adducts (X = Et). More substituted alkenes are unreactive.[42] Trimethylaluminium reacts with the iridium complex, $[\{(C_5Me_5)I_r\}_2Cl_4]$, to afford $\{(C_5Me_5)IrMe_3\}AlMe$ (XXVI). Treatment of XXVI with ethylene or $PPh_3(L)$ results in the formation of the complexes $[(C_5Me_5)IrMe_2L]$, whilst oxygenation results in the formation of $(C_5Me_5)IrMe_4$ in 40% yield.[43] Reaction of the nitrosylmolybdenum complexes, $Mo^{II}Cl_3(NO)(OPPh_3)$ and $Mo^{0}Cl_2(NO)_2(PPh_3)_2$ with $EtAlCl_2$ afford a molybdenum(0) intermediate of the type $[Mo^{0}Cl(NO)\cdot xAlCl_3\cdot yAl(Et)Cl_2]$, which reacts with carbon monoxide and $[Et_2NCS_2]_2$:[44]



Norbornane substituted with amine groups undergoes ring-opening polymerisation with $W(CO)_5(CPh_2)$ or $W(CO)_3(C_6H_3Me_3)$ associated with $EtAlCl_2$ and molecular oxygen.[45]

2 Reactions and Applications in Organic Synthesis

The formation of $(EtO)_2AlOOEt$ on the oxygenation of $(EtO)_2AlEt$ in toluene proceeds by a free-radical mechanism. The chemiluminescence accompanying the oxidation process is induced by two types of reaction.[46] The peroxides, $(PhCH_2O)_2AlOOCMe_3$ are prepared by heating the chloride, $(PhCH_2O)_2AlCl$, with t-butyl hydroperoxide. At temperatures in the range 20-80°, heterocyclic decomposition of $(PhCH_2O)_2AlOOCMe_3$ to Me_3COH, C_6H_5Me, and $(PhCH_2OAlO)_x$ occurs.[47] The intermediate species formed during the hydrolysis of Al_2Me_6 in benzene comprise polyalumoxanes and alumina aggregates as shown by infrared, Raman, and cryoscopic data. Cryoscopic studies showed that the hydrolysed species

undergo associative-dissociative processes through the formation of a network of Al-O coordinative bonds as the solutions age.[48] The reaction of ethylzinc hydroxide with Al_2Me_3 in a 1:0·5 molar ratio most probably involves the formation of the complex XXVII.[49] Methanolysis of Me_2GaOMe yields $MeGa(OMe)_2$.[50] The glyoximato-metallates, $(R_2C_2N_2(O)OH)_2M$ (M = Ni, Pd, Pt, Cu), react with trimethylaluminium, -gallium, and -indium affording the complexes, $(Me_2M^{III})_2[M(R_2C_2O_2N_2)_2]$ (M^{III} = Al, Ga, In). The crystal structures of two of the products, $(Me_2Ga)_2[Ni(H_2C_2O_2N_2)_2]$ and $(Me_2Ga)_2[Pt(Me_2C_2O_2N_2)_2]$ were determined, showing them to possess non-planar structures with weak metal(III)---metal(II) interactions.[51] Triphenylgallane reacts in benzene with alkyl- and aryl-thiols with the formation of organothiogallanes:[52,53]

$$Ph_3Ga + RSH \rightarrow Ph_2GaSR + C_6H_6$$

$$Ph_3Ga + 2RSH \rightarrow PhGa(SR)_2 + 2C_6H_6$$

$$Ph_3Ga + 3RSH \rightarrow Ga(SR)_3 + 3C_6H_6$$

Diphenyl(ethylthio)gallane possesses the expected dimeric structure with a central four-membered $[Ga_2S_2]$ ring. Iodine cleaves the Ga-C bond of phenylbis(alkylthio)gallanes:

$$PhGa(SR)_2 + I_2 \xrightarrow{CH_2Cl_2} PhI + IGa(SR)_2$$

Cleavage also occurs with disulphides:[54]

$$I_2MPh + RSSR \rightarrow I_2MSR \qquad (M = Ga, In).$$

The reactions between $MeGaCl_2$ and silylsulphides, Me_3SiSR in benzene result in the formation of the extremely moisture-sensitive chloro(methyl)(organylthio)gallanes, MeGa(Cl)(SR).[55]

α,ω-1,5-Dienes undergo cyclisation under the action of organoaluminium compounds. Thus, reaction of $CH_2{=}CRCH_2CH_2CR'{=}CH_2$ (R,R' = H, Me) with diisobutylalane in ether gives $Et_2O.(Me_2CHCH_2)_2AlCH_2CHRCH_2CH_2CR'{:}CH_2$ and the corresponding diadduct. The solvating ether molecule can be removed by addition of triisobutylaluminium, and the free organoaluminium adducts then, via a further intermediate, cyclise to (cyclopentylmethyl)-

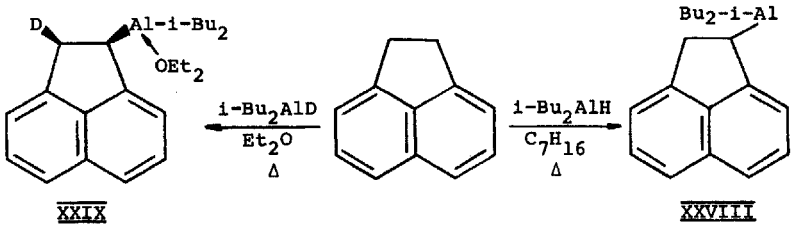
aluminium products.[56] The reaction of R_3Al or R_2AlCl compounds with $PhSO_2CH_2CH{=}CH_2$ is catalysed by a number of transition metal systems (most efficient Li_2CuCl_2-PPh_3) to afford the alkenes, $RCH_2CH{=}CH_2$ (R = Me_2CHCH_2, hexyl, cyclohexyl, octyl, decyl, dodecyl).[57]

Several papers report the interaction of organoaluminium compounds with ketones. The addition of dimethyl(alkynyl)-aluminium compounds to acetone and acetophenone leads to the products of alkynylation, but methylated products are also formed, eg:

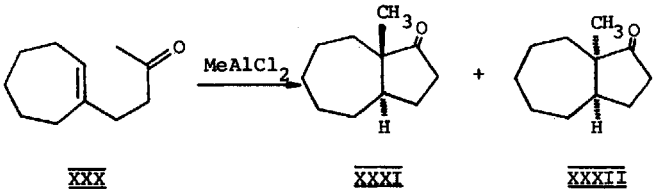
$$nMe_2CO + (Me_2AlC{\equiv}CR)_2 \xrightarrow[2.\ H_2O]{1.\ \Delta t,\text{cyclopentane}} \underset{\text{main product}}{Me_2(RC{\equiv}C)COH} + \underset{\text{by-product}}{Me_3COH}$$

(R = Me, Et, Ph).

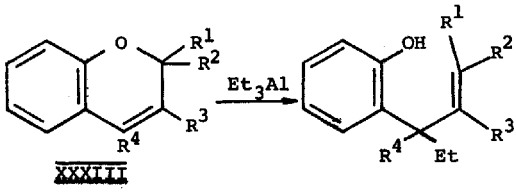
The selectivity of the alkynylaluminium compounds for alkynylation increases in the order $(Me_2AlC{\equiv}CEt)_2 < (Me_2AlC{\equiv}CMe)_2 < (Me_2AlC{\equiv}CPh)_2$. The selectivity also increases when an excess of the organo-aluminium compound is employed, or when it is used as a complex with a Lewis base.[58] Tris (S)-2-methylbutyl aluminium rapidly reduces α-alkynyl ketones to afford optically active α-alkynyl carbinols, which can be recovered after hydrolytic work-up.[59] Similar results are also obtained using {[(1S,2R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl}aluminium dichloride as the reducing agent. The extent of the enantioselectivity, along with the stereochemistry of the process, was found to depend on the structure of the ketone employed.[60] Bis(N-methylpiperazinyl)aluminium hydride is a useful reagent for the reduction of carboxylic acids to aldehydes. The reagent is best prepared *in situ* immediately prior to use by the addition of one equivalent of N-methylpiperazine dihydrochloride to a suspension of two equivalents of $LiAlH_4$ in tetrahydrofuran, followed by addition of three equivalents of the amine itself. Yields of aldehyde are generally >70%.[61] The benzylic reagent 1-acenaphthenyldiisobutyl-aluminium, **XXVIII**, which is formed by the addition of diisobutylalane to acenaphthylene, exhibits a ^1H n.m.r. spectrum at 25°C consistent with aluminium bonding at the C_1 position:



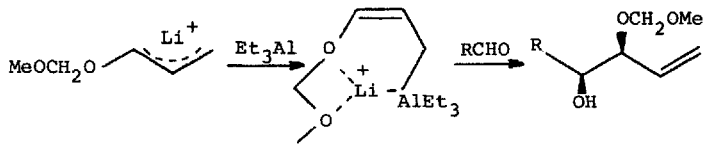
However, at 110°C the Al-C bond undergoes configurational inversion (cis and trans C_2 protons become magnetically equivalent). At -78°C, XXVIII reacts with ketones to give upon hydrolysis 3-(α-hydroxy-disubstituted methyl)-1,3-dihydroacenaphthylenes. In contrast, at temperatures of 80-100°C, the same reagent affords 1-(α-hydroxy-disubstituted methyl)acenaphthenes. Similar reactions with acyl chlorides and Me_3SiCl lead to the formation of 3-acylnaphthylenes and 1-(trimethylsilyl)acenaphthene, respectively. Reaction of the stereochemically-defined deuteride, XXIX, with 9-fluorenone at 65°C yields a 1:1 mixture of cis- and trans-2-deuterio-1-acenaphthenylcarbinols. With oxygen, XXIX affords a 1:1 mixture of cis- and trans-2-deuterio-1-acenaphthenols.[62] The $MeAlCl_2$-initiated cyclization of the enone XXX gives an 85% yield of a 9:1 mixture of the trans- and cis-fused hydroazulenones, XXXI and XXXII:



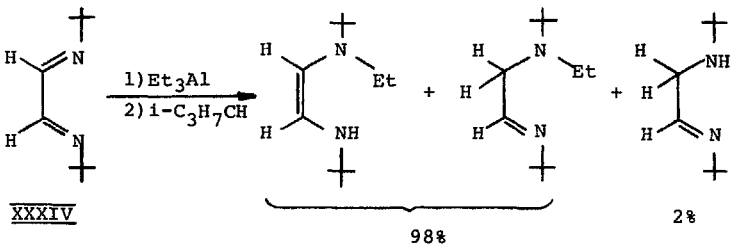
Similar transformations also occur with other cyclopentanones.[63] 2,3-Dialkyl- and 2,2,3-trialkyl-2H-1-benzopyrans, XXXIII, react with triethylaluminium to yield substituted o-allylphenols:



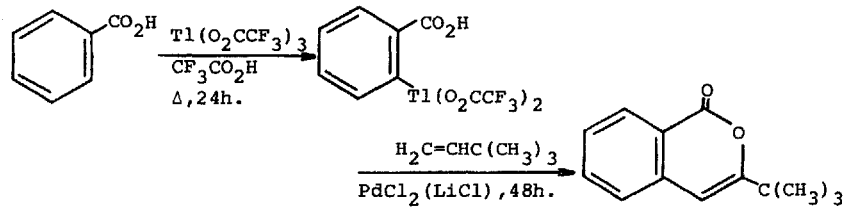
The reactions with 2,3-dialkyl-2H-1-benzopyrans are stereoselective, with either the E or Z isomers being formed preferentially depending on the experimental conditions.[64] The reaction of $LiAlEt_3OR^*$ with (-)-menthyl pyruvate (R*OH = (-)-N-methylephedrine) and with (+)-menthyl pyruvate (R*OH = (+)-N-methylephedrine) in hexane-ether produces the corresponding 2-hydroxy-2-methylbutanoic acids enriched in S- or R- enantiomers, respectively, with an enantiomeric excess close to 60%.[65] The regiochemistry in reactions of heterosubstituted allylic carbanions is highly controlled via allylic aluminium "ate" complexes, which direct both carbonyl compounds and reactive halides to the α-position with high regioselectivity, eg:[66]



Treatment of the diazadiene XXXIV with Et_3Al followed by isopropanol affords a 98% yield of the N-alkylated products, with only 2% of C-alkylation:[67]



Benzoic acid and substituted benzoic acids are readily thallated by thallium(III) trifluoroacetate. Subsequent reaction with palladium chloride and simple alkenes, allylic or vinyl halides, or vinyl esters result in the formation of isocoumarins; eg:



The organic halide reactions are catalytic in palladium.[68] Simultaneous two-electron and one-electron pathways have been shown to occur during the thallation of homologous methylbenzenes. Side-chain substitution, dimerization, and oxidative nuclear substitution derived from the radical cation $ArCH_3^{+\bullet}$ produced as a common intermediate by electron transfer from the methylbenzene to $Tl(O_2CCF_3)_3$ in trifluoroacetic acid. The striking colour changes accompanying thallation are due to charge-transfer transitions in the transient 1:1 π-complexes of the methylbenzene donors and the thallium(III) acceptor. Cationic $Tl(O_2CCF_3)_2^+$ was identified as the active electron acceptor, and also serves the dual function of active electrophile and active oxidant.[69]

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6

Group IV: The Silicon Group

BY D. A. ARMITAGE

1 Introduction

A series of reviews cover the use of organosilicon compounds in organic synthesis[1], with particular reference to silicon containing carbonyl equivalents, silicon-nitrogen compounds, Si-C cleavage, stereochemistry at silicon, and organofluorosilicates.[2] Articles on intramolecular interactions, n.m.r. spectroscopy, notably for ^{29}Si, and theoretical aspects of organosilicon compounds[3] complement several on sila substituted odorous compounds, silylation of hydroxy compounds with arylhydrosilanes, the structural chemistry of heterocyclic silanes, notably 1,3,2-dioxasilacycles, and steric effects in organosilicon chemistry.[4]

Disilenes, p_π-p_π bonded M=C and M=N (M=Si,Ge) homologues, and silyl, germyl, and stannyl derivatives of diazene N_2H_2 are reviewed along with gas phase reactions of dichlorosilylene,[5] organosilicon synthesis of isocyanates, peroxidation of organopolysilanes, polysilylated silacyclohexadienes, gas chromatographic separation of enantiomers on substituted silicones, and the synthetic chemistry of R_3Si-transition metal complexes.[6] Similar topics are reviewed in the oriental[7] and Russian literature[8], together with the photochemistry of unsaturated compounds of the silicon group elements and of their heterocyclic chemistry.[9]

Organogermanium reviews cover reactive intermediates, structural features, and germanium rich heterocycles and polygermanes.[10]

The use of silicon and tin derivatives as covalent templates, and of α-heterosubstituted stannanes in synthesis are surveyed,[11] together with general[12] and specific applications to industrial development.[13] The direct synthesis of organotin halides is critically reviewed, along with pentacoordinate tin compounds, while hydrostannation, cyclopentadienyl tin compounds, stannenes and distannenes, and trimethyltin radicals are assessed for ground state

[For References see page 118

stability.[14]

Annual surveys cover silafunctional compounds, the Si-C bond, and lead for 1981 and 1982, and silicon mechanisms for 1981.[15] Personal appreciations appear for M.Kumada and R.Calas.[16] This article contains about 1010 references.

2 The Carbon-Metalloid Bond

Ab Initio calculations suggest Si=C of $(Me_3Si)_2Si{=}C(Ad)OSiMe_3$ (176 pm) is electronically elongated and should be 170 pm long, while substituents reduce the reactivity of Si=C through reversed π-polarity.[17] Silyl substituted silacyclopropenylidene is the most stable of $C_2Si_2H_4$ cyclic compounds, while silene-silylene interconversions are thermoneutral, but with a high (24-58 kcal) activation energy barrier.[18] This isomerisation explains some earlier conflicting results,[19] with 1-methyl-1-silene isomerising to Me_2Si: (trapped on Me_3SiH and buta-1,3-diene) and Me_2Si: isomerising on photolysis to the silene (stretching frequency 988 cm^{-1}).[20] Dimethylsilylene can be generated from 2,3,4-trisilacyclopent-1-enes (with 2,3-disilacyclobut-1-ene), dibenzodisilacyclohexadienes and silanorbornadienes, while silacyclobutanes give silylene at low pressure.[21] This rationalises the thermal isomerisation of $(Me_3Si)_2Si$: to $Me_2\overline{Si}SiH_2CH_2SiMe_2\overline{C}H_2$ (60%).[22] Me_2Si: absorbs at 350 nm, while $Me_2Si{=}CD_2$ and $(CD_3)_2Si{=}CD_2$ show peaks in their i.r.spectra at ~120 cm^{-1} above and below 1000 cm^{-1}, due to mixing of the Si=C vibration with the scissoring $\alpha(CD_2)$ vibration.[23] BuLi(n, s, or t isomer) and $vinylSiMe_2F$ give 1,3-disilacyclobutane, while at high temperatures, $Ph(Me)Si{=}CHCH_2Bu^t$ is not configurationally stable to cis-trans isomerism.[24] $Me_5C_5W(CO)_3CH_2SiMe_2H$ undergoes β-H transfer photochemically to give the metallosilacyclopropane, a representation preferable to a silene complex.[25] The esters $(Me_3Si)_3CO_2R$ do not isomerise to silenes, but lose CO, while the THF complex $(Bu^t_2MeSi)(Me_3Si)C{=}SiMe_2.THF$ has the shortest Si=C bond reported to date (174 pm) and a long Si-O bond (187.8 pm). This supports a zwitterion with charge on O, and sp^2 C (cf P ylids). The IR spectrum of Si_2C, deposited from the gas phase, supports a C_{2v} structure, angle 110° and stretching frequencies at 1189 and 658 cm^{-1}.[26]

Silabenzene results from the pyrolysis of silacyclohexadienes and is best considered as a symmetry distorted 6π-electron ring. Photolysis induces interconversion of silabenzene with Dewar-silabenzene,

though calculations indicate the latter to be some 40 kcal less stable. Of the 3 disilabenzene isomers, meta is most stable and para the least, though only thermodynamic factors are considered.[27]

Dibenzo-1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclohepta-4,6-diene photolyses to silafluorene and dibenzo-1,2-disilacyclohexadiene. The disilene and silylene were both detected by trapping. The germanium analogue gives Me_2Ge: (λ_{max} 430 nm -cf Me_2Si: at 450 nm) which can be trapped as a diene adduct, and inserts into the C-Br bond of $PhCH_2Br$ via a cage abstaction-recombination reaction. Generated $\bullet GeMe_2Br$ gives Me_2GeBr_2, Me_2Ge: then inserting Ge-Br bonds to form oligomers. $[(Me_3Si)_2CH]_2Ge$: has a $C\hat{G}eC$ angle of 107°, while calculations show Sn_2H_4 to be trans-folded (fold angle 46°) and more stable than the planar structure by 26 kJ mol^{-1}.[28]

Me_3SiCH_2D results from Me_3SiCH_2Cl on lithiation followed by deuterolysis, while $Me_3SiCH_2C(=CH_2)CH_2X$ (X=Cl or OAc) with Os and Ir complexes form Me_3SiCH_2 derivatives.[29] 30% H_2O_2 cleaves the alkyl-Si bond with retention of configuration at carbon.[30] H_2PtCl_6 catalyses the redistribution of tetrasubstituted silanes with $HSiCl_3$, with the least hindered groups exchanging the most readily. Chemical shift correlations have been extended to ^{73}Ge with ^{29}Si and ^{119}Sn, and ^{13}C assignments made for naphthyl- and 9-phenanthryl-trimethylsilanes.[31] Me_4Sn activates MoO_3 catalysts for alkene metathesis while non-phosphine coordinated Pd complexes catalyse the coupling of $ArSnMe_3$ with aryl iodides and alkyl bromides.[32] Excess heat capacity and excess volume for R_4Sn/R'_4Sn is correlated with molecular orientations and hindrance, and volume of activation and of reaction measured for S_E2 brominolysis of R_4Sn.[33] Internal trans-olefins result in high yield regio- and stereo-specifically through elimination of Me_3SnCl from $Cl(PhS)CH(CH_2)_nCH(SnMe_3)CH_2R$ with H-transfer. Keto-olefins result from γ-hydroxyalkyl stannanes and $Pd(OAc)_4$, which induces α-alkenylation of β-dicarbonyl compounds using alk-1-enyl$SnBu^n_3$.[34] $ArPb(OAc)_3$ induces C arylation in malonic ester and Meldrun's acid, while Pb(II) and MePb(IV) is methylated in aqueous solution by MeCo(III) giving Me_2Pb^{2+} and Me_4Pb.[35]

The trimethylsilylmethyl anion adds to N_2O, then eliminates CH_2N_2 and Me_3SiO^-, while the trimethylsilyl anion gives N_2. The total synthesis of the indole alkaloid Vallesiachotamine uses the ester enolate $Me_3Si(CO_2Et)CH^-$, and α-silyl carbanions couple with ketones to give alkenes, but α-phenylthiosilanes give β-silyl carbinols. $Ph_3MCH(I)Li$ and PhCHO give oxirans stereospecifically, which

hydrolyse to iodohydrins, or with PhLi give olefins.[36]

Lithiated o-substituted biphenyl $(Li^+TMED)_2[(2\text{-}CHRC_6H_4)_2]^{2-}$ is polymeric (R=H) but a monomer ($R=Me_3Si$), with the rings separating the lithium ions. The α-silyl-p-xylene derivative $(Li^+TMED)_2[p\text{-}C_6H_4(CHSiMe_3)_2]^{2-}$ has the 2 lithium ions bonding symmetrically to C_α and its adjacent ring-carbon atom, and on opposite sides of the ring. p-$(Me_3SnCH_2)_2C_6H_4$ results from the appropriate Grignard reagent, and $Ph_2Sn([2\text{-}CH(SiMe_3)C_6H_4]_2)$ from the lithiated dianion, crystallising as a racemic mixture. $(Li^+TMED)_2[1,8\text{-}(CHSiMe_3)_2C_{10}H_8]^{2-}$, prepared from bis(chloromethyl)-naphthalene, decomposes in hexane to the 2-silaphenalene derivative $(Li^+TMED)_2[\overline{CHSiMe_2C(SiMe_3)}C_{10}H_6]^{2-}$, which is dimorphic (α and β), these forms differing in the mode of interaction of the 2 cations and the conformation of the heterocyclic ring.[37]

$Pr^iOMe_2SiCH_2MgCl$ hydroxymethylates aldehydes and ketones to give diols on oxidation, and couples with halides and epoxides, while copper catalyses the addition of allylMe_2SiCH_2MgCl to α,β-enones to give γ-hydroxyketones. $KGa(CH_2SiMe_3)_2H_2$, stable to 200°C, reduces $(Me_3SiCH_2)_2GaBr$ to give $(Me_3SiCH_2)_2GaH$ which decomposes to $(Me_3SiCH_2)_3Ga$ at room temperature.[38]

Pyrrolidines, pyrrolines and pyrroles result from azomethine ylid intermediates formed from the desilylation of silylamino compounds or immonium salts, and $Me_3SiCH_2N(NO)CONH_2$ hydrolyses with similar kinetics to the neopentyl analogue, though its bioactivity resembles that of $MeN(NO)CONH_2$.[39] $R_2NCH_2SiCl_3$ result from $HSiCl_3$ and $(R_2N)_2CH_2$, and are covalent, while the tin analogues (from $CH_2NH_2^+X^-$ and $SnCl_2$) are ionic. The diamines $R_3Si(CH_2)_nNHCH_2CH_2NH_2$ have been prepared from the haloalkylsilane and are demethylated (R=Me) by conc. H_2SO_4 to the disiloxane.[40]

Me_3SiCH_2NC (from MeNC) adds 2^y amines (giving $Me_3SiCH_2N{=}CHNR_2$) and thiols, while N-(trimethylsilyl)carbodiimides and ketenimines give the 2-azaallyl anion on desilylation, which forms 1,3-oxazolidines on addition to aldehydes.[41] Bu^tMe_2SiCN results in 75% yield from KCN in CH_2Cl_2 if 1/3 eqt. of 18-crown-6 is added, pyrimidine carbonitriles result from the N-oxide and Me_3SiCN, which gives the cyanodihydrobenzothiazole or Reissert's compound, using benzothiazole or oxazole, and ArCOCl. Cyanonaphthalenes from benzocyclohexenones and Me_3SiCN/BF_3 on desilylation and reduction.[42] Opening epoxides with Me_3SiCN/ZnI_2 using cyclohex-2-en-R^*-1-ol establishes 3 contiguous chiral centres, and $Me_3SiCH(Li)CN$ forms

1,2- and 1,4- adducts with α,β-unsaturated carbonyl compounds. The ^{13}C n.m.r. spectra of Me_3MCN, $Me_3MCH_2CH_2R$ (M=C,Ge,Sn) and $Me_3MCH_2CHRCH_2CH_2R$ (R=CN,CH_2NH_2 for all) show Ge affecting δ-values of α-carbon atoms and Sn, also the β-carbon atoms.[43]

With α,β-unsaturated nitriles, $Me_3SiC(Li)N_2$ gives pyrazoles, and $Me_3SiCH_2N{=}PR_3$ (from $Me_3SiCH_2N_3$) forms heterocumulenes with CX_2 (X=O,S) and cyanates, while ketenes yield N-silylmethyl imines. The first stable methyleneoxophosphorane $ArP(O){=}C(SiMe_3)Ph$ results from O_3 and 2,4,6-$Bu^t{}_3C_6H_2P{=}C(SiMe_3)Ph$, this phosphaalkene coordinating axially to $Fe(CO)_5$ despite steric hindrance.[44] Acylsilanes give 1-siloxy-1,2-propadienes and 1,6-diones with acetylene derivatives, photolysis yields products consistent with both siloxycarbene intermediates and γ-H abstraction, while with RCHO and acetals, $RCH(SiMe_3)COCH_2R'$ gives different aldols depending on the catalyst used.[45]

β-Ketosilanes result from α-silyl esters and are used to prepare homoallyl alcohols and aldols, while cyclic β-silyl ketones form olefinic nitriles from the silicon-directed Beckmann fragmentation.[46] 2-(Trimethylsilylmethyl)cyclopropane carboxylates are ring opened in the presence of F^- unlike the siloxy derivative, which is desilylated. Effects of α- and β-silyl and germyl groups on the proton affinity of alcohols and amines permit discussion of the origin of the stereospecificity of the α-effect.[47] α-, β-, and γ-silylated allyl alcohols undergo Rh-catalysed isomerisation to acylsilanes, α- and β-silylketones, β-silyl ethoxymethanephosphonates are attacked by electrophiles at OCH_2P, while nitrogen of pyrrole and indole can be readily protected by the 2-$Me_3SiCH_2CH_2OCH_2$ group located using the chloride and NaH.[48] 8-MeO-7-Me_3Si-6-tridecanol undergoes Me_3SiO elimination to the olefin, and α-silylsulphones give vinylsulphones with ketones.[49]

The trimethylsilylmethyl complexes $[(Me_5C_5)_2Ln(CH_2SiMe_3)_2]^-$ and $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3R_2SiMe_3)$ have been studied, $(Me_3SiCH_2)_2Ni(PMe_3)_2$ shown to be square planar trans, TMS and $(Me_5C_5)_2\overline{ThCH_2CMe_2CH_2}$ giving $(Me_5C_5)_2Th(CH_2SiMe_3)CH_2Bu^t$ which recyclises to the thorasilacyclobutane with Me_4C elimination, while the ring of $(Me_3P)_4\overline{OsCH_2SiMe_2CH_2}$ is flat.[50] In the presence of CO, $(CO)_5WC(OEt)SiPh_3$ hydrolyses to the ketene $(EtO)(Ph_3Si)CCO$ and anhydride $[(Ph_3Si)(EtO)CHCO]_2O$, and decomposes on heating to $W(CO)_6$, Ph_3SiH and C_2H_4, while the Cr complex also gives $Et(Ph_3Si)CO$ and π-bonded $EtCOSiPh_2PhCr(CO)_3$.[51]

Me_3SnCH_2Li converts ketones to alkenes, α-chloroketones to allyl alcohols and oxiranes to cyclopropanes, and substitutes indium and organoindium chlorides.[52] The n.m.r. parameters of $(Me_3MCH_2)_4Sn$, $Me_3MCH_2SnMe_3$, $(Me_3MCH_2)_2Hg$, and $Me_3MCH_2HgBu^i$ show linear trends for the corresponding Sn and Hg compounds.[53]

The aminomethylstannanes $Bu^n{}_3SnCH_2NR_2$ result from $R_2NCHR'OR''$ (from R_2NH, R'CHO, and R"OH) and $Bu^n{}_3SnMgCl$, while $Bu^n{}_3SnCH_2CN$ couples with ArBr, albeit with low yield in the absence of good electron withdrawing groups on the ring.[54] α-Stannyl esters form from $RR'C(Li)CO_2R''$ and $Bu^n{}_3SnCl$, with $Bu^n{}_3SnCH_2OMe$ coupling ArBr.[55] δ-$Bu^n{}_3Sn$ alcohols 1,4-fragment with iodosylbenzene to provide a new method of synthesis of unsaturated carbonyl compounds. $Cl_3SnCH_2CH_2CO_2H$ is intramolecularly coordinated so is a stronger acid than $FtCO_2H$.[56]

$(Me_3Si)_2CHLi$ is a monomer in the gas phase [cf $(Me_3Si)_2NLi$ dimer] and a polymer with 3 repeating monomer units as a solid with the single alkyl bridge between 2 Li atoms unprecedented. The dilithiomethylsilanes $(Me_3Si)_2CLi_2$ (26%) and $Me_3SiCHLi_2$ (11%) result from the chloride and lithium in the gas phase, while $(Me_3Si)_2C(Cl)Li$ couples fluorosilanes to give $(Me_3Si)_2C(SiFRR')X$ (X=Cl,H,SiFRR') and $(Me_3Si)_2CCl_2$. For X=Cl, further coupling gives $(Me_3Si)_2C(SiFMePh)SiFMe_2$ and $PhMeSiC(SiMe_3)_2SiMePhC(SiMe_3)_2$. Selective population transfer techniques greatly enhance the ^{29}Si n.m.r. signals of substituted bis-silylmethanes, providing unambiguous assignments.[57]

2-$(Me_3Si)_2C(Li)C_5H_4N$ is monomeric in amine solvents, but dimeric in ether, with Li^+ coordinating to η^3-aza-allyl, while Ag^+ coordinates directly with C in the dimeric Ag complex.[58] The borandiylborirane $Bu^tB{=}C\overline{C(SiMe_3)_2B}Bu^t$, which results on reducing $(Me_3Si)_2C{=}C(BBu^tCl)_2$ with Na/K, adds butynes across the B=C double bond, inserts $Me_3SiC{\equiv}CSiMe_3$ to give $(Me_3Si)_2C{=}C{=}\overline{CBBu^tC(SiMe_3)_2B}Bu^t$, and shows topomerisation at room temperature.[59]

The base 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) couples $(Me_3Si)_2CHP(H)GeCl_3$ to give $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$, this diphosphene complexing to $Fe(CO)_4$, $Cr(CO)_5$, and $Ni_5(CO)_6$ residues.[60] The ambivalent derivative $[Ph_2PC(SiMe_3)_2]^-[LiDME]^+$, which results from $Ph_2PCH(SiMe_3)_2$ and Bu^nLi, reacts with phosphorus, alkyl, and acyl halides to give the R-substituted phosphorane $Ph_2P(R){=}C(SiMe_3)_2$. The lithium phosphide $[(Me_3Si)_2CH]_2PLi$ is dimeric with lithium bridges, and complexes with TMED. The sodium derivative reduces $(Me_3P)_2NiCl_2$

to give $(Me_3P)_2NiP[CH(SiMe_3)_2]C(SiMe_3)_2$, while $(Me_3Si)_2C{=}PCl$ gives 2,4,6-$Bu^t{}_3C_6H_2P{=}C(SiMe_3)_2$ with 2,4,6-$Bu^t{}_3C_6H_2Li$, and cyclic adducts with 1,3-dipoles and dienes.[61] The mesityl derivative is readily oxidised by sulphur to $mesP(S)SC(SiMe_3)_2$ and $mesP(S){=}C(SiMe_3)_2$. Ozone and selenium give similar derivatives.[62]

The phospharsene $mesAs{=}PCH(SiMe_3)_2$ and 2,4,6-$Bu^t{}_3C_6H_2As{=}AsCH(SiMe_3)_2$ both η^1-bond to $Cr(CO)_5$,[63] while $Na_2Fe(CO)_4$ reduces $(Me_3Si)_2CHSbCl_2$ to the complexes $(Me_3Si)_2CHSbSbCH(SiMe_3)_2Fe(CO)_4$ and $(Me_3Si)_2CHFe(CO)_4Fe(CO)_4$. With Mg, $(Me_3Si)_2CHSbCl_2$ gives the cyclostibines $[(Me_3Si)_2CHSb]_n$ (n=3,4).[64]

The more hindered diphosphene $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (TsiP=PTsi) (P=P stretching frequency 595 cm^{-1}) results from TsiLi and $TsiPCl_2$, adds sulphur across the P=P bond, and is ozonised to $(TsiPO_3)_2$ $TsiP(O)O_2P(O)TsiO_2$.[65] $(Me_3Si)_2C{=}PN(R)SiMe_3$ results from $(Me_3Si)_2NP{=}NR$ and TsiLi or $(Me_3Si)_2CHLi$ through silyl migration from C to N, and by coupling TsiLi and $Me_3SiN(R)PF_2$, followed by elimination. With $(Me_3Si)_3SiLi$, however, only coupling occurs, no N=P or Si=P products resulting.[66] $TsiPH_2$ relieves steric strain by compressing Me_3Si groups. TsiAs=AsTsi decomposes in solution by a radical pathway to give $(TsiAs)_n$.[67] $TsiGeMe_2Cl$ exchanges with silver salts AgY but with $(Me_3Si)_2C(GeMe_3)SiMe_2Br$, a 1,3-methyl migration from Ge to Si also occurs. $TsiCH_2CH_2OH$ undergoes a base catalysed 1,4-silyl migration from C to O.[68]

The hydrolysis of TsiSiRR'I is now thought likely to involve an S_N2(intermediate) mechanism rather than S_N1, though a comparison of the reactivity of $Bu^t{}_3SiX$ with $TsiSiMe_2X$ suggests a closer similarity in reactivity for established S_N2 mechanisms, with the latter much more reactive to solvolysis and exchange with silver salts where a silicocation intermediate is possible. $Bu^t{}_3SiCl$ is more reactive than the iodide. Ph-Si cleavage of $TsiSiMe_2Ph$ by CF_3CO_2H supports anchimeric assistance in the rearrangements.[69]

The ^1H n.m.r. spectrum of $(Me_3Si)_2C(SiMePh_2)SiMe_2ONO_2$ shows 3 peaks at room temperature which split into 9 at -90°C with $Si\underline{Me}Ph_2$ unaffected. The X-ray structure of $(PhMe_2Si)_3CH$ shows wide (114°) angles at C, though somewhat less than those in the gas phase structure of $(Me_3Si)_3CH$ (116.3°). $(HOMe_2Si)_4C$ results from $(IMe_2C)_4Si$ and AgOCN in moist ether, and rearranges in base to $HOMe_2SiCH(SiMe_2O)_2SiMe_2$.[70] TsiLi gives aminosilyl derivatives TsiSiF(R)NHR' which undergoes 1,3-silyl migration from C to N, while

with Ph_2BCl, the borane $TsiBPh_2$ results which shows B planar, but a small (110.4°) angle between the tilted phenyl rings to compensate for silyl hindrance. $LiAlH_4$ reduces $(PhMe_2Si)_3CBF_2$ to $(PhMe_2Si)_3B(\mu\text{-}H)_3Li(THF)_3$, which has C_3 symmetry.[71] The three 'ate' complexes $[Li(THF)_4]^+[M(Tsi)_2]^-$(M=Li,Cu,Ag) are isomorphous with the silver derivative, the first crystal structure of a mononuclear silver complex. The methyl groups are cleaved from $(Me_3Sn)_4C$ and $(Me_3Sn)_3CH$ by electrophiles to give mono or disubstitution (Br_2). The inner Sn-C bonds remain intact.[72]

Vinylsilanes have been prepared by an extensive range of methods utilising halogen,[73] oxygen, and sulphur substituted precursors,[74] acetylenes[75] and CO (with Me_3SiCH_2Li),[76] while $Me_3SiCH{=}CHCO_2H$ behaves as an acetylene equivalent in Diels-Alder reactions, and trimethylsilylvinyl triflate as an alkylidene carbene source.[77] Grignard reagents add to vinylsilanes to give silyl hydrocarbons on hydrolysis, and bromination of (E)-1-trimethylsilylcyclooctene gives (Z)-1-bromocyclooct-4-ene in 70% yield.[78] Vinylsilanes add C_2F_4 to give cyclobutylsilanes, and add dienes to give cyclohexenylsilanes, both of which can be silylated with F^- to the cyclobutene or cyclohexadiene, while oxidation gives ketones and optically active alcohols.[79] $R_2C{=}C(R)Si(CH_2Cl)Me_2$ undergoes $AlCl_3$ catalysed rearrangements to the allyl- and/or cyclopropyl-chlorosilane depending on R, chiral vinylsilanes with optically active functional groups on Si are precursors for chiral α-hydroxy alkyl anion equivalents, while Michael addition/Peterson olefination of $CH_2{=}C(SiMe_3)CO_2Me$ provides a convenient method of forming consecutive C-C and C=C bonds.[80]

Substituted vinylsilanes have been used in the synthesis of the natural products methyl jasmonate, (-)-propanolol, relatives of the Prelog-Djerassi lactone, (±)-rhodinose, the alkaloid (+)-epielwesine, the cardiac agent pumiliotoxin B and pumiliotoxin 251D,[81] together with trans-hydrindane diones, and silyl enol ethers of 2,2-disubstituted aldehydes, while 6-silylated uracil and uridine are readily converted to 5,6-dihalogen derivatives using NBS or NCS.[82]

Ruthenium salts catalyse the metallation of $(EtO)_3SiCH{=}CH_2$ to trans-$(EtO)_3SiCH{=}CHSi(OEt)_3$, nickel the hydrogenation of alkenylchlorosilanes and the co-oligomerisation of vinylsilane and butadiene.[83] $Me_3SiCH{=}CHCH(SiMe_3)OAc$ behaves as a synthon for a propenyl 1,3-dipole for diene synthesis in the presence of a nucleophile,

RCHO, and a Mo catalyst, and for vinylsilane synthesis from its silylallyl-palladium complex.[84] PhPdOAc and ArN_2^+ arylate $RCH{=}CHSiMe_3$.[85] $H_2C{=}C(SiMe_3)Li$ undergoes E/Z-diastereotopomerisation in solution on warming, while Bu^nLi, Me_3SiCl, and $F_2C{=}CFCl$ give trifluorovinylsilanes which form trans-difluoro-olefins with RLi.[86] Tris(Z-trimethylsilylprop-1-enyl)borane is trigonal planar. The products of shock-tube decomposition of vinylsilane indicate several pathways, while calculations show vinyl groups to stabilise the positive charge of the silylenium ion better than the carbenium ion.[87]

The I.R. spectra of N-alkylidene alkylimines $Me_3Si(CH_2)_nCH{=}NR$ are analysed, the ^{13}C n.m.r. spectra of $Ph_3MCH{=}CHMe$ (M=C-Pb) are compared, and the X-ray structure of $Ph_3SnCH{=}CH_2$ shows 2 non-equivalent molecules in the unit cell.[88]

Palladium catalyses the coupling of vinylstannanes to vinyl iodide/CO, to give divinyl ketones (diallyl ketones prepared similarly), and vinyltriflates to give pleraplysillin-1 and $\Delta^{9(12)}$-capnellene.[89] Stannylated vinyl ethers of defined stereochemistry result from the thermolysis of substituted bicyclo[2.2.1]hept-5-enes, while attempts to prepare $[Me_3Sn(Me)C{=}CEt]_2BEt$ gave a stannylated derivative of $C_4BH_5^{2-}$.[90]

The allylstannanes $(R_3SnCH_2)_2C{=}CH_2$ (R=Me,Ph) behave similarly, but with steric and electronic factors making the methyl derivatives a little more reactive. The stereochemistry of allylstannane--aldehyde condensation supports synclinal over antiperiplanar transition state geometry.[91] 1-Buten-3-yl-n-butyldichlorotin and aldehydes give linear alcohols and/or 2,3,4,6-tetrasubstituted tetrahydropyrans, homoallyl alcohols resulting from the allyl or crotyl trialkylstannane.[92] The stereoselectivity of α- and β-hydroxyaldehyde addition is explored,[93] allyl halides regioselectively couple $allylSnR_3$ head to tail at room temperature under pressure, while E-1-alkoxymethoxybut-2-enyl (tri-n-butyl)stannanes give 4-hydroxy-3-methyl-cis-1,2-enol ethers with PhCHO. γ-Stannyl alcohols cyclise using $SOCl_2$ to fused cyclopropanes, including 3-carene and isosesquicarene.[94]

2-(Trifluoromethyl)allyltrimethylsilane results from Me_3CH_2MgCl and CF_3CO_2Et, and with aldehydes and ketones gives trifluoromethylated alcohols and silyl ethers. Synthesis of allyl and allenylsilanes is stereospecific from hydroalumination or hydroboration of propargyl silanes, from silyl cuprates and allyl and propargyl acetates, or from α,β-unsaturated esters.[95] Epoxyallylsilanes result

from the lactol and $Ph_3\overset{+}{P}-\bar{C}HCH_2SiMe_3$, and can be cyclised with $TiCl_4$, which catalyses the addition of electrophiles to α-(trimethylsilyl) β,γ-unsaturated esters and, with $Ti(OPr^i)_4$, induces 1,3-syn diastereofacial selectivity (2.8:1) to the substitution of β-alkoxy acetal by $allylSiMe_3$.[96] Allylsilanes convert iminium salts to 2-allylpyrrolidines, ω-alkoxy lactams to azabicyclic compounds and γ-amino acids,[97] geraniol to karahanaenol, and are used to prepare dihydronepetalactone, hexestrol derivatives, Z-9-tricosene and the gypsy moth sex pheromone.[98] They substitute PhSCl adducts of alkenes and vinyl ethers, ring open γ-alkenyl-γ-butyrolactones stereoselectively to give methyl-(E)-4,8-alkadienones, and mediate in the carbocyclisation of (R,E)-1-Me_3Si-1-buten-3-ol to (1S,2S)-(+)-2-methyl--3-cyclopenten-1-ol.[99] They show diastereofacial selectivity in Lewis acid mediated reactions with chiral aldehydes, enones and α-keto amides, α-halo substituted allylsilanes give alkenyl halides with electrophiles, and show high (Z)-preference.[100] Optically active allylsilanes are oxidised by MCPBA anti with respect to the silyl group, CF_3CO_2D deuterates γ to Si in 3-methyl but-2-enylSiMe$_3$, while the gas phase decomposition of $allylSiMe_3$ has been shown by D labelling not to involve the vinylsilane, but propene elimination to give the silene, and Si-C homolysis.[101] $(Ph_3P)_4Pd$ converts the protected esters $RCO_2CH_2CH{=}CHCH_2SiMe_3$ into silyl esters and diene, and Mo catalyses the addition of silyl substituted allylic acetates to cyclic enols.[102]

The one dimensional poly-yne polymers involving phthalocyanine silicon or Me_2Si coupling p-diethynylbenzene as the backbone have good air and thermal stability.[103] 1,6-Bis(trimethylsilyl)hexa-1,5--diyn-3-ene, the precursor to polydiacetylenes, results from $Me_3SiC{\equiv}CMgBr$ and trans-ClCH=CHCl [Ni(II) catalyst], while $C_2H_4Br_2/Zn$ reduces conjugated and non-conjugated silylated diacetylenes.[104] Silyl acetylenes result through iodine catalysed dehydrocondensation of R_3SiH and $RC{\equiv}CH$,[105] can be reductively alkylated by R_3Al in the presence of $hex^n{}_2Mg$, specificity depending upon the alkyne, while 1-halo-olefins are formed stereoselectively.[106] Allylzincation of $RC{\equiv}CSiMe_3$ gives unconjugated dienes with selectivity, while silylated haloalkynes cyclise to methylene cycloalkanes with Mg.[107] Propargylic silanes result from methyl acetylenes, and are used to synthesise allylic silanes, allenic alcohols, and 1,3-bis(trimethylsilyl)allene,[108] γ-allenyl-GABA (an inhibitory neurotransmitter), dihydrofurans, and (±)-trans-Maneonene-B, a 15-C halogenated cyclic

ether marine natural product.[109]

$Me_3SiC{\equiv}CC(OEt)_3$ provides a convenient propiolate anion equivalent, $Me_3SiC{\equiv}CLi$ substitutes $N_3P_3F_6$ both geminally and non-geminally[110] while $Me_3SiC{\equiv}CR$ adds $(Bu^tClB)_2$ to give $R(Me_3Si)C{=}C(BBu^tCl)_2$. With stannyl acetylenes, however, elimination of Me_3SnCl gives 1-t-butylborirenes $Bu^t\overline{BC(R){=}CB}Bu^tCl$.[111] $Me_3SiC{\equiv}CSiMe_3$ and WCl_6 in C_2Cl_4 gives the centrosymmetric chloride bridged complex $(Me_3SiC{\equiv}CSiMe_3WCl_4)_2$ with the acetylenes coordinating to one W atom each, but to both Fe and W in a Fe_2W cluster.[112] $Fe_3(CO)_{12}$ catalyses the trans-addition of perfluoroalkyl iodides to $Me_3SiC{\equiv}CSiMe_3$ but iodination of the methyl group also occurs. With $Me_3SiC{\equiv}CH$, E-addition dominates. Alkenes gove adducts similarly, while allylsilanes yield 3-perfluoroalkylprop-1-enes.[113]

The acetylenes $Me_3SiC{\equiv}CX$ (X=H,D) and $H_3MC{\equiv}CCF_3$ (M=Si,Ge) have been characterised by vibrational analysis, the latter pair also by electron diffraction and microwave studies.[114] Condensing Ge and Sn with C_2H_2 gives air sensitive but non-conducting copolymers.[115] Catalysed coupling of allenylstannanes with allylic esters gives 1,5-enynes while 1,4-pentadiyne adds Me_3SnNEt_2 with conjugation to give the 1,3-enyne.[116] Stannylated ynamines undergo electrophylic substitution at Sn, $Ph_3SnC{\equiv}CCR_2Cl$ give stannyl allenes using RCu, while $Bu^n{}_3SiC{\equiv}CX$ (X=CN or CO_2Et) gives the 1-stannyl cyclohexa-1,4--diene through Diels-Alder addition to buta-1,3-dienes. $Me_3SiC{\equiv}CCH_2I$ and Sn/Al with RCHO and R_2CO provides for the synthesis of silylated alcohols of acetylenes and allenes.[117]

While $Me_3SiCH{\equiv}CHCH_2SiMe_3$ gives (E)-$Me_3SiCH{\equiv}CHCH_2CR_2OH$ selectively with carbonyl compounds,and its Li derivative gives silylated dienes, which also result from $Me_3SiC{\equiv}CH$ and $R_2CuMgCl$ through coupling and electrophilic attack. $Me_3SiCH{=}CHC(OAc){=}CH_2$ gives tetracyclic anthracyclinone derivatives through Diels-Alder addition to quinizarin quinone, and $Me_3SiCH_2C{\equiv}CCHO$ is a synthetic equivalent for the butadienyl carbonium ion and is used to prepare terminal 1,3-dienes and for macrocyclic expansion of cyclic ethers.[118] Metal substituted silyl allenes are threo-selective in their addition to imines, while $(Me_3SiCH_2)ClC{=}C{=}O$ adds to double bonds with stereocontrol, giving cyclobutanones.[119]

Hexamethylsilirane is ring opened by RLi, which then metallates methyl substituents on Si, and olefins and acetylenes insert to give 5-membered heterocycles.[120] RCHO and R_2CO yield oxasilacyclopentanes, while benzoxasilacyclohexenes result from

benzosilacyclobutene.[121] The bicyclic disilabicyclo[1.1.0]butane is formed by condensing $Me_3SiCCl_2SiMe_2Cl$ with Bu^tLi in THF. The reaction is thought to proceed via the cis- and trans-isomers of $Me_3Si(Cl)CSiMe_2C(Cl)(SiMe_3)SiMe_2$ which can be isolated if ether is used as the solvent. The cis-isomer has a ring fold angle of 17.9°. $Me_3SiCCl_2SiMeCl_2$ gives cis- and trans-ethylene derivatives $Me_3Si(Cl_2MeSi)C{=}C(Cl_2MeSi)SiMe_3$.[122] The metallocycles $(C_5H_5)_2MCH_2SiMe_2CH_2$ (M=Ti,Zr,Nb,Mo) result from $[Mg(CH_2)_2SiMe_2]_n$ and show a decrease in the $\widehat{CMC}$ angle (81-72°) as M-C and the ring fold angle increase (M=Zr,Nb,Mo). The Zr derivative inserts formaldehyde.[123]

$R_2Si(CH_2)_4$ (R=Me,Ph) undergoes R group exchange at Si using RLi, but $Me_2SiCHPh(CH_2)_3$ ring opens then exchanges with the benzylic hydrogen.[124] Electrophiles cleave the allyl group of 1-allyl-1,2,5--trimethyl-1-silacyclopentane.[125] Me_2Si: reacts with 1,3-dienes through a concerted 1,2-addition followed by ring opening to diradicals, which then give silacyclopentenes, and displaces Me_2Ge: from the phenyl substituted germacyclopentadiene. UV light induces coupling of $Me_2SiCPh{=}CHCH{=}CPh$ at Si-Me, while $Me_2SiCH{=}CHCH{=}CH$ readily coordinates to metal carbonyls.[126] The far-IR spectra of 1-silacyclopent-3-ene and the 1-deuterio derivative provide for the assignment of ring puckering and twisting modes, while 3-silabicyclo[3.1.0]hexanes thermally isomerise to silacyclo-pentenes and -hexenes.[127] $Me_2Si(CH_2)_3CMe{=}CBr$ results from the 1,5-dihalopentene and has been used as a precursor for sila-β-ionone, sila- and germa--cyclohexan-4-ones from divinyl-silane or -germane and $Cl_2CHOMe/LiOCR_3$, while IR spectroscopy indicates that the larger rings show reversible conformation changes on compression, but no enhancement of transannular interactions.[128]

1-Sila-2,4-cyclohexadienes $Bu^t(X)SiCH{=}CHCH{=}CHCH_2$ (X=Cl,OMe) can be mono, bis, or tris-silylated, while for X=H, metallation with Bu^tLi results in ring opening to give $Me_3SiCH_2CH{=}CHCH{=}CHSiBu^t{}_2H$ on silylation. trans-1,4-$(Me_3Si)_2$hexamethyl-1,4-disilacyclohexa-2,5-diene is nearly planar (slight chair deformation) but the cis-isomer has a slightly twisted boat conformation. Silylation of 1-silacyclohexadienes at positions 2 and 6 provides steric shielding for the ring silicon atom. $Me_2Sn(C{\equiv}CPh)_2$ and R_3B give bis(alkenyl)stannanes as adducts, together with 1-bora-4-stannacyclohexadienes, stanna-cyclopentadienes, and -cyclopentenes.[129]

1-Trimethylsilylmethylnaphthalene is nitrated more readily than

benzylsilane and 9,9-$(Me_3Si)_2$-10-lithio-9,10-dihydroanthracene undergoes a [1,4]-silyl migration. The route to disilaanthracenes is simplified through an improved synthesis of $(\underline{o}\text{-}ClC_6H_4)_2SiHMe$, while bending along the Si---Si axis is hardly affected by complexing 2 $Cr(CO)_3$ residues <u>cis</u> or <u>trans</u> to $C_6H_4(SiMe_2)_2C_6H_4$. The η^6 complex of 1-silylated dibenzosilacyclopentadiene with $Cr(CO)_3$ is desilylated by RLi to give the silole, but $PhMe_2SiLi$ substitutes 4 to the silole Si atom. Photolysing 1-Me- and 1-Ph-1-(Me_3Si)dibenzosilole in the presence of $Me_2C{=}X$ (X=O or CH2) induces silyl migration to position 2 and insertion of $Me_2C{=}X$ into the Si-H bond so formed.[130] Appearance potential measurements of 1,1-dimethyl-1-silaphenalene indicates short range delocalisation of the positive charge unlike phenalene, and of the negative charge on the 1-silaphenalenyl anion.[131] Germyl anthracenes result from 9-methylanthracene and $HGeCl_3$, which reductively couples Ph_2O to give $\underline{p}\text{-}PhOC_6H_4\overline{C(GeCl_3)(CH_2CHGeCl_3)_2CH_2}$ remarkably.[132]

2-Trimethylsilyl- and 2-trimethylsilylmethyl-aziridines result from Me_3SiR (R=vinyl or allyl) and methyl <u>N</u>,<u>N</u>-dichlorocarbamate, while α,β-trimethylsilyl epoxides are ring opened by <u>N</u>-silylated 2^y carboxamides $Me_3SiNMeCOR$, to give the acetamide $MeCON(Me)CH(SiMe_3)CH_2OH$ with acid, and silylated thiirans give thiosulphinates on oxidation with peracids through coupling.[133] $Ph_3\overset{+}{As}\text{-}\overset{-}{C}HSiMe_3$ and benzylidene acetophenones give silylcyclopropanes, and ring open with $Bu^n_4N^+X^-$ (X=F,Cl) if halo substituted, to give fluorodienes.[134] A series of functionalised 1-(trimethylsilyl)cyclopropanes have been prepared with alkene derivatives useful intermediates for the synthesis of spirocyclic sesquiterpenes and dicyclopropylidene ethane.[135] The configurational instability of 2,2-diphenyl-1-(trimethylsilyl)cyclopropyl carbanion tends to refute $p_\pi\text{-}d_\pi$ bonding as the mode of stabilisation, but does not confirm an interaction with σ^* on Si.[136]

1-Trimethylsilyl-7,7-dihalobicyclo[4.1.0]heptanes give the diacetals with $AgOCOCF_3$ in alcohol solvents, and bicyclo[n.1.0]trimethylsilanes result from the cycloalkene on silylation of the CCl_2 adduct.[137] Their n.m.r. spectra have been extensively analysed.[138] Cyclobutylsilane exists as both equatorial and axial conformers in the gas phase, while ring distortion is not thought to involve d orbital participation. However the behaviour of $Me_3Si\overline{CH(CH_2)_n}$ does support d orbital participation for n=2 unlike the larger rings. Strong intermolecular H-bonding in the solid stabilises

trans-2-methoxycyclohexanol, equatorially silylated at 2.[139]

1-Silylated adamantanes and 1,3-bis(dimethylsilyl)adamantane result from coupling haloadamantanes with silanes.[140] Reversed phase HPLC separates Si-methylated carbosilanes, the Si_6-Si_9 carbosilanes from Me_4Si pyrolysis, but not Si-Cl compounds. $Si_8C_{18}H_{40}$ is the smallest unit to show the adamantane and Wurtzitane frames of the common 4H-III modification of silicon carbide.[141]

Ynamines and silylketenes couple to give allenecarboxamides, the silyl substituent inducing H migration to give silyl cyclobutenones and silylacetylenes, while 1-silyl cycloalkenes result from the cyclisation of ω-halo-1-silyl-1-alkyl metals.[142] The racemic diastereomers $C_5H_5Co(\eta^4\text{-}\overline{C(SiMe_3)C(SiMe_3)CHC}CHMeR$ result from $C_5H_5Co(CO)_2$, $Me_3SiC{\equiv}CSiMe_3$, and $HC{\equiv}CCHMeR$, and interconvert through a unimolecular reaction thought to involve bis(alkyne)cobalt intermediates.[143]

The hydrolysis of silylated imidazoles and pyridine involves OH^- attack at the Me_3Si group, while (Me_3Si)-1-(methyl)pyrazoles can be selectively halogenated at the 4-position using Br_2 or ICl. Pyrroles and indoles can be silylated at the 3-position with $Me_3SiOSO_2CF_3$, while indole or 1-(Me_3Si)indole can be silylated at the 4-position using Li/Me_3SiCl to give the 1,4-disilyl indole. This reacts with MeOH to give the 4-silyl indole which is attacked at the 3-position by electrophiles.[144]

The spiro silane $\overline{OC(CF_3C_6H_4\text{-}o\text{-}Si}\text{-}\overline{o\text{-}C_6H_4C(CF_3)_2O}$ complexes with o-phen to give a 6-coordinate adduct with C_1 symmetry which isomerises in solution through ligand dissociation, while monodentate ligands induce racemisation if able to shift from equatorial to apical sites. 3-(Me_3Si)-2,5-dihydrofuran both inserts $:CCl_2$ at 2 and 5, and adds it to the double bond. With the 2-silyl-4,5-dihydrofuran however, the pyran results through isomerisation of the bicyclic adduct, while 3-chloromethyl-2-silylfurans behave as butenolide equivalents in the synthesis of biologically active natural products.[145] 2-R_3M-2-butene-1,4-diols (M=Si,Ge) cyclise to the 3-silyl- or 3-germyl-2,5-dihydrofurans, and a series of 3-furyl tin mono- and di-halides have been prepared.[146] 2,5-Bis(trimethylstannyl)thiophene has been used to substitute estrone 3-methyl ether, which on iodination gives a molecule with both biologically active and a radionuclide. Cis- and trans-(4-alkylcyclohexyl)$SnPr^i_3$, prepared from the Ph_3Sn derivative, undergo trifluoroacetolysis with retention of configuration at carbon. Electrophilic brominolysis

favours inversion by equatorial and retention by axial Sn-C bonds.[147] Iron tricarbonyl complexes of 2-(Me_3Si)-1,3-cyclohexadienes give symmetric η^5 cations on hydride abstraction.[148]

Calculations of the structures of the 4 isomers of silylcycloheptatriene support a [1,5]-shift of the silyl group in the η^1-isomer as the only migration pathway. Substituting the ring of cycloheptatrieneFe$(CO)_3$ by exo-7-Me_3M (M=Si or Ge) lowers the activation energy for [1,3]-Fe shifts. Heating the epimers of bicyclic α-bromotrimethylstannanylcyclopropane in C_6H_6 give the spirodiene or cycloheptatriene oligomers, but more polar conditions gave stannylcycloheptadi- and -trienes, supporting an ionic rather than a carbene intermediate.[149] $Me_3SiC_5H_5$ and R_2SO give mono-, bis-, and tris-sulphonio derivatives in the presence of $(CF_3CO)_2O$.[150]

A series of metallaindanes $(C_5H_5)_2\overline{MCH_2C_6H_4CH_2}$-o (M=Ti,Hf,Nb), silylated at either 5-membered ring, have been prepared, while the structure of $(Me_3SiC_5H_4)^-(LiTMED)^+$ shows Li to be trigonal planar to the 2 nitrogen atoms and the ring centroid.[151] $[(Me_3Si)_2C_5H_3]_2Zr(CO)_2$ results on reduction of the dichloride and is a useful synthetic precursor, while $Me_2Si[C_5H_4Fe(CO)_2]_2$ readily complexes with $Ph_2P(CH_2)_nPPh_2$ (n=1-3) to give chelation across the Fe-Fe bond or bridging.[152]

Germanocene, which is formed from C_5H_5Na and Cl_2Ge.dioxane, has a ring apature angle of 50.4° (X-ray) and Ge-C distances ranging from 235-273 pm. With t-BuOH, it gives $[(Bu^tO)_2Ge]_2$ which coordinates to $Ni(CO)_4$ through Ge.[153] Permethylgermanocene has an apature angle of 22° (electron diffraction) while Me_5C_5GeCl shows a short ring-Ge distance and long Ge-Cl bond. A C_{5v} structure is indicated for $C_5H_5Ge^+$ and $Me_5C_5M^+$, while (η^1-indenyl)$_4$M (M=Ge,Sn) have S_4 symmetry.[154] $(Me_5C_5)_2M$ (M=Ge,Sn) form ionic derivatives with $(MeO_2C)_5C_5H$, containing $Me_5C_5M^+(MeO_2C)_5C_5^-$, excess $(MeO_2C)_5C_5H$ giving $[(MeO_2C)_5C_5]_2M$, associated through carboxylate coordination.[155] The apature angle of $[(Me_3Si)_3C_5H_2]_2Sn$, which results on silylation of stannocene, is 18° while decaphenylstannocene provides the first symmetrical main group sandwich, with S_{10} symmetry.[156] The first tetradecker sandwich with a non-transition element, $(C_5H_5CoC_3B_2H_5)_2Sn$ results from $C_5H_5CoC_3B_2H_5^-$ and $SnCl_2$, while $Me_3Si(Me)C_2B_4H_7^-$ and $SnCl_2$ give the stanno-closo-carborane which complexes with bipyridyl to give a π-slipped adduct.[157] The closo-carborane $(Me_3Si)_2C_2B_4H_4Sn$ gives the osmcarborane $(Me_3Si)_2C_2B_4H_4Os(CO)_3$ almost quantitatively using

$Os_3(CO)_{12}$, but with nido-$(Me_3Si)_2C_2B_4H_6$, yields are much lower. However this nido-carborane provides a useful Me_3SiH elimination route to nido-$(Me_3Si)_2C_4B_8H_{10}$.[158]

2-Trimethylsilyl-3-triflyl benzamide gives benzyne intermediates through fluoride-mediated 1,2-elimination, while other silylated benzamides are used in the synthesis of natural anthraquinones, and erythrolaccin tetramethyl ether.[159] The α-chlorobenzylsilanes $RPhClSiMe_3$ result from $Me_3SiCHClPh$ on lithiation and alkylation, while $TeCl_4$ condenses Me_3SiCH_2Ph to give $(p\text{-}Me_3SiCH_2C_6H_4)_nTeCl_{4-n}$ (n=1,2).[160] The IR spectra of Ph_4Si are interpreted based on S_4 symmetry, while the photoelectron spectra of Ph_4M (M=C-Pb) strongly resemble that of benzene. $(o\text{-}MeC_6H_4)_4Ge$ does not possess the D_{2d} symmetry characteristic of the tetra(tolyl)stannane isomers and Ph_4Ge, due to the shorter Ge-C bond.[161]

Macrocycles containing 2 or 4 Ph_2Sn units result from $Ph_3Sn(CH_2)_2SnPh_3$ on dephenylation with HBr, followed by coupling with a diGrignard reagent. Further dephenylation leads to the barrel derivative, while the hindered 3^y proton of $(Ph_3SnCH_2)_3CH$ reacts with Ph_3C^+ slower than the 2^y one of $(Ph_3SnCH_2)_2CH_2$.[162] B_2H_6 reductively exchanges with Ar_4Sn and Ph_3SnX to give Ar_2SnH_2 and Ar_2BH or $ArBH_2$, and $PtCl_6^{2-}$ is arylated by Ar_4M (M=Sn,Pb).[163] A number of tin substituted derivatives of pyridine and its N-oxide have been characterised, while the coupling constants for Ph_3SnX show a linear correlation with Pauling's electronegativity for X.[164]

The first trifluoromethyl organochlorosilanes result from $(Et_2N)_3P/CF_3Br$ and R_nSiCl_{4-n} (R=Ph,Me), while the molecular structures of $(F_3Si)_2CX_2$ (X=H or Cl) shows the $Si\hat{C}Si$ angles to be 117° and 119° respectively, indicating chlorine substitution to have little influence on hindrance.[165] IF_5 cleaves $(C_6F_5)_4Si$ in the presence of pyridine to give $C_6F_5IF_4$, and $p\text{-}RC_6H_4SiMe_3$ (R=H,CN,Cl) is attacked by F_2 to provide a route to ^{18}F labelled compounds.[166] $Pt(PPh_3)_n$ inserts the Ge-Hg bond of $[(CF_3)_3Ge]_2Hg$, while $(CF_3)_2Cd.glyme$ and SnI_2 are thought to yield $CF_3Sn(II)$ products.[167]

3 Catenation

Photoelectron-photoion coincidence PEPICO technique on $Me_6Si_2^+$ gives a Si-Si bond strength of 265 kJ. Though the high temperature Me/Cl exchange between Me_6Si_2 and Si_2Cl_6 involves rupture of the Si-Si bond, H/Cl exchange between $Me_2Si_2Cl_4$ and $Me_2Si_2H_4$ proceeds

catalytically and cleanly at room temperature, so providing a useful route to $Me_2Si_2Cl_xH_{4-x}$. Halomethylsilanes $Cl_2XCSiMeCl_2$ result from the base catalysed cleavage of methylchlorodisilanes by polyhalomethanes Cl_3CX (X=Cl,H,F,$SiMeCl_2$).[168] Palladium catalyses the addition of organodisilanes to conjugated dienes and the cleavage of Me_6Si_2 by allylic esters.[169] Me_6Si_2 reduces CO in the presence of Ni, and nitrobenzenes to azo and azoxy compounds in the presence of fluoride.[170] Hydrogen atoms cleave Me_6Si_2 at room temperature, Me_8Si_3 has $\underline{C}_{2v}$ symmetry, and the vibration spectra of trisilanes have been analysed.[171] Aryl polysilanes give a strong $2p_\pi^* - 3d_\pi$ charge transfer in the excited state, which affects both photochemical reaction and photophysical processes, while phenyl substituted disilanes, digermanes, and mixed derivatives with tin also, show σ-π conjugation.[172]

Both $EtMeSiCl_2$ and Et_2SiCl_2 react with alkali metals to give cyclopolysilanes $(R_2Si)_n$ (n=4-8), $(Et_2Si)_4$ readily inserting isoprene and alkynes, oxygen alternately using MCPBA, and sulphur at 190°.[173] $(RR'Si)_n$ (n=4-7) result from Li/THF and the dichloride, bulky groups giving smaller rings, while dichlorosilacyclopentane yields the spirocyclic cyclopolysilanes $[(CH_2)_4Si]_n$ (n=5-12) with 2 equivalents of Li, but excess Li gives the septamer $[(CH_2)_4Si]_5Si(CH_2)_4Si(CH_2)_4$. $(CH_2)_5SiCl_2$ and K give $[(CH_2)_5Si]_n$ (n=4-6), the cyclopentasilane showing chair conformations for all SiC_5 rings (flattening at silicon) while for $[(CH_2)_4Si]_5$, the SiC_4 rings have different conformations. The Si-Si bonds are also shorter, indicating less steric hindrance of the smaller silacycloalkane ring. Both groups of compound undergo ring contraction on photolysis to give the cyclic silylene which can be trapped using Et_3SiH.[174] A series of α,ω-dihydroperchloropolysilanes $H(SiCl_2)_nH$ (n=3-7) can be prepared from $(Ph_2Si)_x$ (x=4 or 5) by ring opening and coupling to give $H(SiPh_2)_nH$, which can be chlorinated using $HCl/AlCl_3$.[175]

The first spiropentasilane $(Me_2Si)_2Si(SiMe_2)_2$ results from Li and $(XMe_2Si)_4Si$ (X=Cl,Br), but is too unstable to have been fully characterised. It reacts with MeMgBr, $LiAlH_4$, and PCl_5, all of which symmetrically open the 3-membered rings.[176] The structure of $[(Bu^tCH_2)_2Si]_3$ has Si-Si bond lengths comparable to those in $(Ar_2Si)_3$ (~240 pm), while those in $(Bu^t{}_2Si)_3$ of 251 pm are the longest reported. The Si-C bond (197 pm) is also exceptionally long.[177] Oxidation of $(Bu^t{}_2Si)_3$ with O_2, DMSO, or MCPBA inserts one,

two, or three oxygen atoms into the ring, while S and Se insert one.[178] Cyclotetrasilanes with hindered substituents ring contract on irradiation to the cyclotrisilane and disilene,[179] while laser photolysis of $(Me_3Si)_2SiMePh$ gives the short lived silylene PhMeSi: which dimerises to the disilene of unexpectedly low reactivity. Irradiating $[(2,6\text{-}Me_2C_6H_3)_2Si]_3$ yields the disilene, reacting with CH_2N_2 to give the disilacyclopropane, itself inserting oxygen from MCPBA, decomposing thermally to a benzo-1,3-disilacyclohexene and giving silene and silylene on irradiation.[180] The photoinduced fragmentations of $[Bu^t(mes)Si]_3$ gives cis:trans disilene in the ratio 1.6:1, heating subsequently giving the trans isomer through rotation about the Si=Si double bond. This also results on photolysing $(Me_3Si)_2SiBu^t(mes)$, and adds oxygen to give the oxa- and dioxa-cyclodisilane, the latter isomerising to the cyclodisiloxane.[181] The structure of $(mes_2SiO)_2$ shows the trans-annular Si---Si distance to be less than a single bond length, reduction with $Li/C_{10}H_8$ followed by hydrolysis giving the disilane-1,2-diol, in support of a trans-annular Si-Si single bond.[182] 2,3:5,6-Dibenzo--7,7,8,8- -tetraisopropyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene on photolysis loses disilene, which gives the cyclotetrasilane through π-dimerisation, a mechanism suggested for the formation of $[(Me_3Si)_2Si]_4$ from $(Me_3Si)_3SiOMe$.[183]

Dodecamethyl-3,4,7,8,11,12-hexasilacyclododeca-1,5,9-triyne results from $ClMe_2SiSiMe_2Cl$ and Grignard derivatives of HC≡CBr and BrC≡CBr. Pyrolysis extrudes Me_2Si: stepwise to give ultimately the trisilacyclononatriyne which with α-pyrone gives the trisilacyclophane with a twisted saddle conformation. The original hexasila--1,5,9-triyne is oxidised by $Me_3\overset{+}{N}\text{-}\overset{-}{O}$ with insertion into the Si-Si bonds, the product inverting to the substituted benzene on pyrolysis. Irradiating dibenzotetramethyldisilacyclohexadiene in the presence of TCNE extrudes Me_2Si: which also results from the disilaoxacycloheptadiene.[184]

1,2,3-Trisilacyclopent-4-enes generate silylene from the central position regiospecifically on thermolysis, but substituents determine which is ejected on photolysis. The disilacyclobut-3-ene is the other product. Octamethyl-1,2-disilacyclobutane is very air sensitive and the Si-Si bond readily cleaved by acid, halogen and RLi. $(Ph_3P)_2PdCl_2$ catalyses insertion of acetylenes, dienes and allene through initial formation of the Pd(0)disilacyclopentane.[185] Condensing $MeClSiR(CH_2)_4SiR'ClMe$ (R=R'=Me,Et;R=Cl,R'=Me) with H_2O,

$MeNH_2$ or H_2S gave heterocycles, single or coupled, together remarkably with 1,2-disilacyclohexanes, single, coupled and fused. These also result from $ClMe_2Si(CH_2)_3SiMeClR$ with Na/K alloy or Li.[186]

The digermane $([(Me_3Si)_2CH]_2Ge)_2$ has a trans-folded structure with Ge-Ge bond 234.7 pm (4% short of single), a fold angle of 32°, and in solution behaves as singlet germylene, adding EtOH by insertion into O-H. $[(2,6\text{-}Et_2C_6H_3)_2Ge]_2$ has a shorter bond (221.3 pm), a smaller fold angle (15°) and retains its double bond in solution. It results from the photolysis of the trigermane, and adds MeOH across the Ge=Ge bond.[187] As with silicon derivatives, 1,2-digermacyclohex-4-enes and 7,8-digermabenzo[2.2.2]cyclooctadiene eliminate the digermene thermally, a Ge-Ge bond of 230 pm and a fold angle of 37° best fitting the matrix vibrational spectra.[188]

Coupling constants indicate the Ge-Ge bond to be a better transmitter of substituent effects than Si-Si. Cl_3CCO_2H cleaves 2 Ph groups from Ph_6Ge_2 to give $[(Cl_3CCO_2)Ph_2Ge]_2$ with bridging trichloroacetate, and the structures and vibrational spectra are reported for $(Ph_2Ge)_5.C_6H_6$ and $(Ph_2Ge)_n$ (n=4,5,6).[189] The first 1,2-digermacyclobutene results from 3,3,6,6-tetramethyl-1-thia--cyclohept-4-yne and $C_4H_8O_2.GeCl_2$. It has a planar ring with Ge-Ge bond of 238.0 pm, shorter than those of digermane and Ph_6Ge_2.[190]

Pd catalyses the preparation of silyl enol ethers from $Me_3SiSnBu^n_3$ and α-haloketones, vinylstannanes from Me_6Sn_2 and allenes, $RSnMe_3$ from Me_6Sn_2 and RX (R=allyl,X=acetate or halide; R=aryl,X=I), and the preparation of R_6Sn_2 from R_3SnCl and $LiAlH_4$, which in excess gives R_3SnH.[191]

4 Hydrogen Derivatives

Calculations suggest that the Si-C bond of $MeSiH_3$ should be 3 pm longer than observed from its microwave spectrum, while that of allylsilane supports the skew isomer. 1^y silanes and disilanes decompose with silylene formation,[192] while IR photochemistry of alkyl and aryl silanes supports SiH_4 formation first.[193] The IR band shape of the Si-H valence vibration in organosilanes depends on vibrational dephasing relaxation.[194]

The fluoride catalysed addition of ketones to silanes R_3SiH shows predominant inversion at Si, while reduction of ketones by silanes provides a useful route to optically active 1,2-diols and 2-amino alcohols.[195] Phosphinamides are reduced by $PhSiH_3$ to diphosphines

via R_2PNEt_2 and R_2PH, and optically active P,N ligands and N-chelating ligands are used in the Rh catalysed hydrosilation of ketones and oximes by diarylsilanes, which are enantioselective.[196] Heterogeneous fluorination of R_2SiH_2 by SbF_3 gives both mono- and difluoro-silanes, while $ArN_2^+BF_4^-$ salts yield ArCHO on Pd catalysed formylation by CO/Et_3SiH or $[SiMe(H)O]_n$ (PMHS).[197]

PMHS can be metallated with $Co_2(CO)_8$ or $[C_5H_5Fe(CO)_2]_2$ at Si to give metallocyclosiloxanes $[MeSi(R)O)_n$ ($R=Co(CO)_4, C_5H_5Fe(CO)_2$; n=4,5). Titanocene derivatives result on condensing $TiCl_4py_2$ with $(C_5H_5Me_2Si)_2O$ or $[MeSi(C_5H_5)O]_n$ (formed from the Si-H precursors), while of phosphino and arsino substituted polystyrenes treated with $[IrCl(C_8H_{12})_2]_2$ and Et_3SiH, only the phosphino ones show reasonable activity in catalysing the reaction of EtOH with $Me_3SiO[MeSi(H)O]_nSiMe_3$ (n~50).[198] Dehydrocondensation of R_3SiH with silanols is catalysed by $ZnCl_2$, while the reactivity of terminal Si-H bonds in $H(SiMe_2O)_nSiMe_2H$ (n=1-5) to $Ph_2Si(OH)_2$ decreased for n increasing from 1 to 3, then remained constant.[199]

Both Rh and Ir form disilyldihydrides from $[(Me_5C_5)M]_2Cl_4$ and Et_3SiH, while hydrosilation of trans-$Ir(PPh_3)_2(CO)Cl$ is greatly assisted by a chelating β-phosphino group on the silane.[200] $Co_2(CO)_8$ catalyses the ring opening of oxiranes by R_3SiH/CO to give 1,3-diols. Silyl exchange on $R_3SiCo(CO)_4$ occurs photolytically through addition of R'_3SiH to $R_3SiCo(CO)_3$, while cis-mer-$HM(SiEt_3)(CO)_3PPH_3$ (M=Fe,Ru) lose R_3SiH as the 1^y photoprocess, together with CO.[201]

A comparison of the structures of $C_5H_5(CO)_2FeSiR_3$ and $MeC_5H_4(CO)_2Mn(H)SiR_3$ show the Fe compounds to have the shorter M-Si bond, with the Mn derivatives possessing a Mn-H-Si bent 3-centre bond, which influences the stereochemistry of insertion of Mn into Si-H and Ge-H bonds.[202] Catalysed hydrosilylation of alkenes and alkynes has been extensively explored.[203]

The gas phase IR spectra of silanes and germanes, appropriately deuterated, have been used to obtain the σ^* values for cyclopentyl and cyclopropyl groups, and the geometry of the germanes. IR studies indicate that Et_3SiH and Et_3GeH complex with donor solvents.[204]

Bu^n_3SnH has been used in the synthesis of bicalicene, tetradentate organosulphur ligands, and to give the allylic stannane $H_2C=C(CH_2SnBu^n_3)_2$, which is a useful isobutene synthon.[205] The photoreduction of carbonyl compounds by Bu^n_3SnH has been shown to give the tin ethers as major and pinacols as minor products, rather

than the alcohols, and Fischer's carbene catalyses the condensation of R_3SiH and norbornadiene to organotin elastomers.[206] The temperature dependence of rates of radical rearrangements relative to H abstraction from $Bu^n{}_3SnH$ has provided a new expression for the neophyl rearrangement and the rates of ring formation in 2-allylbenzyl and 2-(2-vinylphenyl)ethyl radicals.[207]

5 Radicals and Metal Derivatives

E.s.r. studies show the radical cations R_3SiPh^+ have the ψ_S orbital semi-occupied like radical anions (alkyl benzenes have ψ_A semi-occupied). The anion $(COT)_2SiMe_2^{\bar{\cdot}}$ shows the electron localised on one ring, with no conjugation through Si, and heterosubstituted carbon radicals result from photoionised, sequential electron transfer-desilylation in $RXCH_2SiMe_3$ (X=O,S) systems.[208] Photolysing R_2S_2 and acylsilanes gives radicals $R'\dot{C}(OSiMe_3)SR$, whose structure is ascertained by alternatively reacting $Me_3Si\cdot$ with PhC(O)SMe, while rate constants are determined for the addition of $Et_3Si\cdot$ and N-O spin traps.[209] The preferred conformation of $(R_3MCH_2)_2CX$ (M=Si,-Ge,Sn;X=H,Me,$OSiMe_3$) shows the two metalloid groups almost eclipsing the singly occupied carbon p orbital.[210]

Mes_6Si_2 dissociates reversibly between -60° and -32°C, and mes_6Ge_2 between -12° and 53°C. The radicals react irreversibly by substitution or H abstraction.[211] Polygermyl radicals result from hydride precursors using $Bu^tO\cdot$, and give $R_2Ge:$, $R_3Ge\cdot$, α-digermyl diradicals (or digermanes), and β- or γ-polygermyl diradicals <u>via</u> homolytic monoelectronic α-elimination.[212] While $Me_2(Me_3CCH_2)Ge\cdot$ has the neopentyl group free-rotating, $Me_2(Me_3SiCH_2)Ge\cdot$ has Me_3SiCH_2 eclipsing the singly occupied Ge orbital, and $Me(Me_3SiCH_2)_2Ge\cdot$ shows 2 kinds of methylene proton due to slow invertion.[213]

$Bu^n{}_3M\cdot$ (M=Ge,Sn) react more slowly than $Et_3Si\cdot$ with electrophiles,[214] while RX (X=I,OC(S)SMe) couples with alkenes in the presence of $Bu^n{}_3Sn\cdot$.[215] Alkoxythiocarbonyl radicals, which result from ROC(S)SMe and $Me_3Sn\cdot$, decompose to COS and alkyl radicals, themselves also formed by ultrasonic radiation (55 kHz) of R_4Sn, R_6Sn_2 and $(PhCH_2)_3SnCl$.[216] Heavy atoms are shown not to block intramolecular energy transfer in $Me_3M(CH_2)_2\dot{C}HMe$ (M=Sn,Pb). γ-Radiation of stannanes gives radical cations which show strong sp hybridisation at Sn for $Me_{4-n}SnH_n^+$ (n=1,2,3), but Me_4Sn^+ has spin density on one methyl group and loss of 5s character in the singly

occupied molecular orbital.[217]

Both Me_3SiLi and Me_3SnLi couple with AdBr, while K reduction of organosilanes gives relatively stable radical anions for methylphenylsilanes, Ph_4Si and Ph_6Si_2 but that for other less stable ones, the site of highest free electron spin density is that of highest reactivity, leading to a prediction of decomposition products.[218] Calcium inserts Et_3SiCl at 900°C to give the $Et_3SiCaCl$, which couples with both chlorosilanes and germanes.[219] Cu(I) catalysed silyl magnesation by $PhMe_2SiMgMe$ of $CH{=}C{=}CH(CH_2)_6$ gives $PhMe_2SiC{=}CH(CH_2)_7$, Pd(0) and $PhMe_2SiAlEt_2$, predominantly $PhMe_2SiCHCH{=}CH(CH_2)_6$, Pd(II) both isomers with $PhMe_2SiAlEt_2$ or $(PhMe_2Si)_2Zn$. Reductively condensing $Me_2SiCH_2CH_2SiMe_2NPCl_2$ with $(Me_3Si)_2Hg$ gives the diphosphene.[220] The silylboranediyl Ph_3SiB: results on photolysing $(Ph_3Si)_3B$ (from BBr_3 and Ph_3SiLi), inserts THF and adds to $Me_3SiC{\equiv}CSiMe_3$ to give the boracyclopropene. The first silyl lanthanide $(C_5H_5)_2Sm(SiMe_3)_2$ results from $[(C_5H_5)_2SmCl]_2$ and Me_3SiLi in DME.[221]

The first organoGe-Mg compound $(Me_3Ge)_2Mg.2DME$ results from $(Me_3Ge)_2Hg$ and Mg, $(CF_3)_3GeH$ [from $(CF_3)_3GeI$ and Et_3GeH] and Et_2Hg yield $[(CF_3)_3Ge]_2Hg$, while B-mercurated carboranes and digermanes yield compounds with B-Hg-Ge or Ge-Hg-B-B-Hg-Ge chains.[222]

Lithium bis-silyl cuprates have been used in the diastereoselective alkylation of β-silylenolates, and in the preparation of silyl alkenes.[223] Germyl cuprates react with terminal acetylenes to give vinylgermanes in good yield, while stannyl cuprates are intermediate in the annulation of cyclic unsaturated esters to stannyl derivatives further substituted α to the double bond.[224] 2,3-Dichlorobuta--1,3-diene and 1,4-dichlorobut-2-yne with excess Me_3SnLi give the 2,3-distannyl buta-1,3-diene which is easily destannylated or inserted by electrophiles.[225] $(CH_2)_2CHCH_2X$ (X=Br,I) and Me_3SnM (M=Li,Na,K) give cyclopropylcarbinyl and 3-butenyltrimethylstannanes as major products, proportions and yields depending on the conditions employed.[226] The poor selectivity on stannylation of 1-chloro-1-silacyclopentanes results through the operation of 2 mechanisms, S_N2 substitution (with inversion) and Cl/Sn exchange (retention or epimerisation at Si).[227] Pd(0) catalyses the stannylation of allyl acetates using $Et_2AlSnBu^n_3$, which gives β-hydroxy carbonyl compounds from α-halo carbonyl derivatives via enolates. Organolead-aluminium compounds behave similarly.[228]

$Me_3SiMn(CO)_5$ inserts CO, aldehydes and cyclic ethers to give

functionalised acyl derivatives, while alkylation and acylation of $[Me_3SiFe(CO)_4]^-$ induces a 1,3-silatropic shift to the acyl oxygen atom.[229] GeF_2 desilylates $Ph_3SiCo(CO)_4$ to give the germylene $[(CO)_4Co]_2Ge$: which gives the germacyclopentene with 1,3-dienes, while $[(Me_3Si)_2CH]_2Sn$: adds to one edge of $Os_3H_2(CO)_{10}$, remarkably incorporating the H atom across one Sn-Os bond.[230]

Ph_3MLi (M=Ge,Sn) displaces CO from $C_5H_5M'(CO)_2NO$ (M'=Mo,W), the anion coupling with MeI at room temperature to form the square pyramidal $C_5H_5M'(MPh_3)(CO)(NO)Me$ with CO/NO trans, but at -78°C a cis-mixture results in addition. $[MeC_5H_4Mn(CO)_2MR_3]^-$ (M=Si,Ge) and RX give trans-substituted square pyramidal piano stool complexes which with Ph_3P eliminate Ph_3MR or Ph_3MH, while alkenyl halides give η^1,η^2 and η^3 complexes depending on metal and ligand.[231] The 7-coordinate anion $(Ph_3Sn)_3Cr(CO)_4^-$ reacts with nucleophiles (eg Ph_3SnLi, Ph_3P) to give $(Ph_3Sn)_2Cr(CO)_4^{2-}$. $Et_4N^+[(C_5H_5)Nb(CO)_3SnPh_3]^-$ has a highly distorted tetrahedral structure at Sn, while $C_5H_5M(CO)_nPbPh_3$ (M=Fe,Cr,Mo,W) give the sulphinatophenyl complexes with SO_2 through migration.[232] The stability of the radical anion of $C_5H_5Fe(CO)_2MPh_3$ (M=Si,Ge,Sn) and $Ph_3MCo(CO)_3L$ decrease as the size of M increases, while those of $RGeCo_3$, $RGeCo_2M$ and RGeCoMM' clusters become less stable the different metals there are in the cluster.[233]

6 Nitrogen Derivatives

Aminosilanes have been used to silylate the surface of hydrated silica, to transaminate DMF, to give the silyl enol ethers of β-amino ketones and 1,3-bis(dialkylamino)-1-alkenes using α,β--unsaturated ketones and aldehydes.[234] Bis-silyl carbohydroxamic acids occur predominently as the keto isomer, while the dianion of $Me_3SiNHCOCH_3$ couple electrophiles without N to C rearrangement.[235] Alkyl(trialkylsilyl)aminyl radicals are π-radicals, the R_3Si +I/-M substituent effects being insufficient to switch from a π- to a σ-SOMO.[236]

$(Me_3Si)_2NLi$ couples and lithiates $HC{\equiv}CCH_2Br$, thereby providing a route to protected 1^y amines, while $ROCH_2N(SiMe_3)_2$ [from $(Me_3Si)_2NNa$ and $ROCH_2Cl$] gives 1^y amines on alkylation and protolysis, and α-aminomethylation of esters using ketene silyl acetals.[237]

The structures of $(Me_3Si)_2NH$, $(Me_2HSi)_2NH$, $Me_{3-n}SiH_nNMe_2$ (n=1,2,3) and $(H_3Si)_3N$ are determined, the latter's supporting non-polarity of Si-N bonds as the N atoms are stacked above each

other.[238] The electron diffraction of $(Me_3Si)_2NLi$ shows it to be dimeric in the vapour state, and $(Me_3Si)_2NLi.12$-crown-4 monomeric in the solid, the first structurally characterised mononuclear lithium amide.[239] $[(Me_3Si)_2N]_2Zn$ has a linear N-Zn-N skeleton, and with $(C_5H_5)_2Zn$ gives $(C_5H_5)_3Zn_2N(SiMe_3)_2$ which possesses amide and C_5H_5 bridges. The mercury amide and R_2PH give $(Me_3Si)_2NHgPR_2$.[240] The anions $(M[N(SiMe_3)_2]_3)^-$ (M=Eu,Yb), which result from MI_2 and $(Me_3Si)_2NNa$, share 2 disilazane groups with Na^+.[241]

$TiCl_4$ forms complexes with mono- bis- and tris(amino)silanes, while $[(Me_3Si)_2NMCHSiMe_2NSiMe_3]_2$ or $R_2M[N(SiMe_3)_2]_2$ (M=Zr,Hf;R=Me,-Et,Me_3SiCH_2) and DMPE gave the bismetallocycle $Me_3SiNSiMe_2CH_2MCH_2SiMe_2NSiMe_3$.DMPE almost quantitatively.[242] Vanadyl alkoxy chlorides and $Me_3SiN(R)Li$ give amides which isomerise irreversibly by intramolecular silyl migration on heating to give the imide. Binuclear halogen bridged imides result from $Me_3SiNHBu^t$ and M_2Cl_{10} (M=Nb,Ta) and $TaCl(NBu^t)[N(SiMe_3)_2]_2$ with Me_3SiBr. $NbCl_5$ desilylates $(Me_3Si)_4N_2$ to give a stable N_2 complex $NbCl_3(THF)_2N_2$ which with $Me_3SiS_2CNEt_2$ give the dithiocarbamate N_2 complex.[243]

The diazaboracyclopropane$(Me_3Si)_2NBN(SiMe_2Bu^t)N(SiMe_2Bu^t)$ results from the dilithium hydrazide, while tetrazenes $(Me_3M)_nN_4H_{4-n}$ (M=Si,Ge,Sn) have been prepared and thermally decomposed if trisilylated or unsymmetrically disilylated into Me_3SiN_3, while $Me_3SiNHN{=}NNHSiMe_3$ gives $(Me_3Si)_2NNH_2$ and N_2 on prolonged heating.[244] $Bu^t_3SiN{=}NNHSiBu^t_3$ shows coalescence of proton n.m.r. signals at 55°C, supporting a 1,3-proton migration, and decomposes at 150°C to $(Bu^t_3Si)_2NH$ and N_2.[245]

Cyclic silyl azides $R(N_3)Si(CH_2)_n$ photolyse to give both endo- and exo-cyclic silaimines which can be trapped through C-H insertion. Pyrolysing $(Me_3Si)_2NSi(OMe)_2Me$ yields $Me_3SiN{=}NSi(OMe)Me$, isomerising to $Me_2(MeO)SiN{=}SiMe_2$ which adds Me_3SiOMe to provide a route to $Me_3SiN{=}SiMe_2$. These silaimines dimerise to cyclodisilazanes and insert $(Me_2SiO)_3$.[246] However LiF elimination from $(Me_3SiNMe)_2SiF-N(Li)SiMe_2Bu^t$ results in partial group exchange before coupling of these intermediates gives the mixed cyclodisilazane.[247]

Aryl nitrites result in good yield from ArCHO and Me_3SiN_3, which substitutes ketones to give gem-diazides and tetrazoles, gives dithiazines from o-$RC_6H_4(SCl)_2$,[248] and adds iminoboranes to give boratetrazoles.[249] N-Cyanimines result from ketones and $(Me_3SiN)_2C$, which gives dimeric $Cl_4NCNSiMe_3$ with $SbCl_5$, while $Fe_2(CO)_6RNS$ is

formed from $Fe_3(CO)_{12}$ and $(Me_3SiN)_2S$.[250] Nitrosyl salts and disilazanes give diazonium derivatives, while the intermediacy of solvent stabilised Me_3SiBF_4 in the preparation of substituted ketones is refuted.[251]

A series of boron substituted silylaminoboranes have been prepared from $(Me_3Si)_2NBCl_2$, the borirene $(Me_3Si)_2NBCR{=}CR'$ results through ring substitution of trithiadiborolane by acetylenes, while silylated sulphur diimides insert to give the new 1,4-dithia-2,6-diaza-3,5-diborinanes.[252] The ethylperoxyboron unit can be stabilised as vacuum distillable 1,2,5-azasilaboroles, while silylated 2-picoline and 2-aminopyridine, which result from α-picoline and $(Me_3Si)_2NH$ followed by amination, give heterocyclic derivatives with B_2Cl_4 containing both 3- and 4-coordinate boron.[253]

Hydrolysing $Me_2Si(NHBu^t)_2$ in the presence of $MeInCl_2$ gives the adduct $MeInCl_2.Bu^tNH_2$ which is a 1-D polymer through H---Cl association. The acidity of In is greater than that of Sn in $Me_2Si(NBu^t)_2Sn.Bu^tNH_2$, the parent acid resulting from the thermal decomposition of $Me_2(NBu^t)_3Sn_2$, and adding, like $[(Me_3Si)_2CH]_2Sn$: and SnX_2 (X=Cl,Br,I), to 1,3-dienes to give 1-stannacyclopent-3-enes.[254] With PCl_3, $Me_2SiNBu^tMNBu^t$ gives the tris(chlorogermyl)-phosphine (M=Ge), the Sn(IV) dichloride and $(PCl)_n$ (M=Sn), and ring exchange to give $PbCl_2$ (M=Pb).[255]

An extensive series of bis(silyl)aminophosphines have been prepared. They insert epoxides with silyl migration, reduce thiiranes to alkenes, and are oxidised by Me_3SiN_3, CCl_4, nitro- and nitroso-arenes.[256] The phosphene $(Me_3Si)_2NP{=}CHSiMe_3$ and phosphadiene $(Me_3Si)_2NP{=}C(SiMe_3)CH{=}CHSiMe_3$ have been prepared, the former on treatment with RLi/Me_3SiCl giving products showing hindered rotation about the $P{-}CH(SiMe_3)_2$ bond.[257] Silylated P(III) and P(V) imines form phosphazene complexes with Re and chelate complexes with Mn, while $Bu^t(Me_3Si)NP(X)NHBu^t$ (X=S,Se) displaces C_2H_4 from $(Ph_3P)_2PtC_2H_4$ to give a complex through P-X interaction at Pt, showing N---Si coordination.[258] The 2-(N-methyl-N-trifluorosilyl-aminomethyl)pyridine similarly shows Si 5-coordinate as it is in $PhCO_2CH_2CH_2SiX_3$ (X=F,Cl). The disilazane complex $Ni(R)N(SiMe_2CH_2PPh_2)_2$ inserts CO into the Ni-R bond then rearranges with Ni carbonylation and COR migration to N, to give the diphosphine complex, predominently as imide.[259]

$(Me_3Si)_2NH$ silylates $(Cl_2PO)_2NH$ to give N- and O-silylated phosphazenes, Me_3SiCl adds to the P=N bond of $(R_2N)_2P{\equiv}N$, and

$(Ph_2P)_2NLi$ with chlorosilanes give the N-silylamide, the P-diphenylphosphino silylamide or a mixture. Me_2PCl gives only the P-phosphinophosphinimine and $(Me_3Si)_2NPPh_2$ shows silyl inequivalence at low temperature, showing restricted rotation about the P-N bond.[260] $(R^F)_2PN(SiMe_3)_2$ ring expands $S_3N_2Cl_2$ to PN_3S_2 heterocycles which can be further expanded by the NSN fragment, itself lost from $S_4N_4O_2$ in the presence of $(Me_3Si)_2NNa$.[261] This or $Ph_3P{=}NSiMe_3$ couple benzodithiazoles to thiazato aryl disulphides, while $[(Me_3Si)_2N]_2SO_2$ and SCl_2 give $S_6N_4O_4$ which complexes with $TiCl_4$. Silyl sulphonamides occur predominently as the N-silyl tautomer except with electron withdrawing groups.[262] $S(CN)_2$ results from Me_3SiCN and SCl_2, and Se-N rings from $Me_3SiN(Bu^t)Li$ and Se_2Cl_2 or $SeOCl_2$.[263]

A series of 1,2-diaza-3-sila-5-cyclopentenes result from $RNHSiF_3$ and $Me_2C{=}N{-}N(Bu^t)Li$ which dimerise on subsequent lithiation,[264] the kinetics of hydrolysis of silylurethanes examined, ^{15}N-^{29}Si coupling measured for ^{29}Si satellites in natural abundance, and $MeSi(NHMe)_3$ prepared as a precursor for the preparation of $SiC{-}Si_3N_4$ fibres.[265] Silylamino isothiazoles insert PhCN after lithiation to lengthen the side chain, imidazoles complex with silicon, and silylated pyrolles have been used to prepare the antibiotic verrucarin E.[266] Methylsilyl derivatives of cinchocaine have been prepared, N-(Me_3Si)-2-oxazolidine silylates R_2CO, ROH, RSH and RCO_2H, while silylated 1,4-dihydropropyrazines with TCNE undergo single electron transfer to give persistent solvent separated ion pairs R^+R^-.[267]

CCl_3CHO and Me_3GeNR_2 give insertion and elimination products (Me_3GeCCl_3), whereas Me_3GeXR (X=O,S) give insertion only, while ArNCS, PhNCO and PhCN add to Ph_3GeN_3 to give germyl tetrazoles.[268] Vicinal iodothiocyanates result from $Bu^n{}_3SnNCS/I_2$ and cyclohexenes, and n.m.r. spectroscopy supports a transannular N---Sn interaction with $Me_2Sn(CH_2CH_2CH_2)_2NMe$ and $MeSn(CH_2CH_2CH_2)_3N$.[269] The fused B_6N_7 three ring system results from $Me_3SiN(SnMe_3)_2$ and $B(SR)_3$ on loss of Me_3SnSR while Me_3SnOH and $HN(SO_2Me)_2$ give $Me_3SnN(SO_2Me)_2$ which with $MeSO_2Cl$ forms $(MeSO_2)_3N$.[270] The binding energies of organic bases to Me_3Sn^+ show amines to be stronger than oxygen bases, the order for methyl amines showing an increase with methylation, but for ethyl and butyl amines $R_3N < R_2NH$.[271]

7 Phosphorus Group Derivatives

The first phosphasila-alkene results from 2,4,6-$Bu^t{}_3C_6H_2PH_2$ $(ArPH_2)$

and mes_2SiCl_2 using Bu^nLi, adds MeOH (H to P) but has not yet been isolated.[272] The terminal diphospha-allene ArP=C=PAr results from $ArPHSiMe_2Bu^t$ using BuLi and CO_2, or from the phosphaketene ArP=C=O and $ArP(Li)SiMe_3$.[273] The phosphaketene and the Wittig reagent $Ph_3P{=}CPh_2$ give the ethenylidenephosphine which also results from $Ph_2C{=}C{=}O$ and $ArP(Li)SiMe_2Bu^t$, PhNCO yielding ArP=C=NPh.[274] $ArP(SiMe_3)_2$ and $CSCl_2$ give the phosphathiaketene ArP=C=S which dimerises asymmetrically to lose CS_2 and give the diphospha-allene on photolysis.[275] $Me_3SiP(R)CSNMe_2$ (R=mes, Bu^t) results from Me_2NCSCl and $LiP(SiMe_3)R$, the mesityl derivative disproportionating to $mesP(SiMe_3)_2$ and $mesP(CSNMe_2)_2$, with the Bu^t derivative losing Me_3SiNMe_2 to give $Bu^tP(S)PBu^t(CNMe_2){=}CSSiMe_3$.[276] Phosphacarbamic esters dominate the keto-enol equilibrium of the $RP(SiMe_3)_2$-CO_2 adducts.[277] Dicarboxylic acid chlorides are terminally substituted by Ph_2P using Me_3SiPPh_2, cyclohexenoyl chlorides substituted 4,5 give phosphabicyclononanes with $RP(SiMe_3)_2$ whereas the analogous norbornene gives silylated diphosphines for R=Me. For R=Ph, however, the norbornene acid chloride gives the ring opened diphosphabicyclo-undecatriene by a Cope rearrangement. While $PhP(SiMe_3)_2$ and the acid chloride of cyclohexane-1,2-dicarboxylic acid gives the siloxy-3,4-diphosphacyclodeca-1,5-triene, o-$[(Me_3Si)_2P]_2C_6H_4$ and oxalyl chloride give the diphosphanaphthalene.[278]

The structures of the phosphorus ylids $XMe_2P{=}C(SiR_2CH_2)_2SiR_2$ resulting from $X_2C(SiR_2CH_2)_2SiR_2$ and Me_3SiPMe_2 show a flat chair conformation for R=X=Cl, and a boat one for R=Me,X=Br. PCl_3 cleaves the Si-C bond at the ylid carbon atom, while $MeP(SiMe_3)_2$ couples $(Cl_3Si)_2C{=}PMe_2Cl$ to give the diylid $[(Cl_3Si)_2C{=}PMe_2{-}]_2$ and cyclic ylid $Cl_3SiC{=}PMe_2PMePMeSiCl_2$.[279] The last of the series $P_4(SiMe_3)_nBu^t_{4-n}$ (n=3) results from $(Me_3Si)_5P_3$ and Bu^tPCl_2, and $Me_3Si(PBu^t)_3SiMe_3$ exists as the threo-erythro isomer only, for steric reasons.[280] The vibrational spectra of $(Me_3Si)_3P$, $[(D_3C)_3Si]_3P$, $(Ph_3Si)_3P$ and the polycyclic cage $P_6[Si(SiMe_3)_2]_4$, which results from $(Me_3Si)_3SiCl$ and Na/K phosphide, have been analysed.[281]

Me_3SiPPh_2 gives the ylid complex $(CO)_4MnPPh_2C(OSiMe_3)R$ with $RMn(CO)_5$ (R=Me,CH_2Ph,Ph,naphthyl), while $NiCl_2/Ph_3P$ and $CoCl_2(PPh_3)_2$ give Co_4 and Ni_8 cage complexes with $(Me_3Si)_2PPh$.[282] The Ni(II) complex of 2,3-$(Ph_2P)_2$-N-methylmaleimide couples $(Me_3Si)_2EPh$ (E=P,As) to give diphosphene and diarsene complexes with E-E shorter than the single bond length.[283]

Benzo-1,3-diphospholenes with C, Si, Ge and Sn at 2 have been made, and the configurational evolution at P-Si and P-Ge bonds studied through the synthesis of silyl and germyl phospholanes and phospholenes, the latter reacting with electrophiles with inversion at P.[284] Pyrolysing $Me_3SnE(CF_3)_2$ (E=P,As) eliminates Me_3SnF and $CF_3E{=}CF_2$ which can be trapped and characterised at -196°C but associates to give 3 isomeric dimers on warming, and a trimer.[285] The biscyclotriphosphane $Bu^t{}_4P_6$ results from coupling $XPPBu^tPBu^t$ (X=Cl and Me_3Sn), or $X{=}PCl_2$ with $[Me_3Sn(Bu^t)P]_2$.[286] $(Me_3Sn)_3Sb$ is oxidised to $(Me_3Sn)_2O$ and $(Me_3Sn)_4Sb_2$, and gives $(Me_3Sn)_2Fe(CO)_4$ with $Fe_2(CO)_9$, while $(Me_3M)_3Sb$ (M=Si,Ge) form $(Me_3M)_3SbFe(CO)_4$.[287]

8 Oxygen Derivatives

A theoretical study of the 6 isomers of CH_4SiO shows methylsilanone MeHSi=O to be the most stable, and the metathetical reaction with C_2H_4 suggests that the C=O bond is about 10 Kcal.mol^{-1} stronger than Si=O. $Me_2Si{=}O$ is suggested as intermediate in the rapid cleavage of R-Si bonds of $RSiMe_2OMe$ (R=$ArCH_2$ or PhC≡C) in $H_2O/MeOH/MeO^-$ via the siloxide anion RMe_2SiO^-.[288] The epoxides of sila- and germa-cyclopent-3-enes give silanone and germanone on heating, while the di-epoxide of the spirobicyclononadiene $CH_2CHMe{=}CHCH_2SiCH_2CHMe{=}CHCH_2$ gives a spirosiloxane on heating in the presence of $(Me_2SiO)_3$, supporting the intermediacy of O=Si=O.[289]

An extensive series of alkoxy- and siloxy-silanols have been made,[290] and infinite chain structures formed through H-bonding observed for the morpholinoalkylsilanols which, like piperidino, pyrrolidino and hexamethylenimino derivatives, show atropine activity.[291] $Bu^t{}_2Si(OH)_2$, $Pr^i{}_2Si(OH)_2$ and $Bu^t{}_2Si(OH)F$ react with halosilanes to give chain siloxanes $(HOSiR_2)_2O$ and $(HOSiR_2O)_2SiR_2$ which, like $Bu^t{}_2Si(OH)_2$, associate through H-bonding. Cyclotrisiloxanes also result via 1,3-dihydroxydisiloxanes and cyclotetrasiloxanes from $R_2Si(OLi)_2$.[292] Though chloro and aminoalcohols of the type $R_2C(X)OH$ (X=Cl,NH_2) are unknown, the analogous chlorosilanols can be made from $R_2Si(OH)_2$ and PX_5 (X=Cl,Br) and the aminosilanol from $R_2Si(Cl)OH$ and NH_3. The structure of $Bu^t{}_2Si(NH_2)OLi$ shows a cubane-like structure with N-coordination to Li.[293] $Me_3SiO^-M^+$ function as oxide equivalents soluble in non-aqueous solvents (M=K), converting carboxylic acid esters into acid salts, and giving xanthates with CS_2 (M=Li-Cs) which can be readily alkylated.[294] With

CO_2, Me_3MOLi (M=Si-Sn) give the carbonates.[295] Dimethylsilanone enolate $MeSi(=O)CH_2^-$, which results from collision-induced dissociation of Me_3SiO^- (from OH^- and Me_4Si) reacts with CO_2 to give the silicon equivalent of the acetate ion $MeSiO_2^-$.[296]

The binding ability of crown ethers is greatly reduced on ring contraction using CH_2 or Me_2Si, siloxazanes ring open by Si-N cleavage and the mixed germasiloxane $(Ph_2SiOGeR_2O)_2$, formed from R_2GeX_2 and $Ph_2Si(OH)_2$, shown to be more puckered than cyclotetrasiloxanes. Self-diffusion coefficients have been measured for $(Me_2SiO)_4$, and the molecular structure of $(ClMe_2Si)_2O$ (gas phase) indicates a 2-conformer model.[297]

Interlaminar graphite-siloxane results from graphitic oxide and Me_2SiCl_2 or Me_3SiCl, and trimethylsilyl cellulose used as an intermediate to cellulose esters.[298] Trimethylsilyl silicate anions in acid show tetrameric ring structures, while trimethylsilylation of the mica sericite shows octahedral and tetrahedral Al.[299] The anions $ArSi(ORO)_2^-$ formed from diols possess essentially a square pyramidal structure, 1,3,2-dioxasilacyclohexanes exist as a monomer--dimer equilibrium mixture in solution, while $\overline{O(CH_2)_3}CHSiHMe_2$ isomerises to the oxasilacyclohexane in the presence of a Pd catalyst, which also catalyses the epoxidation of olefins by α-siloxyalkyl peroxybenzoates.[300]

$(Me_3Si)_2SO_2$ catalyses γ-lactonisation of cyclopropane carboxylates, while their siloxy derivatives are cleaved by ArXCl (X=S,Se) to give the appropriate 4-oxoesters, and Me_3SiOSO_2Cl gives silyl 2-oxosulphonates with aldehydes, ketones and silyl enol ethers.[301] Functionalised silyl triflates $R_2SiXOTf$ (X=H,Cl) from R_2SiXY (Y= α-Np,Ph,Cl,H) and CF_3SO_3H. $Me_3SiO_3SCF_3$ forms complexes with BX_3 (X=Cl,Br), catalyses the C-allylation of glycopyranosides, glycosidation of anthracyclinones, and the generation of silyl enol ethers from β-ketosilanes (<u>via</u> Me_3SiCH_2Cu and RCOCl), and silylates SO_2 complexes of Mo and W, and $[C_5H_5(CO)(NO)CrCOCH{=}PMe_3]^-$ at the acyl group.[302] Silyl triflate cleaves Si-aryl more readily than Si-alkyl bonds, and siloxyammonium salts, prepared from triflate and 3^y amine N-oxides, give α-siloxyamines $R_2NCH(R)OSiMe_2Bu^t$ in the presence of base, which with electrophiles E^+ give R_2NE.[303] Bu^tMe_2SiCl has been used to silylate 3-arylphthalides, giving the isobenzofuran, Bu^tMe_2SiO derivatives of key intermediates in the synthesis of C-nucleosides, bicyclomycin and one of the nactins, a macrotetrolide antibiotic,[304] in the preparation of enantiomerically pure chiral

alcohols, and of cis-decalones and 1,2-dioxolan-3-ols.[305] Me_2AlCl selectively cleaves tetrahydropyranyl ethers in the presence of Bu^tMe_2Si ethers which result in high yield from ROH and chlorosilanes in the presence of tetramethylguanidine, while the mass spectra of Bu^tMe_2Si derivatives of 4-chlorobutanol indicate Cl migration to Si.[306]

PPSE [polyphosphoric acid trimethylsilyl ester $Me_3Si(PO_3SiMe_3)_4SiMe_3$] catalyses the Pummerer rearrangement of sulphoxides, $PhS(O)CH_2COPh$ giving the unusual thioglycoxylate PhSCOCOPh (22%) and acetophenone $(PhS)_2CHCOPh$ (30%).[307] α-Lithiated α-phenylthiosilanes are used for the homologation of carbonyl compounds, open oxiranes to give siloxycyclobutanes, while γ-siloxyalkyl phenyl thioethers are converted to γ-silyl alcohols by LiDBB.[308]

1^y amines and RCO_2H are converted into amidines using PPSE, which yields nitriles from aldoximes.[309] The reductive silylation of $RR'C(CN)OSiMe_3$ by Me_3SiCl/Li in THF at 0^oC gives enamines $(Me_3Si)_2NC(=CRR')SiMe_3$ and silylmethyl silyl ethers $RR'C(SiMe_3)OSiMe_3$, while LDA induces O to C silyl migration in $RMeC=NOSiMe_2R'$.[310] Disilyl esters of perfluoroalkyl hydroxamic acid pyrolyse to isocyanates R^FNCO, while $ArC(=NCl)OSiMe_3$ gives both isocyanate ArNCO and nitrile ArCN.[311] $(CF_3)_nPF_{5-n}$ gives 6-coordinate carbamate chelates with $Me_2NCO_2SiMe_3$, which reacts with alcohols autocatalytically.[312]

$2\text{-}Me_3SiOC_6H_4PPh_2$ and P(V) halides give complexes involving P(III) to P(V) coordination, and iminodicarboxylic acid is disilylated by mild silylating agents, but trisilylated by $CF_3C(=NSiMe_3)OSiMe_3$, which also disilylates a dibromo-3,8-phosphononanedione 1-oxide to the disiloxy derivative which then isomerises on warming to phosphorin-7-one with accompanying silyl migration from C-O to P-O.[313]

Covalent chlorinated impurities in $MeSi(OMe)_3$ can be readily removed using Na and substantially reduce its rate of hydrolysis, while 3^y amines accelerate the alcoholysis of Ph_2SiCl_2 through silylated quaternary ammonium intermediates.[314] The $Bu^t(Ph)(MeO)Si$ group provides excellent protection to alcohols, its silyl acetal character providing for ready F^- cleavage, unlike Bu^tPh_2Si, while analogues of the antibiotic bicyclomycin used bicyclic piperazinediones as intermediates, and silylene protected dihydroxystyrene derived from o-hydroxyacetophenone adds dienophiles to give peri-hydroxylated polycyclic aromatic compounds in one step.[315]

Photolysing o-diones with Et_3SiH gives 2-siloxyphenoxy radicals.[316]

The first 1,2-silaoxetene results on photolysing the diazo compond $Me_5Si_2C(=N_2)COAd$ which loses N_2 giving the carbene, this isomerising with silyl migration and cyclisation. The silaoxetene decomposes to $Me_3SiC{\equiv}CAd$ and $Me_2Si{=}O$, and adds MeOH across the Si-O bond with ring opening. Irradiation of oxasilacyclopropane mesityl substituted at Si and spiro substituted to an indane residue gives indene and silane diol in the presence of TCNE/pyrylium salt, but silylene (trapped as EtOH adduct) and indanone in the presence of DCA.[317]

Mo(II) and Ti(IV) catalyse the ring cleavage of α,β-epoxysilanes, providing a route to α,β-unsaturated carbonyl compounds, which also result from chloro siloxy cyclopropanes.[318] Spirovetivanes which are key intermediates of spirobicyclic sesquiterpenes, result from silylated 1-vinyl cyclopropanols. Silyl enols add methyl diazoacetate $HC(N_2)CO_2Me$ to give 2-siloxy substituted methyl cyclopropane carboxylates which ring open to 4-oxoalkanoic esters in the presence of F^-.[319]

Silyl enol ethers result from $R_2CO/Bu^tMe_2SiOSO_2CF_3$ in the presence of amines, and from the base induced rearrangement of 1-(Me_3Si)allylic alcohols, from KH/Bu^tMe_2SiCl and a ketone in one step, while tris(enoxy)silanes are formed from <u>in situ</u> $MeSiI_3$ and aldehyde in the presence of a 3^y amine.[320] They have been extensively used as intermediates in the synthesis of cyclobutanones, δ-keto acids[321] and γ-keto esters and 1,4-diketones,[322] α-chloro, α-silyl, and β-seleno ketones, and α-nitroaryl carbonyl compounds,[323] give enones cleanly, add aldehydes,[324] can be formylated, aminated with $Me_2N{=}CH_2^+$ and function as β-acyl anion equivalents in the presence of strong base.[325] They also give C-glycosides stereospecifically and are intermediate in the synthesis of dehydrofukinone, selina-4(14),7(11)-diene-8-one.[326]

Mannich bases result electrochemically from p-disubstituted dimethylanilines in the presence of silyl enol ether, which form selectively from the kinetically generated enolate, $Bu^tC(OSiR_3){=}CHF$ and RCHO interacting through an open transition state.[327] Methylation of open chain enolates with adjacent silyl group is diastereoselective and assist asymmetric induction in ester enolate Claisen rearrangements.[328] Polycyclic silylated ene diols couple in the presence of oxidising agents[329] while 1,3-bis(siloxy)isobenzofuran results from the phthalic anhydride using $ZnCl_2/Et_3N/Me_3SiCl$,

but can normally only be characterised as dienophile adducts.[330] 2,5-Disiloxy-thiophene and -pyrrole result similarly.[331] α-Isocyano silyl enol ether results from 4-methyloxazole and Me_3SiCl while silyl enolates of cyclopentanone and cyclohexanone couple with α-phenylthioalkyl-α,ω-dihalides or α-cyano-ω-halide.[332]

Synthetic routes to siloxy dienes are described, these compounds being used to prepare α- and γ-protected dicarbonyl compounds, (-)-Pestalotin,[333] Zingiberenol and Daunomycinone analogues,[334] while siloxy cross conjugated trienes add acetylenes to give hydronaphthalenes.[335]

Bis(silyl)butadienyl acetals have been prepared and give hydroxy acids with $PhCHO/TiCl_4$, O-silyl ketene acetals (Z-isomer) result from alkanoate esters and Et_3SiClO_4/Et_3N, and isomerise in the presence of R_3NH^+.[336] Silyl methyl acetals are used to synthesise 3-acylamino-3-oxopropanoates, α-trifluoromethyl β-alkoxy- and β-ketoesters,[337] cyclic amines (with bis-acetals), cyclopropanecarboxylic esters (with $CHBr_3/Et_2Zn$), α-siloxysulphides (with R_2SO),[338] add to α,β-unsaturated ketones, and, like bis(silyl)acetals, give β-lactams.[339] α-Silylated esters and lactones result from the O-silylated acetals at 10 kbar through O to C migration.[340]

Diphenylgermanium oxide has been characterised as trimer, tetramer (monoclinic S_4) and polymer, while hydrolysing $PhGeCl_3/Ph_2GeCl_2$ with $AgNO_3$ in aqueous acetone gives the cage germoxane $(PhGe)_2(Ph_2Ge)_3O_6$.[341] Ph_2SnCl_2 hydrolyses to typical oxygen bridged ladder complexes, the methyl analogue resulting from the decomposition of dimethylchlorotin(IV) xanthate. A similar structure is found for $[(Me_2SnO_2CCH_2Cl)_2O]_2$.[342] $R_4N^+X^-$ adds halide to tin of 1,3,2-benzoxathiastannole, the iodide showing a dimer structure through oxygen bridges. Cyclic 1,3,2-dioxastannanes are dimeric similarly, while diptychoxa- and thiaza-stannolidine show internal N---Sn bonding.[343]

The structures of Ph_3SnOAc and Me_2SnMoO_4 show tin 6-coordinate, but in $(Me_3SnSPMe_2O)_n$ 5-coordinate (X-ray), as with $(Ph_3Sn)_2CrO_4$,[344] sulphonates, tropolonates[345] and $(Bu^n{}_3SnO)_2P(O)Ph$, and 4-coordinate in $(Bu^n{}_3SnO)_3PO$ (n.m.r. and Mossbauer). The carbonates show both 4- and 5-coordinate sites.[346]

Organotin phosphates catalyse epoxide polymerisation, and triflates the hydrostannation of aldehydes and ketones,[347] while triorganotin enolates, which result from the alkoxide and alkenyl acetates, are used to couple α-haloketones (to 1,4-diketones and

dihydrojasmone).[348] Optically active diorgano(alkoxy)tin hydrides are used in the asymmetric reduction of racemic haloalkanes, sulphenate esters result from Bu^n_3SnOR and PhSCl, while macrocyclic dilactones are formed from the distannyl derivatives of 2,6-di(hydroxymethyl)pyridine and FCO-R-COF.[349] $(Ph_3Sn)_2O$ complexes with $SbCl_5$ by chloride displacement, and catalyses the reduction of RCHO and R_2CO to alcohols, as does $R_2Sn(OMe)_2$ using PMHS.[350] $(R_2SnO)_3$ ($R=Bu^t, Am^t$) result from the dichloride and are planar.[351]

9 Sulphur, Selenium, and Tellurium Derivatives

The first silicon thiocyanate $(Me_3Si)_2C(SiMe_2OMe)SiMe_2SCN$ results from the chloride and AgSCN. Its m.pt., 266°C is close to that of the isothiocyanate (from KSCN, m.pt. 269°C) and ν_{SCN} and ν_{NCS} are both 2085 cm^{-1}. It reacts much more readily with MeOH than the iso isomer and the ^1H and ^{13}C n.m.r. spectra of the Me_2SiSCN and Me_2SiNCS groups are distinctly different.[352]

Silyl protected 1^y aminomethyl sulphides result from $(Me_3Si)_2NCH_2OMe$ and $Me_3SiSR/ZnBr_2$, while thiopenam derivatives result from $RC{\equiv}CSSiMe_3$ and 4,5-dihydrothiazoles. The ene thiolate of N,N-dimethylthioamides can be silylated stereospecifically to give the (Z)-N,N-dimethyl-S-trimethylsilylketene S,N-acetal which gives β-hydroxythioamides with $PhCHO/F^-$.[353]

The oxasilacyclopentane ring hydrolyses $\sim 10^4$ times faster than the cyclohexane (cf. phosphates and phosphonates) but this difference is only $\sim 10^2$ for thiasilacycloalkanes. The silyl thiophosphate $(MeO)_2P(S)SSiMe_3$ inserts MeN=C=NPh into Si-S to give the P-substituted thioureas,[354] $(mesPS)_4$ results from the dichloride and $(Me_3Si)_2S$, $MeP(SiMe_3)_2$ adds CS_2, silyl migration giving the symmetrical dimer of $MeP{=}C(SSiMe_3)_2$ (P-C 188 pm). $PhP{=}C(SiMe_3)_2$ remains a monomer (P=C 170 pm), while $Me_3SiSC{=}C(NMe_2)PBu^tPBu^t$ is planar.[355]

Pyrolysing 1,1-dimethyl-1-silacyclobutane with cyclosilthianes at 560°C give a variety of heterocycles through $Me_2Si{=}CH_2$ and $Me_2Si{=}S$ coupling,[356] while heating $Me_2HSiOSiHMe_2$ and sulphur at 260°C gives mixed cyclotrisilthioxanes.[357] The ^{29}Si n.m.r. spectra of Si-S rings have been measured. The structure of $Me_2SiCH_2SCH_2$ is determined, $R_2Si(CH_2)_3S(CH_2)_3$ prepared, and a dibenzodithiasilonine with a nine membered hetero ring shows transannular Si---S interactions (343.8 pm).[358] R_3SiH and Ar_2S_2 at 200°C give thiosilanes by a free radical

mechanism, while in THF, Me_3SiCl and PhTeMgBr give $Me_3SiTePh$, $(Me_3Si)_2Te$ and $Me_3SiO(CH_2)_4TePh$ through ring opening.[359]

3-Germathietanes, which result from $Me_2Ge(CH_2I)_2$ and Na_2S, can be ring opened by MeI or Me_2GeCl_2, the latter giving $(Me_2ClGeCH_2)_2S$ which cyclises with Na_2S. The structure of $[(C_6H_{11})_3Ge]_2S_3$ has been refined to give almost equal S-S bond lengths, while Ph_3MSMe (M=C-Pb) show variations in the propeller orientations of the Ph groups as M varies.[360] The bridgehead strain in Sn_3S_3 adamantane formed from $(PhI_2SnCH_2)_3CH$ and Na_2S induced by long Sn-S bonds makes it a good reducing agent for halides, while $Bu^n{}_3SnH$ reduces unsymmetrical sulphides to give Sn-S derivatives. Both $(Et_3Sn)_2S$ and $(Me_2SnS)_3$ give sulphur and the benzoate with $(PhCO.O)_2$, while copper gives Et_6Sn_2 and $(Me_2SnS)_3/Sn$ respectively, MeI giving organotin iodides, and $BrCH_2CH_2Br$ the 1,4-dithiane on hydrolysis.[361] NBS gives the thioamide with thiostannanes, while $Bu^n{}_2SnCl_2$ acts as a template for the preparation of macrocyclic polythiolactones.[362]

A series organotin tris(dithiophosphates) have been prepared from $RSnCl_3$, and $Me_2Sn(S_2AsMe_2)_2$ shown to be 4-coordinate. The Sn-Se bond is readily cleaved by selenenyl and sulphenyl halides, and by alkyl and allyl halides, and a series of R_3M and R_2M (M=Sn,Pb) 1,3-dithiolates shown to be monomeric or dimeric respectively.[363]

10 Halides

Fluoride induces rearrangement of $ClCH_2SiMe_3$ to Me_2EtSiF, $Ph_2SiF_3^-$ shown to have equatorial phenyl groups, and $MeCO.O^{18}F$ used to oxidise $K_2(ArSiF_5)$ to give ^{18}F labelled aryl fluorides in about 20% yield.[364] A series of ^{13}C labelled chlorosilanes have been made using $^{13}CO_2$, and Penning Ionisation electron spectroscopy found to enhance π-type and lone pair bands of phenyl-fluoro- and -chlorosilanes compared with UV photoelectron spectra.[365] Trimethylsilylmethyl chlorosilanes lose Me_3SiCl on electron impact, while reduction potentials for methyl chlorosilanes coorelate well with theoretical calculations, and the far IR of the polymorphism of Me_3SiCl studied.[366]

At 150°C, methyl chlorosilanes Me_nSiCl_{4-n} (n=0-3) equilibrate with esters RCO_2R', through cleavage of C-O (n=3) or C-O and O-R' (n=2,1,0) bonds. $HSiCl_3$ reacts with $R_2SiR'_2$ in the presence of H_2PtCl_6 to exchange the least hindered organic group, while the Rochow process on CH_2Cl_2 or $CHCl_3$ gives unbranched carbosilanes and

trisilacyclohexanes.[367] Thian-4-one S-oxides are reduced to α,β-unsaturated sulphides using Me_3SiCl through a Pummerer rearrangement, and esters to terminal olefins, partially deuterated, using $Ph_2MeSiCl$.[368]

Me_3SiBr results in 96% yield from $(Me_3Si)_2O$ and Ph_3PBr_2 using Zn as a catalyst. This method also gives silyl pseudohalides in good yield. Me_3SiBr deprotects methyl ethers under mild conditions and Me_3SiX gives β-halogeno acetals from unsaturated aldehydes and ketones in the presence of diols. Nitrosyl halides NOX (X=Cl,Br,I) result from Me_3SiX and RONO.[369]

Me_3SiI, generated <u>in situ</u>, has been used to convert epoxides to alkyl iodides, ArCHO to $ArCH_2I$ (and Br), demethoxylates, is used in the lactonisation of hydroxycyclohexyl <u>gem</u>-diesters, and cleaves catachols,[370] it mediates in the addition of dienol silyl ethers to α,β-unsaturated ketones and the biogenetic type cyclisation of acyclic diterpene alcohols, and is used to introduce iodine into carbohydrates and convert corticoids with a dihydroxyacetone group into hydroxyketones.[371] $MeSiCl_3$/NaI/MeCN cleaves esters and lactams more readily than Me_3SiCl/NaI, and reduces R_2SO to R_2S instantly.[372]

Ph_4Sn readily phenylates BCl_3, giving $PhSnCl_3$, while Me_2Cl_2 results from Me_4Sn using both BCl_3 and $SbCl_3$. $(c\text{-}C_6H_{11})_3SnCl$ is formed in 80% yield from $(c\text{-}C_6H_{11})_2AlCl$ and $SnCl_4$.[373] Heats of formation and the geometries have been calculated for a series of organotin halides, iodine atoms attack Et_3SnBr to give Et_2SnX_2 (X=Br,I), and I_2 forms a charge transfer complex with R_3SnX (X=Br,I) through interaction at X and not Sn, while Me_3SnCl forms intercalated compounds with graphite.[374] $MeSnI_3$ results in 33% yield from SnS and MeI in water at 60°C/2 hours in the dark.[375]

A series of bis(organostannyl)methanes have been prepared, the halogen substituted derivatives $(XPh_2Sn)_2CH_2$ showing anti-tumor activity, and complex with HMPA to give fluxional 1:1 complexes.[376] Crown ethers form hydrated complexes with tri and diorganotin chlorides and isothiocyanates, while <u>o</u>-phen coordinates through water to Ph_3SnCl as an outer sphere complex.[377] The pyrazone complex of Ph_2SnCl_2 is a 1:1/1:2 laminate of 6- and 5-coordinated tin, while Ph_3PO complexes with tri-3-thienyltin bromide. The phosphinoalkylstannanes $Me_2Sn(Cl)(CH_2)_nPRR'$, which result from $Me_3Sn(CH_2)_nPRR'$ and Me_3SnCl, are 4-coordinate (n=2) but 5-coordinate (n=3) in non-polar solvents.[378] The complex $R_3Sn(MeCN)_2^+SbF_6^-$ promotes Diels-Alder additions to furan, quinquedentate polyazo cyclic ligands result

from Me_2Sn^{2+} as template, and macrocyclic bipyridines suitable for $MeSnCl_3$ encapsulation have been prepared and are suitable for pvc addition where, as a byproduct, $MeSnCl_3$ needs deactivating.[379] $RSnX_3$ provides $RSnO_2^-Na^+$ as a water repellent finish for cotton, and $Bu^n{}_2SnCl_2$ can be detected in trace amounts by pulse anodic stripping voltammetry.[380]

A series of silatranes have been prepared,[381] notably from $MeRSiR'SiMeR'_2$ (R'=NMe_2,OEt) and from $Me(CH_2CH_2OH)_2$,[382] Raman spectra taken and local symmetry force field assessed, and the molecular structure of 1-fluorosilatrane shows a longer Si---N bond than the chloro derivative.[383] Studies of germatranes include structure determinations.[384]

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7

Group V: Arsenic, Antimony, and Bismuth

BY J. L. WARDELL

1 Tervalent Compounds

Further details have been given[1] of the synthesis, equation (1), spectra (u.v. and n.m.r.) and stability of metal metal double bonded species (1). The crystal structures of (1, M=As, M'=P) and

$$(Me_3Si)_2CHMCl_2 + 2,4,6\text{-}Bu^t{}_3C_6H_2M'H_2 \xrightarrow[THF]{DBU} 2,4,6\text{-}Bu^t{}_3C_6H_2M'{=}MCH(SiMe_3)_2$$

(1, M=As,M'=P or As; M=Sb,M'=P; M=P,M'=As) (1)

(1, M=M'=As) have been determined; both compounds have trans planar arrangements about the central M=M bonds with bond lengths As=P 2.125(1) and As=As 2.224(2) Å. Compound, (1, M=M'=As), is stable in solution but (1, M=As, M'=P) symmetrises in solution. The diarsene $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$, while stable as a solid for months at -20°C, slowly oligomerises[2] in solution at 20°C.

A synthesis[3] of thermochromic 2,2',5,5'-Me_4-bibismole (2) is shown in Scheme 1. Crystal structures of $Me_2SbSbMe_2$ (3) [a red solid but yellow liquid][4] and Ph_2MMPh_2 (4, M=Bi) [a red solid at

$$1,1\text{-}Bu_2\text{-}2,5\text{-}Me_2\text{-stannole} \xrightarrow[iii]{i,ii} 1\text{-}Ph\text{-}2,5\text{-}Me_2\text{-bibismole} \xrightarrow{iv,v} \quad (2)$$

Reagents: i, I_2; ii, BuLi; iii, $PhBiI_2$; iv, Na,liq.NH_3; v, $ClCH_2CH_2Cl$

Scheme 1

r.t. and a yellow solid at -196°C][5] have been determined. Both (3) and (4, M=Bi) have staggered trans conformations in the solid state. The Sb atoms in (3) are aligned in chains with Sb – Sb 2.838(1) Å and intramolecular Sb...Sb contacts ca. 3.66 Å; different conformations are populated in the liquid phase. The Bi-Bi bond length in labile (4, M=Bi), prepared from Ph_2BiI and Na in liquid NH_3, is 2.990(2) Å. Spectral data (i.r. and m.s.) of (4, M=As,Sb or Bi)[5,6] and of $Me_2BiBiMe_2$ (n.m.r.)[7] have been

[For References see page 145

reported. Thermodynamic data for the exchange, equation 2, have been calculated.[6] Insertions into M-M bonds of R_2MMR_2 (5) have

$$Ph_2PPPh_2 + Ph_2AsAsPh_2 \rightleftharpoons 2Ph_2PAsPh_2 \qquad (2)$$

been achieved by p-benzoquinone (5, M=Bi),[5] O_2 (5, M=Bi),[7] S (5, M=Bi),[5,7] Se or Te (5, M=Sb)[8] and CH_2 (from CH_2N_2) (5, M=Bi)[5] and provide R_2M-Y-MR_2 species. The M-M bonds in (5) are also cleaved by I_2 (M=Bi)[5] and $(ArX)_2$ (X=S, Se or Te).[8,9]

Red 2,4-Bu^t_2-bicyclo[1.1.0]tetra-arsane has been isolated from the reaction of Bu^tAsCl_2, $AsCl_3$ and LiH below 0°C. This compound, the first bicyclo[1.1.0]tetra-arsane to be reported, is stable in the absence of air and light at -190°C, but slowly decomposes in solution at -78°C.[10] Reduction of $(Me_3Si)_2CHSbCl_2$ by Mg in THF provides air-sensitive cyclic $[(Me_3Si)_2CHSb]_n$ (n=3 and 4); m.s. and ^1H n.m.r. data have been reported.[11] Russian workers have given details of the preparation and spectral properties of 1,2,3,4,5,6-Ph_6-1,3,5-triphospha-2,4,6-triarsacyclohexane.[12] The adamantane -like $MeC(CH_2As)_3$ (6) reacts with S(or Se), HgO and H_2O_2 to give respectively $MeC(CH_2As)_3E_2$ (7, E=S or Se), $MeC(CH_2AsO)_3$ and $MeC[CH_2AsO(OH)_2]_3$.[13] As revealed by crystal structure determinations (7, E=Se), as well as [7, E=$C(CO_2Et)_2$], contain five membered heterocyclic rings, AsEAsEAs.

The crystal structure of [dioxan $NaAsPh_2$] consists of infinite chains of alternating Ph_2As groups and dioxan-coordinated sodiums,[6] in contrast that of $[Li(12\text{-crown-}4)_2]AsPh_2$.THF involves well separated and non-interacting anions and crown ether-coordinated cations (Li is 8-coordinate).[14] Flash vacuum pyrolysis of $Me_3SnAs(CF_3)_2$ at 300-340°C and condensation at -196°C provided[15] $CF_3As{=}CF_2$ (8). The ^{19}F n.m.r. spectrum has been obtained at -110°C at higher temperatures (8) oligomerises.

Heating powdered Sb and 1,2-$I_2C_6X_4$ (X=F or Cl) in a sealed tube provides per-fluoro- or -chloro-5,10-o-benzenostibanthrene, $Sb_2(C_6X_4)_3$ (9) which very readily forms hemi-solvates, even with hexane.[16] The following Sb(V)compounds have been obtained from (9, X=F): $Sb_2(C_6F_4)_3Cl_4$, $Sb_2(C_6F_4)_3O_2$, $Sb_2(C_6F_4)_3(OH)_2(NO_3)_2$ and $Sb_2(C_6F_4)_3(OH)_4$. Reaction of As or Sb with Na in liquid NH_3, followed by reaction with ArX, under irradiation produced[17] Ar_3M (M=As or Sb). 2-Quinolinyl-$AsPh_2$ and 2- or 4-pyridinylMPh_2 (M=As or Sb) have been obtained from Ph_3M by successive reactions with Na in liquid NH_3 and the appropriate haloheteroarene.[17,18] Arsinoketenes, $Ph_2As(R_nM)C{=}C{=}O$ (R_nM=Ph_2As, Ph_3Ge or Ph_2MeSi)[19] have been

produced from $Ph_2AsC{\equiv}COR'$ and R_nMX via the intermediacy of $Ph_2As(R_nM)C{=}CXOR'$. Ylides, $Ph_3P{=}CHAsPh_2$ and $Ph_3P{=}C(MPh_2)_2$ (10, M= As or Sb) have been prepared (e.g. Scheme 2). The crystal structures of (10) have been determined;[20] in (10, M=As), the central $PCAs_2$ deviates from planarily with the Ph_2As groups

$$Ph_3P{=}CH_2 \xrightarrow{Ph_2AsCl} Ph_3P{=}CHAsPh_2 \xrightarrow{Ph_2AsCl} Ph_3P{=}C(AsPh)_2$$

Scheme 2

adopting a cis-trans conformation relative to the P=C bond and the lone pairs on As directed in the plane of the heavy atoms.

Spectral data have been reported for $R_2SbESbR_2$ (10, E=Se or Te) and $R_2SbTeAs$ (i.r., Raman, ^1H n.m.r. and m.s.)[8] as well as $Me_2BiEBiMe_2$ (O or S)[7] (^1H n.m.r. and ^{13}C n.m.r.) and Me_2BiEPh (11, E=S, Se or Te) (^1H n.m.r.).[9] Compounds (10, R=Me) are thermochromic, e.g. (10, R=Me, E=Te) is a brown liquid and blue-violet solid.[8] At r.t., (11) disproportionates to $MeBi(EPh)_2$ and Me_3Bi.[9] Syntheses and ^1H n.m.r. spectra of $PhSb(OCOR)_2$, $R\underbrace{SbOCO\text{-}Y\text{-}COO}$ (12; R=Me or Ph; Y=CH=CH or o-C_6H_4)[21] and $Ar_{3-n}Bi(OCOR)_n$ (13, n=1 or 2)[22] have been reported. The crystal structure of the EtOH solvate of (12, R=Me, Y=o-C_6H_4), a dimer, revealed hexa-coordinate Sb. The bismuth carboxylate (13) disportionates in solution. Other tervalent species studied[23] included monothio-β-diketonates, $Ph\underbrace{SbOCRCHCRS}$, xanthates, $PhAs(S_2COR)_2$ and O,O-alkylenedithiophosphates, $PhM[S_2\overbrace{P\text{-}O\text{-}Y\text{-}O}]_2$ (Y=CMe_2CMe_2, $CH_2CMe_2CH_2$, etc; M=As or Sb).

2 Quinquevalent Compounds

Silylcyclopropane derivatives have been obtained from reaction of $Me_3SiCH{=}AsPh_3$ and PhCOCH=CHAr.[24] Chiral alkylthioarsonium salts, $[RR^1R^2AsSR^3]^+X^-$, have been prepared from chiral RR^1R^2As, which had been produced by reduction of RR^1AsOR^4 (R^4OH=cinchonine) by R^2Li;[25a] for resolution of asymmetric arsonium salts, see ref. [25b]. Crystal structures of (p-$ClC_6H_4)_3AsO$ (As-O 1.641 Å) and Pr_2PhAsS [As-S 2.079(4) Å],[26] have been determined. Aqueous Me_3AsO has been reduced to Me_3As by thiols, such as cysteine, glutathione or lipoic acid, via $Me_3AsOR(OH)$ and $[Me_3AsSR]^+$. A simple method for the biological methylation of arsenic involves the oxidative methylation of As^{III} by S-adenosylmethionine followed by reduction with a thiol (e.g. lipoic acid).[27] Conversion of Ph_3MO to Ph_3MS

(M=As or Sb) can be readily achieved using Lawesson's reagent [2,4-bis(4-methoxylphenyl)-1,3,2,4-dithiadiphosphitane-2,4-disulphide].[28] Bisalkoxides, $Ph_3Bi(OR)_2$ (R=Bu^s, Bu, Bu^t, cyclohexyl, etc), are unstable at r.t. and decompose to Ph_3Bi, $Bi(OR)_3$, PhH, ROH and carbonyl compounds.[29]

Crystal structures of two hydrolysis products of $Ph_2Sb(OAc)_3$ have been determined;[30a] these were $[Ph_2Sb(OAc)_2]_2O$ (oxygen bridged distorted pentagonal bipyramids, Sb 7-coordinate; bridging OAc) and $[(Ph_8Sb_4O_6)(HOAc)_3]CH_2Cl_2$, which contains a non-admantane Sb_4O_6 cage. Structures have been also determined for $[(CF_3)_2As(O)OH]_2$, obtained by oxidative hydrolysis of $(CF_3)_3As$, $(CF_3)_6As_4O_6(OH)_2$ and $[CF_3As(O)(OH)Cl]_2$ (all contain four-membered As_2O_2 rings).[31]

Crystal structures have been reported for 3 organobismuth(V) compounds:[32] (i) 8-quinolinyl-$OBiPh_3Cl$ [trigonal bipyramid with Ph equatorial: Bi-C 2.168 to 2.214 Å, Bi-O 2.175(7) Å, Bi-N 2.807 (10) Å and Bi-Cl 2.657(3) Å,] (ii) $[Ph_4Bi]^+$ $[OSO_2C_6H_4Me\text{-}p]^-$ (distorted tetrahedral cation: Bi-C 2.17 to 2.22 Å, Bi---O 2.77 Å) and (iii) $[Ph_4Bi]^+$ $[Ph_2BiOCOCF_3]_2^-$ [distorted tetrahedral cation: Bi-C 2.19-2.23 Å and trigonal bipyramidal anion: lone pair and Ph equatorial (Bi-C 2.24-2.26 Å) and apical $OCOCF_3$: Bi-O 2.38-2.41 Å and interionic contact Bi---O 3.11(2) Å].[32]

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8
Metal Carbonyls

BY B. J. BRISDON

1 Introduction

The format of material in this Chapter is similar to that in Volume 13 of this series. Relevant reviews together with a few significant advances of general interest are described below. Papers of a more specific nature are considered in the appropriate section.

The plenary and section lectures presented at the XIth International Conference on Organometallic Chemistry have been published in *Pure and Applied Chemistry*,[1] and five articles on bonding aspects of metal carbonyl clusters have appeared in the first *Polyhedron Symposia-in-Print*.[2] Other reviews include reference to the formation, structures and reactions of C- and O-bonded metal carbonyls,[3] non-homolytic cleavage pathways in the photochemistry of M-M bonded carbonyl dimers,[4] electron transfer reactions of mononuclear organotransition metal complexes including carbonyls,[5] matrix isolation studies of organometallic intermediates,[6] reagent and catalyst induced substitution reactions of metal carbonyl complexes,[7] cobalt carbonyl radicals and radical reactions of cobalt carbonyl,[8] and the use of Pt carbonyls in homogeneous catalysis.[9] A general account of hydrido complexes of the transition metals includes reference to metal carbonyl hydrides,[10] and reviews of the isolobal approach,[11] and the polyhedral skeletal electron-pair method as applied to M-M bonded compounds,[12] provide additional sources of useful information and reference material.

Three reports from the primary literature are particularly noteworthy. A long and detailed theoretical study of the requirements for C-H and H-H activation in transition metal complexes and on surfaces has appeared.[13] Reduction of coordinated NO in $[Ru_3H(CO)_{10}(\mu_2\text{-}NO)]$ to μ_3-NH and μ_2-NH_2 by molecular hydrogen has been observed,[14] and the first complete study of the deoxygenation of a cluster coordinated NO ligand published.[15]

[For References see page 155

2 General, Theoretical and Mechanistic Studies

Many interesting papers appeared in 1984 in which the bonding, stability and reactivity of metal carbonyls were analysed. Calculations on the hypothetical molecule $[cp_3UCO]^{3+}$ have shown that actinide carbonyl complexes may have a stable existence.[16] The concept of absolute electronegativity (χ) has been used to show that transition metals act as Lewis bases and CO is a Lewis acid in neutral metal carbonyls, and values of χ have been calculated for several metal atoms in their low-spin valence states.[17] Another study on σ- and π-bonding effects in metal carbonyl complexes has appeared in which XPS data have been used in conjunction with available VOIE values to compare the bonding properties of CO with those of other ligands,[18] and a specific comparison of the ligand properties of CO, CS, and CSe have been obtained from the integrated infrared intensities of the stretching modes of these groups in $[Cr(CO)_5(CX)]$ and $[Cr(\eta\text{-}C_6H_6)(CO)_2(CX)]$.[19] Several theoretical papers reporting calculations on mononuclear metal carbonyls and their photofragments have appeared,[20] and the problem of semi-bridging versus bridging coordination of CO in bimetallic systems has been addressed.[21,22] The stability of carbonyl clusters has been examined with respect to local considerations based on both LF theory and the 18-electron rule.[23] The electronic structures and stabilities of seven neutral and anionic carbonyl clusters containing 4, 5 or 6 Ni atoms have been investigated by a MO-LCAO-INDO method, and significant interactions between a metal atom and the ligand groups not directly bonded to it, and between different ligand groups, have been identified.[24]

Independent papers have appeared in which the results of MO calculations on Fe_nC (n = 4 or 5) carbonyl clusters are presented,[25,26] and using $[Fe_4H(CO)_{12}(CH)]$ and $[Fe_4H(CO)_{13}]^-$ as model compounds, the bonding capabilities of the butterfly cluster $[Fe_4H(CO)_{12}]^+$ has been explored.[27] It has been shown that the acid-base nature of isostructural organometallic hydrides can be predicted by examining the orbital energetics of the deprotonated species.[28] Related theoretical studies have been carried out on the deprotonation of hydrido carbonyls of Ru and Os,[29] and the electronic structures of $[Cr_2(\mu\text{-}H)(CO)_{10}]^-$, $[MnH(CO)_5]$, $[FeH_2(CO)_4]$ and $[CoH(CO)_4]$ have been investigated.[30,31] A preliminary communication outlining a method for computing the most favourable initial site for nucleophilic attack on a transition-metal complex has been published,[32] and in a theoretical study using H^- attack on $Fe(CO)_5$ as

a prototype, the existence of a low-lying empty orbital pointing towards the attacked CO ligand was shown to be a key factor for rationalising the formation and reactivity of formyl complexes.[33] The gas phase formation of metallocarboxylates from $Fe(CO)_5$ has been described and the implications for the water gas shift reaction discussed.[34]

Studies reported in 1983 on the mechanism of CO substitution in metal carbonyl radicals have been continued. CO substitution by phosphines in $V(CO)_6$ is a second-order process with the rate of reaction dependent upon the basicity and size of the ligand.[35] The kinetics and mechanism of O- and N-Lewis base induced disproportionation of the same metal carbonyl and its phosphine substituted derivatives have also been examined,[36] as have the mechanisms of redox reactions of $V(CO)_6$ with metal carbonylates.[37] At low temperatures, the reactivity of $V(CO)_5NO$ is dominated by associative substitution behaviour whereas at higher temperatures a ligand independent process becomes important. The remarkable reactivity of $V(CO)_5NO$ can be related to the *trans*-effect of the NO ligand.[38]

In carbonylation reactions of a metallacyclic α-hydroxyalkyl complex, the first evidence for a significant intramolecular hydrogen-bond induced rate acceleration effect has been present.[39] This is a significant observation as such complexes are proposed intermediates in metal-catalysed conversions of CO/H_2 to ethylene glycol.

Interest in the stepwise reduction of coordinated CO continues. Further work on determining whether surface methylenes could arise from formyl intermediates has been reported using $Os_3(CO)_{12}$ as a model system. On hydride reduction, $Os_3(CO)_{12}$ yields $[Os_3(CO)_{11}(CHO)]^-$ which can be converted into $[Os_3(CO)_{11}(\mu\text{-}CH_2)]$ by protonation. The methylene complex eliminates CH_4 on heating in H_2 gas, and forms $[Os_3H_2(CO)_9(\mu_3\text{-}CCO)]$ in the absence of H_2.[40] The first stable neutral formyl complex of a 3d-transition metal has been claimed. Reduction of *trans*-$[Mn(CO)_4\{P(OR)_3\}_2]$ or *mer*-$[Mn(CO)_3\{P(OR)_3\}_3]$ yields $[Mn(CO)_3(CHO)\{P(OR)_3\}_2]$, and the crystal structure of the complex with R = Ph was determined.[41] Other reports on the reduction of Cr-, Mo- or Fe-coordinated CO are referenced below.[42,43]

3 Chemistry of Metal Carbonyls

3.1 Mononuclear Carbonyl Derivatives. - Two further reports on the chemistry of highly reduced carbonylate anions have appeared. $[V(CO)_5]^{3-}$ and $[VH(CO)_5]^{2-}$ have been characterised by ^{13}C, ^{51}V and ^1H n.m.r. spectroscopies,[44] and the corresponding tantalum carbonylate

reacted with $Fe(CO)_5$ to give $[Fe(CO)_4(CHO)]^-$ and $[FeH(CO)_4]^-$.[45] The e.s.r. spectra of $V(CO)_5$ and $V(CO)_4$ in Kr matrices have been examined,[46] and $[KrMn(CO)_5]$ and $[KrFe(CO)_5]^+$ isolated and studied in a similar manner.[47] Low temperature γ-irradiation of $Cr(CO)_6$ in Kr has been shown to produce $[Cr(CO)_4]^+$.[48] Infrared laser pyrolysis of several metal carbonyl derivatives has been used for simple preparations of several otherwise awkward compounds, including $Os(CO)_5$.[49] Pulsed laser pyrolysis techniques have also been used to study the gas phase thermal decompositions of $M(CO)_6$ (M = Cr, Mo or W) and $Fe(CO)_5$, and the first M-CO bond dissociation energies determined.[50] Laser induced isomerism of the $Fe(CO)_4$ entity has been reported, and a simple rationalisation of the non-Berry pseudorotation rearrangement mechanism provided.[51] The gas-phase negative ion chemistry of iron carbonyl derivatives has been examined and the relative rate constants for clustering reactions of mono-, bi- and trinuclear iron carbonylate anions measured.[52] Flash photolysis with infrared detection has been used to demonstrate the formation of $[Cr(CO)_5N_2]$ in cyclohexane solution at room temperature,[53] and a brief report has appeared on the generation of $[Fe(CO)(N_2)(NO)_2]$ and $[Fe(N_2)_2(NO)_2]$ by the photolysis of $[Fe(CO)_2(NO)_2]$ dissolved in liquid Kr doped with N_2.[54] The same research group has also published further work on O_2 complexes of $M(CO)_6$ (M = Cr, Mo or W), in which *trans*-$[M(O_2)_2(CO)_4]$ together with another unidentified carbonyl entity were isolated at 10 K.[55] In a complementary study, the gas-phase interaction of O_2 with carbonylate anions has been investigated, and anionic species of the type $[M(CO)_x(O)_y]^-$ (M = Fe, Cr, Mo, Mn, Co; n = 4, 5; x = 0 - 4; y = 1 - 5) identified.[56]

3.2 Binuclear Carbonyl Derivatives. - A method for producing $Co_2(CO)_8$ under relatively mild conditions has been described. An activated form of cobalt metal will react with CO at 100°C and 95 atmospheres to give good yields of the binuclear carbonyl.[57] Direct evidence for bridge-terminal CO exchange in solid $Co_2(CO)_8$ has been obtained from variable-temperature magic angle spinning n.m.r. experiments,[58] and the solution disproportionation reaction of this carbonyl shown to be water dependent in THF.[59] Several studies on $[M_2(CO)_{10}]^n$ (M = Cr, Mo or W, n = 2-; M = Mn or Re, n = 0) have been published.[60-65] The photochemistry of $M_2(CO)_{10}$ (M = Mn or Re) following excitation at 337 nm in the region of their $\sigma^* \rightarrow \sigma$ bonds has been investigated under collision free conditions, and evidence for partially decarbonylated dimetal photofragments obtained.[61] In an alkane matrix at 77 K, the sole process discernible from the

photolysis of $Mn_2(CO)_{10}$ is the photoejection of CO.[62] Equilibrium constants in decalin for the scrambling reaction

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \rightleftharpoons 2[MnRe(CO)_{10}]$$

have been measured. The enthalpy of the product over the temperature range 170-190°C is *ca* 17 kJ mol^{-1} higher than the average enthalpy of the homonuclear complexes.[63]

3.3 Polynuclear Carbonyl Derivatives. - The first structure determinations of two different isomers of a neutral metal carbonyl cluster have been reported. The red isomer of $Ir_6(CO)_{12}$ is isostructural with $Rh_6(CO)_{12}$, whereas a second, black isomer contains four edge-bridging and twelve terminal CO groups.[66] The chemistry of sterically crowded metal carbonyl clusters has been pursued. Treatment of $[Fe_3(CO)_{11}]^{2-}$ with $[M(CO)_3(NCMe)_3]$ (M = Cr, Mo or W) in CH_2Cl_2 leads to high yields of $[Fe_3M(CO)_{14}]^{2-}$. The Cr derivative has a pseudotetrahedral metal framework, but the strain created by CO-CO repulsions is relieved by an approximately isotropic expansion of the M_4 unit, and an increase in M-C bond lengths.[67]

Detailed vibrational studies have been carried out on several carbonyl cluster compounds. Both single crystal and Raman solution data have been obtained for $M_3(CO)_{12}$ (M = Ru or Os),[68] and small changes in frequency of the two-mode $\nu(CO)$ A_1' vibrations of these two carbonyls in mixed crystals have been used as indicators of the molecular geometry changes by which each species adapts to sites in the mixed crystal.[69] Intermediates formed on the interaction of several Group VIII cluster carbonyls with oxide surfaces have also been characterised by spectroscopic means.[70-74]

The 76 valence electron cluster dianion $[RuRh_4(CO)_{15}]^{2-}$ results from reductive carbonylation of mixtures of $Rh_4(CO)_{12}$ and $Ru_3(CO)_{12}$, and the PPN salt has been shown to be isomorphous with $(PPN)_2[Ru_4Ir(CO)_{15}]$.[75] The preparation, structure and properties of $[Re_2Pt(CO)_{12}]$ have been described. The molecule contains a $Pt(CO)_2$ unit bonded to two $Re(CO)_5$ fragments and has ideal D_{2h} symmetry.[76] The crystal structure of the manganese analogue has also been reported.[77] The reactions between *cis*-$[OsH_2(CO)_4]$ and either $Fe_2(CO)_9$ or $Co_2(CO)_8$ have been thoroughly explored. The main carbonyl products are $[FeOs_2(CO)_{12}]$ and $[Co_2Os(CO)_{11}]$, but minor products include $[FeOs_3H_2(CO)_{13}]$, $[Co_2Os_2H_2(CO)_{12}]$ and $[CoOsH(CO)_8]$.[78] Heating the anion $[PtRh_5(CO)_{15}]^-$ with methanol yields $[Pt_2Rh_9(CO)_{22}]^{3-}$, $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ and $[PtRh_{12}(CO)_{24}]^{4-}$.[79] The metal skeleton of $[Pt_2Rh_9(CO)_{22}]^{3-}$ consists of three face-to-face condensed octahedra with Pt on a 3-fold axis in positions of maximum metal-metal

connectivity.[79] The structure of PPN[$Os_3(CO)_{10}(NO)$], which was first prepared several years ago, has been determined and the fluxional properties of the anion examined.[80] A detailed study of the deoxygenation of a cluster coordinated NO ligand has also been published. The $[FeRu_3(CO)_{12}(NO)]^-$ anion contains a linear Fe-NO entity which is reduced by CO to $[FeRu_3N(CO)_{12}]^-$. The nitrido complex has a butterfly metal framework with the N atom coordinated to all four metals, and the Fe disordered over all four sites. Thus two isomers exist, and both persist in solution. Kinetic data is reported on the deoxygenation reaction and possible mechanisms described.[15] Several other structural studies on mixed metal polynuclear carbonyl complexes containing Hg, Cu or Ag have been published, and some novel features noted.[81,82] By reacting $Hg[Co(CO)_4]_2$ with excess Sm, Eu or Yb at room temperature in THF, lanthanide(II) metal carbonyl derivatives $[Co(CO)_4]_2M$ are formed.[83]

4 Cluster Carbonyls containing C, N, O, S or Se

In addition to papers of a theoretical nature which have been referenced in Section 2, a great many structural studies have been carried out on new and known clusters. Many of these complexes have been prepared using the known tendency of O- or S-donor ligands to labilize coordinated CO groups, and hence lead to the formation of metal species of high nuclearity.

The structure of the first example of a peripheral dicarbido metal carbonyl cluster has been announced. $[Co_6(\mu_6\text{-}C_2)(\mu\text{-}CO)_6(CO)_8(\mu_4\text{-}S)]$ is formed in low yields from the reaction of $Co_2(CO)_8$ with CS_2.[84] The Co_6 unit assumes a boat configuration with the C_2 unit (C-C bond distance 1·37 Å) spanning the apex of the boat. The solid-state structures of both $NEt_4[RhFe_5C(CO)_{16}]$[85] and $AsPh_4[\{Ru_6C(CO)_{12}\}_2T\ell]$[86] have been reported. The latter was prepared as part of an investigation of the oxidative activation of transition metal cluster compounds, and the anion contains two Ru_6 octahedra, each linked by two edge-related Ru atoms to a central Tℓ atom.[86] $[Rh_6C(CO)_{15}]^{2-}$ reacts with $[Rh(CO)_2(NCMe)_2]^+$ in the presence of CO to form the $[Rh_{14}C_2(\mu\text{-}CO)_{21}(CO)_{12}]^{2-}$ anion, which contains two Rh_7C moities linked by a short (2·57 Å) Rh-Rh bond and by three bridging CO ligands.[87] The carbido dianion $[Os_{10}C(CO)_{24}]^{2-}$ reacts with $NOBF_4$ to yield $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ in which the NO ligand adopts a novel bonding mode. In solution CO loss and metal cluster rearrangement occurs to yield $[Os_{10}C(CO)_{23}(NO)]^-$.[88] Alkoxy attack on a CO ligand occurs during the reaction of $[Os_5C(CO)_{15}]$ or $[Os_5C(CO)_{15}I_2]$ with alcohols (ROH). The structure of one of the products

$[Os_5C(CO)_4(CO_2R)X]$ (X = H or I) has been determined, and the metal core shown to exhibit the expected bridged-butterfly geometry.[89] Another preliminary report on nucleophilic attack at a coordinated CO of a carbido carbonyl cluster compound has also appeared.[90] The heterometallic carbido cluster anion $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ results from the reaction of $[Co_3(CO)_9(CCl)]$ with $[Ni_6(CO)_{12}]^{2-}$ and contains two C atoms located in a cavity in the cluster and separated by only 1·49 Å. A delocalised rather than a localised C-C interaction is considered probable.[91]

A new family of nitrido carbonyl cluster anions $[Rh_6MN(CO)_{15}]^{2-}$ (M = Co, Rh or Ir) have been characterised. For M = Rh the 100 valence electron metal core consists of a novel square face capped trigonal prism.[92]

The reaction of S_8 with $Fe_3(CO)_{12}$ has been reinvestigated and the structure of the minor product $[Fe_2(CO)_6(S_2CO)]$ determined. The iron coordination sphere is essentially similar to that in $[Fe_2(CO)_6(S_2)]$.[93] Other papers concerning sulphido carbonyl clusters containing 3d-transition metals are given in reference 94. An improved synthesis of $[Rh_3(CO)_6(\mu_3\text{-}S)_2]^-$ has been published, and the Se analogue prepared from KSeCN and $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$. X-ray studies have revealed Rh-Rh separations greater than 3 Å, indicating very weak M-M interactions rather than direct M-M bonds.[95] Irradiation of $[Os_3H(CO)_{10}(\mu\text{-}XPh)]$ (X = S or Se) in the presence of CO yields the new cluster compound $[Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}X)]$,[96, 97] whereas in the absence of CO, the sulphur analogue yields $[Os_6(CO)_{17}(\mu_4\text{-}S)_2]$ which has also been prepared by decarbonylation of $[Os_6(CO)_{19}(\mu_3\text{-}S)]$.[98] Unusual metal-metal bonding and a new type of Os_{10} cluster geometry respectively, have been revealed by structural studies on $[Os_3(CO)_8(\mu_3\text{-}S)_2]_2$ and $[Os_{10}(CO)_{23}(S)_2]$,[99, 100] and by utilising the coordinating properties of bridging sulphido ligands, several new heteronuclear sulphido cluster carbonyls have been prepared.[101]

5 Metal Carbonyl Hydrides

Comparison of second-order rate constants for halide displacement from *n*-BuBr by H^- derived from anionic metal carbonyl hydrides established the order of reactivity $[WH(CO)_5]^- > [CrH(CO)_5]^- > [RuH(CO)_4]^- \gg [FeH(CO)_4]^-$.[102] Low temperature n.m.r. studies of $[Fe_4H(CO)_{13}]^-$ show that two hydrido species are in equilibrium at room temperature. One has a Fe_4 butterfly cluster geometry, and the other contains a closed Fe_4 tetrahedron.[103] The condensation reaction of $[MH(CO)_4]^-$ (M = Fe, Ru or Os) to give $[M_3H(CO)_{11}]^-$ has

been investigated under protic and water gas shift conditions,[104] and reaction of $AgPF_6$ with the trinuclear anion (M = Os) shown to produce $[\{Os_3H(CO)_{10}\}_2Ag]$, in which an Ag(I) atom links two $Os_3H(CO)_{10}$ fragments.[105] Infrared spectral studies of ion pairing in salts of $[M_3H(CO)_{11}]^-$ (M = Fe or Ru) have also been reported.[106] The coordinative unsaturated cluster $[Ru_4H_4(CO)_{11}]$ is produced during the photolysis of $[Ru_4H_4(CO)_{12}]$ in rigid alkane matrices at low temperatures,[107] and reaction of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with $NOBF_4$ gives $[\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$. The NO ligand in this anion holds together two triangular Re_3 moieties by bridging one edge of each triangle through both N and O atoms.[108] Spectral studies of ^{13}C enriched $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ have proved that only localised CO exchange occurs involving two of the four types of CO ligand.[109] Hydroboration of this species in the presence of THF affords a boroxine-supported Os_3 oxymethylidyne cluster system, $\{Os_3(\mu\text{-}H)_3(CO)_9(\equiv CO)\}_3B_3O_3$, which is a useful precursor for other triosmium cluster derivatives.[110] Further studies on the reaction of $Os_3(CO)_{12}$ with base in isobutanol have appeared in which Os_3, Os_4, Os_6 and Os_{10} species have been identified.[111]

The synthesis of several new heteronuclear hydrido carbonyl clusters have also been described. Reaction of $PPN[FeH(CO)_4]$ with $M(CO)_5THF$ (M = Cr, Mo or W) yields $[FeM(\mu\text{-}H)(CO)_9]^-$ in which the H atom is presumed to bridge the Fe-M bond.[112] Other Fe containing anionic heterometallic clusters reported in 1984 include $[FeOs_3H(CO)_{13}]^-$[113] and $[Fe_3Ni(\mu_3\text{-}H)(\mu\text{-}CO)(CO)_8]^-$.[114] Both $[Ru_2Rh_2H_2(CO)_{12}]$[115] and the anion $[Os_3WH(CO)_{14}]^-$ [116] contain bridging H and CO ligands.

6 Metal Carbonyl Halides

A study of the formation of $M(CO)_5X$ (M = Mn or Re; X = halide) from $M_2(CO)_{10}$ and X_2 in MeCN has been published. The rate of halogenation $Re_2(CO)_{10}$ > $MnRe(CO)_{10}$ > $Mn_2(CO)_{10}$ opposes the order expected based on homolysis of the M-M bond, and it has been proposed that X_2 attack results in heterolytic cleavage of the X-X bond to give X^- and an X-bridged metal dimer.[117] A value of *ca* 100 kJ mol^{-1} has been estimated for the Pd-CO bond energy in $Pd_2(CO)_2Cl_4$, and a high yield synthesis of $[Pd(CO)Cl]_n$ reported.[118] Several independent studies on halide derivatives of $Ru_3(CO)_{12}$ have been carried out.[119-121] Reaction of $Ru_3(CO)_{12}$ with Me_3NO in the presence of an alkali halide, followed by protonation, yields mainly edge double-bridged complexes $[Ru_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ (X = Cl, Br or I), with small quantities of $[Ru_3(\mu\text{-}X)_2(CO)_{10}]$ (X = Br or I),

and for X = I, the additional compound $[Ru_3(\mu\text{-}H)(\mu_3\text{-}I)(CO)_9]$. All three contain Ru_3 triangles with internuclear distances which reflect bond orders required to describe a closed shell around each Ru atom.[120] A combination of $Ru_3(CO)_{12}$ with a second metal selected from Ti, Zr, Co, Mn and Re in a melt of $[Bu_4P]Br$ is effective for the selective synthesis of MeOH, EtOH or acetate esters directly from CO and H_2. The anion $[Ru(CO)_3Br_3]^-$ was detected amongst other Ru species present during these particular syntheses.[121]

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9

Organometallic Compounds containing Metal–Metal Bonds

BY W. E. LINDSELL

1 Introduction

The format of this section is similar to that of Volume 13. The abbreviations Cp, Cp' and Cp* are used throughout the chapter for (η^5-C_5H_5), (η^5-C_5H_4Me) and (η^5-C_5Me_5), respectively.

1.1 Reviews.- Accounts of the chemistry of metal complexes containing bridging alkylidene[1] of α,ω-alkanediyl[2] ligands and of complexes containing C- and O-bonded carbonyl ligands[3] describe many species with metal-metal bonds. Reactions of triosmium clusters with organic ligands are reviewed.[4] Other surveys cover platinum carbonyl compounds, including polynuclear systems,[5] and homo- and hetero-nuclear clusters of gold.[6] Recent developments of the Polyhedral Skeletal Electron Pair Theory are presented[7] and "Recent Advances in the Structures and Bonding in Cluster Compounds" is the subject of 5 articles of a published symposium, originating from a meeting at Cambridge, UK, 1983.[8]

Applications of metal-metal and metal-carbon multiple bonds in the synthesis of new metal-metal bonded complexes are discussed in a review stressing the isolobal connection.[9] A number of Russian reviews on metal-metal bonded complexes have been published in Koord.Khim.,[10] the content of part 5 resulting from a Soviet Conference on Cluster Compounds, 1983. Other relevant accounts discuss non-homolytic cleavage pathways in the photochemistry of M-M bonded carbonyls[11] and synthetic applications of transition metal trialkylsilyl complexes.[12]

1.2 Theoretical Studies.- State correlation diagrams are given for photoinduced metal-metal bond cleavage of carbonyl derivatives.[13] An Xα-SW study of $[Cr_2(\mu\text{-}H)(CO)_{10}]^-$ shows that the Cr-H-Cr linkage is more complex than a closed 3-centre 2e interaction and that the LUMO is Cr-Cr bonding.[14] Theoretical studies of linear semi-bridging CO ligands in $[Mn_2(\mu\text{-}CO)(CO)_4$ dppm$]$[15] or in $[M_2(CO)_4Cp_2]$ (M = Cr,Mo,W)[16] support their role as π-acceptors in a 3-centre 2e interaction and not as 4e donors; similar bonding takes place through semi-bridging carbonyls in CrRh heterobinuclear complexes, with little net metal-metal interaction.[17] UV-PE Spectra of

[For References see page 185

$[M_2(\mu\text{-}CO)_2Cp_2]$ (M = Co,Rh) and related nitrosyl species, are also consistent with delocalised bridge bonding without a direct metal-metal bond.[18] UV-PE Spectra of complexes $[Zn(Tm)_2]$ (Tm = $Fe(CO)_2Cp$; $M(CO)_3Cp$;M = Cr,Mo,W) are assigned.[19] Also, theoretical studies are reported for $[Fe_2(\mu\text{-}S)_2(CO)_6]^{n-}$ (n = 0,2)[20] and $[M_3(\mu_3\text{-}S)(\mu\text{-}H)_2(CO)_9]$ (M = Ru,Os).[21]

A new topological electron counting scheme for polyhedral metal clusters is described and applied to species containing 4-20 metal atoms.[22] INDO Studies of penta- and hexa-nuclear nickel clusters indicate that the main bonding interactions are between metal and ligand atoms and not directly between metals.[23] EHMO Analyses are reported for gold phosphine clusters[24] and for clusters with interstitial carbon atoms.[25]

Both concerted oxidative addition to[26] and reductive elimination from[27] dinuclear systems are analysed theoretically, as also is the scission of coordinated alkynes into alkylidyne units which occurs on vacuum flash pyrolytic conversion of $[M_3(CO)(C_2R_2)Cp_3]$ into $[M_3(\mu_3\text{-}CR)Cp_3]$ (M = Rh,Ir).[28] Other theoretical studies deal with the electronic structures of butterfly clusters $[Fe_4(\mu_4\text{-}L)(\mu\text{-}H)\text{-}(CO)_{12}]^-$ (L = CO,CH)[29] and the general reactivity of clusters with exposed carbido-ligands,[30a] in particular systems with butterfly Fe_4C cores.[30b]

1.3 Physical Studies.- Vibrational group frequencies and ^{13}C n.m.r. resonances of cluster bound C_2H_n (n = 1-4) fragments are reported,[31] as are ^{13}C-^{13}C coupling constants in μ_2- and μ_4-alkyne complexes of cobalt.[32] Bridge-terminal CO exchange in $[Co_2(CO)_8]$ has been studied by VT solid state (MAS) ^{13}C n.m.r. spectroscopy.[33] The applications of ^{17}O n.m.r.[34] and ^{57}V n.m.r.[35] measurements to metal-metal bonded systems may also be noted.

Alkane eliminations from μ-alkylidene complexes have been monitored by mass spectroscopy[36] and the utility of Fast Atom Bombardment in mass spectral characterisation of high molecular weight clusters assessed.[37] Reactions of metal cluster positive ions in the gas phase with alkanes and with CO have been studied using FT MS techniques[38] and iron carbonyl cluster negative ions with double Fe=Fe bonds may be identified using ion cyclotron resonance techniques.[39] Electrochemical studies of redox processes of a number of cluster systems, in solution, are reported.[40]

1.4 Surface Bound Species.- There are further examples of carbonyl clusters adsorbed on to oxide surfaces to form catalysts or potent-

ially catalytically active systems; systems studied spectroscopically include: $[Ru_3(CO)_{12}]$, $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$on Al_2O_3, SiO_2 or TiO_2,[41] $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ on Al_2O_3, SiO_2 or zeolites,[42] $[Rh_2Co_2(CO)_{12}]$ on Al_2O_3.[43] Clusters anchored onto SiO_2 by functionalisation of the surface include $[Ru_3H(CO)_{11}]^-$ attached via ammonium or pyridinium groups,[44] $[Os_3Au(\mu\text{-}X)(CO)_{10}L]$ (X = H,CO; L = PPh_2CH_2-CH_2-SiO_2]),[45] $[Ru_3(CO)_9L_3]$[46] and $[Os_3(\mu\text{-}H)H(CO)_{10}L]$.[47] Photochemical studies of the latter two species show Ru-Ru bond rupture for the former[46] but, at 298K, CO loss from the osmium derivative to form $[Os_3(\mu\text{-}H)_2(CO)_9L]$.[47] Clusters attached to polymers and examined spectroscopically include $[Os_3(CO)_{12}]$ on poly-4-vinylpyridine,[48] anionic clusters on resin IRA 401[49] and $[M_xCo_{4-x}(CO)_{12}]$ (M = Rh,Ir) on amine functionalised polymer.[50]

2 Compounds with Homonuclear Transition Metal Bonds

2.1 Zirconium.- The diamagnetism of complexes $[Zr_2(\mu\text{-}X)_2Cp_4]$ (X = Cl,SPh) has been attributed to Zr-Zr bond formation.[51]

2.2 Vanadium and Niobium.- New, paramagnetic dimers $[V_2(\mu\text{-}SCHRCH_2S)_2$-$Cp_2]$ exhibit significant spin coupling and may contain direct V-V bonds (V-V = 2.5421 (1) Å, R = H).[52] 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) reacts with $[V_2(\mu\text{-}S)_2(\mu\text{-}\eta^1\text{-}S_2)Cp'_2]$ to yield $[V_2(\mu\text{-}S)$-$(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}\eta^1\text{-}PTD)Cp'_2]$ and the crystal structure of an adduct of this product with $[Pt(PPh_3)_2]$ has been determined.[53] An electron deficient, paramagnetic cluster $[V_4(\mu_3\text{-}S)_4Cp'_4]$ has been structurally characterised.[54]

The Nb-Nb distance (3.2343(8)Å) in diamagnetic $[Nb_2(\mu\text{-}S)_2Cp_2]$ is stated to support the presence of a bond.[55] The complex $[Nb_2Cl_4Cp^*_2]$ formed from $[NbCl_2Me_2Cp^*]$ and H_2, is probably structurally analogous to derivatives $[Ta(\mu\text{-}Cl)_2Cl_2L_2]$ which incorporate a metal-metal bond.[56]

2.3 Chromium, Molybdenum and Tungsten.- Alkynes react with $[W_2$-$(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$ giving, via an intermediate 1:1 adduct, the fluxional derivatives $[W_2(\mu\text{-}C_3R_2SiMe_3)(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_4]$ (1); the X-ray structure is reported for R = Ph.[57] Thermolysis of $[W\{CH$-$(p\text{-}C_6H_4R\}(CO)_5]$ yields the binuclear $[W_2\{\mu\text{-}CH(p\text{-}C_6H_4R)\}(CO)_{10}]$.[58] A full account is given of the structures and properties of $[Mo_2$-$(\mu\text{-}C_8Me)Cp_2]$ and its protonation product $[Mo_2(\mu\text{-}C_8Me_8)(\mu_{Mo,C}\text{-}H)Cp_2]^+$ which contains a 3-centre C-H-Mo interaction.[59]

More evidence has been adduced for the formation of 19-electron intermediates in the photochemical disproportionation of $[Mo_2(CO)_6$ -

Cp_2'][60a] and such intermediates are effective reducing agents.[60b] Aryl and alkyl isocyanides readily cleave [$Mo_2(CO)_6Cp_2$] giving disproportionation products [$Mo(CNR)_{4-n}(CO)_nCp$][$Mo(CO)_3Cp$] (n = 0, R = aryl; n = 1, R = alkyl);[61] the formal Mo≡Mo bond of [$Mo_2(CO)_4Cp_2$] is disrupted by CF_3NC in the formation of a new bridging ligand, μ-σ,-η^2,σ-$CF_3N{=}C{=}C{=}NCF_3$.[62] The properties and structure of two disymmetrically substituted complexes [$Mo_2(CO)_3LCp_2$] { L = $PhP(OCH_2CH_2)_2NH$ or $P(OMe)_3$} are described (average Mo≡Mo = 2.504Å).[63] The fulvalene-bridged complexes [$M_2(\mu$-η^5,η^5-$C_{10}H_8)(CO)_6$] (M = Cr,Mo,W), as well as related Co_2, Ru_2 and MoRu derivatives, are reported[64a] and the ditungsten complex possesses a "stretched" W-W bond (3.347(1)Å);[65] photolysis of these fulvalene derivatives in the presence of alkynes has produced novel homo- and hetero-bimetallic alkyne complexes.[64b] Redox studies of [$Cr_2(NO)_2Cp_2$] show that a binuclear monoanion is stable and may be isolated as a salt but oxidation causes Cr-Cr fission.[66]

There are many further reports of binuclear complexes containing two, metal-metal bonded {$M(CO)_nCp$} units, bridged by a range of ligands. Thermal decomposition of [$Mo(C{\equiv}CPh)(CO)_3Cp$] produces [Mo_2-(μ-1,2-η^2-$PhC{\equiv}C$-$C{\equiv}CPh$)$(CO)_4Cp_2$][67] and a triclinic form [$Mo_2(\mu$-η^2-$CNPh)(CO)_4Cp_2$] is described.[68] The fully characterised bridging acetaldehyde complex [$Mo_2(\mu$-η^2-$OCHMe)(CO)_4Cp_2$] may be synthesised from mono- or bi-nuclear precursors.[69] The alkylidyne tungsten complex [$W(CMe)(CO)_2Cp$] reacts with $BH_3.OEt_2$ to give the novel product [$W_2(\mu$-$MeCBHEt)(CO)_4Cp_2$], (2).[70] Formally triple bonded [$Mo_2(\mu$-CO)-{μ-o-$C_6H_4(PPh)_2$}Cp_2] (Mo Mo = 2.532Å) adds a range of ligands giving products with formal double or single Mo-Mo bonds.[71] The η^2-P_2 complex [$Mo_2(\mu$-$P_2)(CO)_4Cp_2$] has been structurally characterised[72a] and acts as a bidentate complex ligand to two {$Cr(CO)_5$} units or to {$Re_2(\mu$-$Br)_2(CO)_6$}.[72b] The phosphoalkyne ligand in [$Mo_2(\mu$-$CPBu^t)(CO)_4$-Cp_2] will also coordinate through phosphorus to other transition metal centres, as in the structurally characterised adduct with $Os_3(CO)_{11}$.[73] Reaction of As_4S_4 with [$Mo_2(CO)_4Cp_2^*$] yields, *inter alia*, binuclear products [$Mo_2(\mu$-$As_2)(CO)_4Cp_2^*$] and [$Mo_2(\mu$-$S_2)(\mu$-AsSAs)-Cp_2^*].[74] The thioformaldehyde derivative [$W_2(\mu$-$SCH_2)(CO)_4Cp_2$] can exist in two isomeric forms.[75]

Reactions of [$M_2(\mu$-$PPh_2)_2(CO)_8$] (M = Mo,W) with nucleophiles, BR_3H^- and LiR, are reported.[76]

Three isomers [$Mo_2(\mu$-$S)_2S_2Cp_2^*$], [$Mo_2(\mu$-η^2-$S_2)(\mu$-$S)_2Cp_2^*$] and [Mo_2-(μ-η^2-$S_2)S_2Cp_2^*$] are interconverted photochemically.[77] The uncoordinated sulphur in [$Cr_2(\mu$-η^1-$S_2)(\mu$-η^2-$S_2)(\mu$-$S)Cp_2^*$] is abstracted by PPh_3 and by [$Mn(CO)_2(thf)Cp$], whereas [$Mo_2S_4Cp_2^*$] complexes with the

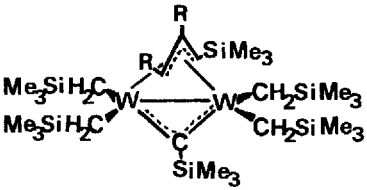
manganese reagent.[78] Both $[Mo_2S_4Cp^*_2]$ and $[Cr_2S_5Cp^*_2]$ have been utilised in photochemical syntheses of homo- and hetero- clusters with M_3S_4 and M_4S_4 cores.[79] The sulphur capped trinuclear anion $[Cr_3(\mu_3\text{-}S)(\mu\text{-}CO)_3(CO)_9]^-$ shows fluxional processes involving CO ligands[80]. A "bow-tie" configuration is found for $[Cr_5(\mu_3\text{-}S)_4(\mu\text{-}SBu^t)_2Cp_4]$ with a central Cr(II) atom and formal double bonds between the two pairs of Cr(III) atoms.[81]

1,2-$[Mo_2(CH_2Ph)_2(OPr^i)_4]$ reacts with PMe_3 to form $[(Pr^iO)_3Mo{\equiv}Mo(CH_2Ph)_2(OPr^i)(PMe_3)]$ which exhibits facile benzyl-alkoxy group migrations at the Mo≡Mo centre.[82] The dialkyl derivatives $[W_2R_2(O_2CEt)_4]$ possess a short W≡W bond (2.186(1)Å, R = CH_2Ph).[83] Full accounts of reactions of alkynes with complexes $[W_2(OR)_6]$ have appeared:[84] the products include simple adducts, mononuclear alkylidyne complexes[84a] and complexes with coupled C_4 ligands, as in $[W_2(\mu\text{-}\eta^1,\eta^4\text{-}C_4R'_4)(\mu\text{-}OR)(OR)_5(\eta\text{-}C_2R'_2)]$(R = Pr^i,R' = H,Me).[84b] The metathesis of alkynes to alkylidyne on $[Mo_2(OBu^t)_6]$ is also described.[85] Although $[M_2(OR)_6]$ complexes (M = Mo,W) are cleaved by isocyanides, the β-diketonate derivatives $[Mo_2(OR)_4(R'COCHCOR')_2]$ form adducts such as $[Mo_2(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_2(acac)_2(CNBu^t)_2]$,[86] and alkyne adducts of $[W_2(OR)_6]$ combine with isocyanides to form 5- or 7-membered heterocyclic rings as bridging ligands.[87] A new structural type (3) is found for $[W_3(\mu_3\text{-}CMe)(\mu\text{-}OPr^i)_3(OPr^i)_6]$, formed by reaction of Me_2C_2 and $[W_2(OPr^i)_6(py)_2]$.[88]

2.4 Manganese and Rhenium.- Equatorially substituted $[Re_2(CO)_9(CNBu^t)]$[89] and 1,1-$[Mn_2(CO)_8(CNBu^t)_2]$,[90] formed by thermal isomerisation of the 1,2-derivative, have been structurally characterised. Kinetic studies are reported for the reformation of $[Mn_2(CO)_8L_2]$ (L = phosphorus ligand) from the transient intermediates $[Mn(CO)_4L]$ and $[Mn_2(CO)_7L_2]$, produced by flash photolysis;[91] the intermediate $[Mn_2(CO)_9]$, formed from the unsubstituted carbonyl, possesses a semi-bridging carbonyl group.[92] Similarly, photochemical decarbonylation of $[Mn_2(\mu\text{-}PPh_2)_2(CO)_n]$ (n = 8) gives complex (n = 7) with one semi-bridging carbonyl.[93]

Complexes $[Re_2(\mu\text{-}L\text{-}L)(CO)_8]$ (L-L = diphosphine) react photochemically with H_2O or MeOH giving $[Re_2(\mu\text{-}H)(\mu\text{-}OR)(\mu\text{-}L\text{-}L)(CO)_6]$ and structural data are reported for R = H, L-L = dppm.[94] The anion $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$ is prepared by deprotonation of the neutral hydride and is a precursor for synthesis of mixed-metal clusters.[95]

Photolyses of $[Re_2(CO)_{10}]$ with simple alkenes yield fluxional $[Re_2(\mu\text{-}H)(\mu\text{-}\sigma,\eta^2\text{-}CRCHR')(CO)_8]$; these μ-alkenyl complexes react readily with phosphorus ligands, liberating alkene, and cause photolytic dimerisation of alkenes.[96] Insertion of either CO or PPh_2 into the σ-bond of the μ-alkenyl group may occur on reaction of $[Mn_2$-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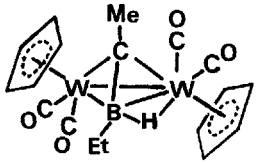
(1)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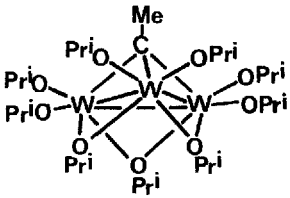
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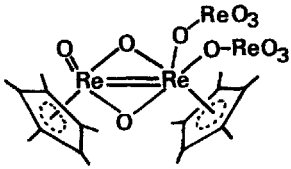
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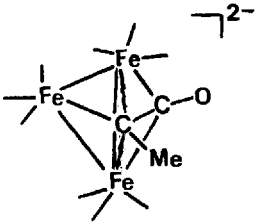
(4)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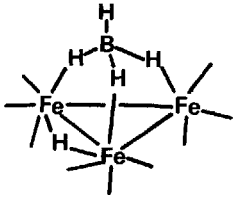
(5)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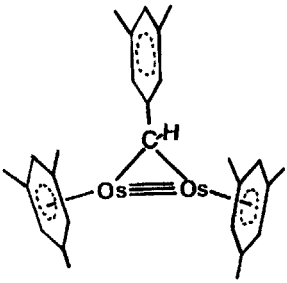
(6)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(7)

$(\mu\text{-}\sigma,\eta^2\text{-CR=CHR})(\mu\text{-PPh}_2)(CO)_7]$ with 2e-ligands, forming μ-acyl or μ-$PPh_2CR{=}CHR$ ligands, respectively.[97] Fluxional, $\mu\text{-}\sigma,\eta^2$-alkylnyl containing complexes $[Re_2(\mu\text{-H})(\mu\text{-}C_2R)(CO)_8]$ (R = Ph,[98] H[99]) have also been studied and show facile CO substitution reactions.[98]

Photochemical carbonyl substitution of $[Mn_2(CO)_{10}]$ with allene produces $[Mn_2(\mu\text{-}\eta^2,\eta^2\text{-allene})(CO)_8]$.[100] Photochemical reaction of 2,4-hexadiene with $[Mn_2(CO)_{10}]$ forms 3 products[101], including the binuclear metallacyclopentadiene complex $[Mn_2(\mu\text{-}\eta^1,\eta^1,\eta^4\text{-}C_4H_2Me_2)(CO)_7]$. Products from photolysis of diphenylacetylene with $[Re_3(\mu\text{-H})_3(CO)_{12}]$ include the metallacyclopentadiene $[Re_2(\mu\text{-}\eta^1,\eta^1,\eta^4\text{-}C_4Ph_4)(CO)_5(C_2Ph_2)]$ and the "fly-over bridged" $[Re_2(\mu\text{-}\eta^1,\eta^3,\eta^3,\eta^1\text{-}C_6Ph_6)(CO)_4(C_2Ph_2)]$.[102]

Cocondensations of Re atoms with benzene and alkanes produce μ-alkylidene species $[Re_2(\mu\text{-H})_2(\mu\text{-CRR'})(\eta\text{-}C_6H_6)_2]$ by oxidative addition of two alkane C-H bonds to Re;[103] similar cocondensations using cyclohexene in place of alkane, produce some mixed valency dimer $[Re_2(\mu\text{-H})_2(\eta\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)_2]$.[104] Complexes with μ-vinylidene, i.e. $[Mn_2(\mu\text{-CCHR})(CO)_4Cp_2]$,[105] and μ-allenylidene, i.e. $[Mn_2(\mu\text{-CCCBu}^t{}_2)(\mu\text{-CO})(CO)_8]$,[106] are also characterised.

Spectroscopic characterisation of rhenocene indicates that it is dinuclear $[Re_2Cp_4]$ and linked by a Re-Re bond.[107] Oxidative decarbonylation of $[Re(CO)_3Cp^*]$ yields $[ReO_3Cp^*]$ although binuclear intermediates $[Re_2O_2(CO)_2Cp^*_2]$ and the structurally characterised $[Re_2(\mu\text{-O})(CO)_4Cp^*_2]$ may be isolated;[108a] the latter complex may also be formed by partial deoxygenation of $[ReO_3Cp^*]$ and this trioxo-complex may also be transformed into Re=Re double-bonded derivatives $[Re_2(\mu\text{-O})_2O_2Cp^*_2]$ and $[Re_2(\mu\text{-O})_2\{OReO_3\}_2Cp^*_2]$ (4).[108b] The crystal structure of $[Re_2(\mu\text{-S})(CO)_4Cp_2]$ has been determined.[109]

The synthesis and structure of $[Mn_2(\mu\text{-CO})_3Cp^*_2]$, with the first Mn≡Mn triple bond (2.170(1)Å) are reported.[110] Ortho-Metallation of 2-(diphenylphosphino)pyridine (Ph_2Ppy) on reaction with quadruply bonded Re(III) dimers $[Re_2Cl_6L_2]$ (L = Cl^-, PR_3) affords Re(II) dimer $[Re_2(\mu\text{-C,P,N-}C_6H_4PPhpy)(\mu\text{-P,N-}PPh_2py)_2Cl_3]$.[111] A Re≡Re triple bond is found in $[Re_2(\mu\text{-}H_3)H_4(PPh_2CH_2)_3CMe]^-$ (Re-Re : 2.597(1)Å)[112] and a multiple Re-H_3-Re bonding system occurs in $[Re_2(\mu\text{-H})_3H_2(PPh_3)_4(CNBu^t)_2]^+$.[113]

The synthesis, crystal structure and fluxional behaviour are described for $[Re_3(\mu_3\text{-H})(\mu\text{-H})(CO)_{10}(\eta^5\text{-}C_7H_9)]$.[114] The X-ray structure[115] is also reported for benzamido bridged $[Re_3(\mu\text{-H})_3\{\mu\text{-OC(Ph)NH}\}(CO)_{10}]^-$ and for $[\{Re_3(\mu\text{-H})_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-NO})]^-$, which contains two Re_3 triangular clusters connected across edges by an N- and O- bonded nitric oxide.[116]

2.5 Iron.- Complex $[Fe(\mu\text{-}CO)(\mu\text{-}CPhCHPh)(CO)_6]^-$ reacts at the μ-alkenyl ligand: (i) with alkynes to give insertion products $[Fe_2(\mu\text{-}CRCRCOCPhCHPh)(CO)_6]^-$ (R = CF_3, CO_2Me) or $[Fe_2(\mu\text{-}CPhCPhCRCHR)(CO)_6]^-$ (R = CF_3);[117a] (ii) with Et_3OBF_4 to give initially $[Fe_2(\mu\text{-}COEt)(\mu\text{-}CPhCHPh)(CO)_6]$ which smoothly transforms to allylic derivative $[Fe\{\mu\text{-}\eta^1,\eta^3\text{-}C(OEt)CPhCHPh\}(CO)_6]$.[117b] The structure of $[Fe_2(\mu\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2NPh)(CO)_6]$, formed from benzalazine,[118] and a study of the formation of bridging (6e) 1,4-diaza-1,3-diene(DAD) complexes $[Fe_2(\mu\text{-}DAD)(CO)_6]$[119] are reported. 2-Nitropropane and $[Fe_3(CO)_{12}]$ in toluene (80°) form $[Fe_2(\mu\text{-}OCCH_2Ph)(\mu\text{-}NCMe_2)(CO)_6]$.[120]

Complexes possessing $\{Fe_2(CO)_6\}$ units bridged by two phosphorus donors include: $[Fe_2(\mu\text{-}P_4R_4)(CO)_6]$ containing catenated polyphosphorus ligands (R = Me, Ph);[121] $[\{Fe_2(CO)_6\}_2(\mu\text{-}P_2Me_2)]$, an organometallic analogue of octabisvalene;[122] and $[Fe_2\{\mu\text{-}o\text{-}C_6H_4(CH_2PPh_2)_2\}(CO)_6]$, which may be deprotonated at a benzylic centre to form an Fe-C bond.[123] The dianion $[Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_5(PPh_2)]^{2-}$ reacts with iodohydrocarbons, and from allyl iodide the structurally characterised $[Fe_2(\mu\text{-}PPh_2)(CO)_5\{PPh_2(C_3H_5)\}(\eta^3\text{-}C_3H_5)]$ is formed.[124] Related nitrosyl species are reported and complexes formed by reaction of CH_2I_2 with anions are $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}P_2Ph_4)(NO)_4]$ and $[Fe(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(NO)_4]$.[125] Structures of Fe_2 and Fe_3 bridged chlorophosphazene complexes are reported.[126] Mechanistic studies of ligand induced heterolytic cleavage of the metal-metal bond in $[Fe_2(\mu\text{-}AsMe_2)(CO)_6(NO)]$ suggest an Fe→Fe bond strength ≥ca. 100 KJ mol^{-1}.[127]

The thioketene cluster $[Fe_2\{\mu\text{-}SC_2(C_5H_6Me_4)\}(CO)_4(PPh_3)_2]$ reacts with excess thioketene to form a di-sulphur bridged, vinylidene complex, $[Fe_2\{\mu\text{-}S_2CC(C_5H_6Me_4)\}\{C_2(C_5H_6Me_4)\}(CO)_4(PPh_3)_2]$.[128] Structures are reported for $[Fe_2(\mu\text{-}S_2CO)(CO)_6]$ formed in low yield from S_8 and $[Fe_3(CO)_{12}]$[129] and for $[\{Fe_2(\mu\text{-}S)_2(CO)_6\}_2]$ containing S-S linked binuclear units.[130] In $[Fe_2(\mu\text{-}SEt)_2(CO)_2Cp_2]^+$ the Fe-Fe distance (2.957(4)Å) corresponds to a one electron interaction.[131]

The primary photolytic products of $[Fe_2(CO)_4Cp_2]$ have been investigated in matrices at 77K[132a] and in solution at RT;[132b] the binuclear product is identified as $[Fe_2(\mu\text{-}CO)_3Cp_2]$, with three bridging carbonyls. Electron transfer to $[Fe_2(CO)_4Cp_2]$[133a] and also oxidation of $[Fe_2(CO)_4Cp^*_2]$[133b] by ferracinium cation cause Fe-Fe bond cleavage; the former process has been studied kinetically.[133a] The structure and fluxional behaviour of several isonitrile derivatives $[Fe_2(CO)_x(CS)_y(CNR)_zCp_2]$ (x + y + z = 4) are reported and the bridging tendency for CNR ligands (x = 2, y = 1, z = 1) increases in the order R = Bu^t<Pr^i<Et<Me.[134] A convenient synthesis of $[Fe_2(\mu\text{-}CO)$-

$(\mu\text{-}CH_2)(CO)_2Cp_2]$ is described[135] and cis- and trans- isomers of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2)(CO)_2Cp_2]$ are characterised.[136] Studies of C-C coupling between 1,2-substituted alkenes and the methylidyne carbon in $[Fe_2(\mu\text{-}CO)(\mu\text{-}CH)(CO)_2Cp_2]^+$ support a concerted alkene-hydrocarbation mechanism followed by equilibration reactions.[137]

1-(Diethylamino)propyne with $[Fe_3(CO)_{12}]$ yields the metallacyclopentadiene complex $[Fe_2\{\mu\text{-}C_4Me_2(NEt_2)_2\}(CO)_6]$ formed by tail-to-tail coupling of alkyne whereas a tetranuclear complex with head-to-tail coupled cyclopentadienone is produced using $[Ru_3(CO)_{12}]$.[138] Thermal or photochemical insertion of alkynes into Fe-P or Fe-Fe bonds, respectively, of $[Fe_3(\mu_3\text{-}PR)(\mu\text{-}CO)(CO)_9]$ give products which may be considered to contain η^4-FeFeCCP or η^5-FeCCFeP rings as ligands to an $\{Fe(CO)_3\}$ unit[139].

X-Ray structures are reported for open-triangular Fe_3 complexes $[Fe_3(\mu_3\text{-}NPh)_2(CO)_9]$,[140] $[Fe_3\{\mu_3\text{-}P(p\text{-}tol)\}(\mu_3\text{-}S)(CO)_9]$[141] and $[Fe_3\{\mu\text{-}CS(CH_2)_2S\}(\mu_3\text{-}S)(CO)_9]$;[142] a structurally related μ-thionyl complex $[Fe_3(\mu_3\text{-}S)(\mu_3\text{-}SO)(CO)_9]$ is also characterised.[143]

Complex $[Fe_3(\mu\text{-}CO)(\mu\text{-}CNCF_3)(CO)_{10}]$ possesses a closed Fe_3 triangle, as in $[Fe_3(CO)_{12}]$.[144] One electron reduction of $[Fe_3(\mu_3\text{-}CO)(\mu_3\text{-}CMe)(CO)_9]^-$ causes coupling of ethylidyne and carbonyl ligand in formation of paramagnetic $[Fe_3(\mu_3\text{-}\eta^2\text{-}MeC{\equiv}CO)(CO)_9]^{2-}$, (5).[145] The equilibrium involving H_2 and CO, between complexes $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}H)_x(CO)_y]$ (x = 1, y = 10 and x = 3, y = 9) has yielded a bond energy for the FeHFe 3-centre interaction (81-85 Kcal mol^{-1}).[146] The following boron containing Fe_3 clusters have been characterised: $[Fe_3(\mu_3\text{-}BH_4)(\mu\text{-}H)_x(CO)_9]^{(1-x)-}$ {x = 0, 1: (6)} and $[Fe_3(\mu_3\text{-}BH_2)(\mu\text{-}H)_x(\mu\text{-}CO)(CO)_9]^{(1-x)-}$ (x = 0, 1).[147]

Benzonitrile acts as a 6e ligand in $[Fe_3(\mu_3\text{-}NCPh)(CO)_9]$ and in the butterfly cluster $[Fe_4(\mu_4\text{-}NCPh)(CO)_{12}]$.[148] The phosphido bridged cluster $[Fe_2(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8]$ undergoes ready intramolecular elimination of benzene to form $[Fe_3(\mu_3\text{-}PPh)_2(CO)_9]$ in the presence of CO.[149] After deprotonation, clusters $[Fe_3(\mu_3\text{-}PR)(\mu\text{-}H)_2(CO)_9]$ react with electrophiles at the PR group: reaction with CH_2I_2 forms a phosphaalkene ligand in $[Fe_3(\mu_3\text{-}RP{=}CH_2)(\mu\text{-}CO)(CO)_9]$.[150] A linked phosphido-phosphine bridge is present in complexes $[Fe_3(\mu_3\text{-}PPr^iCH_2PRPr^i)(\mu\text{-}H)(CO)_9]$ (R = H, Pr^i).[151]

The tetrahedral cluster $[Fe_4(\mu_3\text{-}CMe)(CO)_{12}]^-$ retains its core structure on protonation across an Fe-Fe bond; diprotonation also occurs in neat HSO_3CF_3.[152] The cationic cluster $[Fe_4(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)Cp_4]^+$, with two close Fe-Fe contacts, contains an [3Fe(III), Fe(II)] core.[153]

2.6 Ruthenium and Osmium.- The first characterised homoleptic ruthenium-alkyl is $[Ru_2(CH_2Bu^t)_6]$ containing a formal Ru≡Ru triple bond (2.311(3)Å).[154] Ortho-Metallation of triphenylphosphine occurs on reaction with $[Os_2(O_2CR)_4Cl_2]$ (R = Me,Et) to give $[Os_2(\mu\text{-}O_2CR)_2(\mu\text{-}C_6H_4PPh_2)_2Cl_2]$ with the shortest recorded Os≡Os bonds (2.272(1)Å, R = Me).[155] In the reaction of benzamido complex $[Ru_2(PhCONH)_4Cl]$ with PPh_3, phenyl group transfer occurs to form $[Ru_2\{\mu\text{-}Ph_2POC(Ph)N\}_2(\mu\text{-}PhCONH)_2Ph_2]$.[156] Carboxylato-bridged Ru_2 units are present in structurally characterised complexes $[\{Ru_2(\mu\text{-}O_2CR)_2(CO)_4(RCOOH)\}_n]$ (n = 1, R = Ph; n = 2, R = Bu^s).[157] Structures of complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}Pr^iNCHCHNPr^i)(CO)_4]$,[158] with an 8e-diazobutadiene bridge, and $[Ru_2(\mu\text{-}CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2(CO)_4]$[159] are reported.

Full details are published for syntheses, from $[Ru_2(\mu\text{-}CO)(\mu\text{-}COC_2Ph_2)(CO)Cp_2]$, and properties of μ-alkylidene complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}CHR)(CO)_2Cp_2]$, including a crystal structure for R = H;[160] this μ-methylene derivative may be protonated to form cis and trans μ-methyl cations, whilst the diphosphine substituted derivative forms a μ-methyne cation, $[Ru_2(\mu\text{-}CO)(\mu\text{-}CH)(\mu\text{-}dppm)Cp_2]^+$.[161] Reactions of $[Ru_2(CO)_4Cp^*_2]$ have furnished a range of mono- and bi-nuclear pentamethylcyclopentadienyl containing products;[162] new metal-metal bonded species include μ-alkylidene and μ-vinylidene complexes, reactive $[Ru_2(\mu\text{-}H)(CO)_2Cp^*_2]$ (formally double bonded) and $[Ru_2(\mu\text{-}H)_2(\mu\text{-}CO)Cp^*_2]$ (formally triple bonded).[162a] A μ-methylene unit may be added to the formal Ru=Ru bond in $[Ru_2(\mu\text{-}NO)_2Cp_2]$.[163] Mixed cyclobutadienecyclopentadienyl dimer $[Ru_2(\mu\text{-}CO)\{\mu\text{-}(Z)\text{-}CPhCHPh\}(CO)_2(\eta\text{-}C_4Ph_4)Cp]$ has been structurally characterised,[164] as has a bis-arene dimer (7) (Os≡Os = 2.674(1)Å), formed by cocondensation of Os atoms and mesitylene.[165]

Mechanistic studies of kinetic ^{2}H-isotope effects on μ-H and CO migrations in some trinuclear Ru_3 and Os_3 clusters are reported.[166] The structurally characterised anion $[Os_3(\mu\text{-}NO)(CO)_{10}]^-$ has a lower activation barrier for CO scrambling than related hydrido-bridged clusters.[167] Protonations of complexes $[Os_3(CO)_{12-n}(MeCN)_n]$ (n = 1,2) occur, and the structure of $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2]^+$ is reported.[168] The structure of $[Os(\mu\text{-}H)(\mu\text{-}OH)(CO)_9(PMe_2Ph)]$ is also reported.[169]

A kinetic study of intramolecular bridge formation in the conversion of $[Os_3(CO)_{11}(\eta^1\text{-}dppm)]$ into $[Os_3(\mu\text{-}dppm)(CO)_{10}]$ supports an associative mechanism.[170] New products of trinuclear clusters with diphosphine ligands include isomeric species $[Os_3(CO)_{10}(diphosphine)]$, with bridging or terminal-chelating ligands,[171] $[Ru_2(\mu\text{-}dppm)(CO)_{10}]$[172] and unsaturated $[Os_3(\mu_3\text{-}C_6H_4PPhCHPPh_2)(\mu\text{-}H)(CO)_8]$, with ortho-metallated dppm as ligand.[173]

Nucleophilic alkylations of carbonyl ligands in $[Os_3(CO)_{12}]$ followed by oxidation yield bis-acyl complexes $[Os_3(\mu\text{-}OCR)_2(CO)_{10}]$, initially as vic-isomers but these isomerise to an equilibrium mixture with the more stable gem-isomers; similar reactions on $[Ru_3(CO)_{12}]$ produce vic-$[Ru_2(\mu\text{-}OCMe)_2(CO)_6]$ which does not isomerise.[174] Amines and isocyanates, also attack CO groups of $[Os_3(CO)_{12}]$ to form μ-(O,C)-carboxamido complexes, accompanied, from the second reagents, by μ-(O,C)-formamido and μ-(C,N)-iminylurethane complexes.[175] Ruthenium carbonyl complexes edge-bridged by μ-(OC)-acyl or μ-(OC)-carboxamido groups undergo ready substitution of CO by phosphorus ligands at the O-bonded metal atom.[176] The methoxycarbonyl species $[Ru_3(CO)_{11}(CO_2Me)]^-$, produced by MeO^- attack, is also labile to carbonyl substitution to form $[Ru_3(CO)_{11}L]$ (L = phosphite).[177] Alkylation of $[Os_3(\mu\text{-}OCMe)(CO)_{10}]^-$ by $MeOSO_2CF_3$ affords an unstable bis-acyl complex which disproportionates giving a terminal alkylidene ligand in one product $[Os_3(\mu\text{-}H)(\mu\text{-}OCMe)\{C(OMe)Me\}(CO)_9]$; this product may also be formed by alkylation of $[Os_3(\mu\text{-}H)(\mu\text{-}OCMe)Ac(CO)_9]^-$.[178]

Reduction of CO on $[Os_3(CO)_{12}]$ using $[BH(OPr^i)_3]^-$ forms $[Os_3(\mu\text{-}CH_2)(CO)_{11}]$ via a formyl derivative;[179] decarbonylation of the μ-methylidene cluster produces $[Os_3(\mu_3\text{-}CCO)(\mu\text{-}H)_2(CO)_9]$[179] and reaction with CO the μ-ketene complex $[Os_3(\mu\text{-}CH_2CO)(CO)_{12}]$ containing a triosmacyclopentanone ring.[180] Hydride reduction of $[Ru_3(\mu\text{-}H)(\mu\text{-}OCMe)(CO)_{10}]$ yields an initial formyl derivative which transforms at low temperature into isolable $[Ru_3(\mu_3\text{-}CH)(\mu\text{-}H)(CO)_{10}]$; subsequent rearrangement forms $[Ru_3(\mu_3\text{-}CCO)(\mu\text{-}H)_2(CO)_9]$.[181] Reduction of μ_2-NO in $[Ru_3(\mu\text{-}H)(\mu\text{-}NO)(CO)_{10}]$ by H_2 yields Ru_3 clusters with μ-NH_2 and μ_2-NH ligands and also $[Ru_4(\mu_4\text{-}N)(\mu\text{-}H)(CO)_{12}]$.[182]

X-Ray and neutron diffraction studies give the structure and also information of H atom vibrational modes for $[Os_3(\mu_3\text{-}CH)(\mu\text{-}H)_3(CO)_9]$.[183] Substitution of carbonyls by up to three $AsPh_3$ groups occurs for $[Ru_3(\mu_3\text{-}CX)(\mu\text{-}H)_3(CO)_9]$ with CO dissociation depending on X = OMe ≫ Me > Cl > Ph.[184] Hydroboration of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ forms the boroxine supported cluster $[\{(\mu\text{-}H)_3(CO)_9Os_3CO\}_3(B_3O_3)]$ which is a useful precursor for methylidyne clusters $[Os_3(\mu\text{-}CX)(\mu\text{-}H)_3(CO)_9]$.[185] 3,3-Dimethylcyclopropene is a source of μ-alkylidyne complex $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ which rearranges on thermolysis to μ-alkenyl and μ_3-alkenylidene clusters.[186]

Insertion of methylvinyl ether into $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ gives isomeric alkyl complexes $[Os_3H(\mu\text{-}MeCHOMe)(CO)_{10}]$ which are stabilised by ether coordination.[187] Vinyl complexes $[Os_3H(CO)_{10}(cis\text{-}RCCHCOMe)]$ are formed by metallation of eneones; when R = H an open chain structure is observed but when R = Me a closed triangular Os_3 with terminal

chelating MeC=CHCOMe is present.[169] Full details are given for $[Os_3\{\mu_3\text{-}\eta^2\text{-}CF_3CCH(CF_3)\}(\mu\text{-}H)(CO)_{10}]$ and its reaction with nucleophiles; with PEt_3 metal-metal bond cleavage forms an Os_3 chain complex.[188] Zwitterionic adducts of PMe_2Ph and adducts of ions, especially CN^-, with $\mu\text{-}\eta^2$-alkenyl ligands of $[Os_3(\mu\text{-}H)(\mu\text{-}CHCHR)(CO)_{10}]$ are characterised spectroscopically[189a] and the cis-trans isomerisation of partially deuteriated $\mu\text{-}\eta^2\text{-}CHCH_2$ ligand, catalysed by pyridine, involves a similar zwitterionic alkylidene intermediate.[189b]

The $\mu\text{-}\eta^1,\eta^2$-alkynyl ligand in $[Os_3(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_{10}]$ exhibits a fluxional $\sigma\text{-}\pi$ rearrangement[190a] and also adds to complexes $[M(C_2Ph)(CO)_5]$ (M = Mn, Re) forming C-C bonds in clusters $[Os_3M(\mu_4\text{-}C_4Ph_2)(\mu\text{-}H)(CO)_{14}]$.[190b] Reaction of fluoroalkene complex $[Os_3H(\mu\text{-}CO)(CF_3CHCHCF_3)(CO)_9]$ with Me_3OBF_4 produces four neutral products including a cluster containing $(\mu_3\text{-}C_2CF_3)$ resulting from σ-C-C bond cleavage.[191] Alkynes add as $\mu_3\text{-}\eta^2$- ligands to unsaturated cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$ and also, with loss of CO and Ru-Ru bond rupture, to saturated cluster $[Ru_5(\mu_4\text{-}C_2Ph)(\mu\text{-}PR_2)(CO)_{13}]$.[192] Methylene, from CH_2N_2, adds to $\mu_3\text{-}C_2R$ to form $\mu\text{-}\eta^3$-allenyl and $\mu_3\text{-}\eta^4$-butadienylidene ligands on an Ru_3 cluster.[193]

Sequential hydrogenation of benzonitrile on $[Ru_3(CO)_{12}]$ occurs via isolable μ-NCHPh, $\mu\text{-}NHCH_2Ph$ and $\mu_3\text{-}NCH_2Ph$ complexes;[194a] $[Ru_3(\mu\text{-}H)(\mu\text{-}NCHPh)(CO)_{10}]$ has been structurally characterised.[194b] Related hydrogenations of CF_3CN on Os_3 clusters, including structures of intermediates are reported.[194c] Nitrobenzene with $[Ru_3(CO)_{12}]$ forms $[Ru_3(\mu_3\text{-}NPh)(CO)_{10}]$ and $[Ru_3(\mu_3\text{-}NPh)_2(CO)_9]$ now structurally characterised as open Ru_3 system;[195a] the former cluster reacts with H_2 to give $[Ru_3(\mu_3\text{-}NPh)(\mu\text{-}H)_2(CO)_9]$ which liberates aniline on carbonylation.[195b]

Aryl diazonium cations react with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ giving $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^n\text{-}N_2Ar)(CO)_{10}]$ (n = 1) which can be photochemically isomerised to structurally-characterised dihapto-derivatives (n = 2).[196] Coordinated aryldiazo ligands undergo facile thermal cyclometallation reactions as revealed by the structure of $[Ru_3(\mu_3\text{-}PhAsCH_2AsPh_2)(\mu\text{-}H)(\mu\text{-}N_2C_6H_4)(CO)_8]$.[197] Characterisations of dimethyl diazocarboxylate derivatives $[Os_3(CO)_n(MeOCON_2OCOMe)]$ (n = 10,11 or 12) indicate opened Os_3 structures bridged by organic ligand donating 6e,4e or 2e, respectively.[198] In reaction with $[Os_3(CO)_{10}(MeCN)_2]$ the C-N bond of 1-dimethylamino-but-2-yne is cleaved to form $[Os_3(\mu_3\text{-}MeCCCH_2)(\mu\text{-}H)(CO)_9]$.[199]

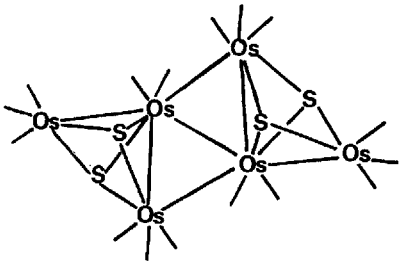
The structure of derivative $[Os_3(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}]$ has been determined.[200] Some new sulphido-osium clusters have been structurally characterised; these include, in increasing nuclearity: $[Os_3$-

$(\mu_3\text{-CO})(\mu_3\text{-S})(CO)_9]$;[201] $[Os_4(\mu_3\text{-S})_2(CO)_{11}L]$ (L = PMe_2Ph, $CNBu^t$),[202] $[Os_6(\mu_3\text{-S})(CO)_{19}]$ and $[Os_6(\mu_4\text{-S})(CO)_{17}]$[203]; $[Os_6(\mu_3\text{-S})_4(CO)_{16}]$ (8),[204] $[Os_6(\mu_4\text{-S})(\mu_3\text{-S})_3(\mu_2\text{-PPh}_2)_2(CO)_{14}]$[205] and the higher nuclearity system, with a new type of metal core geometry, $[Os_{10}(\mu_4\text{-S})(CO)_{23}]$,[206] (9). The cluster $[Os_4(\mu_3\text{-Se})_2(CO)_{12}]$ is also structurally characterised and other selenido clusters of Os_3 and Os_4 reported.[207]

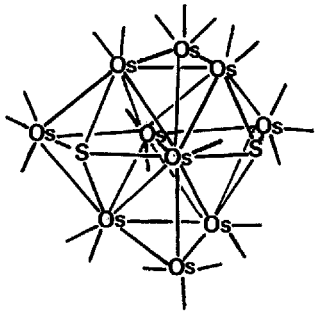
The structure of $[Ru_4(\mu_3\text{-}C_5H_4)_2(CO)_5\{P(OMe)_3\}Cp_2]$ (10) comprises a chain of Ru_4 atoms bridged by two $\mu_3\text{-}\eta^1,\eta^1,\eta^5$-cyclopentadienylidene ligands.[208] The crystal structures and dynamicsare described for $[Ru_4(\mu_4\text{-}\eta^2\text{-MeC}_2\text{Ph})_2(\mu\text{-CO})(CO)_{10}]$[209] and for $[Ru_4\{\mu_3\text{-HC(PPh}_2)_3\}(\mu\text{-H})_4(CO)_9]$,[210] which possesses chirality arising from an asymmetric array of phenyl groups. Phosphorus bridged clusters $[Ru_5(\mu_4\text{-PPh})_2(\mu_3\text{-CCH}_2\text{Pr}^i)(\mu\text{-PPh}_2)(CO)_{12}]$ and $[Ru_5(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_{10}]$ result from stepwise reduction of alkynyl bridge in $[Ru_5(\mu_4\text{-}\eta^2\text{-C}_2\text{Pr}^i)(\mu\text{-PPh}_2)(CO)_{13}]$ by $PPhH_2$.[211] Reactions of PPh_2H with $[Ru_3(CO)_{12}]$ give a range of products including $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$ and, structurally characterised, $[Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7]$.[212]

Clusters $[Os_5C(CO)_{15}]$ or $[(Os_5C(CO)_{15}I_2]$ react with alcohols to give products $[Os_5C(\mu\text{-X})(\mu\text{-OCOR})(CO)_{14}]$ (X = H or I, respectively) which have structures with cores that may be considered as hypho-hexagonal bipyramidal.[213] The X-ray structure of $[Os_6(\mu_4\text{-CO})(CO)_{16}(py)_2]$ (11) reveals an unusual mode of metal-CO bonding.[214] Full details have appeared of syntheses and structures of $[Os_8(\mu\text{-H})(CO)_{22}]^-$ and $[Os_8(\mu_3\text{-H})(\mu\text{-I})(CO)_{22}]$ formed with skeletal rearrangement by reaction of iodine on the former cluster.[215] The first high-nuclearity nitrosyl-carbonyl clusters are $[Os_{10}(\mu_6\text{-C})(\mu\text{-NO})(CO)_{24}]^-$, with nitrosyl group bridging "wing tips" of a butterfly Os_4 arrangement, and $[Os_{10}(\mu_6\text{-C})(CO)_{23}(NO)]$.[216]

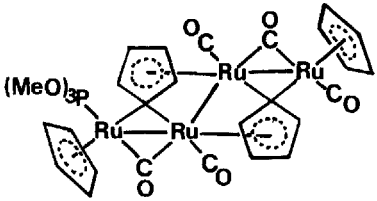
2.7 Cobalt.- Controlled electron-transfer chain-catalysed nucleophilic substitution of carbonyl clusters by polydentate ligands is exemplified by the formation of $[Co_2\{\mu\text{-C}_2(CF_3)_2\}(CO)_3\{MeAs(C_6H_4AsMe_2)_2\}]$ from the parent complex by replacement of three terminal CO groups at one Co atom.[217] Studies of mononuclear radicals, also formed on reduction of complexes $[Co_2(\mu\text{-C}_2R_2)(CO)_6]$, are reported.[218] Several unusual alkyne complexes of the type $[Co_2(\mu\text{-alkyne})(CO)_6]$ have been characterised, including: alkyne = $[PhC{\equiv}CMn(CO)_4(PCy_3)]$,[219] $HC{\equiv}CCH_2\text{-}\{P_3N_3Cl_4R\}$ or $MeC{\equiv}C\{P_3N_3Cl_4R\}$ (phosphazene derivatives)[220] and C_8F_6 (hexafluorodehydrocyclo-octatetraene);[221] in the later case the C_8F_6 ring is severely puckered whereas it is planar in the substituted derivative $[Co_2(\mu\text{-}C_8F_6)(CO)_4(PPh_3)_2]$.[221] Easy coupling of methylene groups of $[Co_2(\mu\text{-CH}_2)_2(\mu\text{-dppm})(CO)_4]$ occurs in reaction with alkynes



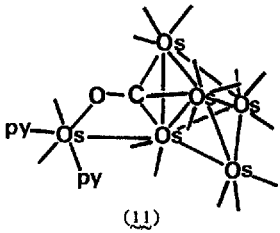
(8)



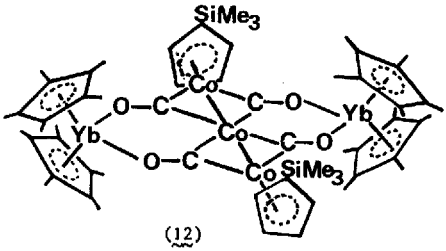
(9)



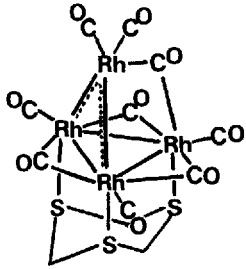
(10)



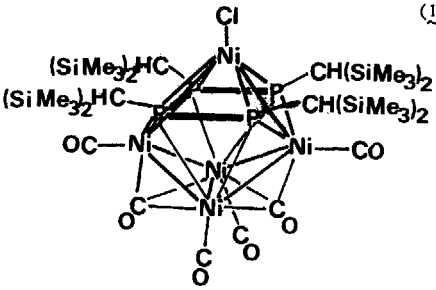
(11)



(12)



(13)



(14)

to give ethylene and $[Co_2(\mu\text{-}C_2R_2)(\mu\text{-dppm})(CO)_4]$ and coupling also, occurs with ethylene, giving propylene, and with hydrogen, giving ethane.[222]

Thioketenes react with $[Co_2(CO)_8]$ to give structurally characterised complexes $[Co_2(\mu\text{-}\eta^1,\eta^2\text{-}SCCR_2)_2(CO)_4]$.[223]

Full details are reported for synthesis of complexes $[Co_2R_2(CO)_2Cp_2]$ and for their thermolysis or carbonylation which forms ketones in some cases;[224] evidence is also presented for an equilibrium between these dimers and 17e monomers. Properties of the bridged cyclopentadienyl dimer $[Co_2(\mu\text{-}C_{11}H_{10})Me_2(CO)_2]$ are described.[224] Radical anions $[Co_2(CO)_2Cp_2]^-$ react with 1,1-dibromoethylene to form $[Co_2(\mu\text{-}CCH_2)(CO)_2Cp_2]$ in which the μ-vinylidene group may be protonated, hydrogenated or reacted with hydrido-complexes to form mixed-metal clusters.[225] The crystal structure of $[Co_2(\mu\text{-}CHMe)(\mu\text{-}CO)_2Cp^*_2]$ is reported.[226] Full synthetic and structural details are given for products of addition of various reagents across the formal double bond of $[Co_2(\mu\text{-}CO)_2Cp^*_2]$.[227] A novel by-product $[Co_2(\mu\text{-}PPh_2C_6H_4CMe)(\eta\text{-}C_5H_4COOMe)_2]$ containing a $\mu\text{-}\eta^3$-benzylic ligand is formed in the reaction between acetylene and $[Co(PPh_3)_2(\eta\text{-}C_5H_4COOMe)]$.[228] The dimer $[Co_2(\mu\text{-}NO)_2Cp_2]$ is cleaved by Na/Hg to form $Na[Co(NO)Cp]$ which is a precursor for syntheses of heteronuclear CoM derivatives.[229]

A 47e unit with an essentially linear Co_3 arrangement and hexagonal-planar coordination around the central Co atom is found in $[\{YbCp^*_2\}_2\ Co_3(\mu\text{-}CO)_4(\eta\text{-}C_5H_4SiMe_3)_2\}]$, (**12**).[230]

The ligand $\{HC(PPh_2)_3\}$ (TPM) forms bidentate and tridentate bridged clusters $[Co_3(\mu\text{-}CR)(\mu\text{-TPM})(CO)_7]$ and $[Co_3(\mu_3\text{-TPM})(\mu\text{-}CR)(CO)_6]$ (R = H,Cl), respectively.[231] Studies of CO exchange and substitution on $[Co_4(\mu_3\text{-TPM})(CO)_9]$ support a dissociative mechanism.[232] Nitrosyl containing anions $[Co_3(\mu\text{-}CY)(CO)_7(NO)]^-$ (Y = Me,Ph,COOH,$CpFeC_5H_4$) are reported.[233]

Structures of two further products from reaction of CS_2 with $[Co_2(CO)_8]$ are described: $[\{Co_3(\mu_3\text{-}S)(CO)_7\}(\mu_3\text{-}SCS)\{Co_3(\mu_3\text{-}C)(CO)_9\}]$ in which two Co_3 clusters are linked by a SCS group <u>via</u> a Co_2 edge and the apical carbon[234] and $[Co_6(\mu_6\text{-}C_2)(\mu_4\text{-}S)(\mu\text{-}CO)_6(CO)_8]$ in which a peripheral C_2 unit bridges a "boat" shaped array of Co_6 atoms.[235] A hexanuclear product of reaction between S_8 and $[Co_2(CO)_8]$ is the exceptionally electron rich cluster $[Co_6(\mu_3\text{-}S)_8(CO)_6]$.[236]

<u>2.8 Rhodium and Iridium.</u>- Binary isocyanide complexes $[Rh_2(\mu\text{-}CNAr)_2(CNAr)_6]$ are described.[237] Crystal structures are reported for $[Ir_2(\mu\text{-}C_2Ph_2)(CO)_4(PPh_3)_2]$ (Ir-Ir:2.689(1)Å)[238] and $[Rh_2(\mu\text{-}CO)_3\{MeGa(pz)_3\}_2]$ (Hpz = pyrazole) (Rh-Rh: 2.5818(8)Å).[239]

Binuclear complexes $[Rh_2(\mu\text{-RNNNR})_2(CO)_2(PPh_3)_2]^n$ (n = 0) are oxidised to a mixed-valence cation (n = +1) with a formal 0.5(Rh-Rh) bond order.[240] Other structurally characterised complexes containing M_2 units bridged by nitrogen ligands include $[Rh_2(\mu\text{-napy})_2(nbd)_2]^{2+}$ (napy = 1,8-naphthyridine);[241] $[Rh_4(\mu\text{-az})_2(\mu\text{-Cl})_2(\mu\text{-CO})_2(CO)_2(nbd)_2]$ (Haz = 7-azaindole), with two directly bonded Rh_2 units in a planar Rh_4Cl_2 framework;[242] $[Ir_2(\mu\text{-pz})(\mu\text{-PPh}_2)(cod)(C_8H_{13})]$ (C_8H_{13} = 1-σ,-4,5-η-cyclooctatetraenyl)[243] and $[Ir_2(\mu\text{-4-Cl-pz})_2Cl_2(CO)_2(PPh_3)_2]$.[244] The latter two complexes are formed by reaction of PPh_2H or Cl_2, respectively, with $[Ir_2(\mu\text{-pz})_2L_2L'_2]$ ($L_2 = L'_2$ = cod or L = PPh_3, L' = CO); these precursors are formally Ir-Ir non-bonded but (for $L_2 = L'_2$ = cod) the long lived excited state $^3B_2(d\sigma^*p\sigma)$ is metal-metal bonding and is active to oxidative addition.[245]

Studies of A-frame derivatives $[Rh_2(\mu\text{-X})(\mu\text{-dppm})_2Y_2]$, and their metal-metal bonded products, include details of protonation and HX oxidative addition,[246a] reactions with isocyanates[246b] and with CO, SO_2[246c,d] and isocyanides;[246c] properties and structures are given for related diphosphine-bridged species $[Rh_2(\mu\text{-dppm})_2(O_2C_6Cl_4)(CO)]$[247] and $[Rh_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-PPh}_2NHPPh_2)_2(CO)_2]Cl$.[248] The chemistry of diiridium species of the type $[Ir_2(\mu\text{-X})(\mu\text{-dppm})_2Y_{4-n}Z_n]$ (X = CO,[249a] alkyne[249b]) is also reported.

Crystal structures of $[Rh_2(\mu\text{-CO})(\mu\text{-dppm})Cp_2]$[250] and $[Rh_2(\mu\text{-CO})(\mu\text{-NO})Cp^*_2][PF_6]$[251] and the reactivity of these and related complexes are described. $[Rh_2(\mu\text{-CO})LCp^*_2]$ { L = $P(OMe)_3$ } contains an unsymmetrical, non-planar Rh_2C_2 core and is structurally related to trinuclear species with L = $Cp^*L'RhP_2Me_4$.[252] As for related cobalt-species, details are provided for syntheses and characterisations of binuclear products of addition to unsaturated $[Rh_2(\mu\text{-CO})_2Cp^*_2]$; hydrazones and MnO_2 form μ-alkylidenes, with cyclic reagents affording dimetallaspiranes,[227a] formyldiazomethane yields $[Rh_2\{\mu\text{-CH(CHO)}\}(CO)_2Cp^*_2]$,[227b] α-diazoketones also yield α-alkylidenes or bridging ligands incorporating a coordinated carbonyl group by C-O or C-C coupling;[253] and inorganic molecules SO_2, Se, $[AuCl(CO)]$ or $[AgCN_2P(O)Ph_2]$ form respective bridged adducts.[227c] The complex $[Rh_2(\mu\text{-PPr}^i_2CHMeCHCCH_2Ph)(\mu\text{-H})Cl(PPr^i_3)Cp]$ is formed by coupling of PPr^i_3 and vinylidene ligands with two H-transfers.[254] Hexafluorobut-2-yne and isocyanates couple on a dirhodium centre to give $[Rh_2\{\mu\text{-}\eta^3\text{-C(CF}_3)C(CF_3)C(O)NPh\}Cp_2]$.[255]

Full details of Rh(IV) complexes derived from $[Rh_2(\mu\text{-CH}_2)_2Me_2Cp^*_2]$ are published, including mono-alkyl species $[Rh_2(\mu\text{-CH}_2)_2RLCp^*_2]^+$ (L = RCN, py, CO)[256a] which exhibit intramolecular alkyl migration, and disubstituted species $[Rh_2(\mu\text{-CH}_2)_2L_2Cp^*_2]^{2+}$;[256b] both complex types form neutral derivatives (L = halide, etc.). Complexes $[Ir_2(\mu\text{-CH}_2)_2MeX$

Cp^*_2] (X = Me,Cl) are also described.[257]

Structures reported for open trinuclear complexes bridged by triphosphines are $[Rh_3\{\mu_3\text{-}PhP(CH_2PPh_2)_2\}_2(\mu\text{-}CO)_2(\mu\text{-}S_2COEt)(CO)(S_2COEt)]^+$ [258a] and $[Rh_3\{\mu_3\text{-}PhP(CH_2PPh_2)_2\}_2(\mu_3\text{-}I)(\mu\text{-}I)_2I(CO)]^+$ [258b] to which CO will add. Several diphenylphosphido-bridged, closed trirhodium clusters can be synthesised, including the structurally characterised $[Rh_3(\mu\text{-}PPh_2)_3(CO)_n]$ (n = 5,7):[259] the pentacarbonyl derivative condenses to $[Rh_4(\mu\text{-}CO)_2(\mu\text{-}PPh_2)_4(CO)_4]$[259] and this tetrahedral cluster shows facile phosphido-ligand migration.[260] Structures have been established for chalogen bridged anions $[Rh_3(\mu_3\text{-}E)_2(CO)_6]^-$ (E = S, Se).[261]

Several alkene substituted tetrairidium carbonyl clusters are described.[262] Crystal structures have been established for the following phosphine substituted clusters: $[Ir_4(\mu\text{-}CO)_3(CO)_5(PMe_2Ph)_4]$,[263] $[Ir(\mu\text{-}CO)_3(\mu\text{-}dppm)_2(CO)_5]$[264] and $[Ir_4\{\mu_3\text{-}(PPh_2)_3CH\}(CO)_9]$,[265] the latter having all CO groups as terminal ligands. The butterfly cluster $[Rh_4(\mu_3\text{-}SCH_2SCH_2SCH_2)(\mu\text{-}CO)_4(CO)_5]$ (13) exhibits fluxionality, possibly involving a tetrahedral intermediate.[266] Neutron diffraction shows the presence of face-bridging H ligands in $[Rh_4(\mu_3\text{-}H)_4Cp^*_4][BF_4]_2$.[267]

Nitrido-cluster $[Rh_6M(\mu_6\text{-}N)(\mu_3\text{-}CO)(\mu\text{-}CO)_4(CO)_{10}]^{2-}$ (M = Rh) contains a novel square face-capped trigonal prisimatic array of Rh_7 atoms, (related heteronuclear clusters M = Co,Ir are similar).[268] In $[Rh_{14}(\mu_6\text{-}C)_2(\mu\text{-}CO)_{21}(CO)_{12}]^{2-}$ two trigonal prisms, monocapped at a triangular-face, are linked by a Rh-Rh bond between capping atoms.[269]

2.9 Nickel.- 1-Alkyne coupling reactions occur on diazadiene (dad) nickel(0) complexes and an intermediate $[Ni(\mu\text{-}CHCRCRCH)(dad)_2]$ has been structurally characterised.[270] $[Ni_5(\mu_4\text{-}P_2\{CH(SiMe_3)_2\}_2)_2(\mu_3\text{-}CO)_2\text{-}Cl(CO)_4]$ (14) incorporates two double bonded P_2 ligands.[271] X-Ray analysis has revealed the structure of $[Ni_8(\mu_4\text{-}PPh)_6(CO)_4(PPh_3)_4]$.[272]

2.10 Palladium and Platinum.- Binuclear complexes $[M_2(\mu\text{-}CO)Cl_2(PPh_3)_3]$ (M = Pd,Pt) are formed by oxidative addition of M^{II}-Cl bonds to M^0 centres.[273] Addition of an Pt-H bond across a terminal alkynyl ligand can form μ-vinylidene complexes, e.g. $[Pt_2(\mu\text{-}CCHPh)(C_2Ph)L_4]^+$.[274] Photolyses of A-frame complexes $[Pt_2(\mu\text{-}H)(\mu\text{-}dppm)_2(Me)X]$ (X = H or Me) cause reductive elimination of HX and the formation of Pt-Pt bonded $[Pt_2(\mu\text{-}dppm)_2Me(S)]^+$.[275] $[\overline{CH_2CH_2CH_2CH_2Pt}(\mu\text{-}dppm)_2PtMe]^+$ contains a dative Pt→Pt bond[276] and a similar bond may be present in a diene-1,4-diyl bridged Pd_2 complex.[277]

A mechanism is presented for formation of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ from a mononuclear precursor.[278] Metal vapour synthesis is described

for structurally characterised $[Pd_3(\mu\text{-CNCy})_3(CNCy)_3]$.[279] ^{31}P and ^{195}Pt Nmr studies and an X-ray structure are reported for clusters $[Pt_4(\mu\text{-CO})_5L_4]$ (L = phosphine).[280] Reactions of phosphine-hydrido clusters $[Pt_4H_x(PBu^t_3)_4]^{n+}$ (x = 1,2,7) include a reversible metallation of a methyl group of a ligand Bu^t group.[281]

2.11 Copper and Gold.- Binuclear cations $[Au_2(\mu\text{-}C_2R)(PPh_3)_2]^+$ (R = Pr, Ph) are described.[282] X-Ray analyses have established structures for binuclear Au^{II}-Au^{II} bonded organo-gold ylide complexes formed by oxidative addition, viz. $[Au_2(\mu\text{-}XPR_2CH_2)_2YZ]$ (X = CH_2, Y = CH_2Cl, Z = I; X = S, Y = Z = I),[283] as well as for a non-Au-Au bonded Au^I/Au^{III} isomer.[283b] Papers on phosphine clusters of copper (Cu_6)[284] and gold (Au_n, n = 7-11)[285] have appeared.

3. Compounds with Heteronuclear Transition Metal Bonds

Tables 1 and 2 list, respectively, the bi- and poly-nuclear complexes containing hetero-transition metal bonds that have been structurally characterised by X-ray diffraction: complexes are entered under the metal of earliest periodic group and arranged in order of (i) increasing group number of other metal(s), (ii) increasing nuclearity (Table 2) and (iii) decreasing number of carbonyl groups.

3.1. Binuclear Complexes.- Other hetero-binuclear derivatives described in 1984 and not listed in Table 1 contain bonding interactions between the following metals: Zr and Re;[286] Cr and W;[306] Fe;[296] Co;[229] Rh;[395] Ni;[288] Pt[290] or Ag;[291] Mo and Mn;[396] Fe,[296] Ru;[64a] Pt,[290,294] Cu[293] or Au;[291] W and Co;[297,306] Rh;[293,300a] Ni;[305] Pd;[305] Pt;[290,294,298,307,397] Cu;[343] Ag[291] or Au;[291] Mn and Co[398] or Rh;[293] Fe and Ru;[172] Ru and Os;[399] Co[362] or Rh;[400] Rh and Cu;[254] Pd and Pt;[276,401] Pt and Cu.[343]

The complex $[WOs(CO)_9(PMe_3)]$, with an unbridged, dative bond Os → W exists in solution as two isomeric forms in a dynamic equilibrium, probably involving non-dissociative CO migration between metal atoms.[299] In related donor-acceptor complex $[(OC)_5RuOsBr(SiCl_3)(CO)_3]$ partial dissociation of the Os→Ru bond does occur in solution.[399] A dative Pt→Pd bond is probably present in the bridged complex $[PtPd(\mu\text{-dppm})_2\{(CH_2)_4\}Me]^+$.[276] Other μ-dppm bridged dimers formally contain normal bonds Mn-Pd;[311] Mo-Pt[294] and Ru-Rh.[400]

The large majority of newly reported binuclear complexes that, at least formally, contain a direct metal-metal bond also contain bridging ligands. Single hydride bridges are observed in $[MFe(\mu\text{-H})(CO)_9]^-$ [296] and $[MM'(\mu\text{-H})(CO)_5(PR_3)]$[291] (M = Cr,Mo,W; M' = Au,Ag) and from

Table 1. X-Ray determined structures of heterobinuclear metal–metal bonded complexes.

Zirconium

$[ZrOs(\mu\text{-}H)_3Cl(PMe_2Ph)_3Cp_2]$[286]

Vanadium

$[VW\{\mu\text{-}C(tol\text{-}p)\}(CO)_2Cp_3]$[287]

Chromium

$[CrCo(\mu\text{-}CO)(\mu\text{-}PBu^t_2)(CO)_4(PMe_3)_2]$[288]

$[CrRh(\mu\text{-}PBu^t_2)(CO)_5(cod)]$[288]

$[CrRh(\mu\text{-}PBu^t_2)(CO)_5(PMe_3)_2]$[289]

$[CrNi(\mu\text{-}PBu^t_2)Cl(CO)_4(PMe_3)_2]$[289]

$[CrPt(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(PEt_3)_2]$[290]

$[CrAu(\mu\text{-}H)(CO)_5(PPh_3)]$[291]

Molybdenum

$[MoW(CO)_5\{\overline{CO(CH_2)_2CH_2}\}Cp_2]$[292]

$[MoRu(\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)O(CO)_2(\eta\text{-}C_2Ph_2)]$[64b]

$[MoRh(\mu\text{-}CO)_2(CO)(PPh_3)_2Cp]$[293]

$[MoPt(\mu\text{-}dppm)(CO)_2(dppm)Cp']^+$ 294

Tungsten

$[WRe\{\mu\text{-}CH(tol\text{-}p)\}(CO)_9]^-$ 295

$[WRe\{\mu\text{-}CH_2(tol\text{-}p)\}(\mu\text{-}dmpm)(CO)_7]$[295]

$[WRe\{\mu\text{-}OCCH_2(tol\text{-}p)\}(\mu\text{-}dppm)(CO)_6\text{-}\{P(OMe)_3\}]$[295]

Tungsten cont'd

$[WFe(\mu\text{-}H)(CO)_9]^-$ 296

$[WFe\{\mu\text{-}C(tol\text{-}p)CMeCMe\}(CO)_5Cp]$[297]

$[WFe\{\mu\text{-}C(tol\text{-}p)\}(CO)_5(HBpz_3)]$[298]

$[WOs(CO)_9(PMe_3)]$[299]

$[WOs\{\mu\text{-}CH(OMe)PPh_2\}\mu\text{-}PPh_2(CO)_6(PMePh_2)]$[300]

$[WCo\{\mu\text{-}\sigma,\eta^3\text{-}C(tol\text{-}p)CMeCHMe\}(\mu\text{-}CO)(CO)\text{-}CpCp^*]^+$ 301

$[WRh\{\mu\text{-}C(tol\text{-}p)CPhCPh\}(CO)_2Cp(\eta\text{-}C_9H_7)]$[302]

$[WRh\{\mu\text{-}C(tol\text{-}p)\}(\mu\text{-}CO)(CO)(PPh_3)_2\text{-}(\eta\text{-}C_2B_9RH_8Me_2)]$ (R = H or C_7H_9)[303]

$[WIr(\mu\text{-}PPh_2)_2H(CO)_5(PPh_3)]$[304]

$[WIr(\mu\text{-}PPh_2)_2H(CO)_4\{C(OMe)Ph\}(PPh_3)]$[304]

$[WPt(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)]$[305]

$[WPt(\mu\text{-}PPh_2)_2(CO)_4(MeO_2CC_2CO_2Me)]$[305]

$[WPt\{\mu\text{-}\sigma,\eta^3\text{-}CH(tol\text{-}p)\}(CO)_2(PMe_3)_2Cp]^+$ 306

$[WPt(\mu\text{-}H)\{\mu\text{-}CH(tol\text{-}p)\}(CO)_2(PMe_3)_2Cp]$[307]

$[WPt\{\mu\text{-}CH(tol\text{-}p)\}(\mu\text{-}CO)(C_2Me_2)(PMe_3)_2\text{-}Cp]^+$ 301

$[WCu(CO)_3(PPh_3)_2Cp]$[293]

$[WAu\{\mu\text{-}CH(tol\text{-}p)\}(CO)_2(PPh_3)Cp]$[308]

$[WAu\{\mu\text{-}C(tol\text{-}p)\}(CO)_2(PPh_3)\text{-}(\eta\text{-}C_2B_9H_9Me_2)]$[303]

Manganese

$[MnFe\{\mu\text{-}\eta^3\text{-}Bu^tNCHCHN(H)Bu^t\}(CO)_6]$[309]

$[MnFe(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_5Cp]$[310]

$[MnCo(\mu\text{-}NO)_2(PMe_3)Cp_2]$[229]

$[MnPd(\mu\text{-}dppm)_2Br(CO)_3]$[311]

Iron

$[FeRu(\mu\text{-}CO)_2(CO)_2Cp_2]$[312]

$[FeCo(\mu\text{-}PBu^t_2)(CO)_5(PMe_3)_2]$[288]

$[FeCo\{\mu\text{-}C(SMe)_2\}(\mu\text{-}CO)(CO)_3Cp]$[313]

$[FeRh\{\mu\text{-}(PPh_2)_3CH\}(CO)_5]^+$ 314

$[FeRh(\mu\text{-}\eta^4,\eta^3\text{-}C_7H_7)(\mu\text{-}CO)(CO)_2(dppe)]$[315]

Ruthenium

$[RuCo\{\mu\text{-}PPh_2C(O)CPhCPh\}(\mu\text{-}CO)(CO)_5]$[316]

$[RuCo(\mu\text{-}PPh_2)H(CO)_6]^-$ 317

Rhodium

$[RhIr(\mu\text{-}H)(\mu\text{-}Cl)X(PEt_3)_3(dppe)]^+$ (X=H or Cl)[318]

crystallographically determined W-Fe and W-Cr distances a significant direct metal-metal interaction may contribute to the overall 3 centre -2e MHM' link. In contrast, long M-M' separations are found in complexes of the type $[Cp_2(OC)M(\mu\text{-}H)M'L_n]$ (M = Nb,Ta; M' = V,Nb,Ta,Mn).[402] Three hydride bridges are present in $[ZrOs(\mu\text{-}H)_3Cl(PMe_2Ph)_3Cp_2]$ and a related Zr-Re complex is also described.[286]

The dynamic cis-trans isomerisation of carbonyl bridged $[FeRu(\mu\text{-}CO)_2(CO)_2Cp_2]$ in solution is described and this complex is a source of a range of binuclear organo-FeRu derivatives.[312] The electronic and molecular structures of $[FeCo(\mu\text{-}CO)\{\mu\text{-}C(SMe)_2\}(CO)_3Cp]$ are reported.[313] Full details of formally unsaturated complexes $[MRh(\mu\text{-}CO)_2(CO)(PPh_3)_2Cp_2]$ (M = Mo,W) are given;[293] reactions of these complexes with $[Fe_2(CO)_9]$ or $[Pt(C_2H_4)(PPh_3)_2]$ yield several new bi-, tri- and tetranuclear mixed metal products including $[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}Ph)(PPh_3)_2Cp]$ containing a $\mu\text{-}\sigma,\eta^2$-phenyl group.[330] The analogy between unsaturated $[MRh(\mu\text{-}CO)_2Cp^*_2]$ (M = Co,Rh) and alkenes is noted in a detailed study of the non-rigidity of adducts with $\{Mo(CO)_5\}$.[329] Studies are also reported on hindered rotation of η-indenyl in $[CrRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_9H_7)(\eta\text{-}C_6H_3Me_3)]$.[395] The semibridging nature of two carbonyl ligands and the two structural forms of polar complexes $[MCu(CO)_3(PPh_3)_2Cp]$ (M = Mo,W) are discussed.[293] Nitrosyl bridges are found in $[MCo(\mu\text{-}NO)_2LCp_2]$ (M = Mn,L = PMe_3; M = Cr, L = NO).[229]

New examples of μ-alkylidyne {especially μ-C(tol-p)} complexes have been prepared, e.g. paramagnetic $[VW\{\mu\text{-}C(tol\text{-}p)\}(CO)_2Cp_2]$;[287] syntheses have involved reactions of $[W(\equiv CR)(CO)_2L]$ (L = Cp,[287,306,308] η-1,2-$C_2B_9H_9Me_2$[303] and $RBpz_3$[298]). Reactions of binuclear complexes containing the {W(μ-CR)M} grouping include insertion of alkynes to form allyl ligands (μ-CRCR'CR') (M = Co,[297] Rh[302]), protonation to form systems $\{W(\mu\text{-}\sigma,\eta^3\text{-}CHR)M^+\}$ (M = Cr,Co,Pt)[306] and related auration with $[Au(PPh_3)]^+$.[308] $[WPt\{\mu\text{-}\sigma,\eta^3\text{-}CH(tol\text{-}p)\}(CO)_2(PEt_3)_2Cp]^+$ is also formed by addition of Pt-H to W≡CR;[397] addition of ligands (CO,PR_3) to such $(\mu\text{-}\sigma\text{-}\eta^3\text{-}CHR)$ containing derivatives causes transformation into normal (μ-CHR) complexes[307] although alkynes may insert into the bridge.[301] Other μ-CRR' complexes have been formed by metal exchange, e.g. $[WAu(\mu\text{-}CHR)(CO)_2(PPh_3)Cp]$,[308] by addition of CuCp* to $[W\{C(OMe)R\}(CO)_5]$,[343] and by hydride addition to $[(OC)_5WRe(\equiv CR)(CO)_4]$.[295] The μ-alkylidene ligand in the product from the latter reaction, i.e. $[WRe(\mu\text{-}CHR)(CO)_9]^-$, can be sequentially transformed into an asymmetric μ-alkyl and a μ-(O,C)-acyl ligand.[295]

A number of new phosphido-bridged dimers containing one or two μ-PR_2 groups have been synthesised - see Table 1 (also ref. 396). Several were prepared by displacement of halide ligand from a metal com-

plex by a mononuclear phosphido-complex anion of second metal;[288,289,300,304,305] other synthetic routes involved addition of P-H in $[M(CO)_5(PR_2H)]$ to a Pt(0) complex.[290] reaction of coordinated-PPh_2X with $[Co_2(CO)_8]$,[362] combination of $[Fe(PR_2)(CO)_2Cp]$ with $[MnH(CO)_5]$,[310] cleavage of Ph from coordinated-PPh_3[330] and photolytic hydrogenolysis of $[MoMn(\mu\text{-}\eta\text{-}C_5H_4PR_2)(CO)_7]$ to $[MoMn(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_6Cp]$.[396] Reactions of such μ-phosphido-complexes normally leave the bridge unchanged, as in ligand substitutions,[288,305] including the interesting site-selective replacement of CO by hydride to form $[H(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]^-$,[317] and the reversible addition of H_2 to a W-Ir bond with bond opening.[304] However, $\mu\text{-}PR_2$ ligands may undergo modifications in some reactions (cf. homonuclear complexes[76,97,125]), as found for reductive couplings of $\mu\text{-}PPh_2$ with alkyl, hydrido and alkylidene ligand in WM (M = Rh,Ir,Os) systems[300] and for addition of CO and PhC≡CPh into $\mu\text{-}PPh_2$ to form $[RuCo(\mu\text{-}CO)(\mu\text{-}PPh_2COCPhCPh)(CO)_5]$[316]

The μ-fulvalene complex $[MoRu(\mu\text{-}C_{10}H_8)(CO)_5]$ furnishes oxo-derivative $[MoRu(\mu\text{-}C_{10}H_8)O(CO)_2(C_2Ph_2)]$ on reaction with alkyne in presence of moisture.[64b] Reversal of the μ-cycloheptatrienyl bonding mode from $\{\eta^4\text{-}Rh,\eta^3\text{-}Fe\}$ in $[(OC)_3Fe(\mu\text{-}C_7H_7)RhL_2]$ (L = CO) to $\{\eta^3\text{-}Rh,\eta^4\text{-}Fe\}$ occurs on substitution of one or two carbonyl groups (L) by phosphine (e.g. L_2 = dppe) and is accompanied by formation of a μ-CO link.[315]

3.2 Tri- and Higher Nuclearity Clusters.- Clusters structurally characterised by X-ray diffraction are listed in Table 2. Limitations of space for this article prevent a discussion of all these mixed metal cluster systems.

The new zirconium complex $[Cp_2Zr\{Ru(CO)_2Cp\}_2]$ contains two Zr-Ru bonds.[319] Reactions of $[M(CO)_3(MeCN)_3]$ with Fe_3 or Os_3 clusters form sterically crowded, tetrahedral MFe_3 (M = Cr,Mo,W)[323] or WOs_3[335] species. $[Fe_3(\mu_3\text{-}CCO)(CO)_9]^{2-}$ is a precursor for carbido-clusters $[Fe_3M(\mu_4\text{-}C)(CO)_{13}]^{2-}$ (M = Cr,Mo,W) and also ketenylidene $[Fe_2Co(\mu_3\text{-}CCO)(CO)_9]$.[355] Butterfly $[FeRu_3(\mu_4\text{-}N)(CO)_{12}]^-$ is synthesised by deoxygenation of tetrahedral $[FeRu_3(\mu\text{-}CO)_3(CO)_9(NO)]^-$.[352]

Alkynes coordinate to heteronuclear clusters in both μ_3- and μ_4-bonding modes, as in $[Fe_2Ru(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)(CO)_9]$[350] and $[Cp_2Ni_2Ru_3(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CO)_2(CO)_6]$;[367] tetrahedral $[CpWOs_3(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}O)(CO)_8]$ with alkyne bridging a WOs_2 face and with 4e(μ-O) bridge is produced by oxidation of Os_3-face-alkyne-bridged $[CpWOs_3(\mu_3\text{-}\eta^2\text{-}C_2H_2)H(CO)_{10}]$.[341] $[Co_2Ru(\mu\text{-}\eta^2\text{-}HC_2Bu^t)(\mu\text{-}CO)(CO)_8]$ thermally rearranges at 60°C into alkenylidene derivative $[Co_2Ru(\mu_3\text{-}CCHBu^t)(CO)_9]$;[361] a related rearrangement of an eneyne forms the bridging ligand in $[Cp_2Ni_2Fe\{\mu_4\text{-}C_2HC(=CH_2)Me\}(\mu\text{-}CO)(CO)_5]$, with spiked-triangular framework, although

Table 2. X-Ray determined structures of heterometallic tri- and higher- nuclearity complexes

Zicronium

$[ZrRu_2(CO)_4Cp_4]$[319]

Chromium

$[(Cr_2Mn(\mu_3\text{-}S)_2(\mu\text{-}SBu^t)(CO)_3Cp_2]$[320]

$[Cr_4Mn(\mu_3\text{-}S)_4(\mu\text{-}SBu^t)_2Cp^*]$ (Cp^* = Cp or Cp')[321,322]

$[CrFe_3(\mu\text{-}CO)_2(CO)_{12}]^{2-}$ 323

$[Cr_4Fe(\mu_3\text{-}S)_4(\mu\text{-}SBu^t)_2Cp'_4]$[322]

$[Cr_2Co(\mu_3\text{-}S)_2(\mu\text{-}SBu^t)(CO)_2Cp'_2]$[320]

$[Cr_3Co(\mu_3\text{-}O)(\mu_3\text{-}S)_3Cp_3]$[324]

$[Cr_4Co(\mu_3\text{-}S)_4(\mu\text{-}SBu^t)_2Cp_4]$[324]

$[M_2Pt_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2Cp_2]$ (M = Cr,Mo,W)[325]

$[Cr_2Au(CO)_6Cp_2]^-$ 326

Molybdenum

$[MoW_2\{\mu\text{-}C(tol\text{-}p)\}_2(\mu\text{-}CO)_2(CO)_4Cp_2]$[327]

$[MoFeCo_2(\mu_3\text{-}S)(\mu\text{-}AsMe_2)(CO)_{10}Cp]$[328]

$[MoRh_2(\mu\text{-}CO)_2(CO)_5Cp^*_2]$[329]

$[MoRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3Cp]$[330]

$[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}\sigma,\eta^2\text{-}Ph)\text{-}(PPh_3)_2Cp]$[330]

$[MoPd_2(\mu\text{-}Cl)(NMe_2CH_2C_6H_4)_2(CO)_3Cp]$[331]

$[MoPd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)_3(8\text{-}mq)_3Cp]^+$ 332

(8-mqH = 8-methylquinoline).

Tungsten

$[W_2Re\{\mu_3\text{-}C(tol\text{-}p)\}(\mu\text{-}Br)(\mu\text{-}L)(\mu\text{-}C(tol\text{-}p)\text{-}(CO)_3Cp_2]$ (L = CO or O)[333]

$[WFe_2\{\mu_3\text{-}C(tol\text{-}p)\}\{\mu\text{-}C_2(SiMe_3)_2\}(\mu\text{-}CO)(CO)_6Cp]$[297]

$[WRu_5Au_2(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{15}(PEt_3)_2]$[334]

$[WOs_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{13}]^-$ 335

$[WOs_3(\mu_3\text{-}S)_2(CO)_{12}(PMe_2Ph)_2]$[336]

$[WOs_3(\mu_3\text{-}S)_2(CO)_{12}(PMe_2Ph)]$[336]

$[WOs_3(\mu_3\text{-}S)_2(CO)_{11}(PMe_2Ph)_2]$[336]

$[WOs_3(\mu_3\text{-}S)(CO)_{11}(PMe_2Ph)_2]$[337]

$[WOs_3(\mu_3\text{-}S)(\mu\text{-}H)(CO)_{11}Cp]$[338]

$[WOs_3\{\mu_3\text{-}C(tol\text{-}p)\}_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_9Cp]$[339]

$[WOs_3\{\mu_3\text{-}C(tol\text{-}p)\}_2H(CO)_9Cp]$[339]

$[WOs_3\{\mu_3\text{-}CCH_2(tol\text{-}p)\}(\mu\text{-}O)(CO)_9Cp]$[340]

$[WOs_3(\mu_3\text{-}C_2H_2)(\mu\text{-}H)(\mu\text{-}O)(CO)_8Cp]$[341]

$[W_2Os_3(\mu_4\text{-}S)(\mu_3\text{-}S)(CO)_{14}(PMePh_2)_2]$[336]

$[W_2Ir_2(\mu_3\text{-}C_3Ph_3)(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_4Cp_2]$[342]

$[WPtCu\{\mu_3\text{-}C(tol\text{-}p)\}(CO)_2(PMe_3)_2CpCp^*]$[343]

$[WPtAu\{\mu_3\text{-}C(tol\text{-}p)\}(CO)_2(PMe_3)_3Cp]^+$ 308

$[W_2Au\{\mu\text{-}C(tol\text{-}p)\}_2(CO)_4Cp_2]^+$ 327

Manganese

$[MnFe_2(\mu_3\text{-}S)(\mu\text{-}CO)_2(CO)_6Cp']$[344]

$[MnFe_2(\mu_3\text{-}Te)(\mu\text{-}CO)_2(CO)_6Cp^*]$[345]

$[MnOs_3(\mu\text{-}H)(\mu\text{-}CHCHPh)(\mu\text{-}CO)(CO)_{11}Cp]$[346]

$[Mn_2Au(\mu\text{-}PPh_2)(CO)_8(PMe_2Ph)]$[95]

Rhenium

$[Re_2Pt(CO)_{12}]$[347]

$[Re_2Cu_2(\mu\text{-}I)_2H_2Cp_4]$[348]

Iron

$[FeRu_2(CO)_{11}(PPh_3)]$[349]

$[FeRu_2(\mu\text{-}CO)_2(CO)_8(PPh_3)_2]$[349]

$[Fe_2Ru(\mu\text{-}CO)_2(CO)_9(PR_3)]$ (R = OMe or Ph)[349]

$[Fe_2Ru(\mu_3\text{-}P_3N_3Cl_4)(\mu\text{-}CO)(CO)_9]$[126]

$[Fe_2Ru(\mu_3\text{-}C_2Ph_2)(CO)_9]$[350]

$[FeRu_3(\mu\text{-}H)_2(CO)_{13}]$[351]

$[FeRu_3(\mu_4\text{-}N)(CO)_{12}]^-$ 352

$[FeRu_3(\mu\text{-}CO)_3(CO)_9(NO)]^-$ 352

$[FeRuCoAu(\mu_3\text{-}PMe)(CO)_9(PPh_3)]$[353]

$[FeOs_3(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_{11}]^-$ 354

$[Fe_2Co(\mu_3\text{-}CCO)(CO)_9]^-$ 355

$[FeRh_5(\mu_3\text{-}CO)_4(CO)_{12}]^-$ 356

$[Fe_5Rh(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_{12}]^-$ 356

$[Fe_2Ni_2\{\mu_4\text{-}C_2HC(=CH_2)Me\}(\mu_3\text{-}CO)\text{-}(CO)_5Cp_2]$[357]

$[Fe_3Ni(\mu_3\text{-}H)(\mu\text{-}CO)_4(CO)_8]^-$ 358

$[Fe_2Pt(\mu_3\text{-}PCBu^t)(CO)_6(dppe)]$[359]

$[Fe_3Ag_6\{\mu_3\text{-}(PPh_2)_3CH\}(CO)_{12}]$[360]

Table 2 continued

Ruthenium

$[RuCo_2(\mu_3\text{-}CCHBu^t)(CO)_9]$[361]
$[RuCo_2(\mu_3\text{-}HCCBu^t)(\mu\text{-}CO)(CO)_8]$[361]
$[RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7]$[362]
$[Ru_3CoAu(\mu\text{-}CO)_3(CO)_{10}(PPh_3)]$[363]
$[Ru_3CoAu_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_{10}(PPh_3)_2]$[363]
$[Ru_3CoAu_3(\mu\text{-}CO)_2(CO)_{10}(PPh_3)_3]$[363]
$[Ru_2Rh_2(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_9]$[364]
$[RuRh_4(\mu\text{-}CO)_6(CO)_9]^{2-}$ [365]
$[Ru_3Rh_2(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{12}(PEt_3)]$[366]
$[Ru_3Ni_2(\mu_4\text{-}C_2Ph_2)(\mu\text{-}CO)_2(CO)_6Cp_2]$[367]
$[Ru_6Cu_2(CO)_{18}(\eta\text{-}C_6H_5Me)_2]$[368]
$[Ru_3Ag(\mu\text{-dppm})_2(O_2CCF_3)(CO)_8]$[369]
$[Ru_3Au(\mu\text{-}Cl)(CO)_{10}(PPh_3)]$[370]
$[Ru_3Au(\mu_3\text{-}PPh)(\mu\text{-}H)(CO)_9(PMe_2Ph)]$[366]
$[Ru_4Au(\mu_5\text{-}C)(\mu\text{-}H)(CO)_{12}(PPh_3)]$[371]
$[Ru_4Au(\mu_5\text{-}C)(\mu\text{-}I)(CO)_{12}(PEt_3)]$[371]
$[Ru_3Au_3(\mu_3\text{-}2\sigma,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$[372]
$[Ru_4Au_2(\mu_5\text{-}C)(CO)_{12}(PMe_2Ph)_2]$[371]
$[Ru_5Au(\mu_5\text{-}C)(\mu\text{-}OCMe)(CO)_{14}(PPh_3)]$[373]
$[Ru_5Au(\mu_5\text{-}C)(CO)_{13}(PPh_3)Cp]$[373]
$[Ru_4Au_3(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$[374]
$[Ru_6Au_2(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{14}(PMePh_2)_2]$[334]

Osmium

$[Os_2Rh(CO)_9Cp]$[375]
$[Os_3Ir(\mu\text{-}H)_3(CO)_{11}(PPh_3)]$[376]
$[Os_3NiAu(\mu\text{-}H)_2(CO)_9(PPh_3)Cp]$[377]
$[Os_3Pt(\mu_3\text{-}S)(CO)_{10}(PMe_2Ph)_2]$[378]
$[Os_3Pt(\mu_3\text{-}S)_2(CO)_9L(PPh_3)]$
(L = CO or PPh_3)[379]
$[Os_3Pt(\mu_3\text{-}S)(CO)_9(PMe_2Ph)_3]$[378]
$[Os_3Pt(\mu_3\text{-}S)(CO)_8(PMe_2Ph)_3]$[337,378]
$[Os_3Pt(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)(\mu\text{-}PPh_2C_6H_4)\text{-}(CO)_8]_2$[380]
$[Os_3Pt(\mu_3\text{-}S)(\mu\text{-}H)(\mu\text{-}PMe_2C_6H_4)(CO)_7\text{-}(PMe_2Ph)_2]$[378]
$[Os_6Pt_2(CO)_{17}(cod)_2]$[381]
$[Os_3Cu(\mu\text{-}H)_3(CO)_{10}(PPh_3)]$[376]
$[Os_6Ag(\mu\text{-}H)_2(CO)_{20}]^-$ [382]
$[OsAu_2(CO)_4(PPh_3)_2]$[383]

Cobalt

$[CoRh_6(\mu_6\text{-}N)(\mu_3\text{-}CO)(\mu\text{-}CO)_4(CO)_{10}]^{2-}$ [268]
$[Co_6Ni_2(\mu_6\text{-}C)_2(\mu\text{-}CO)_8(CO)_8]^{2-}$ [384]

Cobalt continued

$[Co_3Ni_9(\mu_8\text{-}C)(\mu\text{-}CO)_{16}(CO)_4]$[385]
$[CoPd_2(\mu\text{-}Cl)(NMe_2CH_2C_6H_4)_2(CO)_4]$[331]
$[CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3]$[386]
$[Co_4Cu_4(CO)_{16}]$[387]

Rhodium

$[Rh_6Ir(\mu_6\text{-}N)(\mu_3\text{-}CO)(\mu\text{-}CO)_4(CO)_{10}]^{2-}$ [268]
$[Rh_9Pt_2(\mu\text{-}CO)_{11}(CO)_{11}]^{3-}$ [388]
$[Rh_2Cu(\mu\text{-}CO)_2Cp^*_3]$[343]

Iridium

$[Ir_2Pt_2(\mu\text{-}CO)_3(CO)_4(PPh_3)_3]$[389]
$[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3Cp^*_3]$[390]

Platinum

$[Pt_2Ag_2(\mu\text{-}Cl)_4(C_6F_5)_4]^{2-}$ [391]
$[Pt_2Au_2(CN\text{-xylyl})_4(PPh_3)_4]^{2+}$ [392]
$[Pt_3Au(\mu\text{-}CO)_3(PCy_3)_4]^+$ [393]

Silver

$[Ag_2Au_2(C_6F_5)_4L_2]_n$
(L = SC_4H_8 or C_6H_5) [394]

an isomeric cluster containing{μ_4-$HC_2C(=CH_2)Me$} is isolable.[357] Ph_2C_2 reacts with $[W_2Ir_2(CO)_{10}Cp_2]$ to give butterfly species $[Cp_2W_2Ir_2(\mu_4-\eta^2-C_2Ph_2)(\mu-CO)_2(CO)_6]$ by cleavage of W-W, and, independently by alkyne and W-Ir bond scissions, planar $[Cp_2W_2Ir_2(\mu_3-CPh)(\mu_3-\eta^3-C_3Ph_3)(\mu-CO)_2(CO)_4]$.[342]

Alkyne either inserts into the alkylidyne bridge of $[Fe_2W(\mu_3-CR)(\mu-CO)(CO)_8Cp]$ (R = p-tol) to form a binuclear derivative or {e.g. alkyne = $C_2(SiMe_3)_2$} displaces two CO groups to form μ_2-alkyne.[297] A range of alkylidyne clusters containing {μ_3-C(tol-p)} ligands and WRe_2,[333] W_2Re,[333] WRh_2,[298] WCo_2,[298] WPtAu,[308] WCu_2,[343] or W_2PtCu_2[343] systems, have been obtained from controlled syntheses originating from $[W(CR)(CO)_2L]$. Butterfly$[CpWOs_3(\mu_3-CR)_2(\mu-H)(\mu-CO)(CO)_9]$ undergoes a degenerate framework rearrangement and also loses CO thermally to give tetrahedral $[CpWOs_3(\mu_3-CR)H(CO)_9]$.[339] Thermal scission of the acyl C-O bond of a ligand (μ_3-$OCCH_2R$) generates $[CpWOs_3(\mu_3-CCH_2R)(\mu-O)(CO)_9Cp]$.[340] Reaction of $[Co_2(\mu-CCH_2)(CO)_2Cp_2]$ with $[MoH(CO)_2LCp]$ forms cluster $[Co_2Mo(\mu_3-CMe)(\mu-CO)(CO)_2Cp]$.[225] Dibridging {$\mu$-C(tol-p)} ligands are present in species $[W_2M(\mu-CR)_2(CO)_nCp_2]^{z+}$ (M = Mo, n = 6, z = 0; M = Au, n = 4, z = 1) which possess bent M-W-M spines.[327]

Bridging μ_3-S ligands are present in various heteronuclear clusters reported in 1984. Chromium species include triangular $[Cr_2M(\mu_3-S)_2(\mu-SBu^t)(CO)_nCp_2]$ (M = Mn,Co),[320] "bow-tie" clusters $[Cr_2M(\mu_3-S)_4(\mu-SBu^t)_2Cp_4]$ (M = Mn,Fe,Co),[321,322,324] antiferromagnetic $[Cp_3Cr_3Co(\mu_3-O)(\mu-S)_3(CO)_3]$,[324] cubane-like $[Cr_2Mo_2(\mu_3-S)_4Cp_2Cp^*_2]$[79] and paramagnetic $[CrMo_2(\mu_3-S)(\mu-S)_3Cp^*_3]$.[79] Further systematic syntheses have been developed for tri-and tetra-metallic clusters, including chiral examples, containing μ_3-S(and related) ligands: a stepwise route to $[FeRuCoAu(\mu_3-E)(CO)_9(PPh_3)]$ (E = S,PMe)[353] and syntheses of trinuclear clusters of type {$MM'M''(\mu_3-S)$} (M,M',M" = variously Co, Fe, Ru,Cr,Mo,W) by single metal exchanges[403] are described. Cleavage of 16 tetranuclear mixed clusters of type $[M_4(\mu_3-E)(\mu-AsMe_2)]$ (M = Co, Fe,Ru,Mo,W; E = S,PR,CR) by CO at elevated pressures is also reported.[328] Several Os_3W[336-338] and Os_3Pt[378-380] clusters containing μ_3-S groups have been studied and characterised by X-ray diffraction (see Table 2); $[Os_3Pt(\mu_4-S)(\mu_3-S)(\mu-H)(\mu-PPh_2C_6H_4)(CO)_8]_2$ contains two trigonal prismatic $PtOs_3S_2$ units linked on an edge by two 6e μ_4-S bridges that exhibit inverted tetrahedral geometries.[380] Clusters $[MnFe_2(\mu_3-E)(CO)_8Cp]$ (E = S,[344] Te[345]) have been structurally characterised.

Heteronuclear palladium or platinum containing complexes of the

following structural types are noted: Linear M-Pt-M (M = Cr,Mo,W;[325] Mn,Re[347]), triangular CoM_2 (M = Pd,[331] Pt[386]) and $MoPd_2$[331] butterfly Ir_2Pt_2,[389] planar M_2Pt_2 (M = Cr,Mo,W)[325] and planar, "raft-like" Ir_3Pt_3 with a central Pt_3 triangle edge-bridged by Ir atoms.[390] In $[MoPd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)_3(8\text{-}mq)_3Cp]^+$ the $\{MoPd_3Cl(C)_3\}$ atoms define a distorted cubane arrangement.[332] Rational syntheses of mixed tetranuclear clusters from $[PdPt(\mu\text{-dppm})_2Cl_2]$ are described.[401]

A wide range of heteronuclear clusters containing group 1B metals (especially Au) are reported - see Table 2. Simple linear anions $[L_nM\text{-}AuML_n]^-$ (M = Cr,Mo,W,Mn,Fe,Co) have been characterised and some studied by ^{197}Au Mössbauer spectroscopy.[326] In $[Ag\{(Os_3(\mu\text{-}H)(CO)_{10})_2]$ the silver atom links Os_3 triangles by two edge bridges.[382] Most species have been prepared by addition of Group 1B metals as metal(I) complexes {e.g. by using [LMX] (M = Cu,Ag,Au); $[Cu(NCR)_4]^+$; $[(AuPR_3)_3O]^+$ or $[PPh_3CuH]_6$} to preformed clusters: single metal additions are reported of Cu, Ag or Au to Mn_2,[95] Fe_3,[404] Ru_3[366] or Ru_4;[404] of Cu to Os_3;[376] of Cu or Ag to Ru_3[369] or MCo_3 (M = Fe,Ru);[405] and of Au to Ru_3,[370] Ru_5,[373] Ru_3Co,[363] Os_3Ni[377] or Pt_3[393]; related additions of Rh or Ir are of interest.[95,366,376] Additions of more than one Group 1B metal also occur, forming: $[Ru_6Cu_2(CO)_{18}(n\text{-}C_6H_5Me)_2]$, with separated Cu atoms,[368] and $[CoRu_3H_n(CO)_{12}(Au\text{-}PPh_3)_{3-n}]$ (n = 0,1);[363] $[Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$[372] and $[Ru_4Au_3(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$,[374] all incorporating direct Au-Au interactions. Au-Au bonds are also present in $[Ru_5MAu_2(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_n(PR_3)_2]$ (M = W; n = 15) but not in related cluster (M = Ru, n = 14).[334] Removal of Ru from $[Ru_5Au_2C(CO)_{14}(PR_3)_2]$ gives butterfly $[Ru_4Au_2(\mu_5\text{-}C)(CO)_{12}(PR_3)_2]$, from which sequential removal of Au-moieties yields $[Ru_4C(H)_2(CO)_{12}]$.[371]

There is a direct Cu-Cu interaction in $[Cp_4Re_2(H)_2\{Cu(\mu\text{-}I)\}_2]$[348] and in $[OsAu_2(CO)_4(PPh_3)_2]$ the Au-Au distance (2.929(1)Å) supports a bond.[383] $[Ag_6Fe_3(CO)_{12}\{(PPh_2)_3CH\}]$ possesses a distorted tricapped octahedral core.[360] Tetranuclear planar or "flattened-butterfly" structures are found for clusters containing cores Pt_2M_2 (M = Ag,[391] Au[392]) and Ag-Au bonded rings (Ag_2Au_2) are linked in polymeric chains of $[AuAg(C_6F_5)_2L_n]$ (L = SC_4H_8, C_6H_6).[394]

Higher nuclearity heteroclusters reported in 1984 incorporate the following core polyhedra: Rh_4Rh, elongated trigonal bipyramid;[365] Ru_3Rh_2, square pyramid;[366] $Fe_5Rh(\mu_6\text{-}C)$,[356] Rh_5Fe[356] and Rh_5Pt,[406] octahedra; Rh_6M (M = Co,Ir), square-face capped trigonal prism;[268] Rh_9Pt_2, three face-condensed octahedra;[388] Os_6Pt_2, bicapped octahedron;[381] $Co_6Ni_2(\mu_6\text{-}C)_2$, two square-face-condensed trigonal prisms;[384] $Co_3Ni_9(\mu_8\text{-}C)$, tetracapped square antiprism.[385] Fluxional trigonal bipyramidal clusters $[Rh_4Pt(CO)_n]^{2-}$ (n = 14,12; with, respectively 76 and 72 valence electrons) are in equilibrium in solution and have

been studied by VT multinuclear n.m.r. spectroscopy.[406]

4 Compounds Containing Bonds between Transition Metals and Elements of Groups IA and II-VB

4.1 Lithium.- Crystal structures are reported for lithium containing clusters $[Pt_2Li_2(C_2Ph)_4(Bu^n)_2(PEt_3)_2]$,[407] $[Cu_3Li_2Ph_6]^-$ [408] and $[Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$.[409]

4.2 Zinc and Mercury.- $[Nb(ZnCp)H_2Cp_2]$[410] and $[Ta(ZnCp)_2HCp_2]$[411] have been structurally characterised and related derivatives with Nb-Zn[410] and Nb-Ta[411] bonds are also described.

A range of mercury-transition metal bonded complexes have been subjected to X-ray structural analysis: complexes with M-Hg-M links include $[Hg\{cis\text{-}RuMe(PMe_3)_4\}_2]$[412] $[Hg\{Pt(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2\}_2]$[413] and $[Hg\{PtGe(CF_3)_3(PPh_3)_2\}_2]$ with a Ge-Pt-Hg-Pt-Ge chain.[414] In $[Hg\{Co(CO)_4\}_3]^-$, mercury links three separate Co atoms,[415] in $[Hg\{Ru_3(NO)(CO)_{10}\}_2]$ mercury links the two Ru_3 triangles by edge-bridging each unit[416] and in $[\{(OC)_4Co\}Hg\{RuCo_3(\mu\text{-}CO)_3(CO)_9\}]$ mercury links the unique Co atom to the Co_3 face of the Co_3Ru tetrahedron.[417] Raft-like cluster $[Os_9Hg_3(CO)_{33}]$ contains a central Hg_3 triangle[418] and a central, metal-metal bonded Hg_4 ring is edge-bridged by Re units in $[Hg_4\{Re(CO)_2Cp\}_4]$.[419]

Bridging μ-HgX units are present in $[Rh_2(\mu\text{-}HgCl)(\mu\text{-}H)\{\mu\text{-}(PhO)_2PNEtP(OPh)_2\}_2(CO)_2]$,[420] in mixed oxidation state $[(PPh_3)(OC)ClRh(\mu\text{-}HgCl)(\mu\text{-}pz)_2Rh(CO)(PPh_3)]$,[421] and in $[Mn_2(\mu\text{-}HgX)(\mu\text{-}PPh_2)(CO)_8]$.[422] Four-coordinate mercury is found in $[Rh_2(\mu\text{-}HgCl_2)(\mu\text{-}CO)(\mu\text{-}dppm)Cp_2]$.[423]

Physical studies of M-Hg (M = Fe,Rh,Pt) complexes, including reports of ^{199}Hg n.m.r., are described.[424]

4.3 Aluminium and Thallium.- X-Ray analysis has established a short unbridged Rh-Al bond in $[CpRh(Al_2Me_4Cl_2)(PMe_3)]$[425] and a species with Ir-Al bonds is described, *viz* $[MeAl(IrMe_3Cp^*)_2]$.[257] However, in $[Cp_2W(\mu\text{-}H)_2AlMe_3]$ there are two hydride bridges and the direct dative bond W→Al (3.110Å) appears to be insignificant.[426]

A central Tl atom in $[Tl\{Ru_6(\mu_6\text{-}C)(CO)_{16}\}_2]^-$ links two Ru_6 octahedra by edge-bridging two Ru-Ru bonds.[427]

4.4 Group IVB.- Of the numerous derivatives incorporating Si or Ge bonds to transition metals, structurally interesting molecules reported in 1984 include: $[HSi\{Fe(CO)LCp\}\{Co_2(\mu\text{-}CO)(CO)_2\}]$ with a ferriosilanediyl unit bridging a Co-Co bond,[428] $[Co_9(\mu_8\text{-}Si)(\mu\text{-}CO)_8(CO)_{13}]^{2-}$[429] with Si atom encapsulated in a capped square-antiprismatic cluster, and complexes $[Ge\{Mn(CO)_2Cp\}_n]$ (n = 2,3) with multiple Ge-Mn bonds.[430]

Full reports of X-ray crystal structure determinations are given for complexes $[Nb(SnPh_3)(CO)_3Cp]^-$,[431] $[Nb(SiX_3)(CO)Cp_2]$ (X = Ph and X = Cl, Cp = Cp'),[432] $[Cr(SnPh_3)_3(CO)_4]^-$,[433] $[Mo(SnCl_3)HCp_2]$,[434] $[Mo_2\{M'(M'Me_3)_3\}_2(NMe_2)_4]$ (M' = Sn,Si)[435] and $[Re_2(CO)_8\{\mu\text{-Sn(X)Re(CO)}_4\text{-PPh}_3\}_2]$ (X = Cl,I).[436]

In $[Os_3Sn(\mu\text{-H})\{CH(SiMe_2)_2\}_2(CO)_{10}]$ there is a closed planar Os_3Sn unit with one H atom bridging an Os-Sn bond.[437] The structures of $[Co\{SnCl(Co\{CO\}_4)_2\}_2(CO)_3]^-$[438] and $[Pb(MoHCp_2)_2(OAc)_2]$[439] are reported.

4.5 Bismuth.- Structures have been established for the closed Fe_3Bi cluster $[Fe_3(\mu_3\text{-Bi})(\mu_3\text{-CO})(CO)_9]^-$[440] and for $[Co(BiPh_2)(CO)_3(PPh_3)]$.[441]

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10

Ligand Substitution Reactions of Metal and Organometal Carbonyls with Group V and VI Donor Ligands

BY D. A. EDWARDS

1 Introduction and Reviews

The coverage follows that of previous Volumes, priority being given to substitution reactions of mononuclear metal carbonyl complexes as these are unlikely to receive attention in other Chapters.

A review of substitution reactions of metal carbonyls which are known to be either reagent-promoted or catalyst-induced is particularly timely.[1] The specific use of trimethylamine N-oxide in decarbonylation and ligand displacement reactions has been reviewed.[2] Other reviews on phosphenium ion ligands,[3] diphosphenes and diarsenes,[4] secondary phosphine chalcogenides,[5] thio- and seleno-carbamates,[6] inorganic cyclic compounds,[7] cyclometallated complexes incorporating heterocyclic donors,[8] and organometallic chelate complexes formed by ligands such as alkenyl pyridines and allyl or aryl phosphines[9] all contain information on ligand substituted metal carbonyls. Reviews have also appeared on reactions of triosmium clusters with organic compounds,[10] cobalt carbonyl radicals,[11] alkyl cobalt tetracarbonyls,[12] palladium and platinum carbonyl phosphine clusters,[13] and platinum carbonyls and their use in homogeneous catalysis.[14] Reviews of electron-transfer reactions of mononuclear organo-transition metal complexes[15] and the stereodynamics of metal complexes of S-, Se-, and Te-containing ligands[16] will have lasting value. The photochemical cleavage of metal-metal bonded carbonyl dimers has also been surveyed.[17]

2 Papers of General Interest

This Section considers ligands that have been reacted with metal carbonyls from more than one group of the Periodic Table. Complexes containing DAB ligands (RN=CHCH=NR; R=alkyl) continue to be explored. Reactions between $Fe_2(CO)_9$ and $[Fe(CO)_3(DAB)]$ lead to $[Fe_2(CO)_6(DAB)]$ products containing six-electron donor DAB.

[For References see page 219

The intermediates $[Fe_2(CO)_7(DAB)]$ which possess four-electron donor DAB together with bridging and semi-bridging carbonyls were detected.[18] Decarbonylation of $[Ru_2(CO)_6(DAB)]$ (R = Pr^i, Bu^t, or Cy) affords $[Ru_2(CO)_5(DAB)]$ in which DAB acts as an eight-electron donor (2σ-N + $2\eta^2$-C=N attachments). These pentacarbonyls react with excess DAB to give $[Ru_2(CO)_5L]$ complexes in which L is a bis[(alkylimino)(alkylamino)ethane] ligand formed by joining two DAB ligands <u>via</u> their imine carbon atoms. Thermal decomposition of $[Ru_2(CO)_5(DAB)]$ gives the known $[Ru_4(CO)_8(DAB)_2]$ and reactions with $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ produce $[FeRu(CO)_6(DAB)]$ (R = Pr^i, Bu^t, or Cy) and $[Ru_3(CO)_8(DAB)]$ (R = Bu^i or neo-pentyl; eight-electron donor DAB), respectively.[19] The complexes $[M(CO)_3Br(DAB)]$ (M = Mn, R = Bu^t, Cy, or <u>p</u>-tol; M = Re, R = Pr^i or Bu^t) and a few 2,3-dimethyl-DAB analogues react with $[HFe(CO)_4]^-$ to give $\{(OC)_3Fe[RN{=}{=}C(R'){=}{=}C(R')NHR]Mn(CO)_3\}$ (R' = H or Me). The σ-N, σ-N' chelate DAB has been converted into an eight-electron donor 3-amino-1-azaallyl monoanion in which the new -NHR group is coordinated to manganese and the azaallyl group η^3-bonded to iron and σ-N-bonded to manganese.[20] The metal→ligand charge transfer photochemistry of $[Fe(CO)_3(DAB)]$ has been studied.[21] Photolysis of $[(OC)_5MM'(CO)_3(DAB)]$ (M, M' = Mn or Re; R = Pr^i) in 2-MeTHF effects both homolytic and heterolytic splitting of the metal-metal bond depending on temperature. However, in a methane matrix $[(OC)_3MM'(CO)_3(DAB)]$ is formed in which DAB acts in an eight-electron donor bridging manner.[22] Various DAB ligands (R = Cy or 4-XC_6H_4; X = H, OH, Me, or OMe) react with $[Rh(CO)_2Cl]_2$ to yield $[Rh(CO)_2(DAB)][Rh(CO)_2Cl_2]$ or $[Rh(CO)_2Cl(DAB)]$.[23] Complexes containing Tcbiim, the dianion of 4,4',5,5'-tetracyano-2,2'-biimidazole, have been isolated. Products characterized include $[L(OC)_3Mo(\mu\text{-Tcbiim})Mo(CO)_3L]^{2-}$ (L = CO or PPh_3), $[M_4(CO)_8(Tcbiim)_2]$, $[Ir_4(CO)_4(PPh_3)_4(Tcbiim)_2]$ and $[M(CO)_2(Tcbiim)]^-$ (M = Rh and Ir). The planar anions of $[NEt_4][Ir(CO)_2(Tcbiim)]$ pack as weak intermolecular dimers in the solid state, (Ir---Ir 3.19Å), forming an overall slipped stack array.[24]

Further studies on complexes containing pyrazolylgallate ligands have been reported. Reaction of $[RhCl(CO)_2]_2$ with $Na[MeGa(pz)_3]$ gives the metal-metal single bonded complex $\{Rh_2(\mu\text{-CO})_3[MeGa(pz)_3]_2\}$ containing tridentate $MeGa(pz)_3$ ligands. The complex $\{Rh(CO)_2[Me_2Ga(pz)_2]\}$ with a bidentate $Me_2Ga(pz)_2$ ligand and the derivatives $\{Rh(CO)_{2-n}(PPh_3)_n[Me_2Ga(pz)_2]\}$ (n = 1 or

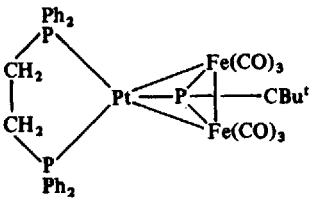
2) have also been isolated. Similar reactions using $[Re(CO)_4Cl]_2$ have led to the chelate complexes $\{Re(CO)_3L[Me_2Ga(pz)_2]\}$ and $\{Re(CO)_3L[Me_2Ga(pz)(OH)]\}$ (L = CO, PPh_3, or pyrazole). Some 3,5-dimethylpyrazolyl analogues have been characterised. The novel anions $\{Me_2Ga(pz)[OCH_2(C_5H_4N)]\}^-$ and $\{Me_2Ga(3,5\text{-}Me_2pz)[OCH_2(C_5H_4N)]\}^-$ containing both N-pyrazolyl and N,O-pyridylmethoxy donor atoms behave as tridentate ligands in fac-$\{M(CO)_3[Me_2Ga(3,5\text{-}Me_2pz)\{OCH_2(C_5H_4N)\}]\}$ (M = Mn and Re), and fac-$\{Mo(CO)_2(\eta^3\text{-}C_3H_4R)[Me_2Ga(pz)\{OCH_2(C_5H_4N)\}]\}$ (R = H or 2-Me).[25]

The new phosphite $P(OCH_2CF_3)_3$, L, undergoes photochemical reaction with $[(\eta^6\text{-mesitylene})Cr(CO)_3]$ and $[CpFe(CO)_2I]$ to give $[(\eta^6\text{-mesitylene})Cr(CO)_2L]$ and $[CpFeIL_2]$, respectively. Thermal reaction with $Ni(CO)_4$ leads to $[Ni(CO)_{4-n}L_n]$ (n = 2 or 3).[26] 3,3',4,4'-Tetramethyl-1,1'-diphosphaferrocene, (DPF), forms the P-unidentate complexes $[M(CO)_5(DPF)]$ (M = Cr, Mo,or W) and $[Mn_2(CO)_9(DPF)]$ and the P,P'-ligand-bridged complexes $\{[M(CO)_5]_2(DPF)\}$ and $\{[Mn_2(CO)_9]_2(DPF)\}$.[27] The secondary phosphine $(Pr^i_2N)_2PH$ displaces THF from $[M(CO)_5(THF)]$ (M = Cr, Mo, or W), $[Fe(CO)_4(THF)]$ or $[(\eta\text{-}C_5H_5)Mn(CO)_2(THF)]$ giving the corresponding phosphine complexes. One of the Pr^i_2N-groups in these complexes can be cleaved with HCl affording $\{M(CO)_5[Pr^i_2NP(H)Cl]\}$ and $\{Fe(CO)_4[Pr^i_2NP(H)Cl]\}$, this halogenophosphine being unknown in the free state. Reactions of $(Pr^i_2N)_2PH$ with $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ are less straightforward giving $\{Mn_2(CO)_8(\mu\text{-}H)[\mu\text{-}P(NPr^i_2)_2]\}$ and $[Co_3(CO)_9(\mu_3\text{-}PNPr^i_2)]$, respectively. The complexes $[M(CO)_5(Cy_2NPH_2)]$ (M = Cr or W) and $[Fe(CO)_4(Cy_2NPH_2)]$ have also been isolated.[28]

The mixed-metal phosphaalkyne complexes $[M_2(\mu\text{-}Bu^tC{\equiv}P)M']$ [M = $Co(CO)_3$, M' = $W(CO)_5$; M = $CpMo(CO)_2$, M' = $W(CO)_5$, $Os_3(CO)_{11}$, or $Ru_3(CO)_{11}$] are of structural type (1). The complex $[Pt(dppe)(Bu^tC{\equiv}P)]$ reacts with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ to give (2) in which the phosphorus of $Bu^tC{\equiv}P$ is coordinated to all three metals.[29]

Complexes containing small-bite bidentate $Me_2PCH_2PMe_2$, dmpm, have been isolated including the chelate complexes $[M(CO)_4(dmpm)]$, (M = Cr, Mo, or W), $[CpMn(CO)(dmpm)]$ and $[Ni(CO)_2(dmpm)]$, ligand-bridged $[M_2(CO)_6(\mu\text{-dmpm})_2]$, (M = Mn or Re), $[Mn_2(CO)_8(\mu\text{-dmpm})]$, $[Fe_2(CO)_{9-2n}(\mu\text{-dmpm})_n]$, (n = 1 or 2), $[Cp_2Fe_2(CO)_2(\mu\text{-dmpm})]$ and $[Ni_2(CO)_2(\mu\text{-dmpm})_3]$ and the unidentate dmpm complexes fac-$[M(CO)_3(dmpm)_3]$, (M = Mo or W). One bridging and two chelating

(1) M = $Co(CO)_3$, M' = $W(CO)_5$;
M = $CpMo(CO)_2$, M' = $W(CO)_5$, $Os_3(CO)_{11}$,
or $Ru_3(CO)_{11}$



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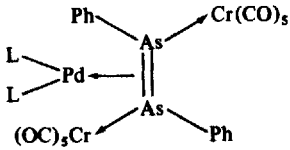
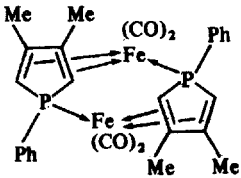


(3) L = $P(OMe)_3$ or $\frac{1}{2}$ bipy



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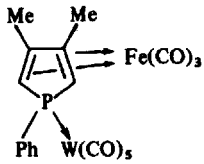


(5)

dmpm ligands are present in fac-$[M_2(CO)_6(dmpm)_3]$ (M = Cr, Mo, or W) whereas mer-$[Cr(CO)_3(dmpm)_2]$ and fac-$[W(CO)_3(dmpm)_2]$ contain chelating and unidentate dmpm ligands.[30] Metal-metal bonded $[Pd_2Cl_2(\mu\text{-dmpm})_2]$, prepared from $[PdCl(CO)]_n$, takes up CO, CS_2, or SO_2 to give the A-frame complexes $[Pd_2Cl_2(\mu\text{-L})(\mu\text{-dmpm})_2]$ which do not possess direct metal-metal interactions.[31]

Complexes containing tripodal phosphines, particularly $(Ph_2P)_3CH$, tpm, have received attention. Reactions of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with tpm lead to $[Fe(CO)_n(tpm)]$ (n = 4 or 3) with unidentate and bidentate tpm, respectively, as well as $[(OC)_4Fe(\mu\text{-tpm})Fe(CO)_3]$. The complexes $[RCCo_3(CO)_n(tpm)]$ (n = 7 or 6) containing bridging bidentate and capping tridentate tpm, respectively, result from stepwise reactions of $[RCCo_3(CO)_9]$ (R = H or Cl) with tpm. Routes to the complexes $[Mo(CO)_5(tpm)]$ (unidentate tpm) and cis-$[M(CO)_4(tpm)]$(bidentate tpm; M = Cr, Mo, or W) have been published. Since many of these complexes contain uncoordinated phosphorus atoms, they can be used in the syntheses of heterobimetallic complexes e.g. $[(OC)_4Fe(\mu\text{-tpm})Mo(CO)_4]$, $\{(OC)ClRh[(\mu\text{-tpm})Mo(CO)_4]_2\}$, $[(OC)_2Rh(\mu\text{-tpm})Fe(CO)_3]^+$, and $\{Cl_2Pt[(\mu\text{-tpm})M(CO)_4]_2\}$ (M = Cr, Mo, or W).[32] The structures of $[M_4(CO)_9(tpm)]$ (M = Co or Ir) and chiral $[Ru_4(CO)_9(\mu\text{-H})_4(tpm)]$ have been determined by X-ray crystallography. It is notable that the iridium complex is the first phosphine-substituted Ir_4 cluster which retains the all-terminal carbonyl ligand array of the parent $Ir_4(CO)_{12}$. The kinetics of the reactions of $[Co_4(CO)_9(tpm)]$ with ^{13}CO, phosphines and phosphites point to the importance of CO dissociative processes, although the reactions with P-donor ligands are complicated by ligand-dependent pathways for carbonyl substitution.[33] Tripodal $(Me_2P)_3CMe$ and the chelates $\{Cr(CO)_4[(Me_2P)_3CMe]\}$ and $\{Cr(CO)_4[CH_2PMe_2C(Me)(PMe_2)_2]\}$ have also been prepared, the latter possessing a CrCPCP ring in an envelope-like conformation.[34] The complexes fac-$[M(CO)_3L]$ (M = Cr, Mo, or W; L = $RSi(OCH_2EMe_2)_3$; R = Me or Ph; E = P or As) also involve novel tripodal ligands.[35]

Both phosphorus atoms of $[Cp_2Mo_2(CO)_4P_2]$, L_2, can act as donors, the complexes $\{[Cr(CO)_5]_2(\mu\text{-}L_2)\}$, $\{[Re(CO)_3(\mu\text{-Br})]_2(\mu\text{-}L_2)\}$ with a Re_2Br_2 ring bridged by the P_2 edge of a P_2Mo_2 cluster, and $\{[ReBr(CO)_3]_2(\mu\text{-}L_2)_2\}$ with a planar RePPRePP ring having been isolated.[36]

Some reactions involving diphosphenes, diarsenes and

phosphaarsenes have been investigated. Products isolated include $\{M(CO)_n[\eta^1-(Bu^t{}_3C_6H_2)_2P_2]\}$ (M = Fe, n = 4; M = Ni, n = 3), both linkage isomers of $\{Fe(CO)_4[\eta^1-Bu^t{}_3C_6H_2As{=}PCH(SiMe_3)_2]\}$, and $\{Cr(CO)_5[\eta^1-(Me_3Si)_2CHAs{=}AsC_6H_2Bu^t{}_3]\}$. Dehydrogenation of $[Cr(CO)_5(AsPhH_2)]$ in toluene at 45° gives $\{[Cr(CO)_5]_2(\mu-PhHAsAsHPh)\}$ which can be exhaustively dehydrogenated in the presence of $P(OMe)_3$ or 2,2'-bipyridyl to produce (3). The complex $\{(dppe)Pd(\eta^2-PhP{=}PPh)[W(CO)_5]_2\}$ also has a structure of type (3). The structure of $\{Ni_5(CO)_6Cl[\{(Me_3Si)_2CH\}_2P_2]_2\}$ has been determined.[37]

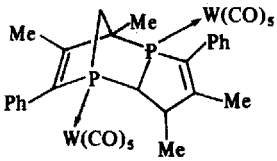
The novel chemistry of complexes containing 1-phenyl-3,4-dimethylphosphole, dmpp, continues to invoke interest. Routes to the diene complex $[Fe(CO)_3(\eta^4-dmpp)]$, the derivatives $[Fe(CO)_3(\eta^4-dmppE)]$ (E = O or S) and the complexes (4) and (5) have been established. Above 150° dmpp is in equilibrium with its 2H-phosphole isomer so when metal carbonyls are reacted with dmpp at elevated temperatures and CO pressures they preferentially form complexes derived from the 2H-phosphole e.g. (6) which arises from [4+2] Diels-Alder dimerization of the 2H-phosphole. At higher temperatures phospholyl- or dihydrophospholyl-bridged complexes e.g. (7) are produced. Starting from (3,4-dimethylphospholyl)lithium, related species, e.g. $Li\{[W(CO)_5]_2(\mu-PC_4H_2Me_2)\}$ have been prepared. This anion can be protonated to the novel complex (8) the P=C bond of which acts as a σ,η^2-four electron donor.

Reactions of metal carbonyls with EtOC(=S)SC(=S)OEt produce bidentate chelating dithioketone radical complexes e.g. cis-$\{M(CO)_4[SC(OEt)SC(OEt)S]\}$ (M = Mn or Re), $\{CpMo(CO)_2[SC(OEt)SC(OEt)S]\}$ and $\{Fe(CO)_3[SC(OEt)SC(OEt)S]\}$.[39]

Irradiation of metal-metal carbonyl dimers, e.g. $[Cp_2Mo_2(CO)_6]$, in the presence of appropriate ligands affords organometallic radicals that are powerful reducing agents. The radicals will induce substitution reactions that otherwise may not occur e.g. irradiation of a mixture of $Ru_3(CO)_{12}$, PMe_2Ph and $[Cp_2Mo_2(CO)_6]$ in THF gives $[Ru_3(CO)_{11}(PMe_2Ph)]$, presumably via the intermediacy of $[Ru_3(CO)_{12}]^-$.[40]

3 Groups IV and V

Reactions of $[\{\eta-MeC_5H_4\}_2Ti(CO)_2]$ with perthiophosphinic acid anhydrides $R_2P_2S_4$ yield $[(\eta-MeC_5H_4)_2Ti(S_4P_2R_2)]$ (R = p-$MeOC_6H_4$ or



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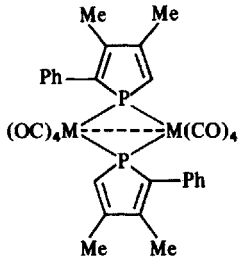
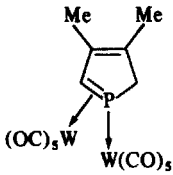


(7) M = Mo or W



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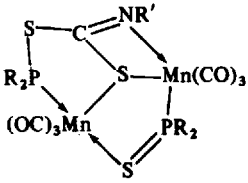

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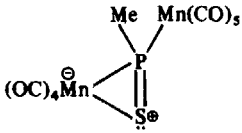


(10)

p-$EtOC_6H_4$) containing a $\overline{TiSP(=S)(R)SP(=S)R}$ ring or $[(\eta\text{-}MeC_5H_4)_2Ti(S_3PR)]$ (R = Bu^t or 3-cyclohexenyl) containing a $\overline{TiSP(=S)(R)S}$ ring.[41]

Carbonyl substitution in $V(CO)_6$ at or below room temperature gives $[V(CO)_5L]$ (L = phosphine or phosphite) by an associative mechanism, the reaction rate being dependent on the basicity and size of the incoming ligand. The substitution of a second carbonyl ligand also proceeds by an associative mechanism but with a much slower reaction rate. Disproportionation of $V(CO)_6$ in the presence of O- and N-donors producing $[VL_6][V(CO)_6]_2$ species, occurs via isocarbonyl-bridged$[(OC)_5VCOV(L)_4OCV(CO)_5]$ intermediates (isolable when L = Et_2O).[42] The kinetics of carbonyl substitution of $[V(CO)_5(NO)]$ by phosphines and phosphites has also been studied. This nitrosyl is thermally unstable as a result of facile carbonyl dissociation.[43] The complexes $[V(CO)_{5-n}(NO)L_n]$ (L = a di- or tri-tertiary phosphine; n = 2 or 3) result from reactions of $[V(H)(CO)_{6-n}L_n]$ with $[CoX(NO)_2]_2$ (X = halide).[44]

Photolytically-induced reactions of $Et_4N[Nb(CO)_6]$ with dppe, $PhP(CH_2CH_2PPh_2)_2$, or $P(CH_2CH_2PPh_2)_3$ lead to octahedral $[Nb(CO)_4(\text{phosphine})]^-$ chelate anions which are converted on silica gel treatment to neutral $[Nb(H)(CO)_4(dppe)]$ or $[Nb(H)(CO)_3(\text{phosphine})]$ complexes.[45]

Reactions of $[CpV(CO)_4]$ with alkanedithiols afford $[CpV(\mu\text{-}SCHRCH_2S)]_2$ dimers (R = H or Me).[46]

4 Group VI

4.1 Carbonyl Complexes of Cr^0, Mo^0, and W^0.- Space limitations allow only a selective coverage of the many reports of mono- and di-ligand-substituted Group VI metal carbonyls. Some are merely listed below, others being accorded some discussion.

Monosubstituted complexes $[M(CO)_5L]$ with L = $Ph_3P{=}CH(CN)$,[47a] radical anions of 2,1,3-benzoxadiazole, 2,1,3-benzothiadiazole, or 2,1,3-benzoselenadiazole,[47b] $[P(CN)_2]^-$,[47c] $Ph_2PCH_2\overline{CHO(CH_2)_3}$,[47d] $R_2EE'R$ or $R_2EER'_2$ (R,R' = Me or CF_3; E = P or As; E' = S, Se, or Te),[47e] η^1-cyclo-$MeC(CH_2P)_3$,[47f] $Ph_2PEC_6H_4R$-p (R = alkyl, aryl, alkoxy, or halo; E = O, S, or NH),[47g] $BiBu^n_3$,[47h] substituted thioureas,[47i] or $S(NR_2)_2$ (R = Me or Bz, R_2 = piperidino or morpholino)[47j] have been characterised.

Among the disubstituted complexes $[M(CO)_4L_2]$ studied have been those with chelate ligands L_2 = 4,4'- or 5,5'-disubstituted-

2,2'-bipyridyls,[48a] chiral diazadienes,[48b] Schiff bases derived from either ethylenediamine or $MeSC(=S)NHNH_2$ and various aldehydes,[48c] $R_2P(CH_2)_2PR_2$ (R = F, Cl, C_6F_5, MeO, Ph, Me, or Cy),[48d] 2,2'-bis(pyridyl)methane,[48e] $(Bu^t{}_2P)_2Te$,[48f] P,S-bonded $Ph_2PC(=S)NR_2$ (R = H, Me, Ph, or Me_3Si),[48g] and dialkyl- or tetra-alkyl dithiooxamides.[48h] Unidentate ligand $[M(CO)_4L_2]$ complexes investigated include those with L = R_2PEMe (R = Me or CF_3; E = S or Se),[48i] $RP(\overline{C{=}CHCH{=}CHO})_2$ (R = Me or Ph),[47d] P-bonded $Ph_2PC(=S)NR_2$,[48g] or dialkylthioamides.[48h]

The kinetics of ligand substitution in cis-$[Mo(CO)_4(py)_2]$ and $[Mo(CO)_5L]$ (L = py, 4-Mepy, or 4-CNpy) by bipy, phen, or RN=CHCH=NR (R = aryl) have been examined. The $[Mo(CO)_4(chelate)]$ products arise via dissociative mechanisms.[49] The synthesis and photochemical properties of $[(OC)_5M(\mu\text{-pyrazine})M'(CO)_5]$ (M,M' = Cr, Mo, or W) have been studied.[50] Oxidation of the arylamine ligands of $[Cr(CO)_5(NH_2R)]$ using lead(IV) acetate produces $[Cr(CO)_5$(N-aryl-1,4-benzoquinone diimine)] complexes.[51] The intermediates $[W(CO)_5L]$ containing unidentate bipy or $Bu^tN{=}CHCH{=}NBu^t$ have been detected in the photoinitiated reactions of $W(CO)_6$ with the potentially chelate ligands.[52] Improved syntheses of cis-$[M(CO)_2(L_2)_2]$ (M = Mo or W; L_2 = bipy or phen) have been reported. Oxidation of these dicarbonyls permits the isolation of several metal(I) and (II) cations e.g. $[Mo_2(CO)_4(bipy)_4]^{2+}$ trans-$[Mo(CO)_2(bipy)_2]^+$, cis-$[Mo(CO)_2(bipy)_2L]^{2+}$ (L = MeCN, Me_2CO, or H_2O), and cis-$[W(CO)_2(bipy)_2]^{x+}$ (x = 1 or 2).[53] Bridging bidentate benzotriazole complexes $[Mo_2(CO)_6(\mu\text{-}\overline{RNN{=}NC}_6H_4)]$ (R = H or Me) have been prepared from $[Mo(CO)_3(NCMe)_3]$.[54] The radical complexes $\{[M(CO)_4]_n(bpym)\}^{\bar{\cdot}}$ and $\{[M(CO)_4(ER_3)]_2(\mu\text{-}L_2)\}^{\bar{\cdot}}$ (M = Cr, Mo, or W; bpym = 2,2'-bipyrimidine; ER_3 = phosphine, phosphite or arsine; L_2 = pyrazine or 4,4'-bipyridyl) have been studied using e.s.r. spectroscopy.[55] Tridentate $\overline{HN(CH_2)_2NH(CH_2)_2NH(CH_2)_2}$, tacn, reacts with $M(CO)_6$ (M = Cr, Mo, or W) to give fac-$[M(CO)_3(tacn)]$. Various oxidation reactions of these tricarbonyls have been reported.[56] The complex $\{Et_4N\}\{Mo(CO)_3[HB(3\text{-}Mepz)_3]\}$ has been isolated and the related species $M'\{M(CO)_3[HB(3,5\text{-}Me_2pz)_3]\}$ (M = Mo or W; M' = K or Et_4N), reacted with $N_3S_3Cl_3$ to give the thionitrosyls $\{M(CO)_2(NS)[HB(3,5\text{-}Me_2pz)_3]\}$ and the sulphido-complexes $\{M_2(CO)_4(\mu\text{-}S)[HB(3,5\text{-}Me_2pz)_3]\}$.[57]

The cis-trans-isomerizations of $[M(CO)_4(^{13}CO)(PR_3)]$ (M = Cr, R = Et; M = W, R = Me, Et, Pr^i, or OMe) and of $[M(CO)_4(PR_3)_2]$ (M = Cr, Mo, or W; R = Bu^n, OMe, or OPh) proceed intramolecularly. Diene displacement by PR_3 in $[M(CO)_4(\eta^4\text{-nbd})]$ (M = Cr, Mo, or W; R = Bu^n, OMe, or OPh) occurs by a stepwise ligand-assisted dechelation of the diene.[58] Photochemical syntheses of $\{M(CO)_5[P(C{\equiv}CPh)_nPh_{3-n}]\}$, cis-$\{M(CO)_4[P(C{\equiv}CPh)_nPh_{3-n}]_2\}$ and fac-$\{Cr(CO)_3[P(C{\equiv}CPh)Ph_2]\}$ (M = Cr or W; n = 1, 2, or 3) have been reported.[59] Phosphinous acid, $H_2P(OH)$, unknown in the free state, has been stabilized as its $W(CO)_5$ complex which thermally decomposes to $\{[W(CO)_5]_2(\mu\text{-}H_2POPH_2)\}$. The related complexes $[W(CO)_5(XPH_2)]$ (X = Et_2N, OH, OMe, or Cl) have also been characterised.[60] Cathodic reduction of $[Cr(CO)_5(PX_3)]$ (X = Cl or Br) gives $\{[Cr(CO)_5]_2(\mu\text{-}P_2X_4)\}$; reductive dehalogenation of $[Cr(CO)_5(PRX_2)]$ (R = Me or Ph) in the presence of Me_2S_2 gives $\{Cr(CO)_5[PR(SMe)_2]\}$.[61] The phosphinidene complex $\{[Cr(CO)_5]_2(\mu\text{-}PBu^t)\}$ arises from the reaction of $[Cr(CO)_5(PBu^tCl_2)]$ with $Na_2[Cr_2(CO)_{10}]$. The arsinidene analogue reacts with $[(Ph_3P)_2N]Cl$ to produce the chelate complex $\{Cr(CO)_4[Bu^tAs(Cl)As(Bu^t)As(Bu^t)AsCl(Bu^t)]\}$ containing a $CrAs_4$ ring.[62] Routes to fac-$\{Mo(CO)_3[MeN(PF_2)_2]_2\}$ (one unidentate and one bidentate phosphine), $\{(OC)_2Mo(\mu\text{-}CO)[\mu\text{-}MeN(PF_2)_2]_3Mo[MeN(PF_2)_2]\}$ and $\{(OC)_2Mo[\mu\text{-}MeN(PF_2)_2]_2(\mu\text{-}PF_2)(\mu\text{-}Cl)Mo(PF_2NHMe)\}$ have been established.[63] The first phosphorus analogue of 2,2'-bipyridyl, 4,5-dimethyl-2-(2-pyridyl)phosphorin, acts as a P-unidentate ligand in $[M(CO)_5L]$ (M = Cr or W), but facile elimination of CO gives the P,N-chelates $[M(CO)_4L]$. Direct reaction of $Mo(CO)_6$ with the phosphorin at 155° affords $[Mo(CO)_4L]$.[64] Syntheses of the bi- and trimetallic species $[(OC)_5Mo(\mu\text{-}Ph_2POPPh_2)M(CO)_n]$ (M = Cr, n = 5; M = Fe, n = 4) $\{(OC)_5Mo[\mu\text{-}(EtO)_2POP(Ph)OP(OEt)_2]Mo(CO)_5\}$ and $\{[(OC)_5Mo]_3[\mu\text{-}(R_2PO)_3P]\}$ (R = Ph or OEt) have been devised.[65] Many other heterobimetallic complexes have been characterised e.g. $[(OC)_4(Me_3P)\overline{Cr(\mu\text{-}PBu^t_2)}MX(PMe_3)]$ (M = Ni, X = Cl; M = Rh, X = CO), $\{[Mo(CO)_4]_2(\mu\text{-}H)[\mu\text{-}Ph_2P(CH_2)_nPPh_2]\}^-$ (n = 1-4), $\{[Mo(CO)_4]_2(\mu\text{-}L_2)(\mu\text{-dppe})\}$ (L_2 = dppm, dppe, or dpae), $[(OC)_3M(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CR)Pt(C{\equiv}CR)]$ (M = Mo or W; R = Me, Ph, or p-tol), $[(OC)_3M(\mu\text{-dppm})_2M'(CO)Cl]$ (M = Cr, Mo, or W; M' = Rh or Ir) and $[(OC)_3M(\mu\text{-dppm})_2M'(CO)_2]^+$ (M = Cr, Mo, or W; M' = Rh or Ir).[66]

Deprotonation of $[M(CO)_4(dppm)]$ (M = Cr, Mo, or W) gives the

carbanions $[M(CO)_4(Ph_2PCHPPh_2)]^-$ which may be acylated to the chelates $\{M(CO)_4[Ph_2PCH(COR)PPh_2]\}$ (R = Ph or p-tol). These acyl derivatives can be further converted to $\{M(CO)_4[Ph_2PC(=COR)PPh_2]\}^-$ enolate anions or to $\{M(CO)_4[Ph_2PC(=C(R)OCOR)PPh_2]\}$ complexes. Irradiation of $\{W(CO)_4[Ph_2PCH(COPh)PPh_2]\}$ gives, initially, the chelate complex $\{W(CO)_4[Ph_2POC(Ph)=CHPPh_2]\}$ which is, in turn, converted into $[W(CO)_4(Ph_2POH)(Ph_2PCH_2COPh)]$ in the presence of light and traces of water.[67]

The redox couples $[M(CO)_3(PR_3)_3]^{x+}$, [M = Cr or Mo; x = 0 or 1; PR_3 = $P(OMe)_3$, $P(OPh)_3$, $P(OMe)_2Ph$, or PMe_2Ph] have been examined by electrochemical and spectroscopic techniques. Both fac- and mer-isomers exist in each oxidation state. The chemical and electrochemical oxidation of trans-$[Cr(CO)_4(PPh_3)_2]$ to the trans-monocation has also been studied.[68]

The first ^{95}Mo n.m.r. chemical shift values for Mo(0)-sulphur donor complexes $\{Mo(CO)_5[SC(S)NMe_2]\}^-$ and $[Mo(CO)_4L_2]^-$ (L_2 = dithiocarbamato, xanthato, or phosphorodithioato) have been reported.[69]

Dynamic n.m.r. studies of $\{[M(CO)_5]_n[MeS(CH_2S)_xMe]\}$ (M = Cr or W; n = 1, x = 2; n = 2, x = 2 or 3) have provided accurate data for pyramidal sulphur inversions. At higher temperatures, 1,3-intramolecular shifts of the $M(CO)_5$ groups between ligand sulphur atoms have been detected.[70] Other sulphur donor ligand complexes reported include fac-$[Mo(CO)_3(ttct)]$, $\{[W(CO)_4]_2(\mu\text{-ttct})\}$, fac-$[Mo(CO)_3(ttnt)]$, cis-$[W(CO)_4(ttnt)]$ (ttct = 1,4,8,11-tetrathiacyclotetradecane; ttnt = 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene)[71] and anionic $[M(CO)_4(SC_6H_4SMe)]^-$, $[M(CO)_4(S_2C_6H_4)]^{2-}$, $\{[M(CO)_3(\mu\text{-}S_2C_6H_4)]_2\}^{2-}$ and $\{[Cr(CO)_4]_2(\mu\text{-dttd})\}^{2-}$ (M = Cr or W; dttd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane).[72] U.v. irradiation of $[M(CO)_5(NCR)]$ (M = Cr or W; R = Bu^t, Ph, Cy, or Bz) in the presence of 1,3-dithiane or $PhSCH_2SPh$ produces cis-$[M(CO)_4(CNR)(\text{thioether})]$ complexes.[73] Oxidative decarbonylation reactions of $M(CO)_6$ with PhSSPh and $PhC(O)CH_2C(S)Ph$ afford $[M(\mu\text{-SPh})_3]_n$ (M = Mo or W) and the chelate $\{Mo[SC(Ph)CHC(Ph)O]_3\}$, respectively.[74]

4.2 Carbonyl Complexes of Mo^{II} and W^{II}.- Reactions of $MoCl_2(CO)_4$ and $[MCl_2(CO)_3(PPh_3)_2]$ (M = Mo or W) with $Ph_2PC(S)NHR$ (R = Ph or Me) yield two isomers of $\{MCl_2(CO)_2[Ph_2PC(S)NHR]_2\}$. One is a 1:1 electrolyte with P,S-chelate ligands, the other neutral with one

chelate and one P-unidentate ligand. Deprotonation of these isomers produces $\{M(CO)_2[Ph_2PC(S)NR]_2\}$ the complex with M = Mo and R = Me being a dimer with chelating and bridging ligands. The related $\{M(CO)_2L[Me_2NC(S)NPh]_2\}$ (L = CO or PPh_3) and $\{M(CO)_2(PPh_3)[Ph_2P(S)C(S)NPh]_2\}$ have also been isolated, the latter showing dynamic behaviour with respect to ligand coordination. Routes to $[M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2]$ and $[Mo(CO)_3(\eta^2\text{-}SPPh_2)_2]$ were also established.[75] Reaction of $MoBr_2(CO)_4$ with $Ph_2P(S)SH$ in methanol yields $[Mo(CO)_3(S_2PPh_2)_2]$. This product shows no tendency to form a dicarbonyl but will react with ligands to form $[Mo(CO)_2L(S_2PPh_2)_2]$ (L = Ph_3P, Ph_2EtP, or py).[76] The complexes $[M(CO)_n(PMe_3)_{3-n}(S_2CNR_2)_2]$ (M = Mo or W; n = 1 or 2; R = alkyl) have been prepared from $[MCl_2(CO)_2(PMe_3)_3]$.[77]

4.3 Cyclopentadienyl and Other Complexes.- Chiral complexes $\{CpMo(CO)_2[N(R')=C(R)C(O)O]\}$, containing N,O-chelating 2-imino-carboxylate groups, have been synthesised from $[CpMo(CO)_3Cl]$, $RC(O)COO^-Na^+$ and $R'NH_2$ [R = H, Me, Et, or Pr^i; R' = H, OH, NH_2, NHPh, Me, Ph, CH_2CO_2Et, or (S)-CHMePh].[78] Irradiation of $[(\eta\text{-}MeC_5H_4)Mo(CO)_3]_2$ in the presence of $P(OMe)_3$ effects both substitution and disproportionation. The products are $\{(\eta\text{-}MeC_5H_4)Mo(CO)_2[P(OMe)_3]\}$, $\{(\eta\text{-}MeC_5H_4)Mo(CO)_2[P(OMe)_3]_2\}^+$ and $[(\eta\text{-}MeC_5H_4)Mo(CO)_3]^-$. The importance of 19-electron intermediates in such disproportionations is supported by the observation that $[(\eta\text{-}MeC_5H_4)Mo(CO)_2(triphos)]^+$ containing bidentate triphos is a product of the irradiation of $[(\eta\text{-}MeC_5H_4)Mo(CO)_3]_2$ with triphos.[79] The complexes $\{CpMo(CO)_2Br[Ph_2PO(CH_2)_nCl]\}$ (n = 2 or 3), obtained from $[CpMo(CO)_3Br]$ and $Ph_2PO(CH_2)_nCl$, undergo reductive cycloelimination giving the metallacycles $\{CpMo(CO)_2[Ph_2PO(CH_2)_n]\}$. The metallacycloalkanes $\{CpM(CO)_2[Ph_2P(CH_2)_n]\}$ (M = Mo or W; n = 1-3) have been prepared by analogous reaction sequences.[80] Reaction of $[CpMo(CO)_2]_2$ with the bicyclic aminophosphorane $PhP(H)(OCH_2CH_2)_2N$ results in the formation of $[Cp_2Mo_2(CO)_3L]$, which retains the metal-metal triple bond, and $[Cp_2Mo_2(CO)_nL]$ (n = 4 or 5). In these complexes L is the open tautomeric form of the ligand i.e. $PhP(OCH_2CH_2)_2NH$.[81] The metallophosphenium ion complexes $\{CpMo(CO)_2[POCH_2CH_2NR]\}$ (R = Me, Et, Bu^t, or Ph) result from reactions of $Na[CpMo(CO)_3]$ with $RNCH_2CH_2OPX$ (X = F or Cl).[82]

The complexes cis- and trans-$[CpM(CO)_2H(XPOCH_2CH_2O)]$, which result from the reactions of $[CpM(CO)_3H]$ with $XPOCH_2CH_2O$ (M = Mo or W; X = Cl or NMe_2), undergo elimination of HX to afford the novel species $[CpM(CO)_2(POCH_2CH_2O)]$ containing M-P double bonds.[83] The phosphavinylidene complex $\{CpMo(CO)_2[P{=}C(SiMe_3)_2]\}$ has a two-coordinate phosphorus atom engaged in multiple bonding to both carbon and molybdenum.[84]

The complexes $[CpW(CO)_3(AsR_2)]$ (AsR_2 = $AsPr^i_2$ or $AsMeBu^t$) undergo intermolecular carbonyl substitution to yield $[CpW(CO)_2(\mu\text{-}AsR_2)]_2$ dimers. However, the $AsBu^t_2$ analogue gives monomeric $[CpW(CO)_2(=AsBu^t_2)]$ on decarbonylation as a consequence of the presence of bulky t-butyl groups.[85] The action of heat or u.v. irradiation on $\{CpW(CO)_3[SC(S)NMe_2]\}$ induces formation of the chelate $[CpW(CO)_2(S_2CNMe_2)]$.[86] The reaction of $[CpM(CO)_3Cl]$ with $Ph_2P(S)C(S)NHR$ (M = Mo or W; R = Me or Ph) in the presence of a base leads to three different products depending on reaction conditions. They are the S,S-chelate and S(C), N-bonded isomers of $\{CpM(CO)_2[Ph_2P(S)C(S)NR]\}$ and $[CpM(CO)_2(\eta^2\text{-}SPPh_2)]$.[75]

5 Group VII

5.1 Carbonyl, Carbonyl Halide and Related Complexes.- The photochemical disproportionation of $Mn_2(CO)_{10}$ in the presence of the nitrogen donors py, NEt_3 and dien occurs by a radical chain pathway, the key step being the formation of 19-electron intermediates $[Mn(CO)_3L_3]$.[87] The reactions of $Mn_2(CO)_{10}$ with diazoles may result in the substitution products $[Mn_2(CO)_9L]$, or the disproportionation products $[MnL_4]^{2+}[Mn(CO)_5]_2^-$ (L = pyrazole or imidazole). Anion-bridged $[Et_4N][Mn_2(CO)_6(\mu\text{-pyrazolato})_3]$ was also isolated.[88]

A number of metallacyclic compounds containing phosphorus have been studied e.g. $[Mn(CO)_4(\mu\text{-}PH_2)]_n$ (n = 2 and 3), $\{M(CO)_4[PO(OEt)_2]\}_2$ (M = Mn or Re) and $\{Mn(CO)_4[Ph_2P(CH_2)_2C(O)O]\}$ with MPOMPO and MnPCCCO rings, respectively, $\{Mn(CO)_4[(Ph_2PO)_2H]\}$ containing a MnPO-H-OP hydrogen-bonded ring, and thermally labile $[Mn(CO)_4(Ph_2POCHRCHR')]$ (R,R' = H or Me). Decomposition of the latter type gives $[Mn(CO)_4(OPPh_2)]_2$ and an alkene. Action of CO or HBr on the metallacycle with R=R'=H gives $[Mn(CO)_5(PPh_2O)]$ and $[Mn(CO)_4Br(PPh_2OH)]$, respectively.[89]

When $[Mn(CO)_4(SPR_2)]_2$ (R = Me or Ph) react with R'NCS (R' = Me, Et, or Ph) novel tricyclic complexes (9) are formed.[90]

Dehalogenation of $MeP(=S)Cl_2$ by magnesium gives the thioxophosphane MeP=S which can be trapped by reaction with $Mn_2(CO)_{10}$ giving complex (10).[91]

On treatment of the μ-alkenyl complexes $\{Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}C(R)=CR'R'']\}$ (R, R', R" = combinations of H and alkyl) with ligands olefin is eliminated producing 1,2-dieq-$[Re_2(CO)_8L_2]$ [L = py, $P(OMe)_3$, or $P(OPh)_3$], 1,2-ax,eq-$[Re_2(CO)_8L_2]$ (L = PPh_3 or PBu^n_3) or 1,2-dieq-$[Re_2(CO)_8(\mu\text{-}L_2)]$ (L_2 = dmpm, dppm, dmpe, or dppe). However, the related μ-alkynyl $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)]$ undergoes simple carbonyl substitution on reaction with py, PPh_3, or PBu^i_3 giving $[Re_2(CO)_{8-n}(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)L_n]$ (n=1 or 2).[92]

The first low-valent teflate complex $[Mn(CO)_5(OTeF_5)]$ results from the reaction of $[MeMn(CO)_5]$ with $HOTeF_5$ in CH_2Cl_2.[93]

The complexes fac-$[M(CO)_3(NCR)_3]ClO_4$ (M = Mn or Re; R = Et, Pr, or Bz) have been prepared, subsequent RCN displacement leading to other fac-$[M(CO)_3L_3]^+$ cations (L = NH_3; L_3 = dien or triphos).[94] Many manganese carbonyl cations containing both nitrogen chelates and isocyanides have been characterised including the first mer-tricarbonyl examples mer-$[Mn(CO)_3(CNBu^t)L_2]^+$ (L_2 = bipy or phen).[95] The complexes trans-$\{Mn(CO)_4[P(OR)_3]_2\}\{PF_6\}$ (R = Me, Et, Pr^i, Ph, or p-tol), mer-$\{Mn(CO)_3[P(OMe)_3]_3\}\{PF_6\}$ and cis-$\{Mn(CO)_2[P(OMe)_3]_4\}\{PF_6\}$ have been synthesised from the corresponding neutral hydrido-complexes.[96] New methods for the preparation of the bipy complexes cis, trans-$[Re(CO)_2(PPh_3)_2(bipy)][PF_6]$, cis, trans-$[Re(CO)_2(PMe_2Ph)_2(bipy)][PF_6]$ and cis-$[Re(CO)_2(bipy)_2][PF_6]$ have been reported, and their electronic spectra and electrochemistry studied.[97] The complexes $[Re(CO)_5(OH_2)]X$ (X = BF_4 or AsF_6) and $[Re(CO)_3L_2(OH_2)][BF_4]$ [L_2 = bipy, dppe or 2 $P(OPh)_3$] have been prepared by reaction of $Re(CO)_5Br$ or $[Re(CO)_3BrL_2]$ with $AgAsF_6$ or $AgBF_4$ in undried CH_2Cl_2. However, AsF_6^- and BF_4^- are coordinated in the labile complexes $[Re(CO)_3(bipy)(FAsF_5)]$ and $[Re(CO)_3(tmen)(FBF_3)]$. The fluoro-complexes $[Re(CO)_3L_2F]$ (L_2 = bipy, dppe, tmen, or 2 $SbPh_3$) have also been characterised.[98]

The five-coordinate, 16-electron, chelate complex $\{Mn(CO)_3[RNP(Br)(NR_2)NR]\}$ (R = Me_3Si) results from the reaction of $Mn(CO)_5Br$ with the double ylid $R_2NP(=NR)_2$. Addition of CO affords the octahedral, 18-electron, tetracarbonyl.[99] The NN'-diaryl-amidines R'NHC(R)NR' (R = H, Me, or Ph; R' = Ph or p-tol) react

with $Re(CO)_5X$ or $[Re_2(CO)_8X_2]$ (X = Cl or Br) to give $\{Re(CO)_4X[R'NC(R)NHR']\}$ containing unidentate amidine ligands. Use of the corresponding lithioamidines (R = Me or Ph) leads to the carbamoyl species $\{Re(CO)_4[CON(R')C(R)NR']\}$ which may be converted thermally to $\{Re(CO)_4[R'NC(R)NR']\}$ containing bidentate amidinate groups and to ortho-metallated $\{Re(CO)_4[R'NC(R)NHC_6H_3R'']\}$ (R" = H or Me).[100] The diastereomeric diazaphosphole ligands cis- and trans-$PhPC(H)(Ph)C(Ph)=NNPh$ (L_c and L_t, respectively) react with $M(CO)_5Br$ (M = Mn or Re) to give cis-$[M(CO)_4Br(L_c)]$, mer-$[M(CO)_3Br(L_c)_2]$, fac-$[Re(CO)_3Br(L_c)_2]$, cis-$[M(CO)_4Br(L_t)]$ and mer-$[M(CO)_3Br(L_t)_2]$. The product variation has been related to the size of the metal and the greater steric demands of L_t.[101] Reactions of $Mn(CO)_5Br$ with $(EtO)_2POP(OEt)_2$, L_2, give either $[Mn_2(CO)_{10-2n}Br_2(\mu-L_2)_n]$ or $[Mn_2(CO)_{8-2n}(\mu-Br)_2(\mu-L_2)_n]$ (n = 1 or 2). Reduction of the latter complexes followed by acidification affords $[Mn_2(CO)_{8-2n}(\mu-Br)(\mu-H)(\mu-L_2)_n]$ (n = 1 or 2).[102] Several other complexes of the type $[M_2(CO)_6(\mu-X)_2(\mu-L_2)]$ have been characterised e.g. $[M_2(CO)_6(\mu-X)_2(\mu-E_2Ph_4)]$ (M = Mn or Re, X = Br or I, E = P, As or Sb) and $[Re_2(CO)_6(\mu-Br)_2(\mu-L_2)]$ [L_2 = P,N-bonded $Me_3SiN(Bu^t)P=NBu^t$ or P,P-bonded $MePN(R)P(Me)NR$, R = Me or Bu^t].[103]

The electrochemical properties of fac- and mer-$[Re(CO)_3Cl(PMe_2Ph)_2]$ and $[Re(CO)_2Cl(PMe_2Ph)_3]$ in MeCN have been investigated, including the synthesis of the oxidation products $[Re(CO)Cl(NCMe)_2(PMe_2Ph)_3][ClO_4]_2$ and $[Re(CO)_2Cl_3(PMe_2Ph)_2]$.[104] Bromine oxidation of a range of $[Re(CO)_3Br(PR_3)_2]$ complexes leads to $[Re(CO)_2Br_3(PR_3)_2]$ only for the least sterically demanding phosphines.[105]

Complexes fac-$[Mn(CO)_3XL_2]$ containing P,S-chelating thioformamides or isomeric thioformimido esters (X = Cl, Br, or I; L_2 = $Ph_2PC(S)N(R)Me$ or $Ph_2PC(NR)SMe$; R = H, Me, or Ph) have been prepared from $Mn(CO)_5X$.[106] The dynamic n.m.r. spectra of the four diastereoisomers of each fac-$[Re(CO)_3X(MeSCH_2SCH_2SMe)]$ complex (X = Cl, Br, or I) have been recorded and energy data associated with the pyramidal inversion of sulphur atoms and rotation of the chelate ligands obtained. Similar data have been acquired for fac-$[Re(CO)_3XL_2]$, [X = Cl, Br, or I; L_2 = $MeS(CH_2)_2SeMe$, o-$MeS(C_6H_4)SeMe$, or o-$C_6H_4(SMe)_2$].[107]

5.2 Cyclopentadienyl Complexes.- The light- and air-sensitive $\{[\eta\text{-}C_5H_4Me)Mn(CO)_2]_2(\mu\text{-}L_2)\}$ [L_2 = pyrazine, 4,4'-bipy, 1,2-bis(4-pyridyl)ethane, or 1,2-bis(4-pyridyl)ethene] and $\{[(\eta\text{-}C_5R_5)Mn(CO)_2]_2(\mu\text{-pyrazine})\}$ (R = H or Me) have been prepared from $[(\eta\text{-}C_5R_5)Mn(CO)_2(THF)]$. The radical anions of the pyrazine complexes are reasonably stable.[108] Ligand substitution kinetics of $[(\eta\text{-}C_5H_4Me)Mn(CO)_2L]^+$ (L = 3- and 4-substituted pyridines) have been measured for a variety of phosphine nucleophiles of differing steric and electronic properties. The cations were generated by electrocatalysis of the neutral $[(\eta\text{-}C_5H_4Me)Mn(CO)_2L]$ precursors. The results indicate an associative mechanism.[109] The first compound possessing a manganese-manganese triple bond, $[(\eta\text{-}C_5Me_5)_2Mn_2(\mu\text{-}CO)_3]$, reacts with $P(OEt)_3$ to give a mixture of $\{(\eta\text{-}C_5Me_5)Mn(CO)_2[P(OEt)_3]\}$ and $\{(\eta\text{-}C_5Me_5)Mn(CO)[P(OEt)_3]_2\}$.[110] Whereas $[CpMn(CO)_3]$ is rather inert to thermal substitution reactions, $[(\eta^5\text{-indenyl})Mn(CO)_3]$ and $[(\eta^5\text{-fluorenyl})Mn(CO)_3]$ react with a variety of phosphines and phosphites to give mono-substituted products. The η^5-fluorenyl complex also undergoes a second substitution stage with PBu^n_3 and PCy_3 via a $[(\eta^1\text{-}C_{13}H_9)(CO)_3L_2]$ intermediate. All reactions take place by second-order processes.[111] Photolysis of $\{[\eta^5\text{-}C_5(CO_2Me)_5]Mn(CO)_3\}$ in the presence of PBu^n_3, PPh_3, or $P(OEt)_3$ affords monosubstituted products.[112] The first arsinidene complex of manganese $\{[(\eta\text{-}C_5Me_5)Mn(CO)_2]_2(\mu\text{-AsH})\}$, isolated from the reaction of $[(\eta\text{-}C_5Me_5)Mn(CO)_2(THF)]$ with AsH_3, can be dehydrogenated to the diarsene complex $\{[(\eta\text{-}C_5Me_5)Mn(CO)_2]_2As_2\}$ which has a 'butterfly' skeleton with two As_2Mn triangles and not the expected tetrahedrane array.[113] Thiols react with $[(\eta\text{-}C_5R_5)Mn(CO)_2(THF)]$ (R = H or Me) to give solutions which probably contain $[(\eta\text{-}C_5R_5)Mn(CO)_2(R'SH)]$ species. In the presence of oxygen, paramagnetic $[(\eta\text{-}C_5R_5)Mn(CO)_2(SR')]$ complexes containing stabilized R'S· radicals can be isolated (R' = Bu^t or 2-adamantyl).[114]

The η^5-pentadienyl $[(\eta^5\text{-}C_5H_7)Mn(CO)_3]$ reacts at room temperature with PMe_3, PMe_2Ph, or PBu^n_3 to give the η^3-allyls $[(\eta^3\text{-}C_5H_7)Mn(CO)_3L]$. However, in refluxing C_6H_{12} a further reaction step leads to $[(\eta^5\text{-}C_5H_7)Mn(CO)_2L]$ complexes (L = phosphines, phosphites, or $AsPh_3$).[115]

6 Group VIII: Iron, Ruthenium, and Osmium

6.1 Iron Carbonyl Complexes.- Stepwise degradation of $S(NSiMe_3)_2$ occurs on reaction with $Fe_3(CO)_{12}$ giving $[Fe_2(CO)_6(Me_3SiNS)]$ then $[Fe_2(CO)_6(HNS)]$ in which sulphur imide, which is unknown in the free state, is stabilized as a bis- η^2-bridging ligand.[116] The amino(methylene)phosphine $(Me_3Si)_2C{=}PN(SiMe_3)_2$ reacts with $Fe_2(CO)_9$ giving a trigonal bipyramidal $[Fe(CO)_4L]$ complex, the equatorial ligand L having a severely twisted P=C bond.[117] Photochemical conditions are necessary for the preparation of the bridging diphosphine complexes $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}R_2PXPR_2)]$ and $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}R_2PXPR_2)_2]$ (X = CH_2, R = Ph, Me, OMe, or OPr^i; X = NEt, R = OPh, or OMe; X = NMe, R = OPr^i or OEt) from $Fe_2(CO)_9$. Thermal conditions result in the formation of $[Fe(CO)_3(R_2PXPR_2)]$ chelate complexes.[118] The clusters $[Fe_3(CO)_9(\mu\text{-}H)(RR'PCH_2PR)]$ and $[Fe_3(CO)_9(\mu_3\text{-}PR)(\mu_2\text{-}PMeR)H]$ arise from oxidative addition and cleavage of the diphosphines $(RR'P)_2CH_2$ (R = Me, Pr^i, Bu^t, or Bz; R' = H or R) on reaction with $Fe_2(CO)_9$.[119] The complex $\{[Fe(CO)_4]_2[HPN(Bu^t)P(H)NBu^t]\}$, containing a P,P-bonded diazadiphosphetidine ring, results from the reaction of $[Fe(CO)_4]^{2-}$ with $ClPN(Bu^t)P(Cl)NBu^t$.[120]

Reactions of $[(OC)_2(ON)Fe(\mu\text{-}AsMe_2)Fe(CO)_4]$ with P-, As-, or Sb-donor ligands occurs by heterolytic cleavage of the metal-metal bond and addition of ligand at the $Fe(CO)_2(NO)$ moiety.[121] The complexes $[Fe(CO)_4\{Sb(EMe_3)_3\}]$ (E = Si or Ge) and $[Fe(CO)_4(BiR_3)]$ (R = Et, Pr^n, or Bu^n) have been prepared.[47h,122]

Photolysis of $Fe(CO)_5$ in the presence of Ph_2S_2 gives $[(OC)_3Fe(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3Fe(CO)_3]$.[74] Reaction of $Fe_3(CO)_{12}$ with Me_2S_2 in refluxing benzene gives the known syn- and anti-isomers of $[Fe_2(CO)_6(\mu\text{-}SMe)_2]$ together with a low yield of $\{[Fe(CO)_3]_4(\mu\text{-}SMe)_2(\mu_4\text{-}S)\}$.[123]

Dithioformate esters and O-alkyl thioesters react with $Fe_2(CO)_9$ to give complexes of type (11) but use of HC(S)OEt affords (12).[124] The complexes fac-$[Fe(CO)_3(S_2CR)I]$ and cis-$[Fe(CO)_2(S_2CR)_2]$ (R = OEt, OCy, NEt_2, or NHPh) can be prepared from $Fe(CO)_4I_2$.[125]

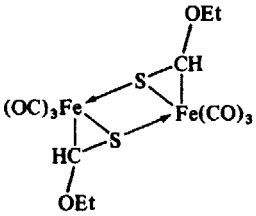
6.2 Ruthenium and Osmium Carbonyl Complexes.- The rates of substitution of the equatorial CO group by $P(OMe)_3$ have been determined for 24 complexes of the type mer-$[Ru(CO)_3L(SiCl_3)_2]$

(L = P-donor). The results are consistent with a dissociative mechanism.[126] Substitution occurs preferentially at ruthenium centres when $[FeRu_2(CO)_{12}]$ and $[Fe_2Ru(CO)_{12}]$ react with PPh_3 and $P(OMe)_3$.[127] Isomers of $[Os_3(CO)_{10}(L_2)]$ (L_2 = dppe, dppp, or dppb) in which the phosphines are either chelating or bridging can be prepared from $[Os_3(CO)_{10}(C_4H_6)]$ or $[Os_3(CO)_{10}(NCMe)_2]$.[128] The conversion of $[Os_3(CO)_{11}(\eta^1\text{-dppm})]$ to $[Os_3(CO)_{10}(\mu\text{-dppm})]$ occurs by an intramolecular process which is associative in type.[129] Thermal or photochemical reactions of $Ru_3(CO)_{12}$ with $(RO)_2PN(R')P(OR)_2$ (R = Et or Pr^i, R' = Me; R = Me or Ph, R' = Et) yield $\{Ru_3(CO)_{10}[\mu\text{-}(RO)_2PN(R')P(OR)_2]\}$ and $\{Ru_2(CO)_4(\mu\text{-}CO)[\mu\text{-}(RO)_2PN(R')P(OR)_2]_2\}$ complexes.[118] Some ruthenium(II) complexes have been characterised e.g. cis,trans-$[Ru(CO)_2X_2(terpy)]$, the bidentate terpy ligand of which can be mono-protonated, cis- and trans-$[Ru(CO)X_2(terpy)]$ (X = Cl or Br), cis-$[Ru(CO)_2L_2L'_2]$ and trans-$[Ru(CO)Cl(PPh_3)_2L'_2]$ (L_2 = bipy or phen; L'_2 = chelating anions e.g. β-diketonato, salicylaldehydato, or oxinato).[130]

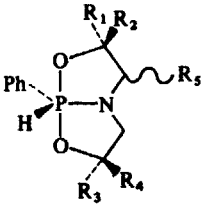
Benzoic and 2-methylbutyric acids react with $Ru_3(CO)_{12}$ to give $[Ru(\mu\text{-}O_2CPh)(\eta^1\text{-}PhCO_2H)(CO)_2]_2$ and $[Ru_2(\mu\text{-}O_2CBu^s)_2(\eta^1\text{-}Bu^sCO_2H)(CO)_4]_2$, respectively.[131] An oxidative reaction of $[Ru(CO)_3(PPh_3)_2]$ with 2-nitrophenol produces $[Ru^{II}(CO)(PPh_3)_2(o\text{-}OC_6H_4NO)(o\text{-}OC_6H_4NO_2)]$ containing O,N-chelating o-nitrosophenolate and O-bonded o-nitrophenolate ligands.[132]

6.3 Cyclopentadienyl Complexes.- Synthetic methods for the preparation of a range of $[(\eta\text{-}C_5Me_5)Fe(CO)_{3-n}L_n][PF_6]$ complexes have been published: [n = 1, L = THF, Me_2CO, MeCN, py, PPh_3, or $P(OPh)_3$; n = 2, L = MeCN, 2L = dppe; n = 3, L = MeCN]. The key step is the oxidation of $[(\eta\text{-}C_5Me_5)Fe(CO)_2]_2$ by $[Cp_2Fe][PF_6]$ in a donor solvent. Substitution of coordinated solvent by other ligands follows. Other similar complexes e.g. $\{(\eta\text{-}C_5Me_5)Fe(CO)_2[SC(S)NMe_2]\}$, all six species of general formula $[(\eta\text{-}C_5Me_5)Fe(CO)_x(PMe_3)_y(NCMe)_z][PF_6]$ (x + y + z = 3), and some $\eta\text{-}C_5H_5$ analogues have also been isolated.[133] Stable thiophosphinito-complexes $\{CpFe(CO)_2[P(R)_2{=}S]\}$ (R = alkyl, Cy, or Ph) have been prepared from $R_2P(H){=}S$ and $[CpFe(CO)_2Br]$ in the presence of Et_3N.[134] An improved synthesis of $[CpFe(CO)_2H]$ has been reported. Reaction with PMe_2Ph yields $[CpFe(CO)(PMe_2Ph)H]$.[135]

(11); E = S, R = H,
R′ = Me, Et, or $CH_2C(O)Me$;
E = O, R = Me or Et, R′ = Et



(12)



(13)

The complexes $[CpFe(CO)_{3-n}(ER_2)_n][BF_4]$ (n = 1 or 2; E = S, R = Me or Bu^t; E = Se or Te, R = Me; ER_2 = thiophene or tetrahydrothiophene) have been prepared from $[CpFe(CO)_2(THF)][BF_4]$.[136]

Group V donor ligands react with $[CpRu(CO)_2I]$ in the presence of either $[(\eta\text{-}C_5Me_5)Fe(CO)_2]_2$ or $[CpRu(CO)_2]_2$ as catalyst to give good yields of $[CpRu(CO)(L)I]$, [L = PPh_3, PMe_2Ph, $PMePh_2$, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, or ½dppm] and $[CpRu(CO)(L)_2]I$, [L = PMe_2Ph, $PMePh_2$; L_2 = $Ph_2P(CH_2)_nPPh_2$; n = 1-4].[137] Phosphines and phosphites react with $[(\eta\text{-}C_5H_4R)Ru(CO)_2X]$ to give resolvable diastereoisomers $[(\eta\text{-}C_5H_4R)Ru(CO)(L)X]$ containing a chiral metal atom, [R = menthyl, X = Cl, L = $PMePh_2$ or $PPh_2(CH_2OMe)$; X = Br, L = PBu^n_3 or $P(OPh)_3$; R = neomenthyl, X = I, L = PPh_3].[138]

Reactions of $[(\eta\text{-}C_3H_4R)Fe(CO)_2(NO)]$ with the (S)-aminophosphines $Ph_2PN(R')CH(Me)Ph$ give diastereoisomers of $\{(\eta\text{-}C_3H_4R)Fe(CO)(NO)[Ph_2PN(R')CH(Me)Ph]\}$ (R, R' = H or Me) that can be separated by fractional crystallisation and preparative liquid chromatography.[139]

7 Group VIII: Cobalt, Rhodium, and Iridium

7.1 Cobalt Complexes.- The reactivity of $Co_2(CO)_8$ towards E_2Ph_4, has been explored. Substitutive oxidative addition occurs for E = As or Sb giving $[Co(CO)_3(\mu\text{-}EPh_2)]_n$ whereas for E = Bi the product is mononuclear $[Co(CO)_4(BiPh_2)]$, the terminal $BiPh_2$ group showing no tendency to become bridging. The derivative $[Co(CO)_3(PPh_3)(BiPh_2)]$ has trigonal bipyramidal geometry.[140] The complex $[Co_2(CO)_6(PBu^n_3)_2]$ is photostable in the absence of free phosphine, but the addition of excess phosphine results in photosubstitution giving $[Co_2(CO)_{6-n}(PBu^n_3)_{2+n}]$ (n = 1 or 2) or disproportionation giving $[Co(CO)_2(PBu^n_3)_3][Co(CO)_4]$ and $[Co(CO)_3(PBu^n_3)_2][Co(CO)_3(PBu^n_3)]$.[141] Ligand exchange between $[Co_2(CO)_6(PMe_2Ph)_2]$ and electrolytically generated $[Co(CO)_3(PMe_2Ph)]^-$ produces $[Co_2(CO)_5(PMe_2Ph)_3]$ and $[Co(CO)_4]^-$.[142]

Controlled electron-transfer chain catalysed nucleophilic substitution reactions of di- and trinuclear metal carbonyls allows sequential and regioselective coordination of polydentate ligands. This type of reaction has been illustrated by the syntheses of $\{[CF_3)_2C_2]Co_2(CO)_{6-n}L_n\}$ (n = 1-3; L = $(o\text{-}C_6H_4AsMe_2)_2AsMe$. The three arsenic donor atoms are sequentially coordinated to the same cobalt centre finally yielding the novel complex $\{LCo[(CF_3)_2C_2]Co(CO)_3\}$ containing tridentate L.[143]

Reactions between 1:1 mixtures of $Co_4(^{12}CO)_{12}$ and $Co_4(^{13}CO)_{12}$ and PR_3 (R = OMe or Ph) afford only $[Co_4(^{12}CO)_{11}(PR_3)]$ and $[Co_4(^{13}CO)_{11}(PR_3)]$, the absence of CO scrambling showing that substitution occurs without cluster fragmentation.[144]

7.2 Rhodium and Iridium Complexes.- A great variety of rhodium(I) carbonyl complexes have been reported. Examples, most of which have been prepared from $[RhCl(CO)_2]_2$, include $[RhCl(CO)_2L]$ (L = 4-Mepy, benzotriazole, or phenothiazine), trans-$[RhCl(CO)L_2]$ {L = $PX[CH(SiMe_3)_2]_2$, X = H or Cl; $FPN(Bu^t)P(F)NBu^t$; $PF(NMe_2)_2$; PBu^t_2X, X = H, Me, Et, Bu^n, or Ph; 9H-telluroxanthene, 10-ethyl-3,7-dimethylphenotellurazine or phenothiazine} and the 5-coordinate complexes $[RhCl(CO)_2L_2]$ (L = 2-diphenylphosphinothiophene) and $[Rh(CO)(PPh_3)_2L_2]$ (L_2 = monobasic bidentate chelate anions e.g. acac, oxinate, salicylaldehydato, or dibenzoylmethanato).[145] Ligand-bridged complexes studied include $\{[RhCl(CO)_2]_2(\mu\text{-}L_2)\}$ (L_2 = 4,4'-bipyridyl and $FPN(Bu^t)P(F)NBu^t$),[145] $\{[Rh(CO)_2]_2(\mu\text{-}L_2)\}$ (L_2 = di-deprotonated 1,8-diaminonaphthalene), $\{[Rh(CO)_2]_2(\mu\text{-}L_2)_2\}$ [L_2 = anion of 1,8-naphthyridine-2(1H)-one], and $\{[Rh(CO)_2]_2(\mu\text{-}L_4)\}$, {$L_4$ = quadridentate Schiff bases e.g. ethylenebis(salicylideneiminato) and o-phenylenebis(salicylideneiminato) and p-xylylenebis[3-(2,4-pentanedionato)]}.[146] Cationic examples include $[Rh(CO)_2L_2]^+$, [L_2 = $CH_2(pz)_2$, $CH_2(3,5\text{-}Me_2pz)_2$, or $CH_2(4\text{-}NO_2pz)_2$; L = unidentate 1,8-naphthyridine; L_2 = 1,4-dithiane, $MeS(CH_2)_3SMe$, or $Bu^tSCH{=}CHSBu^t$].[147]

Diphenylphosphinoacetic acid reacts with $[RhX(CO)_2]_2$ or with $[Rh(CO)_2(acac)]$ to give trans-$[RhX(CO)(Ph_2PCH_2CO_2H)_2]$ (X = Cl, Br or I) and $[Rh(CO)(Ph_2PCH_2CO_2)(Ph_2PCH_2CO_2H)]_2$ each half of the hydrogen-bonded dimer containing one P-unidentate acid ligand and one O,P-chelate acidato anion.[148] Reactions of $[Rh(CO)_2(acac)]$ with 1,3,2-dioxaphosphorinanes or 1,3,2-oxazaphosphorinanes $R'POCH_2CH_2CH(R)E$ [E = O, R = H, R' = Me_2N, Et_2N, Ph_2N, morpholino, or piperidino; E = O, R = Me, R' = Et_2N, Cl, or morpholino; E = NPr^i, R = H, R' = Me_2N, Et_2N, EtO, or $H_2N(CH_2)_3O$] lead to P-bonded complexes of the type $[Rh(CO)(acac)L]$.[149] Stepwise reactions of $[Rh(CO)_2(S_2CNR_2)]$ with phosphines produce $\{Rh(CO)_{2-n}(S_2CNR_2)[P(C_6H_4X\text{-}p)_3]_n\}$ (n = 1 or 2; R = Me or Et; X = Cl, F, Me, or OMe).[150] The A-frame complex $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}Ph_2PN(H)PPh_2)_2]$ has been synthesised from

$[RhCl(CO)_2]_2$, and the intermediates $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PN(H)PPh_2)_2]Cl$ and $[Rh_2Cl(\mu\text{-}Cl)CO(\mu\text{-}CO)(\mu\text{-}Ph_2PN(H)PPh_2)_2]$ characterised. Alterations in the reaction conditions permit isolation of $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PN(H)PPh_2)_2]X$ [X = Cl or $Rh(CO)_2Cl_2$].[151]

Treatment of $[Ph_4As][Rh(CO)_2(1,2\text{-}O_2C_6Cl_4)]$ with dppm gives $[Rh_2(CO)(1,2\text{-}O_2C_6Cl_4)(\mu\text{-dppm})_2]$ containing planar and square pyramidal ligand arrays around the two metal atoms. The dppm ligands are arranged such that they are mutually trans at one metal, but mutually cis at the other metal.[152] The bicyclic aminophosphorane (13; R^1, R^2, R^3, R^4 = Me, R^5 = H) reacts with $[RhCl(CO)_2]_2$ to give either [RhCl(CO)L] or $[(OC)_2ClRh(\mu\text{-}Cl)Rh(CO)L]$ depending on the ratio of reactants, L being the monocyclic P,N-chelating tautomer $PhP[OC(Me)_2CH_2]_2NH$. The chiral aminophosphoranes (13; R^1, R^2, R^3, R^4 = H, R^5 = Me or Et and R^1, R^2 = H, R^3, R^4 = Me, R^5 = Me or Et) afford diastereoisomeric pairs of [RhCl(CO)L] complexes where again L is the monocyclic P,N-chelating tautomer of (13).[153] The macrocycles $ROPO(CH_2)_2N(Me)(CH_2)_2N(Me)(CH_2)_2O$ [R = Me, Et, Bu^s, menthyl, or (S)-(-)-2-Me-1-Bu] form complexes of the type [RhCl(CO)(macrocycle)] in which the macrocycle bonds via the phosphorus and two nitrogen atoms. However, one Rh-N bond is very long resulting in a geometry intermediate between four- and five-coordination.[154] The dipodal macrocycle $Ph_2P(CH_2)_2N[(CH_2)_2O(CH_2)_2]_2N(CH_2)_2PPh_2$ functions as a double P,N-chelate on reaction with $[RhCl(CO)_2]_2$, the product being $\{[RhCl(CO)]_2(\text{macrocycle})\}$.[155] The complex $[(OC)ClRh(\mu\text{-}Ph_2AsCH_2PPh_2)_2PtCl_2]$, produced from cis-$[PtCl_2(Ph_2PCH_2AsPh_2)_2]$ and $[RhCl(CO)_2]_2$, has an unusual geometry with ligand-bridged cis-PtP_2Cl_2 and trans-$RhCl(CO)As_2$ units.[156]

The iridium(I)-pyrazolyl complexes $[Ir(CO)(PPh_3)(\mu\text{-pz})]_2$ and trans-$[Ir(CO)(PPh_3)_2L]$ (L = unidentate 3,5-Me_2-, 3,5-Me_2-4-NO_2- or 3,5-$(CF_3)_2$-pz) have been characterised. For the latter type, protonation of the nitrogen atom not coordinated to the metal is possible.[157] New mono- and binuclear iridium(I) complexes containing dppe or dppp have been prepared e.g. $[Ir(CO)_nX(dppe)]$ (n = 1 or 2; X = Br or I), $[Ir(CO)_2I(dppp)]$ and trans-$[Ir(CO)X(\mu\text{-dppp})]_2$ (X = Cl, Br, or I).[158] The novel five-coordinate complexes $[Ir(CO)R\{R'P[(CH_2)_nPPh_2]_2\}]$ (R = p-tol, CH_2CMe_3, or CH_2SiMe_3; R' = Ph, n = 2 or 3; R' = Me, n = 3) have been prepared by reactions of $[Ir(CO)R(PPh_3)_2]$ with terdentate phosphines.[159] The P,S-chelate complex

$[Ir(CO)(PPh_3)(Ph_2PCH_2CH_2S)]$ results from the reaction of trans-$[Ir(CO)Cl(PPh_3)_2]$ with $Ph_2P(CH_2)_2SH$ in methanol with the addition of NaOMe. However, in $CHCl_3$ oxidative addition also occurs to give $[Ir(CO)Cl(H)(PPh_3)(Ph_2PCH_2CH_2S)]$. In CH_2Cl_2 the product is $[Ir(CO)H(Ph_2PCH_2CH_2S)(Ph_2PCH_2CH_2SH)]Cl$.[160]

7.3 Cyclopentadienyl Complexes.- The chelate complexes $[CpCo(bid)I]I$ (bid = dppp, dppb, or dpae) result from the reactions of $[CpCo(CO)I_2]$ with the Group V donor ligands.[161] The reactions of $[(\eta^5\text{-}R)Rh(CO)_2]$ (R = C_9H_7, C_9Me_7, or $C_5H_4NO_2$) and $[(\eta\text{-}C_5H_4PPh_3)Rh(CO)_2]^+$ with PPh_3 proceed by an associative mechanism to give monosubstituted products. The reaction rates are much faster than those of $[CpRh(CO)_2]$.[162] The complex $[Cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ is produced by the reaction of $[Cp_2Rh_2(CO)_2(\mu\text{-}CO)]$ with dppm. Some insertion and oxidative addition reactions of this dppm complex are also reported.[163] Phosphine ligands displace one or two carbonyl groups from $[(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2]$ exclusively at the rhodium centre. The products $[(\mu\text{-}C_7H_7)Fe(CO)_2(\mu\text{-}CO)Rh(CO)_{2-n}(PR_3)_n]$ (n = 1, R = Me or Ph; n = 2, R = Me or PR_3 = ½dppm, ½dppe, or ½dmpe) have the $\mu\text{-}C_7H_7$ ring bonded in an η^4-mode to iron and in an η^3-mode to rhodium, the reverse bonding pattern to that of the initial pentacarbonyl.[164]

8 Group VIII: Palladium and Platinum

The mechanism of formation of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][CF_3CO_2]_2$ from $Pd(O_2CMe)_2$, dppm and CF_3CO_2H has been elucidated and a number of intermediates characterised.[165] The syntheses of tri-, tetra-, and deca-nuclear palladium clusters containing carbonyl and triaryl phosphine ligands have been reported.[166] Bimetallic $[MM'Cl_2(\mu\text{-}CO)(PPh_3)_3]$ arise from reactions of $[M(CO)(PPh_3)_3]$ with $(M'Cl_2(NCPh)_2]$ (M, M' = Pd or Pt).[167] The cluster complexes $[Pt_4(\mu\text{-}CO)_5L_4]$ (L = PEt_3, PMe_2Ph, $PMePh_2$, or PEt_2Bu^t) have been synthesised from $[Pt(cod)_2]$. In $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ the Pt_4 unit is arranged as a distorted edge-opened tetrahedron. The complex $[Pt_4(\mu\text{-}CO)_5(PEt_3)_4]$ has also been prepared from $[Pt(CO)_2]_n$ and its solution structure investigated.[168]

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11

Complexes Containing Metal–Carbon σ-Bonds of the Groups Scandium to Manganese, including Carbenes and Carbynes

BY M. J. WINTER

1. Intoduction

This chapter is organised into Sections for the Groups IIIA-VIIA each of which is ordered in topics concerning syntheses and reactivities of classes of complexes with similar ligand systems.

For brevity, in this chapter Cp denotes C_5H_5, Cp' represents C_5H_4Me and Cp* indicates C_5Me_5.

Several review articles of relevance have appeared.

The structural consequences of bonding for carbene complexes are discussed.[1] Photochemical reactions of metal alkyl complexes result in very reactive intermediates that can be trapped and used preparatively.[2] Matrix isolation studies of organometallic intermediates are considered in detail.[3] Transition metals in organic synthesis for the year 1982 are reviewed extensively[4] and a further article concerns σ-(1,n)-alkanediyl complexes.[5]

2. Group IIIA (Sc, Y, and La), Lanthanides, and Actinides

Published abstracts of a conference concern the chemistry and technology of the lanthanides and actinides.[6] The stoicheiometric and catalytic reactions of actinides including C-H activation is discussed[7] and the chemistry of organolanthanoids, particularly homoleptic alkyls and $LnCp_2$ (Ln = lanthanoid) derivatives, is extensively reviewed.[8]

The reactions of YCl_3, $LaCl_3$, or $LnCl_3$ with MeLi in Et_2O in the presence of tmeda afford $[Li(tmeda)_3][LnMe_6]$ which are the subjects of X-ray crystallographic studies in two cases. Treatment of $Lu(OBu^t)_3$ with Bu^tLi and tmeda in pentane results in $[Li(tmeda)_2][LuBu^t_4]$ while $LnCl_3$ and Bu^tLi similarly provide $[Li(tmeda)_2]LnBu^t_4]$ (Ln = Tb, Er, and Lu). The complexes $[Li(tmeda)_3][LnMe_6]$ (Ln = Pr or Sm) have potential as methylating agents, they tend to methylate α,β-unsaturated aldehydes and ketones 1,2 rather than 1,4 in high yield reactions.[9]

In the presence of dme, the reaction of $LuCl_3$ and MeLi proceeds

[For References see page 252

to give $[Li(dme)]_3[LuMe_6]$ which is octahedral about Lu.[10]

The interaction of 7MeLi with $ThCl_4$ in the presence of tmeda provides the seven coordinate Th complex $[Li(tmeda)]_3[ThMe_7]$.tmeda which although apparently coordinatively saturated is reactive.[11]

Treatment of $MCl_4(dmpe)_2$ with $4PhCH_2Li$ proceeds with formation of $M(CH_2Ph)_4(dmpe)$ (M = Th or U) whereas the corresponding reaction with $3PhCH_2Li$ + 1MeLi affords $M(CH_2Ph)_3Me(dmpe)$.[12]

A mixture of $LnCl_3$, 2NaCp*, and 2MeLi reacts in THF/tmeda to form $LnCp^*_2(\mu\text{-}Me)_2Li(tmeda)$ (Ln = La or Lu) whereas the reaction of $LuCl_3$, 2NaCp*, $2LiCH_2SiMe_3$, and dme provides $[Li(dme)_2][Lu(CH_2SiMe_3)_2Cp^*_2]$ while $LnCl_3$, NaCp*, 3MeLi, and dme gives $[Li(dme)_2]_2[LnMe_3Cp^*]$ (Ln = Lu or Yb).[13]

The ylide PPh_3CH_2 reacts with $Lu(thf)Cp_3$ forming $Lu(CH_2PPh_3)Cp_3$ and $LuCl(CH_2PPh_3)Cp_2$ reacts with MeLi affording $LuMe(CH_2PPh_3)Cp_2$ which decomposes with CH_4 evolution to the cyclic compound 1.[14]

Sterically hindered alkyl and hydride Th complexes of type $Th(R^1)(OR^2)Cp^*_2$ (R^1 = H, alkyl; R^2 = alkyl or aryl) are available by a number of methods including alcoholysis of Th alkyls, metathesis of the halide with Li reagents, and ketone insertion reactions into M-H bonds. Most react irreversibly with CO by migratory insertion forming η^2-acyls $Th(OR^2)(\eta^2\text{-}COR^1)Cp^*_2$.[15]

Reaction of $LuCl_3$ with $Li(CH_2)_2PBu^t_2$ affords the alkyl $Lu[CH_2P(Bu^t_2)CH_2]_3$ which is octahedral about Lu and dynamic in solution while the same Li reagent with $LuClCp_2$ leads to isolation of the stable $Lu[CH_2(PBu^t_2)CH_2]Cp_2$.[16]

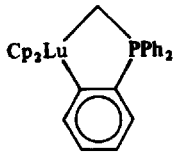
The dimethylphosphino<u>bis</u>(methanide) compound $Lu(CH_2PMe_2CH_2)Cp^*_2$ is the subject of an <u>X</u>-ray crystal structure.[17]

The hydride complexes $[Y(H)(thf)L_2]_2$ (L = Cp or Cp') react with $R^1CH{=}CH_2$ forming alkyls $Y(CH_2CH_2R^1)(thf)L_2$ while allene provides $Y(\eta^3\text{-}CH_2CHCH_2)(thf)L_2$, Bu^tCCH results in alkynide $Y(\text{-}CCBu^t)L_2$, and R^2CCR^2 leads to the vinyl $Y(CR^2{=}CHR^2)(thf)L_2$.[18]

Treatment of $Yb(MeOCH_2)_2Cp_2$ with an appropriate HgX_2, TlX, CuX, or AgX_2 forms $YbXCp_2$ [X = CCPh, $CH(COMe)_2$, $CH(COPh)_2$, or C_6F_5].[19]

Phenylethyne reacts with $M(OEt_2)Cp^*_2$ in toluene giving the mixed valence compound $Yb_3(\mu\text{-}CCPh)_4Cp^*_4$ 2 in the Yb case whereas the product for M = Eu is $Eu_2(\mu\text{-}CCPh)_2(thf)_4Cp^*_2$ after crystallisation from THF, the former has idealised D_{2d} geometry.[20]

A sterically demanding chelate complex arises in the reaction of anhydrous MCl_3 with $Li(C_6H_4CH_2NMe_2\text{-}\underline{o})$ (M = Lu, Er, and Yb) as indicated by the <u>X</u>-ray crystal structure of $Lu(C_6H_4CH_2NMe_2\text{-}\underline{o})_3$.[21] The same chelate cleaves the $[YClCp_2]_2$ dimer producing the Y aryl



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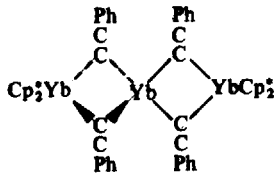

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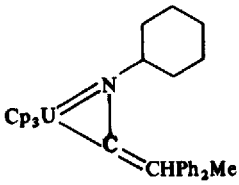

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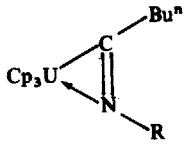
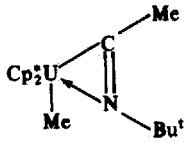


(4) R = Bu^t, C_6H_{11}-*c*, $C_6H_3Me_2$-2,6



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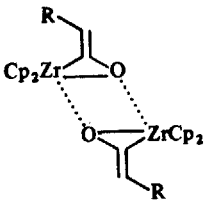
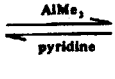
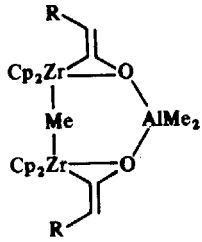
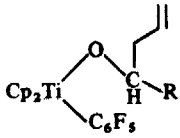






(6) R = CH_2Bu^t

(7)



(8)

$\overline{Y(o\text{-}C_6H_4CH_2NMe_2)}Cp_2$.[22]

The isonitrile CNC_6H_{11}-c inserts into the U=C bond of $U[C(H)PPh_2Me]Cp_3$ forming the X-ray crystallographically characterised uranaazacyclopropene complex **3**.[23] Equimolar quantities of $U[C(H)PPh_2Me]Cp_3$ and MeCN give the insertion product $U[NC(Me)=CHPPh_2Me]Cp_3$ which is an example of UN multiple bonding.[24]

Isonitrile (RNC) insertion into the U-C bond of UBu^nCp_3 results in the η^2-iminoacyl **4** (R ▫ Bu^t, C_6H_{11}-c, and $C_6H_3Me_2$-2,6). However only a single insertion proceeds for UMe_2Cp_2 where the product is **5**. The remaining methyl is unreactive towards further Bu^tNC but is replaced by Cl upon treatment with CCl_4.[25]

3. Group IVA (Ti, Zr, and Hf)

The carbonylation reactions of zirconocene complexes of type ZrR_2Cp_2 (R = alkyl, aryl, and H) are discussed in a review[26] and some relevant material is incorporated into reviews on Ti for the literature years 1981[27] and 1982.[28]

Attaining the lowest energy electronic excited states for $TiMe_2Cp_2$ involve transfer of electron density from the Ti-Me orbitals to d-orbitals. This explains the Ti-Me bond cleavage on low energy irradiation.[29]

Addition of $AlMe_3$, MeLi, or $ZnMe_2$ to $TiCl_3Cp$ affords $TiCl_2MeCp$ while $ZnEt_2$ provides the partially characterised $TiCl_2EtCp$.[30]

An approximately trigonal bypyramidal methyl group exists in the product **6** arising from reaction of $AlMe_3$ with **7**. The methyl bridges two zirconacene ketene centres, the ∠ Zr-C-Zr is 147.8°. Treatment of **7** with pyridine regenerates **6**.[31]

One equivalent of $AlMe_3$ reacts with $TiCl_2Cp_2$ to form the chloro bridged compound $Cp_2TiMe(\mu\text{-}Cl)AlMe_3$ in which the Al binds weakly to the chloride. Addition of a Lewis base such as an ether releases $TiClMeCp_2$. A second equivalent of $AlMe_3$ exchanges with $AlMe_2Cl$, the resulting $Cp_2TiMe(\mu\text{-}Cl)AlMe_3$ extrudes CH_4 by alpha abstraction producing the methylene $\overline{TiCH_2AlMe_2Cl}$.[32]

Aldonolactones are alkylated using $\overline{TiCH_2AlMe_2Cl}$ resulting in potentially useful substrates for glycosidase enzymes.[33]

Addition of C_3H_5MgCl to chiral racemic $TiCl(C_6F_5)Cp(\eta\text{-}C_5H_4Bu^t)$ proceeds with formation of the allyl $Ti(C_3H_5)(C_6F_5)Cp(\eta\text{-}C_5H_4Bu^t)$ which on reaction with RCHO afford adducts of type **8** with diastereomeric excesses of 12 - 40%. However reaction of the optically active (+)-Ti complex with C_3H_5MgBr, followed by PhCHO,

and hydrolysis yields a product with only 11% enantiomeric excess, loss of chiral information occurs at the C_3H_5MgBr stage.[34]

Addition of $ZrCl_2Cp_2$ to (tmeda)$\overline{LiPMe_2Li(tmeda)CH_2P}Me_2$ or $LiCH_2PMe_2$ gives materials formulated as $ZrX(CH_2PMe_2)Cp_2$ (X = Cl and CH_2PMe_2).[35,36] The chloride carbonylates without isolation to the binuclear ketene **9** (R = Me), apparently via a mononuclear η^2-acyl intermediate[35] (Scheme 1) while facile CO insertion is observed for X = CH_2PMe_2 in pentane at 0°C resulting in the zirconacycle **10**.[36] Analogous carbonylation of $ZrCl(CH_2PPh_2)Cp_2$ results in formation of Ph_2PMe and **9** (R = Ph). The acyl **11** is probably the primary product, the acidity of the CH_2 is enhanced sufficiently to allow cleavage of the Zr alkyl of the starting material resulting in **10**. Electron density is delocalised around the ring.[37,38]

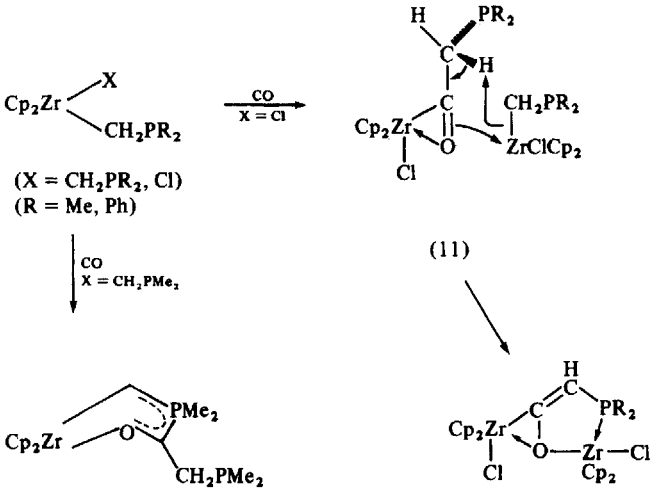
Metallaindane derivatives **12** arise in the reactions of $[Li(tmeda)_2][C_6H_4(CHSiMe_3)_2\text{-}o]$ with MCl_2Cp_2 (M = Ti, Zr, or Hf). These complexes are assigned the meso structure on the basis of n.m.r. spectroscopy and an X-ray analysis for M = Zr.[39]

A mixture of s-cis and s-trans Zr(hexa-2,4-diene)Cp_2 reacts with alkenes $RCH{=}CH_2$ providing the zirconacycles **13** which carbonylate eliminating the cyclic ketones $\overline{CH_2CHRCHRCH_2C}O$. Reaction of the same mixture with MeCCMe provides the zirconacycle **14** (R = Me).[40]

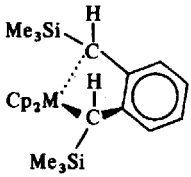
The photochemical reaction of RCCR with $Zr(CO)_2Cp_2$ leads to the zirconacyclopentadiene $\overline{Zr(CR{=}CRCR{=}C}R)Cp_2$ **14** (R = Ph or Pr^n) while heat is effective for R = C_6F_5 as well as Pr^n. The corresponding hafnocycles are obtained under thermal conditions.[41] Substituted zirconacyclopentadiene rings adopt an envelope type structure but all four carbons are within bonding distance of the metal. There is a continuous transition from an η^4 to a σ^2,π configuration depending upon the nature of the diene substituents. The different configurations affect the reaction rates with CO.[42]

Grignard reagents $C_6H_4(CH_2MgCl)_2\text{-}o$ react with MCl_2Cp_2 or $MCl_2(C_5H_4SiMe_3)_2$ (M = Ti, Zr, and Hf) generating the metallacycle **15**. Two conformers of **16** result from carbonylation of **15** (M = Hf, R = $SiMe_3$).[43]

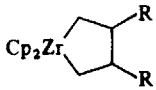
Pseudotetrahedral metallacycles **17** are formed in the reaction of $[Mg(CH_2)_2SiMe_2]_n$ with MCl_2Cp_2 (M = Ti, Zr, Nb, or Mo). All four molecules are subjects of X-ray crystal analysis. Their thermal stability is greater than the corresponding metallacyclobutanes.[44] The electronic configuration of the metal exerts an influence upon the conformational structure of the MC_2Si ring in the series **17** M = Zr, Nb, and Mo). An increase in the number of metal valence



Scheme 1



(12) M = Ti, Zr, Hf, Nb



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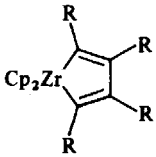
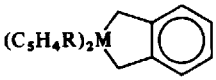
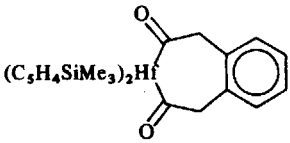


(14) R = Me, Ph, Pr^n



(15) R = H, $SiMe_3$
M = Ti, Zr, Hf



(16)

electrons from d^0 (Zr) to d^1 (Nb) to d^2 (Mo) is manifested by a gradual decrease in the Δ C-M-C and a gradual increase in the M-C distance. This is an anti-bonding influence.[45]

The cyclic structure **18** arises from the reaction of zirconacycle **17** (M = Zr) with H_2CO. X-ray crystallography confirms the H_2CO insertion into the ring. There is a donation from filled O 2p orbitals into empty Zr d orbitals.[46]

Carbon dioxide is incorporated in the titanacycle **19** arising from coupling of CO_2 with $Ti(\eta^2\text{-PhCCPh})CpCp^*$.[47]

Complex reactions of $TiCl_2Cp_2$ with bidentate substituted pyrazolones $R\overline{COC{=}C(OH)NPhN{=}C}Me$ (R = alkyl or aryl) (L) lead to $TiCl(L)Cp_2$, $TiCl(L)_2Cp_2$, and $[C_5H_4Ti(L)_2]_2$ **20**.[48]

Interaction of the hydride $ZrH_2Cp^*_2$ with $ZrL(CO)Cp_2$ (L = CO or PMe_3 gives a zirconoxy carbene **21** which is a rare example of Group IV MC multiple bonding (Scheme 2). Reaction with pyridine provides the ketene **22** which with MeI gives the corresponding iodo complex and methane. Reaction of **21** (L = PMe_3) with MeI results in (Zr)-H for I exchange; this product carbonylates to vinyl **23**.[49]

The carbenes $Zr[C(H)CH_2R]PPh_3Cp_2$ react with aldehydes giving preferential Z alkenation but imines give reverse selectivity.[50]

Methyllithium reacts with $MCl_2(tritox)_2$ (M = Ti or Zr, $tritox^-$ = $[Bu^t{}_3CO]^-$, a steric equivalent of Cp^-), with methyl for halide exchange yielding $MMe_2(tritox)_2$. In a corresponding reaction $TiCl_3(tritox)$ and MeLi provide $TiMe_3(tritox)$ while tritoxH reacts with $Zr(CH_2Bu^t)_4$ by elimination of CMe_4 and formation of $Zr(CH_2Bu^t)_3(tritox)$.[51]

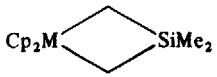
Addition of excess $MgMe_2$ to $ZrCl_4(dmpe)_2$ gives $ZrCl_2Me_2(dmpe)_2$ while excess MeLi affords $ZrMe_4(dmpe)_2$, and $LiCH_2SiMe_3$ forms $Zr(CH_2SiMe_3)_4(dmpe)$. The benzyl $Zr(CH_2Ph)_4$ adds dmpe generating $Zr(CH_2Ph)_4(dmpe)$.[52]

Thermal decomposition of $Ti(CH_2R)_9$ (R = Ph or $SiMe_3$) containing no β-hydrogens proceeds by either i) radical or σ-bond homolysis or ii) carbene or α-disproportionation pathways.[53]

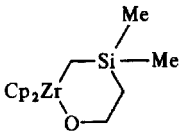
4. Group VA (V, Nb, and Ta)

The bis-Grignard $C_6H_4(CH_2MgCl)_2$-o reacts with $NbCl_2(C_5H_4SiMe_3)_2$ to form the metallacycle $Nb(CH_2C_6H_4CH_2)(C_5H_4SiMe_3)2$.[43]

The anionic poly(pyrazolyl)borate ligands $[HB(pz)_3]^-$ (pz ■ pyrazolyl) and $[HB(3,5\text{-}Me_2pz)_3]^-$ undergo reaction with the alkyl $TaCl_2Me_3$ resulting in $TaClMe_3[HB(pz)_3]$ and $TaClMe_3[HB(3,5\text{-}Me_2pz)_3$.



(17) M = Ti, Zr, Nb, Mo



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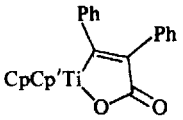

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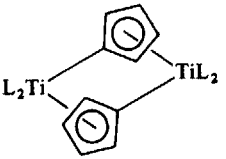

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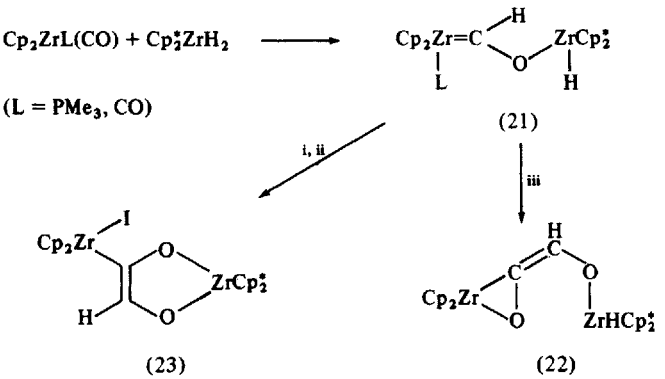
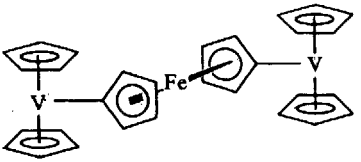


Reagents: i, MeI (L = PMe_3); ii, CO; iii, pyridine

Scheme 2



(24)

The solid state structure of these consists of a virtually octahedral N_3Me_2Cl set around Ta with the final Me group capping the Me_2Cl face. However in solution there are two isomers with similar geometries but either Me or Cl capping.[54]

Addition of $[Li(tmeda)_2][C_6H_4(CHSiMe_3)_2\text{-}o]$ to $NbCl_2Cp_2$ results in the metallaindane **12** (M = Nb).[39]

Carbonylation of $Ta(H)(\eta^2\text{-}C_2H_4)Cp_2$ results in the insertion product $TaEt(CO)Cp_2$. Photolysis of $TaEt(CO)Cp_2$ in a hydrocarbon solvent yields $Ta(H)(\eta^2\text{-}C_2H_4)Cp_2$ and $Ta(H)(CO)Cp_2$.[55]

Addition of the acetylide $LiCCBu^t$ to $VClCp_2$ results in the vanadium alkynide $V(CCBu^t)Cp_2$ which is the subject of an X-ray crystallographic study.[56]

The Grignard reagent $BrMgCH_2CMe_2CH_2MgBr$ reacts with VCl_2Cp_2 to give moderate yields of the vanada(IV)cyclobutane $V(CH_2CMe_2CH_2)Cp_2$ which only has limited stability.[57]

Paramagnetic VCp_2 or VCp'_2 units bridged by ferrocene are formed in the reaction of $VClCp_2$ or $VClCp'_2$ with $Fe(C_5H_4Li)_2$, the product **24** has perpendicular ring systems. There is no exchange of unpaired electrons across the ferrocene unit down to 234 K.[58]

Vanadocene reacts with $R_2C{=}C{=}S$ to form the X-ray crystallographically characterised η^2-thioketene $V(\eta^2\text{-}CR_2{=}CS)Cp_2$.[59]

The $\eta^2\text{-}CS_2$ complex $NbBu^n(\eta^2\text{-}CS_2)Cp_2$ is alkylated by RX resulting in $[NbBu^n\{\eta^2\text{-}C(SR)S\}Cp_2][X]$ which in turn reacts with $[BH_4]^-$ to $NbBu^n[\eta^2\text{-}CH(SR)S]Cp_2$, a compound apparently produced *via* a Nb coordinated $[BH_4]^-$.[60]

The carbene $Nb(H)_2Me(=CH_2)$ is calculated to have a stronger M=C(carbene) bond than that of $Cr(=CHOH)(CO)_5$, the atomic charges are calculated to be negative.[61]

Calculations suggest that the covalent character and bond strength increases in the order V < Nb < Ta for M-Me bonds. The same order is followed for the stability of $M{=}CH_2$ *vs.* M-Me and for the rotational barrier about the $M{=}CH_2$ bond.[62]

5. Group VIA (Cr, Mo, and W)

Treatment of $MoCl_5$ or $MoCl_3O$ with MeLi leads to mixtures of $MoCl_nMe_{3-n}(=CH_2)$ (n = 1 - 3), $MoCl(=CH_2)O$ or their dimers according to the stoicheimetry and reaction conditions. They convert aldehydes RCHO to alkenes $RCH{=}CH_2$ or act as alkylating agents.[63,64]

The Grignard reagents $C_6H_4(CH_2MgCl)_2\text{-}o$ react with WCl_4O with halide elimination and formation of either **25** or $W(CH_2C_6H_4CH_2\text{-}o)_3$,

although the actual product is critically dependent upon reaction conditions. Compound **25** is the precursor to $W(CH_2C_6H_4CH_2\text{-}\underline{o})_3$, which is capable of undergoing reversible one electron oxidation.[65]

The seven coordinate Mo complexes $MoX_2(CO)_2(PMe_3)_3$ (X = halide or NCO) undergo reaction with the appropriate Grignard reagents or alkyl lithium reagents providing the η^2-acyl complexes **26** (R = Me, CH_2SiMe_3, CH_2Bu^t, or CH_2CMe_2Ph), one example of which is the subject of an X-ray crystal structure. These compounds undergo phosphine replacement for carbonyl upon carbonylation rather than the acyl adopting $\eta^{\frac{1}{2}}$ coordination.[66]

The photochemical reactions of $M(norbornyl)_4$ (M = Cr or Ti) in hexane or CCl_4 lead to 1,1'-binorbornyl and this is rationalised through interpretation of their electronic spectra.[67]

Trimethylphosphine attacks $M(CH{=}CHCR^1{=}O)(CO)_2(\eta\text{-}C_5H_4R^2)$ (R^2 = various, M = Mo or W) at the α-C in producing **27** (L = CO). In a related process the acyl $W(COMe)(CO)_2(\eta^2\text{-}HCCH)Cp$ requires two equivalents of PMe_3 to form **27** (R^1 = Me, R^2 = H, L = PMe_3) which has a very high electron density at the metal.[68] The same acyl gives two of the possible four diastereomers of the tungstenacyclopropane **28** on ClNO treatment, addition of HX to **28** gives the cycle **29**.[69]

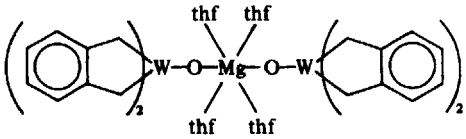
The sulphur ylide $Cr[CH_2S(O)Me_2](CO)_5$ reacts with asymmetric diphosphines to form chelate complexes $Cr(CO)_4(CH_2PR^1{}_2CH_2PR^2{}_2)$, the more nucleophilic phosphorus binding to the methylene.[70]

The X-ray crystal analysis of the anion cis-$[WMe(CO)_4(PMe_3)]^-$ formed in the reaction of $[W(CO)_4(PMe_3)]^{2-}$ and methyl tosylate reveals a W-Me distance of 2.18 Å.[71]

Cocondensation of W atoms, PMe_3 and cyclopentene provides several products, one of which is **30**.[72] Treatment of **30** with MeOH at ambient temperature forms a compound represented as **31** which is an η^2-formaldehyde complex.[73]

Metal carbonyl radicals result from electroreduction of $Cr(CO)_6$ and they accept hydrogen atoms from $Bu^n{}_3SnH$ to form the formyl $[Cr(CHO)(CO)_5]^-$ which in turn is reduced to the hydroxymethyl $[Cr(CH_2OH)(CO)_5]^-$.[74] The $t_{\frac{1}{2}}$ of $[M(CHO)(CO)_5]^-$ (M = Cr or W) is increased by approximately x5 on addition of $Bu^n{}_3SnH$.[75]

A possible insight is gained into the mechanism by which a ligand migrates to a coordinated alkyne is suggested by the η^2-vinyl complex **32** which is the result of the metathesis of TlSR (R = alkyl) with $WCl(F_3CC_2CF_3)Cp$. Different products arise when the R group is electron withdrawing.[76]



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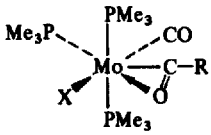
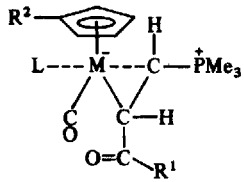
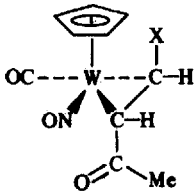


(26) X = Cl, Br, I, NCO
R = Me, CH_2SiMe_3, CH_2Bu^t, CH_2CMe_2Ph



(27) M = Mo, W
L = CO, PMe_3



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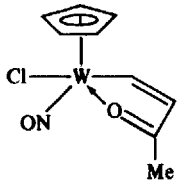

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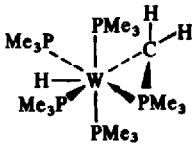

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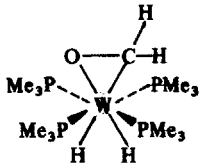

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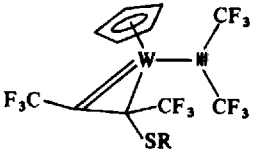

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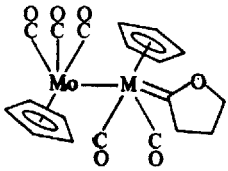
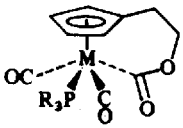
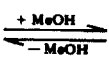
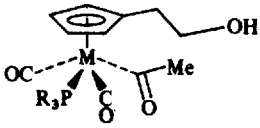


(33) M = Mo, W



(34) M = Mo, W
R = Ph, C_6H_4Me-*p*





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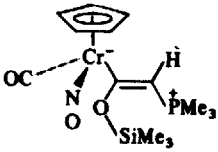

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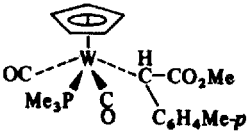

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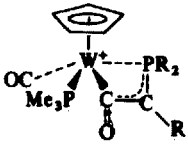

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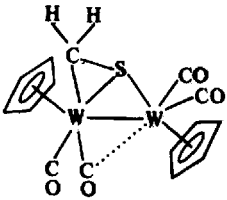


(39)

The action of BX_3 (X = Cl or Br) on $MoR^1(CO)_3Cp$ (R^1 = CF_3 or C_2F_5) causes alpha F abstraction with resulting formations of $M(R^2)(CO)_3Cp$ (R^2 = CX_3 or CCl_2CF_3); a reaction seeming to proceed via intermediate dihalocarbenes.[77] Acidification of $M(CF_3)(CO)_3Cp$ (M = Mo or W) with aqueous HBF_4 leads to the cations $[M(CO)_4Cp]^+$ probably through difluorocarbene intermediates.[78]

The initial products of photochemical reactions of $MR(CO)_3Cp$, $MR(CO)_3Cp'$ or $MR(CO)_3Cp^*$ (R = alkyl, Ph, CH_2Ph) in matrices are the β-eliminates MH(alkene)$(CO)_2Cp$ (M = Mo or W).[79,80]

Dihaloalkanes $I[CH_2]_nI$ undergo halide replacement at both ends of the chain upon treatment with the anions $[M(CO)_3Cp]^-$ resulting in the dimetallaalkanes $Cp(OC)_3M[CH_2]_nM(CO)_3Cp$ (M = Mo, n = 4; M = W, n = 3 or 4). The alkyl $Mo[(CH_2)_3Br](CO)_3Cp$ is attacked by $[Mo(CO)_3Cp]^-$ and cyclises to carbene **33** (M = Mo) but the product with $[W(CO)_3Cp]^-$ is **33** (M = W), a result of carbene migration.[81]

The anions $[M(CO)_3Cp]^-$ (M = Mo or W) react with N-(chloromethyl)phthalimide resulting in the substituted methyl complexes $M[CH_2\overline{NC(O)C_6H_4C}(O)\text{-}o](CO)_3Cp$.[82]

Thermolysis of the alkynide $Mo(CCR)(CO)_3Cp$ in octane produces $Mo_2(CO)_4(\mu\text{-RCC-CCR})Cp_2$ (R = Ph or C_6H_4F) in a complex reaction.[83]

An 82% yield of the alkynide $W(CCPh)(CO)_3Cp$ is isolated from the CuI catalysed reaction of $WCl(CO)_3Cp$ with PhCCH and $NHEt_2$.[84]

Reaction of the cation $[M(CO)_3(PR_3)(C_5H_4CH_2CH_2OH)]^+$ with base provides the trans intramolecular ester **34**. The ester is in equilibrium with MeOH and **35**.[85]

Interaction of $PMe_3CHSiMe_3$ with the nitrosyl $Cr(CO)_2(NO)Cp$ in benzene or silylation of the acylate $[Cr(COCHPMe_3)(CO)(NO)Cp]^-$ results in the vinyl **36**.[86]

Methanol reacts with η^1-ketene $W[\text{-}C(C_6H_4Me\text{-}p)=C=O](CO)_2(PMe_3)Cp$ providing the substituted methyl acetate complex **37**, the X-ray crystal structure of which confirms the trans configuration.[87]

The result of adding PR_2Cl to the ketene $\overline{W(CO)(PMe_3)(\eta^2\text{-}CRCO)}Cp$ is conversion to the unusual cationic cycle **38**.[88]

Addition of allyl halides to the anions $[M(GePh_3)(CO)(NO)Cp]^-$ (M = Mo or W) results in the η^1-allyl $Mo(\eta^1\text{-}C_3H_5)(GePh_3)(CO)(NO)Cp$ which undergoes decarbonylation upon thermolysis with the formation of the η^3-allyl $M(GePh_3)(NO)(\eta^3\text{-}C_3H_5)Cp$. A number of derivatives show related behaviour.[89]

The hydride $WH(CO)_3Cp$ reacts with $S(NMe)_2$ providing $S[W(CO)_3Cp]_2$ which reacts with CH_2N_2 to form the $\mu_2\text{-}CH_2S$ complex **39** which exists in two isomeric forms.[90]

Reaction of the alkyl $MoMe(CO)_3Cp$ with $LiEt_3BH$ leads to the acetaldehyde complex **40** via the formyl $[Mo(CHO)Me(CO)_2Cp]^-$ and the acyl $[MoH(COMe)(CO)_2Cp]^-$.[91] Reaction of **40** with $[Mo(CO)_3Cp]^+$ or several other one electron oxidising agents provides the η^2-acetaldehyde complex **41**, this species is also attained by the addition of hydride from $LiEt_3BH$ to the bridged acyl complex $[Mo_2(\mu_2\text{-}COMe)(CO)_4Cp_2][BF_4]$.[92]

Spectroscopic data concerning the reaction of $[Mo(CO)_3(C_7H_7)]^+$ with OMe^- at low temperature suggests attack takes place exo at the ring and at the metal forming $Mo(OMe)(CO)_3(C_7H_7)$ which rearranges to $Mo(CO_2Me)(CO)_2(C_7H_7)$ and to the same exo ring compound.[93]

The vinyl $Cr[\eta^1\text{-}C(OSiMe_3)=CHPMe_2](CO)(NO)Cp$ arises from reaction of $PMe_3CHSiMe_3$ with $Cr(CO)_2(NO)Cp$.[94]

The lead species $Pb(O_2CMe)_2[Mo(H)Cp_2]$ reacts with HCC-CN in forming the bis-η^1-vinyl $Mo(\eta^1\text{-}CH=CHCN)_2Cp_2$.[95]

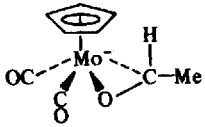
A bridging alkynide **42** is produced in the reaction of $M(CO)_3(CNMe)_3$ (M = Mo or W) with the platinum alkynide $Pt(CCR)_2(PMe_2CH_2PMe_2)_2$.[96]

The isolobal connections of carbynes $W(CO)_2(CR)Cp$ with alkynes and carbene $Cr[C(OMe)Ph](CO)_5$ with alkenes are reviewed.[97] They react with late transition metal centres forming heterobimetallic bridging alkylidene and alkylidyne derivatives, there are many such examples and their chemistry towards species such as nucleophiles protons, alkynes, and metal fragment precursors is prolific.[98-108]

There is kinetic evidence for the transient presence of $Cr(CH_2)(CO)_5$ in the reaction of $Cr[CH_2S(O)Me_2](CO)_5$ with $P(aryl)_3$ whose ultimate products are dimethyl sulphoxide and the phosphonium ylide $Cr(CH_2PPh_3)(CO)_5$.[109]

The tungsten carbene $W(CPh_2)(CO)_5$ undergoes carbonyl substitution under photochemical reaction conditions at $^-60^oC$ with trans cyclooctene giving trans-$W(\eta^2\text{-}C_8H_{14})(CPh_2)(CO)_4$. This geometry is observed since there is no competition for the alkene for backbonding electron density from a trans carbonyl.[110]

Photolysis of $W(CPh_2)(CO)_5$ in the presence of $H_2C=CPh(C_6H_4OMe\text{-}p)$ allows isolation of the metathesised carbene $W[CPh(C_6H_4OMe\text{-}p)](CO)_5$ in a reaction that is suppressed by CO. The reaction probably proceeds by dissociation of a cis CO followed by ligand coordination, and metallacyclobutadiene formation. The purpose of photochemical excitation is the promotion of an electron into the $d_{x^2-y^2}$ orbital, which is antibonding with respect to the cis carbonyls, enhancing the rate of cis CO loss.[111]



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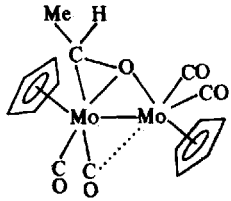

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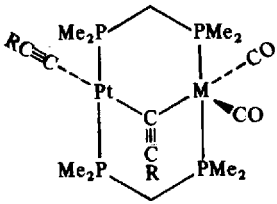
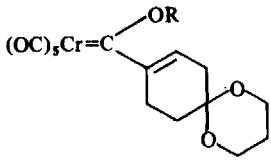


(42) M = Mo, W



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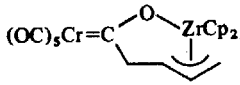

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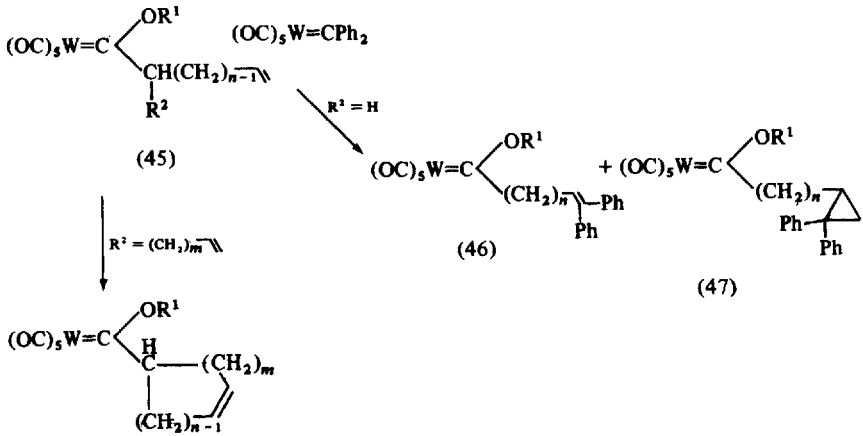


Scheme 3

The carbenes $W(CPhR^1)(CO)_5$ (R^1 = OMe or Ph) are low activity metathesis catalysts for heteroallenes $R^2N{=}C{=}NR^2$ but also undergo stoicheimetric reaction with $R^2N{=}C{=}CNR^2$ (R^2 = Pr^i or cyclohexyl) forming the metathesised complex $W(=C{=}NR^2)(CO)_5$ and $R^2N{=}CR^1Ph$.[112]

Linear correlations in the stoicheoimetric cyclopropanation by $W(CHPh)(CO)_5$ with alkenes in a comparison with the catalytic reactions of $Rh_2(OAc)_4$ suggest a unifying mechanism. Cyclopropanation stereochemistry is determined by interactions in the π-complex and at the ring forming stage.[113]

Organyl cyanates RECN (R = alkyl or aryl, E = O or S) undergo reaction with $W(CPh_2)(CO)_5$ by an insertion reaction leading to the new carbenes $W[C(ER){=}NCPh_2](CO)_5$.[114]

One of the pathways followed during thermolysis of solid $Cr[C(OEt)SiPh_3](CO)_5$ is elimination of $Ph_3SiC(O)Et$ and formation of the arene complex $Cr(CO)_3[n\text{-}C_6H_5SiPh_2C(O)Me]$[115] while thermolysis of $W[C(R)SiPh_3](CO)_5$ (R = OEt or NEt_2) gives Ph_3SiH, C_2H_4, $W(CO)_5L$ (L = CO or CNEt).[116]

Cyclisation of the chromium carbene complex **43** with alkynes is used as part of a strategy to produce an intermediate in the synthesis of anthracyclines relevant to antitumour activity.[117]

The structure of the metallacyclic zirconaoxycarbene **44** which is the result of reacting $Cr(CO)_6$ with $Zr(C_4H_8)Cp_2$ at ambient temperature is similar at the chromium centre to those of other Fischer type carbenes.[118]

Compound **45** (R^2 = H) containing a remote alkene, gives both the metathesised complex **46** and the cyclopropanation product **47** in its reaction with $W(CPh_2)(CO)_5$ (Scheme 3). If the initial carbene complex has two pendant alkenes as in **46** (R = $[CH_2]_3CH{=}CH_2$) then the product is an intramolecular metathesised species **48** whose double bond replaces a carbonyl ligand upon thermolysis.[119]

One of the products from reaction of $W[C(OMe)Ph](CO)_5$ with LiSeCCPh followed by Se_8/HCl is the cyclic carbene $W(CO)_5[\overline{CSeSeC(Ph){=}C}(Ph)]$.[120]

Acidification of the methoxyalkyl $[M\{CH(OMe)(C_6H_4R\text{-}\underline{p})\}(CO)_5]^-$ with $HBF_4.OEt_2$ results in methoxide abstraction and formation of the highly electrophilic carbenes $M[C(C_6H_4R\text{-}\underline{p})H](CO)_5$ (M = Cr, R = OMe; M = W, R = OMe, Me or H). Thermolysis of the W examples result in carbene loss and formation of the bridged alkylidene $W_2(CO)_{10}[\mu\text{-}C(C_6H_4R\text{-}\underline{p})H]$.[121]

Methyllithium or phenyllithium attack the tungsten carbonyl group of **49** resulting in an acyl **50** (Scheme 4) which is alkylated

by Me_3O^+ providing the carbene **51**. Acidification of the acyl does form the hydroxy carbene but the product is unstable over 0°C.[122]

The thermal reaction of $W[C(OMe)(OCH_2R^1)](CO)_5$ (R^1 = H or Me) with alkynes $PhCCR^2$ (R^2 = Ph or Me) in toluene provides vinyl ethers and enones. This reaction probably proceeds via CO loss, alkyne coordination and the intermediacy of $W[C(OMe)(CH_2R^1)CR^2{=}CPh](CO)_4$ which, in turn, undergoes β-exocyclic hydride elimination.[123]

The isonitrile complex $W(CNR)(CO)_5$ is formed in a complex reaction of $W[{=}C(SMe)_2](CO)_5$ with NH_2R. The intermediate is $W[C(SMe)_2NH_2R](CO)_5$ arising from NH_2R attack at the carbene atom which undergoes NH_2R catalysed losses of SMe^-. Related processes are observed for $H_2N[CH_2]_nNH_2$ in which the second amine is contained in a pendant group of the intermediate.[124]

The X-ray crystal structure and spectroscopic data suggest that there is little back-bonding associated with the carbene ligand in $W[C(NHMe)Ph](CO)_5$.[125]

Cyclic aminocarbene thioether chelate complexes containing Cr-S or W-S bonds arise in complicated reactions of $M(CNR)(CO)_4(S[CH_2]_3SCH_2)$ with Bu^nLi, followed by PEt_3, and $[Et_3O]^+$. Variation of the ligands results in carbene $Cr[CS(CH_2)_2S](CO)_5$.[126]

A chromium "nitrene" complex is probably the result of addition of PhN=NPh to the carbene $Cr[C(OMe)Me](CO)_5$ in a photochemical reaction. This is formed by cycloaddition to the carbene followed by metathesis forming the iminoether PhN=C(OMe)Me and the nitrene, inferred by its reaction with acid resulting in $PhNH_2$.[127]

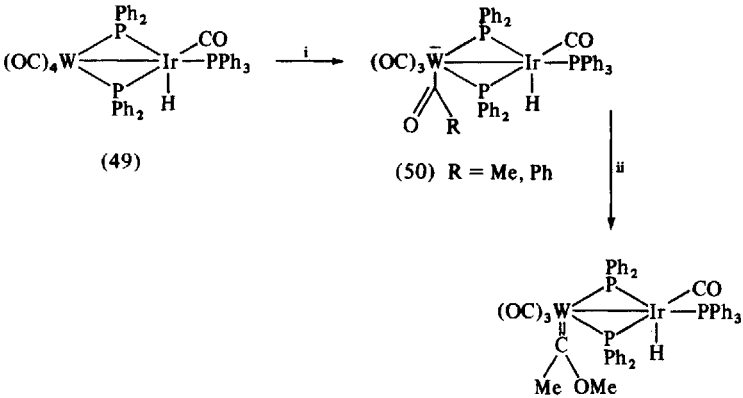
The carbyne complex $W(CO)_2(CNEt_2)Cp$ adds HCl so forming the chlorocarbene complex $WCl(CO)_2[CH(NEt_2)]Cp$.[128]

The carbene $Cr({=}CPh_2)(CO)(NO)Cp$ arises from interaction of $Ph_2C{=}N_2$ with $Cr(CO)(NO)(thf)Cp$. There is no rotation apparent around the Cr=C bond, the Cr=C distance (1.912 Å) is very short, and the carbene plane is nearly coplanar with the N-Cr-C(carbene) fragment. This is different to the situation in a corresponding Mn complex.[129]

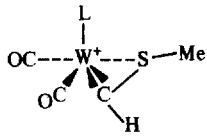
Addition of R^1CCR^1 to $W(SR^2)(CO)_3Cp$ gives among others η^2-vinyls $W(CO)_2[{=}C(R^1)-C(R^1)(COSR^2)]Cp$ (R^1 = CF_3 or CO_2Me).[130]

Treatment of mercaptocarbyne $W(CO)_2(CSMe)[HB(pz)_3]$ with HX (X = CF_3SO_3, BF_4, or CF_3CO_2) results in the formation of X-ray structurally characterised cation **52** containing an η^2-CHSMe ligand. The reaction is reversed by the addition of base.[131]

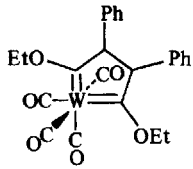
The reaction of the bis-carbene complex **53** with the alkyne



Scheme 4



(52) L = $HB(pz)_3$



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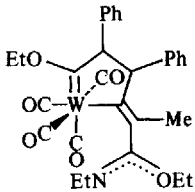

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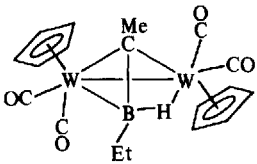


(55)

$MeCCNEt_2$ results in an insertion reaction providing the unsaturated metallacycle **54**.[132]

In an extension of earlier work $M(CO)_6$ reacts with $C_6H_4Li_2$-p followed by $[Me_3O]^+$ providing an intermediate bis carbene $(OC)_5M[C(OEt)C_6H_4C(OEt)]M(CO)_5$ which yields the bis carbyne $MX(CO)_4[CC_6H_4C]MX(CO)_4$ (M = Cr or W) upon treatment with BX_3 at $^-30^oC$. X-ray crystallography and i.r. spectroscopy suggest that the π-electron density is influenced by the carbyne and that it is localised in the ring bonds parallel to the molecule axis.[133]

The carbyne trans-$WX(CO)_4[C(aryl)]$ (X = halide) undergoes halide exchange with halide Y^- following kinetics first order in each of the metal complex and the incoming ligand Y^-. This result is consistent with a nucleophilic frontier orbital controlled attack of Y^- at the metal in the rate determining step.[134] This exchange is accompanied by carbonyl substitution reactions, the latter process results in mer-$[WXY(CO)_3(CC_6H_4R\text{-}p)]^-$ and mer-$[WY_2(CO)_3(CC_6H_4R\text{-}p)]^-$.[135]

Nucleophilic replacement at a terminal methylidyne is observed when $Mo(CO)_2(CCl)L$ [L = $HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3$] reacts with ER^- (E ◘ S or Se). The products are $Mo(CO)_2(CER)L$ and in the case for R = Ph, E = Se represents the first organoselenomethylidyne. Treatment of $Mo(CO)_2(CCl)L$ with E^{2-} (E = S, Se, or Te) yields the anion $[M(CO)_2(CE)L]^-$ which is alkylated by MeI to $Mo(CO)_2(CEMe)L$ (E = S or Te) providing the first organotelluromethylidyne.[136]

The product from the reaction of carbyne trans-$WCl(PMe_3)_4(CH)$ with $AlCl_3$ in C_2Cl_6 is the X-ray crystallographically characterised phosphinomethylidyne $[W_2(CPMe_3)_2(PMe_3)_4(\mu\text{-}Cl)_2Cl_2][AlCl_4]$.[137]

The alkynide $Cr(CCPh)(CO)_3Cp$ undergoes a multistage redox process in its reaction with Na/K alloy in forming the bis-carbyne $Cp(OC)_2Cr[C\text{-}CPh{=}CPh\text{-}C]Cr(CO)_2Cp$.[138]

The cationic carbynes $[Cr(CO)_5(CNR_2)]^+$ arise from BCl_3 treatment of $Cr[C(NR_2)N{=}C(Ph)OMe](CO)_5$ (R = Me, Pr^i, or Ph).[139]

Tungsten carbyne complexes are synthesised from alkynide complexes by double addition of electrophiles. Thus addition of FSO_3Me or Et_3O^+ to $[W(CCBu^t)CO)_5]^-$ leads to the vinylidene $W(=C{=}CBu^tR)(CO)_5$ (R = Me or Et). Addition of CF_3SO_3H/Me_4NI to this vinylidene or directly to the alkynide allows the high yield isolation of trans-$WI(CO)_4[C(CHBu^tR)]$.[140]

Interaction of BH_3.thf with carbyne $W(CO)_2(CMe)Cp$ at ambient temperature provides a ditungsten complex **55** containing a transverse BHEt-CMe group. The ethyl group comes from cleavage of

a CW triple bond.[141]

Two equivalents of HCl add to the carbyne $W(CR)(CO)_2Cp$ with the formation of the η^2-acyl $WCl_2[\eta^2\text{-}C(O)CH_2R]Cp$ (R = Me or C_6H_4Me-p) which is the subject of an X-ray crystallographic analysis.[142]

Addition of S_8 to $ML_2(CR)Cp$ [M = Mo, R = CH_2Bu^t, L = $P(OMe)_3$ or CO; M = W, R = C_6H_4Me-p, L = CO)] results in $\overline{ML_2[S(CR)S]}Cp$ in which the MSCS unit is planar.[143]

Addition of RCCR (R = H, Me, Ph) to the bridging alkylidynes $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ yields $W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3R_2SiMe_3)(CH_2SiMe_3)_4$ which is fluxional in solution and characterised by X-ray crystallography for R = Ph.[144]

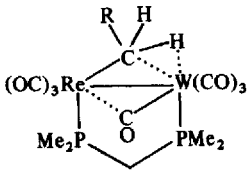
Labelling and n.m.r. experiments suggest that there is an equilibrium between the bridging alkyne complex $W_2(OBu^t)_6(\mu\text{-}HCCH)$ and the alkylidyne species $W(OBu^t)_3(CH)$.[145]

The heterobimetal carbyne species $(OC)_5ReW(CO)_4(\mu\text{-}CR)$ is attacked by hydride from $BH(CHMeEt)_3$ resulting in the anionic bridging alkylidene $[ReW(CO)_9(\mu\text{-}CHC_6H_4Me\text{-}p)]^-$. This anion reacts with $Me_2PCH_2PMe_2$ in the presence of H^+ forming **56** which contains an asymmetric bridging alkyl, confirmed by X-ray crystallography. Compound **56** undergoes $P(OMe)_3$ induced migratory insertion to the bridged acyl **57** in which the acyl is a four electron ligand.[146]

The MoMo triple bond of $Mo_2(OBu^t)_6$ is metathesised upon reaction with PhCCH in pentane with the resulting formation of carbyne $Mo(OBu^t)_3(CPh)$ but the fate of "$Mo(OBu^t)_3(CH)$" is not clear.[147]

Alkynes are metathesised by Mo(VI) alkylidyne complexes, thus reaction of $Mo(CBu^t)[OCMe_2(CF_3)]_3$ with oct-4-yne gives Bu^tCCPr^n and the alkylidyne $Mo(CPr^n)[OCMe_2(CF_3)]_3$ while $Mo(CBu^t)[OCMe(CF_3)_2]3$.dme metathesises but-2-yne eliminating Bu^tCCMe and generating $Mo(CMe)[OCMe(CF_3)_2]_3$.dme. No intermediate molybdenacyclobutadiene intermediates are detectable.[148]

Neopentylidyne $WCl_3(CBu^t)$(dme) reacts with one equivalent of RCCR (R = Me or Et) forming the tungstenacyclobutadiene **58** which in the presence of Bu^tOH gives $\overline{WCl_2(OBu^t)(CBu^tCRCR)}$. Treatment of the last compound with $LiOBu^t$ gives only the alyklidyne $W(OBu^t)_3(CR)$ rather than the expected metallacycle. An excess of MeCCMe with $WCl_3(CBu^t)$(dme) leads to the paramagnetic cyclopentadienyls $WCl_2(\eta^2\text{-}MeCCMe)(\eta\text{-}C_5Me_4Bu^t)$ and $[WCl_4(\eta\text{-}C_5Me_4Bu^t)]_2$.[149] The X-ray crystal structure of **58** indicates the geometry about the metal is trigonal bipyramidal and that the WC_3 system is planar.[150] The alkylidyne WCl_3(CBut)(dme) reacts with LiOR [R = $C_6H_3(Pr^i)_2$-2,6] forming $W(OR)_3(CBu^t)$ which interacts with EtCCEt in a metathetical



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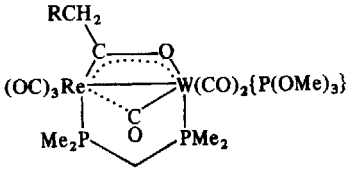

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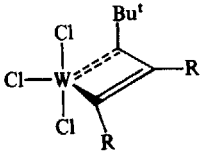

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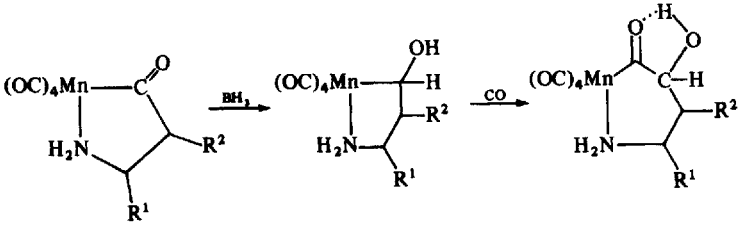
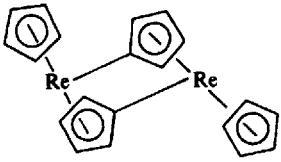


(59) (60) (61)

Scheme 5



(62)

(63)

fashion to Bu^tCCEt and the sterically crowded tungstenacyclobutadiene $W(OR)_3(C_3Et_3)$. The complex $W(OR)_3(CBu^t)$ is a metathesis catalyst for hept-3-yne and non-4-yne.[151]

The reaction of three equivalents of $LiOR^1$ [R^1 = $CH(CF_3)_2$ or $CMe(CF_3)_2$] with alkylidyne $W(CBu^t)Cl_3(dme)$ gives $W(CBu^t)(OR^1)_3(dme)$, each of which react with disubstituted alkynes R^2CCR^2 forming the tungstenacyclobutadiene species $W(CR^2)_3(OR^1)_3$. Both metathesise alkynes very rapidly but the mechanisms differ, for R^1 = $CMe(CF_3)_2$ the mechanism is dissociative but associative for R^1 = $CH(CF_3)_2$ in relatively non-coordinating solvents.[152]

6. Group VIIA (Mn, Tc, and Re)

There is relevant material in a review of the Group VIIA elements for the literature year 1982.[153]

The i.r. spectra of $MMe(CO)_5$ (M = Mn or Re) in the C-H and C-D regions are interpretable in terms of a freely rotating Me group whose individual bond stretching force constants vary during rotation.[154]

Co-condensation of Re atoms, benzene, and alkane (RH) results in alkane activation. The products are dirhenium systems containing bridging hydride ligands and bridging CR^1R^2 whose nature depends upon the alkane. The X-ray crystal structure of the μ-$CHBu^t$ derivative confirms the structural assignments.[155]

One equivalent of BX_3 reacts with $Mn(CF_3)(CO)_5$ with replacement of all three fluorine atoms to form $Mn(CX_3)(CO)_5$ (X = Cl, Br, or I). The order of stability for the complexes is Cl>Br>I. It is also possible to synthesise $Mn(CHX_2)(CO)_5$ or $Mn(CH_2X)(CO)_5$ from the appropriate precursor. Only F atoms alpha to the metal are replaced, thus treatment of $Re(C_2F_5)(CO)_5$ with BX_3 results in $Mn(CX_2CF_3)(CO)_5$ (X = Cl or Br). These reactions appear to go through the intermediacy of dihalocarbenes.[77] The action of aqueous HBF_4 upon $MnCF_3(CO)_5$ results in formation of $[Mn(CO)_6]^+$, the likely intermediate is a dihalocarbene $[Mn(CF_2)(CO)_5]^+$.[78]

The product from the reaction of N-(chloromethyl)phthalimide with $[Mn(CO)_5]^-$ is the alkyl $Mn[CH_2NC(O)C_6H_4C(O)\text{-}o](CO)_5$ which undergoes insertion with CO.[82]

Addition of two equivalents of the alkynide $M(CCPh)(CO)_5$ (M = Mn or Re) with $HOs_3(CO)_{10}(\mu,\eta^2\text{-}CCPh)$ results in a complex cluster $HOs_3M(CO)_{14}(CCPh)_2$ that has been charactised by X-ray crystallographic methods for the Re example.[156]

Stabilisation of the formyls $[Mn(CHO)(CO)_3(PPh_3)_2]^-$, $[ReBr(CHO)(CO)_4]^-$, and $[Re(CHO)(COMe)(CO)_4]^-$ towards metal-hydride formation through CO loss is accomplished by the judicious addition of the radical retarder $Bu^n{}_3SnH$. Although these formyls are not indefinitely stabilised by this reagent the presence of a plateau in a graph of $t_{\frac{1}{2}}$ against $[Bu^n{}_3SnH]$ indicates that subsequent decompositions are by non-chain routes.[75]

The acyl complex $Mn[C(O)CHR(OSiMe_3)](CO)_5$ arises from the reactions of $MnSiMe_3(CO)_5$ with RCHO and CO. Similar reactions employing $\overline{OCH_2[CH_2]_nCH_2}$ (n = 0, 1 or 2) yield $Mn[C(O)CH_2(CH_2)_nCH_2OSiMe_3](CO)_5$, experiments carried out in the absence of CO show that the labile alkyls $Mn[CHR(OSiMe_3)](CO)_5$ or $Mn[CH_2(CH_2)_nCH_2OSiMe_3](CO)_5$ are intermediates.[157]

Decarbonylation results in the reaction of $Re(CO)_5Br$ or $[ReBr(CO)_4]_2$ with $R^1NLiCR^2{=}NR^1$ is decarbonylation and formation of $Re(CONR^1CR^2{=}NR^1)(CO)_4$ (R^1 = aryl, R^2 = Me or Ph).[158]

The manganese acyl **59** reacts with BH_3.thf with reduction of the acyl group generating **60**. A carbonyl group inserts into the metal alkyl bond when subjected to CO pressure, this results in **61** which contains an intramolecular hydrogen bond. The CO insertion is x16 faster than for the corresponding α-$OSiMe_3$ derivative and the hydrogen bonding is proposed to account for this (Scheme 5).[159]

The rhenocene dimer $[ReCp_2]_2$ reacts with $PhCH_2Br$ to give a 1:1 mixture of the η^1-benzyl $Re(\eta^1\text{-}CH_2Ph)Cp_2$ and $ReBrCp_2$ while thermolysis results in the doubly metallated complex **62**.[160]

One of the side products in the reaction of $Mn_2(CO)_{10}$ with <u>cis</u>,<u>trans</u>-hexa-2,4-diene is the metallacycle **63**.[161]

A study on the photochemical reaction of $Re_2(CO)_{10}$ with alkenes at ambient temperatures indicates formation of vinyl complexes $Re_2(\mu\text{-}H)(\mu_2\text{-}\sigma{:}\eta^2\text{-}C_2R^1R^2R^3)(CO)_8$ **64** containing bridging hydride ligands. These molecules are fluxional on the n.m.r. time scale, undergoing rapid interchange of the σ and π bonds. Alkenes are eliminated by donor ligands.[162] The complex $Re_2(\mu\text{-}H)(\mu_2\text{-}\sigma{:}\eta^2\text{-}CHCH_2)(CO)_8$ reacts with ethene under photochemical reaction conditions to form the η^2-vinyl complexes $Re_2(\mu\text{-}H)(\mu_2\text{-}\sigma{:}\eta^2\text{-}CHCHEt)(CO)_8$ and the system is able to catalytically generate but-1-ene and hex-3-ene.[162]

Reduction of the vinyl $Mn(\mu\text{-}PPh_2)(\mu_2\text{-}\sigma{:}\eta^2\text{-}CRCHR)(CO)_7$ (R = H or Ph with $NaBH_4$ results in the anionic crystallographically characterised μ_2-acyl **65** containing a Mn-Mn bond as major product. In turn **65** (R = Ph) reacts with Bu^tNC with Mn-Mn bond cleavage and

CO substitution to form the μ_2-acyl **66** as major product together with a minor bridging μ_2-vinyl **67**.[164]

The dintrogen ligand is displaced by PhCCH from trans-$ReCl(N_2)(dppe)_2$ so forming the alkynide trans-$ReCl(C_2Ph)(dppe)_2$ whose structure is established by X-ray crystallography.[165]

The cation mer-$[Mn(CO)_3(P(OPh)_3)_3]^+$ is transformed to the crystallographically characterised neutral formyl complex mer-$Mn(CHO)(CO)_2[P(OPh)_3]_3$ upon treatment with $KB(OPr^i)_3H$.[166]

The single crystal time-of-flight neutron diffraction study on the metallaacetylacetone complex **68** reveals the presence of an intramolecular O..H..O bond.[167]

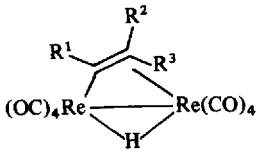
The anion $Mn(MR^1_3)(CO)_2Cp'$ (M = Si or Ge, R^1_3 ◘ Ph_3 or $[C_{10}H_7\text{-}1]PhMe$ reacts with alkyl halides R^2I (R^2 = Me, Et, or benzyl) producing neutral complexes trans-$MnR^2(MR^1_3)(CO)_2Cp'$ reactive towards phosphines.[168]

A series of diazoalkanes $N_2CR^1R^2$ react with $Mn(CO)_2(thf)L$ (L = Cp or Cp' with elimination of N_2 forming the corresponding carbenes $Mn(CO)_2(CR^1R^2)L$. The carbene precursor $C_6H_4[C(N_2)Ph]_2$-p under similar conditions provides a bis-carbene complex. Reaction of the 7-membered carbocyclic carbene **69** with CO results in the η^2-ketene derivative **70**.[169]

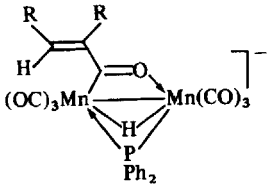
Treatment of $Mn(CO)_2(thf)Cp^*$ with Al_2Te_3/HCl provides a "bare Te" complex μ_2-$Te[Mn(CO)_2Cp^*]_2$ which upon reaction with CR_2N_2 (R = H or Me) provides the unusual **71** containing a μ-η^2-$TeCR_2$ group. Upon heating, compound **71** (R = H) undergoes quantitative CR_2 bridge collapse providing ethene whereas facile carbene isomerisation to propene occurs in the case of **71** (R = Me) upon thermolysis.[170]

The Re acyl $Re(COR)(NO)(PPh_3)Cp$ (R = Me, Ph, or CH_2Ph) reacts with $LiNPr^i_2$ (LDA) followed by MeI to give the Re methyl $ReMe(NO)(PPh_3)(\eta\text{-}C_5H_4COMe)$, a reaction probably proceeding via lithiation at the ring followed by rapid acyl transfer to the ring and alkylation at the metal. On the other hand $Re(CH_2Ph)(NO)(PPh_3)Cp$ under the same conditions gives $Re(CH_2Ph)(NO)(PPh_3)Cp'$; there is no migration of the alkyl group to the initially lithiated ring.[171]

The mechanisms of α-abstraction for $Re(NO)(L)(CH_2R)Cp$ (L = PMe_3, R = Ph; L = PPh_3, R = Ph, C_6H_4Me-o, and mesityl) by $[Ph_3C]^+$ are compared. The pro-R H is abstracted for the CH_2Ph complexes, both the pro-R or pro-S for the C_6H_4Me-o case and exclusively the pro-S H for the mesityl example, explainable in terms of the Curtin-Hammett



(64)



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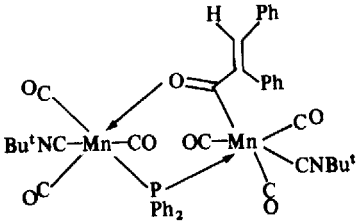

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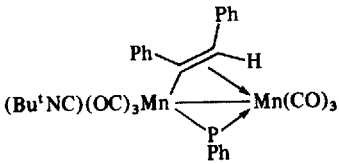

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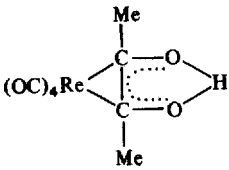

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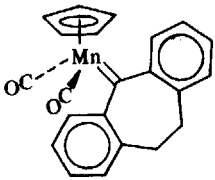

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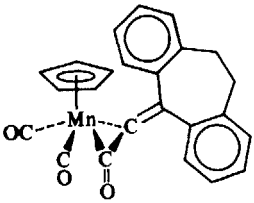

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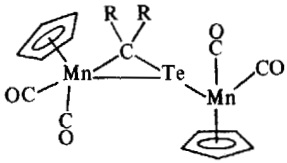
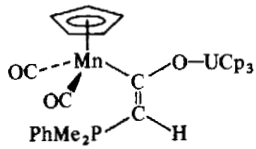
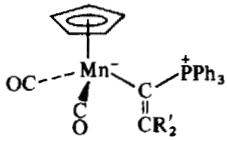


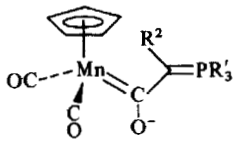
(71) R = H or Me



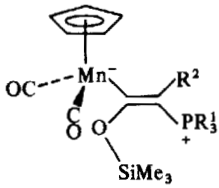
(72)



(73) $R'_2 = Bu^t_2, Ph_2, HR$
[R = CO_2Me, Ph, $C(Bu^t)_2OH$]



(74)



(75)

principle.[172]

The chiral complex (+)-(S)-ReMe(NO)(PPh_3)Cp undergoes loss of methyl in its reactions with HX for a number of X resulting in ReX(NO)(PPh_3)Cp in yields of 63 - 85% and with > 99% retention of configuration at the Re atom.[173]

Treatment of $M_2(CO)_{10}$ (M ◘ Mn or Re) with the dianion $[:C{=}CC(Bu^t)_2O]^{2-}$ results in nucleophilic attack at a carbonyl and formation of $[Mn_2(CO)_9(COC{=}CCBu^t{}_2O)]^{2-}$ which undergoes photolytic decarbonylation yielding the dianionic acetylide $[M_2(CO)_9(C{=}CBu^t{}_2O)]^{2-}$. The main product from reaction of the alkynide with $COCl_2$ is $M(C{=}CCBu^t{}_2OH)(CO)_5$ but the dinuclear allenylidene complexes $Mn_2(\mu\text{-}CO)(\mu\text{-}C{=}C{=}CBu^t{}_2)(CO)_8$ and $(OC)_5ReRe(C{=}C{=}CBu^t{}_2)(CO)_4$ are minor products. The monometallic species are also available from $[:C{=}CC(Bu^t)_2O]^{2-}$ and $MCl(CO)_5$.[174]

Cymantrene, $Mn(CO)_3Cp$, reacts with the uranium carbene complex $U(=CHPMe_2Ph)Cp_3$ by insertion of a Mn carbonyl group into the U=C bond with the formation of the manganese carbene **72**.[175]

Addition of proton acids HX (X = Cl, BF_4, or CF_3CO_2) to $Mn(CO)_2(=C{=}C{=}CR_2)Cp$ (R = Bu^t or Ph) generates the vinyl carbene cation $[Mn(CO)_2(C\text{-}CH{=}CR_2)Cp]^+$, the Mn=C bond is very short at 1.665 Å (R ◘ Ph, X = BF_4). The μ_2-vinylidene $Mn_2(\mu_2\text{-}C{=}CHR)(CO)_4Cp_2$ reacts with HX to form the cation $[Mn_2(\mu_2\text{-}CCH_2R)(CO)_4Cp_2]^+$.[176]

The P atom of PPh_3 adds to the α-carbon atom of the cumulidene ligand of $Mn(CO)_2(=C{=}CHR)Cp$ (R = Ph, CO_2Me, or $C(Bu^t)_2OH$) or $Mn(CO)_2(=C{=}CR^1{}_2)Cp$ (R^1 ◘ Bu^t or Ph) forming the phosphonium ylide **73**.[177]

Photochemical reaction of $Mn(CO)_3L$ (L = Cp or Cp') with $Me_3P{=}CHSiMe_3$ gives the ylide $Mn[CH(PMe_3)SiMe_3](CO)_2L$. On the other hand $Mn(CO)_3Cp'$ reacts with two equivalents of $R^1{}_3P{=}CHR^2$ providing the anion **74**. Addition of Me3SiOSO2CF3 affords the neutral vinyl **75** which in the pure state slowly eliminates Me_3SiOH at ambient temperature forming the β-PMe_3-alkynide $Mn(CCPMe_3)(CO)_2Cp'$.[178]

Reaction of $[Mn(CO)_2(NO)Cp]^+$ with $\overline{YCH_2CH_2}$ provides the cyclic carbene complexes $[Mn(CO)(NO)(\overline{C.O.CH_2CH_2Y})Cp]^+$ (Y = O or NH)[179] while the same reagents with $MnX(CO)_5$ (X = Br or I) give cis-$MnX(CO)_4(\overline{C.O.CH_2CH_2Y})$.[180]

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12

Complexes Containing Metal–Carbon σ-Bonds of the Groups Iron, Cobalt, and Nickel

BY A. K. SMITH

1. Introduction

The format of this chapter follows that adopted in Volume 13 of this series. Thus the chapter is divided into the following four sections: reviews and articles of general interest; metal-carbon σ-bonds of the Group VIII triads in the sequence iron, cobalt, and nickel; carbene and carbyne complexes including complexes containing μ-CH_2 and μ-CH ligands; and a short bibliography giving details of some of the papers that have not been included in the main body of the text due to the continuing pressure on space.

2. Reviews and Articles of General Interest

Reviews published in 1984 cover the photochemistry of alkyl transition metal complexes,[1] carbonyl insertion reactions of square-planar complexes,[2] the preparation and properties, including homolytic and heterolytic Co-C cleavage reactions, of organocobalt compounds,[3] the reactions of alkynes with metal atoms,[4] cyclometallate complexes incorporating a heterocyclic donor atom,[5] μ-(α,ω)-alkanediyl transition metal complexes,[6] transition metal complexes containing μ-alkylidene ligands,[7] carbene complexes in organic synthesis,[8] and the reactions of carbene complexes with unsaturated hydrocarbons.[9] Articles of general interest include a theoretical study of alkyl shifts between transition metals and co-ordinated main group atoms,[10] the role of [2+2] cycloaddition-type reactions in catalysis,[11] dinculear reductive eliminations,[12] M-C and M-M multiple bonds as ligands,[13] a comparison of bonding in molecular cluster carbides with extended metal carbide structures,[14] the reactivity of metal cluster carbides which have an exposed carbon atom,[15] and a review covering n.m.r. studies of the stereodynamics of S-, Se-, and Te- containing ligands in complexes, many of which contain a metal-alkyl bond.[16] A paper describing improved syntheses of a variety of transition metal acetylides has also been published.[17]

[For References see page 285

3. Metal-Carbon σ-Bonds Involving Group VIII Metals

3.1 The Iron Triad. - The gas phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with aliphatic alkanes[18] and cyclic hydrocarbons[19] have been studied. Also in the gas phase, Fe^+ decarbonylates cyclobutanone to generate a stable metallacyclobutane ion.[20] Metallacyclo-hexanes and -heptanes have also been made, and their decomposition has been studied.[20] Photoreversible oxidative addition - reductive elimination reactions have been described for both CH_4 and H_2 with Fe (and Mn) atoms in cryogenic matrices.[21]

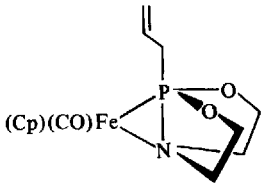
A convenient synthesis of a ferracyclopentane complex involves the reaction of $[Fe(CO)_4]^{2-}$ with tetramethylenebis(trifluoromethanesulphonate).[22] The crystal structure of $[(CO)_4\overline{FeCH_2CH_2CH_2}]$ has been determined.[22] The insertion of CO in $[Fe(CO)_2(PMe_3)_2Me(X)]$ (X=CN, NCS, or I) to give the corresponding acyl complex has been studied by isotopic exchange (with ^{13}CO) measurements and the results explained in terms of a mechanism involving a trigonal bipyramidal intermediate.[23] *Ab initio* LCAO-MO-SCF calculations indicate that $[Fe(CO)_4(COMe)H]$ is thermodynamically more stable than $[Fe(CO)_4Me(CHO)]$, thus providing an explanation for the relative ease of CO insertion into the Fe-H or Fe-Me bond of $[Fe(CO)_4Me(H)]$.[24] The alkyl complexes *cis*-$[Fe(CO)_4(R)(SiMe_3)]$ (R=Me,Et,Bz,$CH_2CH=CH_2$) have been prepared.[25] Studies of the reactivity of these complexes have shown that reduction elimination of $RSiMe_3$ occurs at ambient temperature when R-Me or Bz, and that they react with acylating agents at low temperature to give (silyloxy)carbene complexes $[(CO)_4Fe=C(CH_2R)OSiMe_3]$ which readily undergo a 1,2-hydride shift to give the olefin complex $[(CO)_4Fe(RCH=CHOSiMe_3)]$.[25]

The chemistry of organoiron complexes derived from the complexation of vinyl ethers with $[Fe(Cp)(CO)_2]^+$, in which the complexes behave as vinyl cation equivalents, has been reviewed.[26] Infrared studies have shown that the photoinduced decarbonylation of $[Fe(Cp)(CO)_2(COMe)]$ in a PVC film matrix at 12-200K is thermally reversible, and that the photolysis of $[Fe(Cp)(CO)_2Me]$ leads to the reversible formation of $[Fe(Cp)(CO)Me]$.[27] The solvent dependence of the stereospecificity

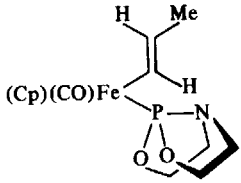
of the insertion of CO into the Fe-C σ-bond in the optically active complexes [Fe(Cp)(CO)(PPh_3)Et] and [Fe(Cp)(CO)(mtpb)Et] [mtpb = $P(OCH_2)_3CMe$] has been investigated.[28] The reaction is catalysed by $BF_3.Et_2O$ with no change in the stereochemistry of the reaction products. In NOMe, NOEt, and MeCN the configuration of the products corresponds to a formal alkyl migration, while in HMPA, Me_2SO, DMF or propylene carbonate, a formal CO migration occurs.[28] In the complexes [Fe(Cp)$(CO)_2(CH_2CH_2R)$](R=Me,Pr^i, or Bu^t) it has been shown that at low temperature in the presence of CO, migratory CO insertion can compete with triphenylcarbenium-induced β-elimination.[29]

The metallation of [Fe(Cp)$(CO)_2$R] [R=Ph,Bz, $(C_5H_4)Mn(CO)_3$] with BuLi followed by treatment with CO_2 yields the carboxylic acid complexes, [Fe(η^5-C_5H_4COOH)$(CO)_2$R].[30] The $LiAlH_4$ reduction of the carbonyl cations [Fe(Cp)(CO)$(L)_2]^+$ (L=PPh_3; L_2=dppp, (+)-DIOP, dppm, dmpe, cis-$Ph_2PCH{=}CHPPh_2$) and [Fe(Cp)$(CO)_2L]^+$ (L=PPh_3, PMe_3) yields the corresponding carbonyl-hydride or -methyl complexes depending upon the electron-donating and chelating abilities of the phosphine ligands.[31] The formation of the carbonyl-methyl complex is favoured by the better electron donating ligand and by the greater chelating ability of the ligand. The hydrido complex [Fe(C_5Me_5)$(CO)_2$H] reduces [Fe(C_5Me_5)$(CO)_3]^+$ to [Fe(C_5Me_5)$(CO)_2$-(CH_2OH)] and further to [Fe(C_5Me_5)$(CO)_2$Me].[32] The repeated deprotonation and alkylation of the complex [Fe(Cp)(CO)(PPh_3)-(=CO $CH_2CH_2CH_2$)$]^+$ has allowed the stereoselective synthesis of quaternary carbon centres to be achieved.[33] The previously assumed most stable conformation of the alkyl complexes [Fe(Cp)(CO)-(PPh_3)R] has been demonstrated to be energetically extremely unfavourable in a conformation analysis study.[34] The cycloaddition of fumaronitrile and maleonitrile to [Fe(Cp)$(CO)_2$(η^1-C_5H_5)] has been shown in a mechanistic study to proceed by a concerted [4π + 2π] cycloaddition pathway.[35]

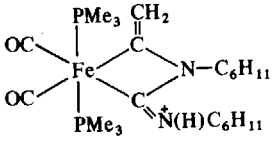
A large range of complexes of the type [Fe(Cp)(CO)(L)(η^1-alkenyl)] have been synthesised by the reaction of [Fe(Cp)(CO)(L)(η^2-alkyne)$]^+$ with a variety of nucleophiles.[36] The η^1-alkenyl complexes [alkenyl = C(Me)=CMe(Ph), C(Me)=C(Me)CH$(CO_2Et)_2$, C(CO_2Me)=C(H)Me, C(Me)=C(H)Ph; L=$P(OPh)_3$] react with oxidising agents such as $[Cp_2Fe]^+$ or Ce(IV) under CO to give the alkenylacyl complexes [Fe(Cp)(CO)L{C(O)C(R)=CR' R"}].[37] Protonation of [Fe(Cp)$(CO)_2$-{C(R)(OEt)(1-norbornyl)}] (R=H or D) with HBF_4 occurs regio-


(Cp)(CO)Fe
P
O
O
N

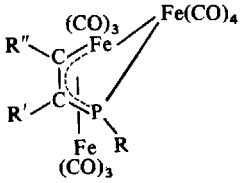
(1)


H
Me
(Cp)(CO)Fe
H
P
N
O
O

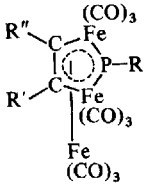
(2)


PMe3
CH2
OC
C
Fe
N—C6H11
OC
C
N(H)C6H11
PMe3

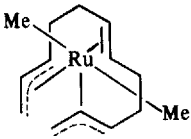
(3)


(CO)3
Fe(CO)4
R"
C
Fe
R'
C
P
Fe
R
(CO)3

(4)


(CO)3
R"
C
Fe
P—R
R'
C
Fe
(CO)3
Fe
(CO)3

(5)


Me
Ru
Me

(6)

selectively to form $[Fe(Cp)(CO)_2(1\text{-norbornylmethylidene})]^+$ which undergoes a ring enlargement to form $[Fe(Cp)(CO)_2(\eta^2\text{-bicyclo-oct-1-ene})]^+$ and finally rearranges to give $[Fe(Cp)(CO)_2(\underline{exo}\text{-}\eta^2\text{-1-R-bicyclo[3.2.1]oct-2-ene})]^+[BF_4]^-$.[38] The iron phosphoramide complex(1) is unstable in solution above 0°C due to conversion into the aminophosphane complex(2).[39] The reaction of $[Fe(CO)_2(PMe_3)_2(Me)I]$ with $C_6H_{11}NC$ gave $[Fe(CO)(PMe_3)_2(COMe)(CNC_6H_{11})I]$ which reacted further with $C_6H_{11}NC$ to give the cationic species $[Fe(CO)_2(PMe_3)_2\{C(=CH_2)NC_6H_{11}C(=NHC_6H_{11})\}][I]$ (3).[40] The product of the reaction between $[Fe(CO)_4]^{2-}$ and PPh_3 in CH_2Cl_2 has been confirmed by X-ray structure analysis as the ylide complex $[Fe(CO)_4(CH_2PPh_3)]$.[41] Ylide complexes of the type $[L_3XFe\overline{CH_2}PMe_2]$ (X=H,Me; L=PMe_3), in addition to the related complexes $[L_2L'Co\overline{CH_2}PMe_2]$ (L=L'=PMe_3; L=PMe_3, L'=CO), $[L_2Me_2Co\overline{CH_2}PMe_2]$, and $[L_3Ni\overline{CH_2}PMe_2]^+$, have been prepared by the treatment of the appropriate phosphine metal halide complexes with $LiCH_2PMe_2$.[42]

The trihaloalkyl complexes $[Fe(Cp)(CO)_2(CX_3)]$ (X=Cl,Br) have been prepared by a halogen exchange reaction between BX_3 and $[Fe(Cp)(CO)_2(CF_3)]$.[43] These complexes are much more reactive with nucleophiles than the corresponding trifluoromethyl derivative.[44] Thus, for example, treatment of $[Fe(Cp)(CO)_2(CCl_3)]$ with NH_3, NH_2Pr^i, or H_2O yields $[Fe(Cp)(CO)_2CN]$, $[Fe(Cp)(CO)_2(CNPr^i)]^+$, or $[Fe(Cp)(CO)_3]^+$, respectively, while the CF_3 analogue is inert to these reagents.[44]

$[Fe_3(CO)_{10}(\mu_3\text{-PR})]$ (R=p-C_6H_4OMe) reacts with alkynes in a thermally activated reaction to give (4), whereas under photochemical conditions (5) is formed.[45] A molecular orbital study of the bonding and reactivity in carbido clusters based on the Fe_4C butterfly structure has been published.[46]

A study of the gas phase reactions of Ru^+, Rh^+, and Pd^+ with ethane has yielded the following bond dissociation energies: $D^o(Ru^+\text{-Me})$ 227±21 KJ mol^{-1}, $D^o(Rh^+\text{-Me})$ 197±21 KJ mol^{-1}, and $D^o(Pd^+\text{-Me})$ 248±21 KJ mol^{-1}.[47]

A benzene C-H bond is activated by the complex $[Ru(C_6Me_6)(PHCy_2)H_2]$ which on irradiation in benzene gives $[Ru(C_6Me_6)(PHCy_2)H(Ph)]$.[48] Treatment of $[Ru_2(O_2CMe)_4Cl]$ or $[Os_2(O_2CMe)_4Cl_2]$ with RMgCl (R=CH_2SiMe_3 or CH_2Bu^t) gives the peralkyl compounds M_2R_6(M=Ru) and $M_2(\mu\text{-}O_2CMe)_2R_4$ (M=Ru,Os).[49] The structure of $[Ru_2(CH_2Bu^t)_6]$ has been determined.[49] The interaction of

$[Ru(C_5Me_5)Cl_2(NO)]$ with $[Al(CH_2R)_3]$ gives the dialkyl complexes $[Ru(C_5Me_5)(NO)(CH_2R)_2]$ (R=H, Me).[50] The thermolysis of the methyl derivative (R=H) in the presence of PMe_3 gives $[Ru(C_5Me_5)(PMe_3)_2(CN)]$, while thermolysis of the ethyl derivative gives the oximate complex $[Ru(C_5Me_5)(PMe_3)_2(ON{=}CHMe)]$.[50] The dialkyl or diaryl complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$ undergo an intramolecular decomposition reaction to yield the ketones R_2CO.[51,52] It is believed that the ketones are formed by reductive elimination from $[Ru(CO)(COR)R(PMe_2Ph)_2]$. Kinetic studies have been carried out on the reactions of Me_3CNC with $[Ru(CO)_2Me(R)(PMe_2Ph)_2]$ (R=Ph, COMe, Me)[53] and $[Ru(CO)_2RR'(PMe_2Ph)_2]$ [R,R'=aryl][54] to yield the acetyl and acyl complexes $[Ru(CO)(CNCMe_3)(COMe)R(PMe_2Ph)_2]$ and $[Ru(CO)(CNCMe_3)(COR)R'(PMe_2Ph)_2]$, respectively.

The treatment of trans-$[RuCl_2(PMe_3)_4]$ with R_2Mg gives either $[Ru(\eta^2\text{-}C_2H_4)(PMe_3)_4]$ or cis-$[RuH(Et)(PMe_3)_4]$ for R=Et, and cis-$[Ru(H)(Pr^n)(PMe_3)_4]$ for R=Pr^n.[55] With trans-$[RuX_2(dmpe)_2]$ (X=Cl, CO_2Me), treatment with Et_2Mg gives cis-$[Ru(Et)_2(dmpe)_2]$ for X=Cl and trans-$[Ru(Et)_2(dmpe)_2]$ for X=CO_2Me.[55] The structure of $[RuH(Et)(PMe_3)_4]$ was confirmed by an X-ray diffraction study. The complexes cis-$[RuCl(Me)(PMe_3)_4]$, $[Ru(CH_2C(Me)_2CH_2)(PMe_3)_4]$, $[Ru(CH_2C_6H_4)(PMe_3)_4]$, and cis-$[\{RuMe(PMe_3)_4\}_2Hg]$ have been synthesised.[56] The reaction of $[Ru(C_5Me_5)(PMe_3)_2Cl]$ with RMgX affords the corresponding alkyl complexes (R=Me, Et, CH_2CMe_3, or CH_2SiMe_3).[57] Treatment of $[Ru(Cp)R(PPh_3)_2]$ (R=Me, Et, Pr) with ethylene (50-150 bar) gives the η^2-ethylenealkyl complexes $[Ru(Cp)(C_2H_4)R(PPh_3)]$.[58] Under lower ethylene pressure, the complexes $[Ru(Cp)R(Ph_2PC_6H_4CH{=}CH_2)]$ are formed, and with $[Ru(Cp)(Ph)(PPh_3)_2]$, the reaction with ethylene affords $[Ru(Cp)H(\eta^2\text{-}PhCH{=}CH_2)(PPh_3)]$.[58] Alkyl cleavage reactions, which are oxidative in nature, of the compounds [Ru(Cp)LL'R] (L,L'=CO, PPh_3; R=Me,Bz) with halogens, HCl, mercury(II) halides and Cu(II) halides, were investigated.[59]

The first ruthenium(IV) methyl complexes have been prepared by the methylation of $[RuCl_2(1\text{-}3{:}6\text{-}7{:}10\text{-}12\text{-}\eta\text{-}C_{12}H_{18})]$ by MeLi or MeMgI to give the methyl derivatives (6) and (7) respectively.[60] Treatment of (7) with CO, Bu^tNC, or phosphites leads to reductive coupling of the Me group and the π-allyl moiety to give π-allylruthenium complexes, $[RuL_3(1\text{-}3\text{-}\eta\text{-}C_{13}H_{21})]$.[61]

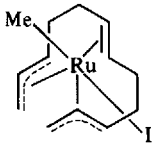
The complex $[Ru_2(PhCONH)_4Cl]$ reacts with PPh_3 to give $[Ru_2Ph_2(PhCONH)_2\{Ph_2POC(Ph)N\}_2]$ in which a phenyl group has been transferred from PPh_3 to the Ru atom.[62]

The reduction of $RuCl_3$ with sodium sand in pure PMe_3 and in a PMe_3/cyclopentene mixture leads to the formation of $[(Me_3P)_3HRu(\mu\text{-}CH_2PMe_2)_2RuH(PMe_3)_3]$ and $[Ru\{\eta'\text{-}C{=}CH(CH_2)_3\}H(PMe_3)_4]$, respectively.[63] The reaction of cis-$[Ru(O_2CMe)Cl(PMe_3)_4]$ with $LiN(SiMe_3)_2$ gives the metallacycle $[Ru(CH_2PMe_2)Cl(PMe_3)_3]$, while cis-$[Ru(O_2CMe)_2(PMe_3)_4]$ reacts with $LiN(SiMe_3)_2$ to give $[Ru(CH_2PMe_2)_2(PMe_3)_2]$.[64] The rhodium complex $[Rh_2(CH_2PMe_2)_2(PMe_3)_4]$ has been prepared in a similar manner.[64]

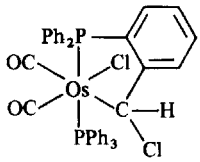
A number of ortho-metallated complexes of ruthenium have been reported. These include $[RuH\{Ph_2PCH_2CH_2P(Ph)C_6H_4\}(dppe)]$,[65] $[Ru\{Ph_2PCH_2CH_2P(Ph)C_6H_4\}_2]$,[65] $[Ru\{(PhO)_2POC_6H_4\}_2\{P(OPh)_3\}_2]$,[66] $[RuH(Ph_2PC_6H_4)(C_6Me_6)]$,[67] $[RuH(CH_2CHMePPr^i_2)(C_6Me_6)]$,[67] and $[RuH(CH_2CMe_2PPh_2)(C_6Me_6)]$ which isomerises to $[RuH(Bu^tPhPC_6H_4)(C_6Me_6)]$.[67]

The organic chemistry at di- and tri- ruthenium centres has been reviewed.[68] The carbido cluster complex $[Ru_4(H)_2C(CO)_{12}]$ has been synthesised via mixed Ru-Au carbido cluster intermediates.[69] The carbido cluster $[Ru_5C(CO)_{15}]$ reacts with LiMe, followed by $[Ph_3PAu][Cl]$ to afford $[Ru_5C(CO)_{14}(\mu\text{-}\eta^2\text{-}MeCO)(AuPPh_3)]$ via attack at a CO ligand, while reaction with NaCp followed by $[Ph_3PAu][ClO_4]$ gives $[Ru_5C(CO)_{13}(Cp)(AuPPh_3)]$ in which the nucleophile has attacked at a metal centre.[70] The structures of the carbido clusters $[Ru_5WC(CO)_{17}(AuPEt_3)_2]$,[71] $[Ru_6C(CO)_{16}(AuPMePh_2)_2]$,[71] and $[AsPh_4][\{Ru_6C(CO)_{16}\}_2Tl]$,[72] have been reported.

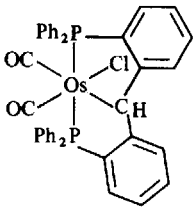
The α-diazoalkylosmium complex $[OsCl(I)(NO)(CN_2CO_2Et)(PPh_3)_2]$ loses N_2 to give, via an intermediate cationic carbyne complex, the complex $[OsCl(I)(NO)(PPh_2C_6H_4CHCO_2Et)(PPh_3)]$, of which the crystal structure has been determined.[73] The complex $[Os(CHF_2)Cl(CO)_2(PPh_3)_2]$ reacts with BCl_3 to give the metallacyclic complex $[OsCl(CO)_2(o\text{-}Ph_2PC_6H_4CHCl)(PPh_3)]$ (8), which undergoes a further reaction with BCl_3 to give $[OsCl(CO)_2(o\text{-}Ph_2PC_6H_4CHC_6H_4PPh_2\text{-}o)]$ (9).[74] Treatment of trans-$[Os(O_2CMe)_2(PMe_3)_4]$ and $[Os_2Cl_2(\mu\text{-}O_2CMe)_4]$ with R_2Mg or RMgX in the presence of PMe_3 generates the alkyl complexes cis-$[OsMe_2(PMe_3)_4]$, $[Os\{(CH_2)_2SiMe_2\}(PMe_3)_4]$, $[OsCl(CH_2PMe_2)(PMe_3)_3]$, and $[Os(CH_2C_6H_4)(PMe_3)_4]$.[75] Treatment of $[Os(CO)_2(PPh_3)_3]$ with $Me_3SiCH_2C(=CH_2)CH_2OAc$, leads to the formation of $[Os_3\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(PPh_3)]$.[76] The ortho-metallated complexes, $[M_2(O_2CMe_2)_2\{Ph_2P(C_6H_4)\}_2X_2]$ (M=Os, X=Cl; M=Rh, X=$MeCO_2H$) have been prepared by treating $[M_2(O_2CMe)_4X_2]$ (M=Os, X=Cl; M=Rh, X=MeOH) with PPh_3 in acetic acid.[77]


Me
Ru
I

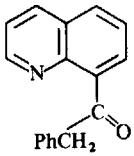
(7)


Ph2P
OC
Cl
Os
OC
C—H
PPh3
Cl

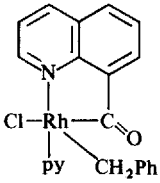
(8)


Ph2P
OC
Cl
Os
OC
CH
Ph2P

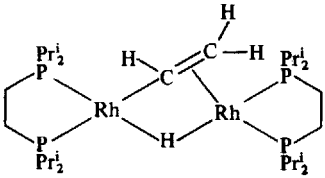
(9)


N
C
O
PhCH2

(10)


N
Cl—Rh—C
O
py
CH2Ph

(11)


H
Pri2
P
H
C
C—H
Pri2
P
Rh
Rh
P
H
P
Pri2
Pri2

(12)

The thermolysis of $[Os_3(CO)_{10}(dppm)]$ in refluxing toluene affords the unsaturated cluster $[Os_3(CO)_8(H)\{Ph_2PCH_2P(Ph)C_6H_4\}]$ in which an ortho-metallated phenyl ring bridges an Os=Os double bond.[78] The carbido clusters $[Os_5C(CO)_{15}]$ and $[Os_5C(CO)_{15}I_2]$ react with alcohols to give derivatives of the type $[Os_5C(CO)_{14}(CO_2R)H]$ and $[Os_5C(CO)_{14}(CO_2R)I]$ (R=Me, Et).[79]

3.2 The Cobalt Triad. - A review of alkylcobalt tetracarbonyls and their derivatives has been published.[80]

In an ion beam apparatus, Co^+ ions react with acetone to form $[CoMe_2]^+$.[81] Similar decarbonylation reactions occur with Fe^+ and Ni^+. Other reactions of Co^+ with aldehydes and ketones producing metal alkyl and metallacyclic products have been studied.[81]

The factors influencing square-planar as opposed to tetrahedral structures in a series of square-planar organocobalt complexes of the type $[CoR_2L_2]$ (R=2,3,4,6-C_6HCl_4 and 2,3,6-$C_6H_2Cl_3$, L=$PEtPh_2$, PEt_2Ph, and PEt_3; R=2,3,5,6-C_6HCl_4 and 2,6-$C_6H_3Cl_2$, L=PEt_2Ph, PEt_3, and ½dppe) have been investigated.[82] The cationic complex $[Co(C_5Me_5)Et\{P(p\text{-tolyl})_3\}]^+$ is formed on protonation of $[Co(C_5Me_5)(C_2H_4)\{P(p\text{-tolyl})_3\}]$.[83] In this cationic ethylcobalt complex there is a strong 3-centre interaction between the metal and a β-C-H, as indicated by ^1H and ^{13}C n.m.r. and a single crystal X-ray study.[83] Treatment of $[CoBr(Cp)(\eta^3\text{-allyl})]$ with RLi or RMgX leads to the formation of the organylcobalt complexes $[Co(Cp)(\eta^3\text{-allyl})R]$ (R=Me,Et,Ph,Bz, $CH{=}CH_2$, CH_2SiMe_3).[84] The cobaltacyclopentadiene complexes $[Co\{CH{=}CHCH{=}CH\}(\eta\text{-}C_5H_4R)(PPh_3)]$ (R=CO_2Me, COMe) have been prepared by treatment of $[Co(\eta\text{-}C_5H_4R)(PPh_3)_2]$ with acetylene.[85] Novel dinuclear complexes $[(\eta\text{-}C_5H_4R)Co(PPh_2C_6H_4)(\mu\text{-}CMe)Co(\eta\text{-}C_5H_4R)]$, are also formed in this reaction.[85] $[Mg(ClO_4)_2]$ acts as a catalyst for the alkyl transfer reaction from cis-$[CoR_2(bipy)][ClO_4]$ (R=Me, Et) to p-benzoquinone derivatives.[86]

The interaction of azidotrimethylsilane with mer-$[CoMe_3(PMe_3)_3]$ gives tetramethylsilane and the azido complex $[CoMe_2(N_3)(PMe_3)_3]$, of which the crystal structure has been determined.[87] The azido complexes $[RhMe_2(N_3)(PMe_3)_3]$, $[IrMe_2(N)_3(PMe_2Ph)_3]$, and cis-$Ru(N_3)_2(PMe_3)_4$ were obtained in a similar manner.[87] Treatment of mer-$[CoMe_3(PMe_3)_3]$ with p-$MeC_6H_4N_3$ leads to the formation of $[CoMe_2(MeNNNp\text{-tolyl})(PMe_3)_2]$, in which the triazenido group appears to be bidentate.[87]

A structural characterisation of the cobalt(III) B_{12} model compound, trans-adamantylbis(dimethylglyoximato)(1-methylimidazole) cobalt(III), has shown that it has a very long Co-C bond of 2.154(5)Å.[88] Alkyl transfer reactions between Cr^{2+} and $[CoR(dmgBF_2)_2(H_2O)]$ (R=Me,Et,Bz,CH_2OMe) have been studied,[89] and the bond dissociation enthalpy of the Co-C bond in $[Co(Bz)(dmgBF_2)_2(H_2O)]$ was found to be 100 ± 12 KJ mol^{-1} by a unimolecular thermal homolysis study.[89] The Co-C bond dissociation energy of coenzyme B_{12} has been determined to be 109 ± 8 KJ mol^{-1} using an adaptation of the kinetic approach previously developed to determine Co-C bond dissociation energies of alkylcobalt Schiff base compounds.[90] The crystal structures of trans-bis(2,3-butanedione dioximato-N,N') (imidazole-N^3)methylcobalt(III),[91] trans-$[Co(mpyim)(Hdmg)_2Et]$ (mpyim=methyl4-pyridine-carboximidate; Hdmg=dimethylglyoximate monoanion),[92] and formylmethyl(tetraphenylporphinato)cobalt(III)[93] have been determined.

The carbido clusters $[Co_3Ni_9C(CO)_{20}]^{3-}$,[94] $Co_6(\mu_6\text{-}C_2)(\mu\text{-}CO)_6(CO)_8(\mu_4\text{-}S)$,[95] and $[Co_6Ni_2C_2(CO)_{16}]^{2-}$,[96] have been synthesised and structurally characterised by X-ray crystallography.

A review of cis-alkyl- and cis-acyl- rhodium and iridium hydrides as model intermediates in homogeneous catalysis has been published.[97] The use of rhodium complexes in the activation of C-H bonds continues to provide much interst. Infrared spectroscopic studies have shown that the photolysis of $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M=Rh, R=Me; M=Ir, R=Me,H) in CH_4 matrices at 12K leads primarily to $[M(\eta^5\text{-}C_5R_5)(CO)(H)(Me)]$.[98] A plenary lecture on the addition of C-H bonds in methane and higher alkanes to soluble rhodium and iridium complexes has appeared.[99] The u.v. irradiation of $[Rh(C_5Me_5)(PMe_3)H_2]$ in alkanes below -30°C leads to the formation of $[Rh(C_5Me_5)(PMe_3)(R)(H)]$ (R=Et,Pr^n, Pr^i, cyclopropyl, Ph, n-hexyl, cyclopentyl, cyclohexyl).[100] Treatment of the alkylrhodium complexes with $CHBr_3$ gave the corresponding bromide complexes $[Rh(C_5Me_5)(PMe_3)(R)(Br)]$, which reacts with Br_2 to give $[Rh(C_5Me_5)(PMe_3)Br_2]$ and bromoalkane.[100] The cyclopropyl derivative $[Rh(C_5Me_5)(PMe_3)(c\text{-}C_3H_6)(H)]$ decomposes above 0°C, not only to regenerate cyclopropane, but in a competitive reaction, the rhodacyclobutane complex $[Rh(CH_2CH_2CH_2)(C_5Me_5)(PMe_3)]$ is formed.[101] The octaethylporphyrinrhodium dimer $[Rh(OEP)]_2$ reacts with arylmethyl C-H bonds to produce octaethylporphyrinbenzylrhodium compounds.[102] A series of alkyl or aryl hydride complexes $[Rh(C_5Me_5)(PMe_3)(R)(H)]$ have been prepared by the

reactions of the corresponding bromide with [Li][$HBBu_3$] or [Na][$H_2Al(OCH_2CH_2OMe)_2$] or by the photochemical reaction of alkane or arene with the dihydrido complex [$Rh(C_5Me_5)(PMe_3)H_2$], (R=Me, Ph, p-tol, 3,4-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$, 2,5-$C_6H_3Me_2$, and $\overline{C{=}CHCH_2CH_2{-}CH_2}$).[103] The aryl complexes were found to be in rapid equilibrium with their η^2-arene derivatives at temperatures above -15°C. It was also found that the Rh-Ph bond is approximately 54 KJ mol^{-1} stronger than the Rh-Me bond in these complexes.[103] The aryl derivatives [$Rh(C_5Me_5)(PR'_3)(R)X$] (X=Cl,Br,I; R = a wide variety of substituted aryl groups) show hindered rotation about the Rh-C bond, with $\Delta G^{\ddagger}$ being insensitive to the nature of the para substituent but dependent on both the halide, X, and the phosphine ligand.[104] The crystal structure of [$Rh(C_5Me_5)(PMe_3)(Ph)Br$] was determined.[104]

The dimer [$RhCl(C_2H_4)_2]_2$ induces C-C bond cleavage in ketone(10) to produce, after reaction with pyridine, the acylbenzylrhodium (III) complex (11).[105]

[$Rh(2,4,6\text{-}Me_3C_6H_2)(CO)(PPh_3)_2$] reacts with $P(OMe)_3$ to give cis-[$Rh(2,4,6\text{-}Me_3C_6H_2)\{P(OMe)_3\}_2(PPh_3)$] and [$Rh(2,4,6\text{-}Me_3C_6H_2)\{P(OMe)_3\}_3$].[106] The reactivity of a number of organorhodium and -iridium complexes towards CO_2[107] and carboxylic acids[108] has been investigated. Thus, for example, [$Rh(4\text{-}MeC_6H_4)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$] reacts with CO_2 to give the peroxocarbonatorhodium complex, mer-[$\overline{Rh(4\text{-}MeC_6H_4)(OOC(O)O)}\{PhP(CH_2CH_2CH_2PPh_2)_2\}$][107] and with aliphatic and aromatic carboxylic acids to yield the carboxylatorhodium complex, [$Rh(O_2CR)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$].[108]

The reaction of [$Rh(PPh_3)_3$][$HC(SO_2CF_3)_2$] with MeI leads to the formation of [$RhI_2(Me)(PPh_3)_2$], a complex that has been shown to have an extensive acid-base chemistry.[109] The oxidative addition of MeI to [$Rh(CO)_2I_2]^-$, the rate determining step in the carbonylation of methyl acetate and methyl halides, has been shown to be promoted by iodide and bases such as 1-methylimidazole.[110] The activation parameters for this reaction have been determined in a number of different solvents. The kinetics and mechanism of the oxidative addition of MeI to [Rh(β-diketone)(CO)(PPh_3)] has been studied, and the rate constant for metal-acyl to metal-alkyl conversion (methyl migration) was determined.[111]

The rhoda- and irida-cyclopentane complexes [$\overline{M(CH_2CH_2CH_2CH_2)}$-($C_5Me_5$)($PPh_3$)] (M=Rh, Ir) undergo β-H abstraction on treatment with the trityl cation to give a σ-3-butenyl intermediate which is

transformed into the η^3-1-methallyl derivative $[M(\eta^3\text{-}CH_2CHCHMe)(C_5Me_5)(PPh_3)][BF_4]$.[112]

Ethylene reacts with the electron-rich hydrido complex $[\{Rh(Pr^i_2PCH_2CH_2PPr^i_2)\}_2(\mu\text{-}H)_2]$ to give the bridging vinylhydride derivative(12).[13]

When the trans dimethyl complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ is treated with acid in the presence of MeCN, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(MeCN)]PF_6$ is formed.[114] N.m.r. studies show that this cationic complex exists as a mixture of cis and trans isomers at -80^oC, and that dynamic behaviour at higher temperatures corresponds to an intramolecular migration of the methyl group from one Rh to the other. Other alkyl complexes such as $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)X]$ (X=Cl or I) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(R)(MeCN)]$ (R=Et,Pr^n, or Bu^n) have also been prepared and show similar dynamic behaviour.[114]

The carbido cluster $[Rh_{14}C_2(\mu\text{-}CO)_{21}(CO)_{12}]^{2-}$ has been synthesised by the interaction of $[Rh_6C(CO)_{15}]^{2-}$ with $[Rh(CO)_2(MeCN)_2]^+$.[115]

Further studies on the activation of C-H bonds in alkanes using $[Ir(C_5Me_5)(PMe_3)(H)_2]$ have been reported.[116] Thus, it was estimated from reversible C-H insertion/reductive elimation reactions that the Ir-C bond energy in the primary complex $[Ir(C_5Me_5)(PMe_3)(H)(n\text{-pentyl})]$ is 23 KJ mol^{-1} stronger than the secondary Ir-C bond in $[Ir(C_5Me_5)(PMe_3)(H)(cyclohexyl)]$. This led to the successful preparation of the hydridomethyl complex $[Ir(C_5Me_5)(PMe_3)(H)(Me)]$ by heating the thermodynamically less stable complex $[Ir(C_5Me_5)(PMe_3)(H)(cyclohexyl)]$ under 20 atm. CH_4 at 140-150^oC.[116] 1,1-dimethyl-cyclopentane reacts with $[IrH_2(Me_2CO)_2L_2]^+$ to form $[Ir(\eta^4\text{-}C_5H_4Me_2)L_2]^+$ (L=P(p-$FC_6H_4)_3$] which rearranges on heating to give $[Ir(\eta^5\text{-}C_5H_4Me)(Me)L_2]^+$, thus providing the first case of homogeneous C-C bond cleavage starting from an alkane.[117]

Determination of kinetic deuterium isotope effects in the oxidative additions of MeI and $MeOSO_2CF_3$ to $[IrCl(CO)(PPh_3)_2]$ show that they are consistent with a Menschutkin-type S_N2 displacement mechanism for this process.[118] The reaction of MeI to $[Ir(CO)(PPh_3)(\mu\text{-}pz)]_2$ (pz=pyrazolyl) is a two-centre oxidative addition to $[(PPh_3)(Me)(CO)Ir(\mu\text{-}pz)_2Ir(PPh_3)(CO)I]$.[119]

The hydroxymethyl complex $[Ir(CH_2OH)(MeCN)(PMe_3)_4][PF_6][BF_4]$ is formed by treating $[IrH(CHO)(PMe_3)_4][PF_6]$ with HBF_4 in acetonitrile.[120] The MeCN ligand undergoes base-catalysed attack by the O atom of the hyroxymethyl group to give the metallacycle

$[Ir\{CH_2OC(Me)=NH\}(PMe_3)_4][PF_6][BF_4]$.[120] The methoxymethyl complex $[Ir(CH_2OMe)(\underline{p}\text{-tol-C}\equiv\text{C-}\underline{p}\text{-tol})(PMe_3)_3]$ reacts with $SiBrMe_3$ to afford the metallacyclobutene complex <u>fac</u>-$[Ir\{CH_2C(\underline{p}\text{-tol})=C(\underline{p}\text{-tol})\}Br(PMe_3)_3]$.[121]

The preparation of organoiridium(I) complexes of the type $[Ir(CO)(R)(\underline{chel}\text{-}P_3)]$ ($\underline{chel}\text{-}P_3=PhP(CH_2CH_2CH_2PPh_2)_2$, $R=CH_2CMe_3$, CH_2SiMe_3; $\underline{chel}\text{-}P_3=MeP(CH_2CH_2CH_2PPh_2)_2$, $R=CH_2SiMe_3$; $\underline{chel}\text{-}P_3=PhP(CH_2CH_2PPh_2)_3$, $R=CH_2SiMe_3$, $4\text{-}MeC_6H_4$) has been reported.[122] The reaction of $Bu^t{}_2PCH_2CHCH_2CH_2$ with $[IrCl(C_8H_{14})_2]_2$ produces the σ-cyclopropane complex $[IrCl(H)(PBu^t{}_2CH_2CHCH_2CH)(PBu^t{}_2CH_2CHCH_2CH_2)]$, which isomerisesin polar solvents to give the σ-vinyl complex $[IrCl(H)\{PBu^t{}_2CH_2C(Me)\ CH\}(PBu^t{}_2CH_2CHCH_2CH_2)]$.[123] The structure of the σ-cyclopropyl complex $[IrCl_2(C_3H_5)(CO)(PMePh_2)_2]$ has been determined.[124] The reaction of $[IrCl(C_8H_{14})_2]_2$ with $PPr^i{}_3$ and $PhC\equiv CPh$ gives the two isomers <u>trans</u>-$[IrCl(\eta^2\text{-}PhC\equiv CH)(PPr^i{}_3)_2]$ and $[IrH(Cl)(C\equiv CPh)(PPr^i{}_3)_2]$.[125] <u>Trans</u>-$[IrCl(PhC\equiv CPh)(PPr^i{}_3)_2]$ reacts with NaCp to give $[Ir(Cp)(PhC\equiv CPh)(PPr^i{}_3)_2]$ which is transformed by treatment with CF_3COOH via the σ-vinyl complex $[Ir(Cp)\{C(Ph)=CHPh\}(OOCCF_3)(PPr^i{}_3)]$ into the iridaindene derivative (13).[125]

The complex $[\{(C_5Me_5)IrMe_3\}_2AlMe]$, prepared from the reaction of $[\{(C_5Me_5)Ir\}_2Cl]$ with Al_2Me_6, reacts with ligands L ($L=PPh_3$ or C_2H_4) to give $[(C_5Me_5)IrMe_2L]$ and with acetone to give $[\{(C_5Me_5)IrMe\}_2(\mu\text{-}CH_2)_2]$.[126] Also, $[\{(C_5Me_5)IrMe_3\}_2AlMe]$ is oxygenated by air to give the iridium(V) complex $[(C_5Me_5)IrMe_4]$. Other methyliridium complexes reported include $[\{(C_5Me_5)Ir\}_2Me(Cl)(\mu\text{-}CH_2)_2]$ and $[\{(C_5Me_5)Ir\}_3(\mu_3\text{-}CH)_2]$.[126] The He-I and He-II photoelectron spectra of $[Ir(C_5Me_5)Me_2(Me_2SO)]$ and $[(C_5Me_5)IrMe_4]$, among a number of other complexes, have been reported.[127]

The methyliridium complex $[(CO)_4W(\mu\text{-}PPh_2)_2IrMe(CO)(PPh_3)]$ undergoes coupling of the methyl and phosphido ligands on heating to 110°C to afford the mono-phosphido bridged complex $[(CO)_4(PPh_2Me)W(\mu\text{-}PPh_2)Ir(CO)(PPh_3)]$.[128] The photochemistry of $[MCl(L)_2]_2$ (M=Ir or Rh;L= 2-phenylpyridine or benzoquinoline) has been investigated.[129]

<u>3.3 The Nickel Triad</u>.- The chemistry of square-planar dialkyl complexes of Ni,Pd, and Pt has been reviewed.[130] A theoretical study of the breaking of a C-H bond in CH_4 on both discrete transition metal complexes and Ni and Ti surfaces has been published.[131]

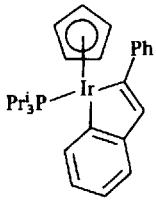
A molecular orbital analysis of the addition of neutral ligands to <u>cis</u>-$[NiR_2L_2]$ complexes, which promotes the reductive elimination of R-R, has been carried out showing how the fifth ligand affects

the elimination step.[132] The alkyl derivatives trans-[Ni(CH_2CMe_3)-Cl(PMe_3)$_2$], [Ni(R)(NCS)(PMe_3)$_2$] (R=CH_2CMe_3, $COCH_2CMe_3$), and [Ni(R)(Cp)L] (L=PMe_3, R=CH_2CMe_3, $COCH_2CMe_3$; L=PPh_3, R=CH_2CMe_2Ph) have been prepared by treating [$NiCl_2$(PMe_3)$_2$] with [Mg(CH_2CMe_3)Cl], and, for the acyl complexes, subsequent reaction with CO.[133] The dialkyl derivatives, [NiR_2(dmpe)] (R=CH_2SiMe_3, CH_2CMe_2Ph) were obtained by phosphine replacement of pyridine or TMED in the corresponding [Ni(CH_2SiMe_3)$_2$(py)$_2$] and [Ni(CH_2CMe_2Ph)$_2$(TMED)] complexes.[133] The insertion of PhC≡CH into the Ni-COR bond of [Ni(COR)Cl(PMe_3)$_2$] (R=Me,CH_2SiMe_3, CH_2CMe_3, and CH_2CMe_2Ph) to give [Ni{C(Ph)=C(H)(COR)}Cl(PMe_3)$_2$] takes place readily, and in the case of the R=CH_2CMe_2Ph complex, a rearrangement occurs in solution to yield the nickelacyclopropane complex [Ni{C(Ph)(PMe_3)C(H)($COCH_2$-CMe_2Ph)}Cl(PMe_3)].[134]

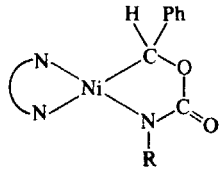
The molecular structures of trans-[Ni{C_6H_3(OMe)$_2$-2,6}$_2$(PR_3)$_2$] (PR_3=PMe_3,PMe_2Ph) and their m-brominated derivatives trans-[Ni{C_6H(OMe)$_2$-2,6-Br_2-3,5}$_2$(PR_3)$_2$] have been determined and show the effect on the conformation of the o-OMe groups of m-Br substitution.[135]

Thermolysis of trans-[Ni(CCl=CCl_2)(C_6H_4Y)(PMe_3)$_2$] (Y=NMe_2-4, Me-4, Me-3, or Cl-4) yields the isomeric complexes trans-[Ni{C_2Cl_2(C_6H_4Y)}Cl(PMe_3)$_2$], the products expected from reductive elimination followed by oxidative addition.[136] The complexes trans-[NiCl(chlorovinyl)(PPh_3)$_2$] have been prepared by the oxidative addition of Cl_2C=CCl_2, Cl_2C=CHCl, trans-HClC=CHCl, and CH_2=CCl_2 to [Ni(PPh_3)$_n$].[137] The addition takes place at the less hindered C-Cl bond with retention of geometry. The action of bidentate N-donor ligands on the chlorovinylnickel complexes leads to the formation of [$NiCl_2$(LL)] and [NiC_2Cl_3)$_2$(LL)] (LL=bipy or phen).[137] Treatment of nickelocene with RLi in the presence of alkenes (C_2H_4 or C_3H_6) gives the organonickel complexes [Ni(Cp)-(R)(alkene)] (R=Me,Et,Pr^n,Pr^i,Ph,CH_2SiMe_3, cyclopropyl, etc).[138]

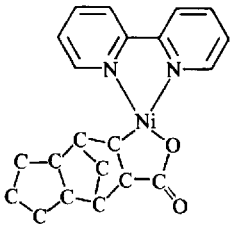
Oxazanickelacyclopentanones (14) are formed by the coupling of isocyanates with benzaldehyde in the presence of cyclododecatrienenickel(0) and a basic ligand such as TMED or bipy.[139] Some properties of these nickelacylic complexes are reported. Nickelacarboxylates are formed on reaction of 1,2-dienes[140] or 1,3-dienes,[141] in the presence of CO_2, with nickel(0) complexes. With alkenes or alkynes in the presence of CO_2, nickel(0)


Ph
Ir
Pr^i_3P

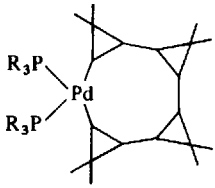
(13)


H
Ph
C
O
N
Ni
N
N
C
O
R

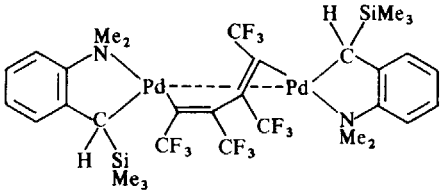
(14)


N
N
Ni
O
C
O

(15)


R_3P
Pd
R_3P

(16)


Me_2
N
Pd
C
H
Si
Me_3
CF_3
CF_3
CF_3
CF_3
Pd
H
$SiMe_3$
C
N
Me_2

(17)

complexes react to give oxanickelacyclopentanones and oxanickelacyclopentenones, respecively.[142] The 5-membered nickelacyclic complex (15) is formed by the reaction of CO_2 and dicyclopentadiene at the complex moiety [Ni(bipy)].[143]

The oxidative addition of cyclic carboxylic anhydrides to metal(0) complexes leads to the formation of [LNiCHRCHR'COO] (L=dppe or bipy; R,R'=H or Me) and [L_nPtCOCH$_2$CH$_2$COO] (L=PCy_3 or dppe; n=1 or 2).[144] The oxidative addition of aryl halides, RX (R=Ph, 2,3-, 2,6-, or 3,5-$C_6H_3Cl_2$, 2-MeC_6H_4; X=I, Br) to [$NiBr(PPh_3)_3$] has been investigated.[145] A kinetic study of the oxidative addition of RC_6H_4CN (R=H, m-CN, p-CN) to [$Ni(DEPB)_2$] [DEPB=1,4-bis(diethylphosphino)butane] gives [$Ni_2(\mu\text{-DEPB})_2(RC_6H_4)_2(CN)_2$] and [$Ni(\eta^1\text{-DEPB})(RC_6H_4)(CN)$] by a template mechanism leading to the fission of a C-CN bond.[146]

The preparation of a number of dialkylpalladium(II) complexes of the type cis - or trans-[$PdR_2(PMe_3)_2$] and cis-[PdR_2(dmpe)] (R=Me, Bz, CH_2CMe_2Ph, CH_2SiMe_3) from the interaction of magnesium reagents with Pd(II) acetate or trans-[$Pd(O_2CMe)(PMe_3)_2$] has been reported.[147] The neopentyl complexes [$Pd(CH_2CMe_3)_2L_2$] (L_2=dppe, bipy; L=PMe_2Ph) have also been prepared by the alkylation of the corresponding dichlorides with [$Mg(CH_2CMe_3)Br$] or [$LiCH_2CMe_3$].[148] Some reactions of these complexes have been studied. The palladacycle [Pd($CH_2CMe_2CMe_2CH_2$)(dppe)] has also been prepared by treating [$PdCl_2$(dppe)] with [$Li(CH_2CMe_2CMe_2CH_2)Li$].[148] The structure of the 9-membered palladacycloalkane(16) has been determined.[149]

The thermolysis of [$PdX(Me)(PEt_3)_2$] (X=Br,I,CN; Me=CH_3,CD_3) produces methane, ethane, and ethene in ratios which vary with temperature.[150] The methane is mainly formed by intramolecular abstraction of hydrogen from PEt_3, while ethane and ethene are produced by P-Et bond cleavage.[150]

Pd-C bond cleavage occurs on reaction of [$Pd(CH_2SR)(PPh_2R')X$] (R,R'=Me or Ph, X=Cl,Br,I, or SCN) with excess CF_3CO_2H or HCl to give [$Pd(PPh_2R')X(A)$] (A=CF_3CO_2 or Cl) and MeSR',[151] although reaction with alkyl halides leads to halide (or pseudohalide) exchange and no Pd-C bond cleavage.[152]

A number of new pentafluorophenylpalladium complexes have been synthesised and some of their properties investigated. New complexes include cis-[$Pd(C_6F_5)_2L_2$] (L=o- and p-aminophenol, o- and p- anisidine, p-phenylenediamine, 2- and 4-cyanopyridine, and

allylamine),[153] trans-$[Pd(C_6F_5)(PEt_3)_2(S_2CPEt_3)][ClO_4]$,[154] $[Pd(C_6F_5)_3(CNR)]^-$ (R=p-tolyl, Me, Cy, Bu^t),[155] $[\{(C_6F_5)Pd(\mu\text{-dppm})_2\text{-}Pd(C_5F_5)\}_2(\mu,\mu'\text{-}CNC_6H_4NC)]$,[156] and $[(\mu\text{-}X)\{Pd(C_5F_5)L_2\}\{Pd(C_6F_5)\text{-}L'_2\}][ClO_4]$ (L,L'=P- or N-donor ligand, X=CN,SCN,N_3, or halide).[157] A series ofpolynuclear pentafluorophenylpalladium-gold complexes have been prepared by reaction of $[PdRR'(\eta^1\text{-dppm})_2]$ (R=R'=C_6F_5, C_6Cl_5; R=C_6F_5,R'=Cl) with the gold complexes [AuCl(tht)], $[Au(C_6F_5)_3(tht)]$, $[Au(C_6F_5)(tht)]$, or $[Au(O_3ClO)(PPh_3)]$ (tht=tetrahydrothiophen).[158]

The mono- and di-organopalladium complexes trans-$[PdR(X)L_2]$ (R=Me,Et,Ph; X=Cl,Br,I, and aryloxo; L=tertiary phosphine) react with CO and secondary amines to produce α-keto amides.[159]

The mechanism of the intramolecular acetylene insertion reaction of $[PdClL_2\{C(O)O(CH_2)_nC{\equiv}CMe\}]$ [L=PPh_3, n=2,3; L=P(p-tol)$_3$, n=2] to give the vinyl complexes $[PdClL_2\{C(Me){=}\overline{CCH_2CH_2OC(O)}\}]$ has been studied.[160] U.V. photoelectron spectra of trans-$[MXY(PEt_3)_2]$ (M=Pd,Pt; X=Y=-C≡CH,-C≡CMe,CN; X=Cl,Y=CN) and molecular orbital calculation on the model compounds trans-$[MXY(PH_3)_2]$ (M=Pd; X=Y=-C≡CH,-C≡CMe,CN; X=Cl,Y=CN) have been reported.[161] The results demonstrate a strong π-interaction between the metal and filled acetylide orbitals both in- and out-of-plane, but no metal-ligand π-back-bonding.

As in previous years, numerous cyclopalladated ligands have been reported. Among the ligands to undergo such cyclopalladation reactions are 1,3-bis(2-pyridyl)propane,[162] 4-methyl-4'-nitrodibenzyl sulphide,[163] N-(benzylidene)benzylamines,[164] P(o-tolyl)$_3$,[165] 2-benzylpyridine,[166] and a new method for the preparation of cyclopalladated benzalimines has also been reported.[167] Reactions involving cyclopalladated ligands include the oxidation of the C-Pd bond in cyclopalladated azobenzenes into the C-OPd function by m-chloroperbenzoic acid,[168] the insertion of isocyanides into the Pd-C bond of cyclopalladated benzylamine,[169] CO insertion in cyclopalladated benzylideneaniline Schiff's bases,[170] the reaction of various cyclopalladated dimers of the type $[\overline{Pd(C^{\frown}N)}Cl]_2$ with carbonylmetalate anions $\{[Co(CO)_4]^-$, $[Fe(CO)_3(NO)]^-$, and $[M(CO)_3(Cp)]^-$ (M=Cr,Mo,W)$\}$ to give chloro-bridged trimetallic complexes,[171] and the exchange of cyclopalladated ligands with free ligand to afford new metallacycles.[172] $[Pd\{CH(SiMe_3)C_6H_4NMe_2\text{-}2\}R']$ [R'=2-(dimethylamino)methylphenyl, 8-methylquinoline) reacts with

$CF_3C{\equiv}CCF_3$ to give selective asymmetric oxidative coupling of the cyclopalladated organo groups leading to the formation of the novel unsymmetrical dinuclear palladium complex (17).[173] The first mixed metal cyclometallated compounds, $[ClPd\{p\text{-}RC_6H_3CH{=}N\text{-}N{=}CH\text{-}(p\text{-}RC_6H_3)\}PtCl]_n$ (R=H,Cl) have been prepared.[174]

A multinuclear n.m.r. study of the organoplatinum compounds $[Pt(COD)(XC_6H_4)_2]$, cis-$[Pt(PBu^n_3)_2(XC_6H_4)_2]$ (X=H,4-Me,4-Bu^t, 4-NMe_2, 3-F,4-F,4-OMe,4-CF_3), trans-$[Pt(PBu^n_3)_2(4\text{-}MeOC_6H_4)_2]$, and trans-$[Pt(PBu^n_3)_2(4\text{-}CF_3C_6H_4)_2]$ has shown a clear correlation of the coupling constants [$^1J(^{195}Pt^{31}P)$, $^nJ(^{195}Pt^{13}C)$, $^nJ(^{195}Pt^1H)$, and $^2J(^{195}Pt^{13}C)$] and the ligand configuration so that the data may be used as a basis for the determination of configuration.[175] A number of new substituted aryl derivatives of platinum(II) have been reported, including trans-$[Pt(PPh_3)_2\{2,6\text{-}(OMe)_2C_6H_3\}_2]$,[176] trans-$[Pt(PPh_3)_2\{2,4,6\text{-}(OMe)_3C_6H_2\}_2]$,[176] cis-$[Pt(PPh_3)_2(C_6H_4X\text{-}2)(C_6H_4Y)]$ (X=CF_3, Y=H, 2-OMe, 3-OMe, 4-OMe, 2-Me, 3-Me, 4-Me, 3-CF_3, 4-CF_3; X=NMe_2, Y=H, 2-OMe),[177] cis-$[Pt(PPh_3)_2(C_6H_4X\text{-}2)_2]$ (X=CF_3, Me, NMe_2, NO_2, F),[178] cis- and trans-$[PtH(C_6Cl_5)(PEt_3)_2]$, cis- and trans-$[Pt(SnCl_3)(C_6Cl_5)(PEt_3)_2]$,[179] $[PtCl(C_6F_5)_3]^-$,[180] and $[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]^{2-}$.[180] The first mononuclear platinum(III) complex $[NBu_4][Pt(C_6Cl_5)_4]$ has been prepared and characterised by X-ray crystallography.[181] A full paper describing the synthesis and reactivity of hydridomethyl and hydridoaryl complexes, trans-$[PtH(R)L_2]$ (R=Me or aryl, L=tertiaryphosphine) has been published.[182] Spectroscopic data providing evidence for a cis influence of aryl groups that is opposite in effect to their trans influence in arylplatinum(II) complexes of the types trans-$[PtX(C_6H_4Y)(PEt_3)_2]$ and $[Pt(C_6H_4Y)(PEt_3)_3][BF_4]$ (X=H or Br, Y= one of a wide range of electron-withdrawing or -releasing substitutents in the meta or para position to Pt) has been presented.[183] The molecular structures of trans-$[PtCl(Ph)(PPh_3)_2]$ [184] and trans-$[PtCl(Me)(PEt_3)(AsPh_3)]$[185] have been determined. The preparation of complexes of the type $[PtR_2(bipym)]$ [bipym=2,2'-bipyrimidyl; R=Me, CF_3, Ph, 1-adamantylmethyl; $R_2=(CH_2)_4$] and $[R_2Pt(\mu\text{-bipym})PtR'_2]$ (R=R'=Me, Ph,1-adamantylmethyl; R=Me, R'=Ph,CF_3,1-adamantylmethyl) has been described.[186] The complexes trans-$[PtCl(R)(PMe_3)_2]$ [R=(1-methylcyclobutyl)methyl, adamantylmethyl, 4-methylpentyl-1,1-d_2, or 4-methyl-4-pentenyl) have been prepared and their decomposition reactions have been studied.[187]

Tetrafluoroethylene reacts by insertion into the P-O bond in [Pt(Me)(OMe)(dppe)] to give $[Pt(Me)(CF_2CF_2OMe)(dppe)]$, which has

been characterised by X-ray crystallography.[188] Reversible alkene insertion into the Pt-alkyl bond in the chelated alkylalkene platinum complex(18) occurs on heating to give the rearranged product (19).[189] p-Chlorophenyl isonitrile inserts into the Pt-H bond in [Pt(dmpe)H(Me)] to give exclusively the E-iminomethylcomplex [Pt(dmpe)(Me){C(H)=NC$_6$H$_4$Cl-4}].[190] The complexes trans-[PtCl(H)-{P(OMe)$_3$}$_2$] and trans-[PtCl(H){PMe(OMe)$_2$}$_2$] react with methyl acrylate to give the insertion products cis-[PtCl{CH(Me)CO$_2$Me}L$_2$].[191] [Pt$_2$(μ-Cl)$_2$(PEt$_3$)$_2$(SnCl$_3$)$_2$] undergoes an insertion reaction with hexafluorobut-2-yne to give [Pt$_2$(μ-Cl)$_2$(PEt$_3$)$_2${C(CF$_3$)=C(CF$_3$)-SnCl$_3$}$_2$].[192] The complexes [PtMe$_2$L$_2$] (L$_2$=bipy or phen) react with alcohols ROH (R=Me,Et,Pr^i) or water(R=H)to give [PtMe$_2$(OR)L$_2$(OH$_2$)]$^+$ [OH]$^-$.[193]

The activation parameters for the reductive elimination of 4,4'-dimethyloxybiphenyl from cis-[Pt(C$_6$H$_4$OMe-4)$_2$(PPh$_3$)$_2$] and a series of derivatives with various substituents on the phenyl groups of the PPh$_3$ ligands have been determined, and show a marked dependence on the electronic character of these substituents.[194] The addition of PPh$_3$ or P(OEt)$_3$ to [PtBr(CH$_2$CH$_2$OPh)(PPh$_3$)$_2$] has been shown accelerate β-aryloxy group elimination by platinum to liberate ethene.[195] The mechanism of the hydrogenolysis of [Pt(CH$_2$CMe$_3$)$_2$-(PEt$_3$)$_2$] to give neopentane and [PtH$_2$(PEt$_3$)$_2$] has been investigated.[196] A preliminary study of β-H elimination from cis-[PtCl(R)(PEt$_3$)$_2$] (R=Pr^n or Bu^n) has been published.[197]

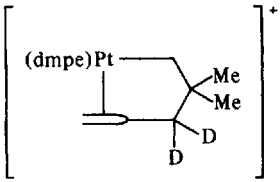
Several new platinacyclic complexes have been reported. These include [Pt{PPh$_2$(2-C$_6$H$_4$CH$_2$)}LL'][BF$_4$] [L=PPh$_3$, L=PPh$_3$ or P(C$_6$H$_4$Me-4)$_3$],[198] [Pt{CHRC(O)CHR}L$_2$] (R=CO$_2$Me, CO$_2$Et, or CO$_2$Pr^n; L=tertiary phosphine or arsine),[199] and [Pt(CH$_2$CH$_2$CH$_2$)(I)$_3$(py)]$^-$.[200]

The complexes cis-[Pt(C≡CR)$_2$(PPh$_3$)$_2$] [R=C(OH)Me$_2$, C(OH)MeEt, CH(OH)Ph, or Ph] are obtained from the reaction of cis-[PtCl$_2$-(PPh$_3$)$_2$] with HC≡CR in 30% aqueous ammonia.[201] When chloroform-diethylamine is used as solvent, the complexes trans-[PtCl(C≡CR)-(PPh$_3$)$_2$] [R=CH$_2$OH, CH(OH)Me, C(OH)Me$_2$, C(OH)MeEt, C$_6$H$_{10}$OH, or CH$_2$NEt$_2$] are obtained.[201] Reactions between cis-[PtCl$_2$(CO)L] (L=PMePh$_2$) and [Hg(C≡CR)$_2$] (R=Me or Ph) lead first to [PtCl(C≡CR)-(CO)L] [L trans to (C≡CR)], then to cis-[Pt(C≡CR)$_2$(CO)L], and finally to [PtCl(C≡CR)(CO)L] (L trans to Cl), showing that treatment of the bis(ethynyl)platinum complexes with HgCl$_2$ specifically removes the ethynyl trans to L.[202] Similarly, treatment of cis-[Pt(Ph)$_2$(CO)L] with HgCl$_2$ or cis-[PtCl$_2$(^{13}CO)L] results in the

specific replacement by Cl of the phenyl group trans to L.[203] By contrast, the ethynyl complex cis-$[Pt(C{\equiv}CPh)_2(CO)L]$ reacts with cis-$[PtCl_2(CO)L]$ to form $[PtCl(C{\equiv}CPh)(CO)L]$ with Cl trans to L.[203] Complexes of the type trans-$[Pt(C{\equiv}CR)_2(PEt_3)_2]$ (R=Me,Bu^n, or Ph) react with LiR'(R'=Bu^n, Bu^t, or Ph) in hydrocarbon solvents to give the dinuclear complexes $[Pt_2(C{\equiv}CR)_4(PEt_3)_2(R')_2(\mu\text{-}Li)_2]$.[204] In the presence of donor solvents, trans-$[Pt(C{\equiv}CR)_2(PEt_3)R']^-$ is formed which reacts further with LiR' (R'=Bu^n) to give cis-$[Pt(C{\equiv}CPh)(PEt_3)(Bu^n)_2]^-$.[204]

Among the new bidentate phosphine complexes of platinum reported are the first methyldiplatinum(I) complexes, $[Pt_2Me(L)(\mu\text{-dppm})_2]^+$ (L=η^1-dppm, PPh_3, PMe_2Ph),[205] $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ (R=Me,Et, Ph),[206] and $[LPt(\mu\text{-I})(\mu\text{-}Me_2PCH_2PMe_2)_2PtMe_3][I_3]$ (L=0.45I + 0.55Me).[207] The reductive eliminations of H_2,CH_4, and C_2H_6 on photolysis of $[Pt_2H(\mu\text{-H})Me(\mu\text{-dppm})_2]^+$, $[Pt_2(\mu\text{-H})Me_2(\mu\text{-dppm})_2]^+$, and $[Pt_2Me_3(\mu\text{-dppm})_2]^+$, respectively, have been shown to be primarily intramolecular by isotopic labelling studies.[208] The metallacycle $[Pt(CH_2CH_2CH_2CH_2)(dppm)]$ reacts with dppm to give $[Pt(CH_2CH_2CH_2CH_2)(\eta^1\text{-dppm})_2]$, and this complex containing monodentate dppm ligands has been used to prepare a number of bimetallic complexes.[209] In a similar manner, several bimetallic complexes have been synthesised using monodentate dppm acetylide complexes of the type trans-$[Pt(C{\equiv}CR)_2(\eta^1\text{-dppm})_2]$.[210,211] The complex $[MePt(\mu\text{-dppm})_2PtMe]^{2+}$ reacts with terminal alkynes to give a μ- η^2-$HC{\equiv}CR$ complex which readily deprotonates to give the μ-η^1-$C{\equiv}CR$ complex $[MePt(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CR)PtMe]^+$ (20), whereas for the bimetallic platinum-rhodium complex the acetylide is σ-bonded to the Pt and π-bonded to the Rh in the complex(21).[212]

The first binuclear tetramethylplatinum(IV) complex $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$, has been prepared by treating $[PtCl_2(SMe_2)_2]$ with excess MeLi and MeI.[213] This complex reacts with donor ligands L, to give cis-$[PtMe_4L_2]$ (L_2=dppm,dppe,bipy,phen, or L=PMe_2Ph, $PMePh_2$).[213] The organoplatinum(IV) complexes $[PtMe_3X(NN)$ (X=Cl,I,OAc,NO_3; NN=bidentate N-donor ligand) and $[PtMe_3(NNN)][PF_6]$ [NNN=tris(1-pyrazolyl)methane or tris(2-pyridyl)methane] have been prepared.[214] Further work on the synthesis of organoplatinum(IV) complexes from $[PtCl_6]^{2-}$ has been published.[215-219] Thus, ^{13}C and ^{195}Pt n.m.r. spectral data for a number of previously reported σ-aryl complexes of Pt(IV) have been reported.[215] The kinetics of the thermal reaction of $[PtCl_6]^{2-}$ with various aromatic



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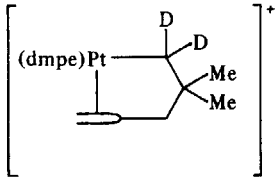

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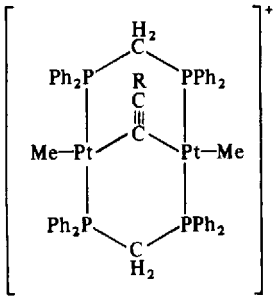

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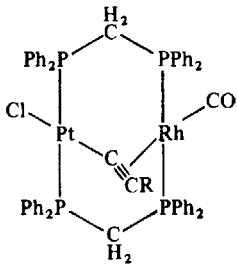

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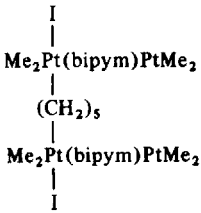
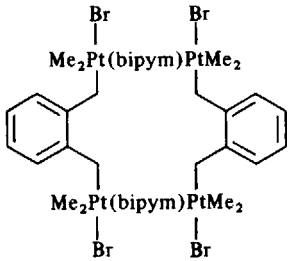


(22)



(23)

compounds in CF_3COOH/H_2O or CH_3COOH have been studied.[216] Irradiation of a $[PtCl_6]^{2-}$ solution in acetone affords the σ-acetonyl complex $[Pt(CH_2COMe)Cl_5]^{2-}$,[217] and the photoinduced or thermal reaction of $[PtCl_6]^{2-}$ with Me_4Sn in CH_3COOH or acetone affords $[Pt(Me)Cl_5]^{2-}$.[218] Aryl derivatives of Hg, Sn, Pb, or B react with $[PtCl_6]^{2-}$ to give σ-arylplatinum complexes.[219]

A series of tetranuclear complexes, such as (22) and (23) have been synthesised by means of the trans oxidative addition of α,ω-dihalogenoalkanes to dimethylplatinum(II) complexes.[220]

4 Carbene and Carbyne Complexes of the Group VIII Metals

4.1 The Iron Triad.- The reaction of $[Fe(CO)_4(C{=}C{=}Bu^t_2)]$ with PPh_3 results in the formation of the ylide complex $[Fe(CO)_4\{C(PPh_3){=}C{=}CBu^t_2\}]$.[221] $[(CO)_4Fe\{\mu\text{-}C{=}C{=}CBu^t_2\}Fe(CO)_4]$ reacts with PPh_3 to give $[(CO)_3(PPh_3)Fe\{\mu\text{-}C{=}C{=}CBu^t_2\}Fe(CO)_3L]$ (L=CO or PPh_3), and with pyridine to give (24).[221] The reaction of $[Fe(CO)_4\{{=}C(OEt)R\}]$ (R=Bu^n, Bu^t, Ph) with alkynes $R^1C{\equiv}CR^2$ gives 6-ethoxy-α-pyrone iron tricarbonyl complexes via a ferracyclobutene intermediate.[222] The reaction of $[Fe(CO)_5]$ with $LiNPr^i_2$ and subsequent treatment with Et_3OBF_4 gives $[Fe(CO)_4\{C(NPr^i_2)OEt\}]$ and the cyclic carbene complex $[(CO)_3Fe\{C(NPr^i_2)OCOEt\}]$.[223] When the carbene complex $[Fe(CO)_3(PPh_3)\{C(NPr^i_2)(OEt)\}]$ is treated with BCl_3 at -100°C, the carbyneiron cation $[Fe(CO)_3(PPh_3)(CNPr^i_2)]^+$ is produced.[224] The reactive intermediate $[Fe\{CSC_2(CO_2Me)_2S\}(CO)_2(PMe_2Ph)_2]$ is stabilised by the addition of $HgCl_2$ which leads to the formation of the bimetallic carbene complex $[Cl_2HgFe\{CSC_2(CO_2Me)_2S\}(CO)_2(PMePh_2)_2]$.[225]

Loss of alkene stereochemistry upon cyclopropane formation occurs during the transfer of ethylidene from $[(Cp)(CO)_2Fe{=}CHMe]^+$ to a series of para-substituted styrenes to give cis- and trans-1-(parasubstituted phenyl)-2-methylcyclopropanes.[226] An investigation of diastereomeric equilibria in vinylidene complexes of the type $[(Cp)Fe(C{=}CHR)(L\text{-}L)][PF_6]$ (L-L= a chiral diphosphine; R=Me, Bu^t, Ph) has been reported.[227] Nucleophilic addition reactions to the cationic carbene complexes $[Fe(CO)(Cp)(PPh_3)({=}CROMe)]^+$ (R=H, Et) are highly stereoselective. The product diastereoisomers $[Fe(CO)(Cp)(PPh_3)(CHEtOMe)]$ undergo epimerisation in MeOH prior to the formation of (E)-$[Fe(CO)(Cp)(PPh_3)(CH{=}CHMe)]$.[228] The cationic carbene complexes $[Fe(CO)(Cp)(PPh_3)(\text{methoxycarbene})]^+$

are stereoselectively deprotonated to (Z)-methoxyvinyl complexes, as shown by the crystal structure of {Z)-[Fe(CO)(Cp)(PPh$_3$){C-(OMe)=CHMe}].[229]

The vinylcarbene complexes [Fe(CO)$_2$(Cp)(=CHCH=CMe$_2$)]$^+$.[230] and [Fe(CO)(Cp)(L)(=CHCH=CRCH$_2$R')]$^+$ [L=CO or P(OMe)$_3$; R=H,R'=Me or R=Me,R'=H)[231] have been prepared and reacted with alkenes to give vinylcyclopropanes. The reaction of [Fe(CO)(Cp)(PPh$_3$)(=C=CMe$_2$)]$^+$ with R$_2$Cu(CN)Li$_2$ (R=Ph, CH=CH$_2$) leads to addition at the vinylidene α-carbon atom to produce the alkenyliron complexes [Fe(CO)-(Cp)(PPh$_3$)(η^1-C(R)=CMe$_2$)][232]. The unsymmetrical vinylidene complex [Fe(CO)(Cp)(PPh$_3$){C=C(Ph)Me}]$^+$ reacts with Me$_2$Cu(CN)Li$_2$ to produce a 93:7 ratio of the Z:E isomers of [Fe(CO)(Cp)(PPh$_3$)-{η^1-C(Me)=C(Ph)Me]].[232] The carbene complex [Fe(Cp)(PMe$_3$)$_2$(=C-(OMe)Me}][X] [X=SO$_3$F, Cp(CO)$_3$W,Cl] has been prepared by treating [Fe(Cp)(PMe$_3$)$_2$(C(OMe)=CH$_2$}] with HSO$_3$F, [HW(CO)$_3$(Cp)], or MeCOCl, respectively.[233] [Fe(Cp)(PMe$_3$)$_2$(C(OMe)=CH$_2$}] also adds CS$_2$ to give [Fe(Cp)(PMe$_3$)$_2$(=C(OMe)CH$_2$CS$_2$}] which may be methylated with MeI to give [Fe(Cp)(PMe$_3$)$_2$(=C(OMe)CH$_2$C(S)SMe}][I].[233]

The cyclic carbene complexes [M=$\overline{\text{COCH}_2\text{CH}_2\text{NH}}$]$^+$ and [M=$\overline{\text{COCH}_2\text{CH}_2\text{O}}$]$^+$ [M=Fe(CO)$_2$(Cp), Ru(CO)$_2$(Cp), or Fe(CO)(Cp)(PPh$_3$)], [M=$\overline{\text{CSCH}_2\text{CH}_2\text{NH}}$]$^+$, and [M=$\overline{\text{CSCH}_2\text{CH}_2\text{S}}$]$^+$ [M=Fe(CO)$_2$(Cp)] has been synthesised by treating the appropriate cationic metal complex with aziridine, oxirane, or thiirane.[234] New carbeneporphyriniron complexes in which the carbene ligand is substituted by two electron-donating substituents have been prepared by reacting [Fe(Por){C(Cl)R }] (Por = TPP or TTP; R=Me or Pr^i) with alcohols or thiols.[235]

Treatment of [Fe$_2$(μ-CH$_2$)(CO)$_8$] with NaOMe gives an unstable methylmetalla-acetate complex which on warming gives [Fe(CO)$_4$-(CH$_2$COOMe)]$^-$, indicating an interaction of the μ-CH$_2$ group with a CO ligand.[236] The reaction of the μ-vinylidene complexes cis- and trans-[Fe$_2$(Cp)$_2$(CO)$_2$(μ-CO)(μ-C=CH$_2$)] with CH$_2$N$_2$ gives the μ-cyclopropylidene complexes cis- and trans-[Fe$_2$(Cp)$_2$(CO)$_2$-(μ-CO)(μ-$\overline{\text{CCH}_2\text{CH}_2}$)].[237] The M=M double bonded complexes [(Cp)Fe(μ-NO)$_2$Fe(Cp)] and [(C$_5$Me$_5$)M(μ-CO)$_2$M(C$_5$Me$_5$)] (M=Co,Rh) react with formyldiazomethane to give formyl-substituted dimetallacyclopropanes, [(Cp)(NO)Fe{μ-CHCH(O)}Fe(NO)(Cp)] and [(C$_5$Me$_5$)(CO)M-{μ-CHCH(O)}M(CO)(C$_5$Me$_5$)].[238] The reaction of [Fe$_2$(CO)$_2$(Cp)$_2$-(μ-CO)(μ-CH)]$^+$ with cis-2-butene has been shown by deuterium labelling experiments to occur via hydrocarbation by equilibration to give cis-[(Cp)$_2$(CO)$_2$Fe$_2$(μ-CO){μ-CCH(Me)CH$_2$(Me)}]$^+$ and a mixture

of (E) and (Z) isomers of cis-$[(Cp)_2(CO)_2Fe_2(\mu\text{-}CO)\{(E)\text{- or }(Z)\text{-}\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(Me)CH_2(Me)\}]^+$.[239] $[Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)H\}]^-$ reacts with Et_3OBF_4 to yield $[Fe_2(CO)_6(\mu\text{-}COEt)\{\mu\text{-}C(Ph)C(Ph)H\}]$ which is transformed at room temperature to $[Fe_2(CO)_6\{\mu\text{-}C(OEt)C(Ph)C(Ph)H\}]$ by intramolecular coupling of the ethoxycarbyne and 1,2-diphenylethenyl ligands.[240] A preliminary account of the organic chemistry of the Fe-Ru centre has been published.[241]

The electrochemical reduction of $[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CMe)][PPh_4]$ gives the μ_3,η^2-propynolate complex $[Fe_3(CO)_9(\mu_3,\eta^2\text{-}MeC{\equiv}CO)][PPh_4]$.[242] The reaction between H_2 and $[Fe_3(\mu\text{-}H)(CO)_{10}(\mu_3\text{-}CMe)]$ to give $[Fe_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CMe)]$ and CO has been shown to be an equilibrium process.[243] The reaction of $[Fe_4(CO)_{12}(CMe)]^-$ with HSO_3CF_3 in CH_2Cl_2 gives $[HFe_4(CO)_{12}(CMe)]$, while in neat HSO_3CF_3, another proton adds to the metal framework producing $[H_2Fe_4(CO)_{12}(CMe)]$.[244]

The propionyl ruthenium complex $[RuCl\{C(O)Et\}(CO)(PPh_3)_2]$ reacts with HCl to yield the hydroxycarbene complex $[RuCl_2\{C(OH)Et\}(CO)(PPh_3)_2]$.[245] The crystal structure of the ruthenium-carbene complex $[RuCl_2\{{=}C(F)OCH_2CMe_3\}(CO)(PPh_3)_2]$ has been determined,[246] and the fluorochlorocarbene complex $[OsCl_2(CFCl)(CO)(PPh_3)_2]$ has been prepared from the reaction between $[OsCl_2(CCl_2)(CO)(PPh_3)_2]$ and $[Cd(CF_3)_2(DME)]$.[246]

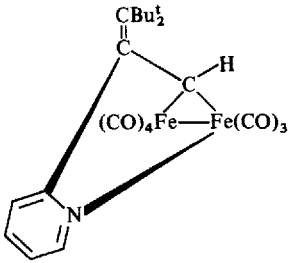
The μ-methylene complex $[(Cp)(NO)Ru(\mu\text{-}CR_2)Ru(NO)(Cp)]$ has been prepared by treating the new Ru=Ru double-bonded complex $[(Cp)Ru(\mu\text{-}NO)]_2$ with CR_2N_2 (R=H,Me).[247] Preliminary results show a considerable effect on the organic chemistry at diruthenium centres on changing from $\eta\text{-}C_5H_5$ to $\eta\text{-}C_5Me_5$ ligands with several new organic transformations being observed.[248] The μ-alkylidene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)(Cp)_2]$ (R=H,Me,Et, or Ph) have been prepared by heating $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(Cp)_2]$ with the ylide $Ph_3P{=}CHR$.[249] A number of reactions of these complexes are reported together with the crystal structure $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(Cp)_2]$.[249] Protonation of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(Cp)_2]$ yields $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3(Cp)_2]^+$ as cis and trans isomers which interconvert on the n.m.r. time scale.[250] Protonation of $[Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)(Cp)_2]$ gives $[Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_3)(Cp)_2]^+$ in a similar reaction, but in solution this converts into the μ-methyne cation $[Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH)(Cp)_2]^+$.[250] The complex $[Ru_3H(CO)_{10}(CH)]$ has been prepared by treatment of

$[Ru_3H(CO)_{10}(COMe)]$ with $LiHBEt_3$ at low temperature. The product rearranges readily into $[Ru_3H_2(CO)_9(CCO)]$.[251] One of the products of the u.v. irradiation of $[Ru_2(CO)_4(Cp)_2]$ is the tetranuclear complex $[Ru_4(CO)_6(\mu_3\text{-}C_5H_4)_2(Cp)_2]$ (25), in which the $\mu_3\text{-}C_5H_4$ ligand was characterised by an X-ray diffraction study on the derivative $[Ru_4(CO)_5\{P(OMe)_3\}(\mu_3\text{-}C_5H_4)_2(Cp)_2]$.[252]

The methylene complexes $[Os(=CH_2)Cl(NO)(PPh_3)_2]$ and $[Ir(=CH_2)I(CO)(PPh_3)_2]$ react with SO_2 to form the C,O-bound sulphene complexes $[Os\{CH_2S(O)O\}Cl(NO)(PPh_3)_2]$ and $[Ir\{CH_2S(O)O\}I(CO)(PPh_3)_2]$, respectively.[253] The co-condensation of Os atoms with mesitylene forms the dimers $[\{(\eta^6\text{-}C_6H_3Me_3)Os(\mu\text{-}H)\}_2\{\mu\text{-}C(H)C_6H_3Me_2\text{-}3,5\}Os(\eta^6\text{-}C_6H_3Me_3)]$ and $[\{(\eta^6\text{-}C_6H_3Me_3)Os(\mu\text{-}C(H)C_6H_3Me_2\text{-}3,5\}Os(\eta^6\text{-}C_6H_3Me_3)]$.[254]

Treatment of $[Os_3(CO)_{12}]$ with $k[BH(OPr^i)_3]$ at 0^oC gives an unstable formyl complex $K[Os_3(CO)_{11}(CHO)]$, which on acidification with H_3PO_4 yields the μ-methylene cluster $[Os_3(CO)_{11}(\mu\text{-}CH_2)]$.[255] Methane is produced when $[Os_3(CO)_{11}(\mu\text{-}CH_2)]$ is heated under H_2,[255] and the reaction with CO gives the ketene complex $[Os_3(CO)_{12}\{\eta^2\text{-}(\underline{C},\underline{C}),\mu_2\text{-}CH_2CO\}]$.[256] X-ray and neutron diffraction studies on $[Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9]$ have been carried out, and the vibrational frequencies of methylidyne hydrogen and hydride hydrogen were calculated.[257] The μ-carbyne complexes $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}CCH{=}CMe_2)(CO)_{10}]$ have been synthesised.[258] On thermolysis, the μ-carbyne complex $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ rearranges to the μ-vinyl complex $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHCHMe_2)(CO)_{10}]$ and the μ-vinylidene complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C{=}CHCHMe_2)(CO)_9]$.[258] The μ-vinyl clusters $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHR)(CO)_{10}]$ (R=H,Bu^n, or Ph) react with PMe_2Ph to give the zwitterionic μ-alkylidene complexes $[Os_3(\mu\text{-}H)(\mu\text{-}CHCHRPMe_2Ph)(CO)_{10}]$.[259]

4.2 The Cobalt Triad.- The μ-vinylidene complex $[Co_2(Cp)_2(CO)_2(\mu\text{-}CCH_2)]$ has been synthesised and characterised by an X-ray diffraction study.[260] Protonation of this complex gives $[Co_2(Cp)_2(CO)_2(\mu\text{-}CCH_3)]^+$, which in turn is reduced by $NaBH_4$ to give $[Co_2(Cp)_2(CO)_2(\mu\text{-}CHCH_3)]$.[260] $[Co_2(Cp)_2(CO)_2(\mu\text{-}CCH_2)]$ also reacts with $[Mo(Cp)(CO)_2(H)L]$ (L=CO or PPh_3) to yield the mixed metal cluster $[Co_2Mo(Cp)_3(CO)_2(\mu\text{-}CO)(\mu_3\text{-}CCH_3)]$.[260] Treatment of $[(C_5Me_5)M(\mu\text{-}CO)_2M(C_5Me_5)]$ (M=Co or Rh) with hydrazones $RR'C{=}NNH_2$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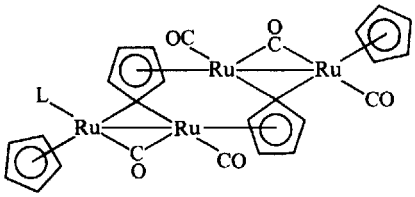
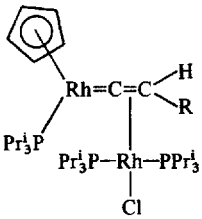
C
C
H
(CO)$_4$Fe—Fe(CO)$_3$
N

(24)


OC
O
C
Ru
Ru
CO
L
Ru
Ru
C
O
CO

(25)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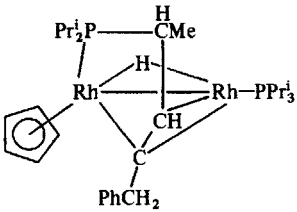
H
R
Pr$^i_3$P
Pr$^i_3$P—Rh—PPr$^i_3$
Cl

(26)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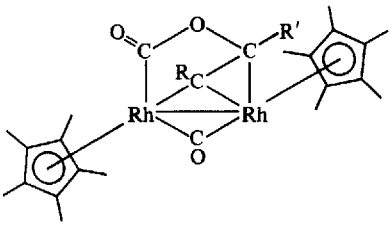
Pr$^i_2$P
CMe
H
Rh
Rh—PPr$^i_3$
CH
C
PhCH$_2$

(27)


O
C
O
C
R'
R
C
Rh
Rh
C
O

(28)

in the presence of MnO_2 gives the μ-alkylidene complexes trans-$[(C_5Me_5)(CO)Rh(\mu\text{-}CCR')\ Rh(CO)(C_5Me_5)]$ and $[(C_5Me_5)Co(\mu\text{-}CO)_2(\mu\text{-}CRR')\ Co(C_5Me_5)]$.[261] The μ-ethylidenecobalt complex $[(C_5Me_5)Co(\mu\text{-}CO)_2(\mu\text{-}CHMe)Co(C_5Me_5)]$ has been synthesised by treating $[(C_5Me_5)Co(\mu\text{-}CO)]_2$ with diazoethane.[262] The electron impact induced decomposition pathways of μ-CH_2 complexes of the type $[(C_5Me_5)M(\mu\text{-}CO)_2(\mu\text{-}CCR')M(C_5Me_5)]$ (M=Co or Rh) have been elucidated.[263] Reactions of alkynes with $[Co_2(CO)_4(\mu\text{-}CH_2)_2(\mu\text{-dppm})]$ lead to the formation of ethene and $[Co_2(CO)_4(\mu\text{-}RCCR)(\mu\text{-dppm})]$.[264] Carbon-carbon coupling reactions also occur with ethene (to give propene) and with hydrogen (to give ethane).[264] The reaction of $[(C_5Me_5)Co(\mu\text{-}CO)(\mu\text{-}CH_2)Co(C_5Me_5)]$ with SO_2 gives $[(C_5Me_5)Co(\mu\text{-}CO)(\mu\text{-}CH_2(\mu\text{-}SO_2)Co(C_5Me_5)]$, but with the complexes $[(C_5Me_5)(CO)M(\mu\text{-}CR_2)M(CO)(C_5Me_5)]$ (M=Co or Rh; R=H or Ph), SO_2 inserts into the M-CH_2 bond to give the μ-thioformaldehyde-S-S-dioxide complex $[(C_5Me_5)\overline{M(\mu\text{-}CO)_2\{CR_2S(O)_2\}M}(C_5Me_5)]$.[265] Treatment of $[(C_5Me_5)Rh(\mu\text{-}CO)(\mu\text{-}CPh_2)Rh(C_5Me_5)]$ with SO_2 gives $[(C_5Me_5)(CO)Rh(\mu\text{-}SO_2)Rh(CPh_2)(C_5Me_5)]$.[265]

Rhodium(I) complexes react with the electron-rich alkenes of general type $[=\overline{C(NR)CH_2CH_2NR}]_2$ (R=Me,Et,Ph,4-MeC_6H_4,4-$MeOC_6H_4$, or 2-$MeOC_6H_4$) to produce carbenerhodium(I) complexes such as $[RhCl\{=\overline{C(NR)CH_2CH_2NR}\}LL']$ (L=L'=PPh_3; L=PPh_3, L'=CO) and $[Rh(cod)Cl\{=\overline{C(NR)CH_2CH_2NR}\}]$.[266] These complexes have been found to be effective catalysts for the hydrosilylation of ketones or alkynes.[267] The complex $[(Cp)(PPr^i_3)Rh(=C=CHR)]$ (R=H or Ph) reacts with diazomethane in the presence of CuCl to give $[(Cp)(PPr^i_3)Rh(\mu\text{-}C=CH_2)CuCl]$, and with $[RhCl(PPr^i_3)_3]$ to give the dirhodium complex (26).[267] In solution, complex (26) (R=Ph) eliminates phosphine to give (27).[267]

Treatment of either cis- or trans-$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ with HCl gives $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Cl_2]$ which reacts with neutral ligands L to give the cationic complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(L)Cl]^+$ and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2L_2]^{2+}$ (L=MeCN, CO, or H_2O).[268] Diazoketones react with $[(C_5Me_5)Rh(\mu\text{-}CO)_2Rh(C_5Me_5)]$ to give the μ-alkylidene complexes $[(C_5Me_5)(CO)Rh\{\mu\text{-}C(R)C(O)R'\}Rh(CO)(C_5Me_5)]$ [R=R'=Me,Ph,4-$MeOC_6H_4$, CO_2Et; R=Me,R'=Ph, C(O)Me], which in some cases react further to give (28) via intramolecular cycloaddition reactions.[269] The heteronuclear μ-methylene complexes $[(Cp)_2Ti(\mu\text{-}CH_2)(\mu\text{-}X)Rh(cod)]$ (X=Cl,OMe) have been synthesised among a number of other such complexes.[270] The reactions of

$[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(Cp)(\eta\text{-}C_9H_7)]$ (C_9H_7=indenyl) with alkynes have been investigated.[271]

The addition of diazomethane to $[IrI(CO)(PPh_3)_2]$ at -50°C gives the carbeneiridium complex $[Ir(=CH_2)I(CO)(PPh_3)_2]$.[272] This complex rearranges in solution to give the ortho-metallated complex $[Ir\{CH_2P(Ph_2)C_6H_4\}(CO)H(I)(PPh_3)]$.[272]

4.3 The Nickel Triad.- The reaction between trans-$[Pt(PEt_3)_2(C{\equiv}CPh)_2]$ and trans-$[Pt(PEt_3)_2(H)(acetone)][BF_4]$ occurs by Pt-H addition to the C≡C triple bonds of the acetylide ligands to give the μ-vinylidene complex, $[(PEt_3)_2(PhC{\equiv}C)Pt(\mu\text{-}C{=}CHPh)Pt(PEt_3)_2][BF_4]$.[273] The mechanism of the formation of A-frame complexes of the type $[Pt_2(PPh_3)_2(\mu\text{-}Y)(\mu\text{-}dppm)_2][PF_6]_2$ (Y=CH_2, CO, S, SO_2) has been investigated.[274] A number of new complexes involving platinum with μ-carbene or μ-carbyne ligands have been reported. Such complexes include $[PtW\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(Cp)][BF_4]$,[275] $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(Cp)]$,[276] and $[AuPtW(\mu_3\text{-}CR)(CO)_2(PMe_3)_3(Cp)][PF_6]$ (R=C_6H_4Me-4).[277]

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13

Metal–Hydrocarbon π-Complexes, other than π-Cyclopentadienyl and π-Arene Complexes

BY J. A. S. HOWELL

A Reviews

Reviews have been published on intramolecular coordination of allyl[1] and diene[2] ligands, on reactions of acetylenes with metal atoms,[3] and on the reactions of coordinated π-hydrocarbons with nucleophiles.[4,5] In addition, reviews on insertion reactions of metal alkyls,[6] on carbonylation of zirconocene complexes,[7] on half-sandwich Rh and Co complexes,[8] on organometallic matrix isolation,[9] on organometallic intramolecular rearrangements,[10] on vinylidene and allenylidene complexes,[11] and on electron transfer reactions[12] contain material of interest. A summary of the Plenary and Section lectures from the 11th International Conference on Organometallic Chemistry contains articles on the organic reactions of Ru_2 centres,[13] and on synthetic uses of $[CpFe(CO)_2(olefin)]X$ complexes.[14]

B Allyl Complexes and Complexes Derived from Monoolefins.

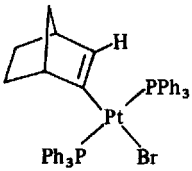
1. Ni, Pd and Pt

A crystal structure determination of $(C_2H_4)_2PtO_2$ reveals the expected trigonal planar (in-plane) coordination.[15] In (cod)Ni[methyl-trans-β-(phenylsulfonyl)acrylate], the cod and olefin bonds are mutually perpendicular in a trigonal planar geometry. The cod ligand may be displaced by a variety of bidentate nitrogen and phosphorus donors.[16] (Diop)$Pt(C_2H_4)$ has been prepared and undergoes displacement of C_2H_4 with ligands such as CO and allene.[17] A variety of halogen substituted (bicyclo[2.2.1]hept-2-ene)$Pt(PPh_3)_2$ complexes have been synthesised, and undergo intramolecular oxidative addition on heating to give complexes such as (1).[18]

Reaction of $(C_2H_4)_3Ni$ with dmpe yields complexes (2) to (4) depending on stoichiometry, eventually giving $(dmpe)_4Ni_2$ in the presence of excess dmpe.[19] Barriers to rotation in a series of $(C_2H_4)_2NiL$ complexes have been reported.[20]

A variety of CpNi(olefin)R complexes (olefin = ethene, propene) have been prepared by reaction of Cp_2Ni with RMgX in the presence of olefin. Olefin rotation in the propene complexes occurs with a barrier of 51 kJ mol^{-1}. Butadiene and its substituted

[For References see page 334



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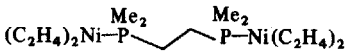

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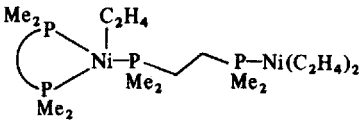

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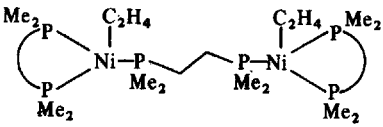

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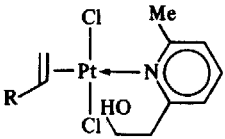

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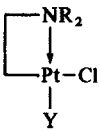
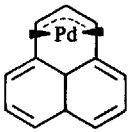
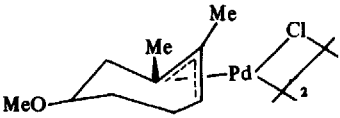


(6) Y = Me_2SO, PPh_3
R = Me



(7)

(8)



(9)

derivatives also form $CpNi(\eta^2\text{-diene})CH_3$ complexes on treatment of Cp_2Ni with CH_3Li/diene, but Cp_2Ni reacts with five- to eight-membered 1,3-cycloalkadienes in the presence of Pr^iMgCl to give the $CpNi(\eta^3\text{-cycloalkenyl})$ complex.[21,22]

A single crystal polarized electronic absorption study of $[PtCl_3(C_2H_4)]^-$ shows a strong σ-donor but weak π-acceptor character of the C_2H_4 towards Pt(II).[23] Molecular orbital calculations on $Ni(C_2H_4)(CH_3)(PH_3)Cl$[24] and $Pd(H_2O)(Nu)_2(C_2H_4)$[25] (Nu = H, CH_3, OH, F) show that cis-methyl migration in the former and cis-Nu migration in the latter requires initial rotation of C_2H_4 into the square plane, and calculated barriers are generally in agreement with available experimental data. In the Pd complex, migration is favoured only for H and CH_3; generally, soft nucleophiles favour cis-migration whereas hard nucleophiles add via external trans-attack. $Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2$ has been prepared; the complex undergoes exchange of C_2H_4 with activated olefins (eg. PhCH = CHPh or PhC ≡ CPh) and bridge cleavage to give $PtClMe(C_2H_4)L$ complexes (L = py, Me_2S, C_2H_4).[26] Trans-Cl_2Pt(olefin)(py) complexes of structure (5) undergo intramolecular catalysis of olefin exchange via formation of a (hydroxyalkylpyridine - O,N) platinum chelate.[27] Attack by amines (am) on cis-$Cl_2Pt(C_2H_4)Y$ complexes yields sequentially neutral acyclic cis-$Cl_2Pt(CH_2CH_2am)Y$ complexes (Y = Me_2SO, PPh_3) and cationic acyclic complexes $[Cl(am)Pt(CH_2CH_2am)Y]Cl$ (Y = NH_3, py, Me_2SO); ring compounds of structure (6) are formed preferentially by bulky amines via deprotonation of the neutral acyclic species by excess amine.[28]

The equilibrium constant of ca. 0.5 for the reaction [Pt](trans-2-butene) + cis-2-butene ⇌ [Pt](cis-2-butene) + trans-2-butene ([Pt] = (methylallyl)$Pt(PPh_3)^+$] indicates a reversal of the usual stability order (cis > trans) for metal binding. Crystal structures show the C = C in the cis-isomer to be in the (allyl)$PtPPh_3$ plane, whereas in the trans-isomer it is rotated out of the plane by 67°.[29] Equilibrium constants for the reaction

$$[Pt]NCPh + C_2H_4 \rightleftharpoons [Pt](C_2H_4) + NCPh$$

increase in the order [Pt] = (methylallyl)$Pt(PPh_3)^+$ > $CpPt(PPh_3)^+$. For the $CpPt(PPh_3)^+$ case, experiments with a variety of p-substituted styrene complexes ($C_2H_3C_6H_4Y$) show an increasing value of K with increasing electron donating character of Y. Olefin rotational barriers are larger in the $CpPt(PPh_3)(olefin)^+$ case, and crystal structure determinations show that olefin is coordinated perpendicular to the plane defined by Pt, P and the

centroid of the Cp ring.[30,31]

(η^3-phenalenyl)Pd(acac) and [(η^3-indenyl)PdCl]$_2$ have been prepared; the calculated minimum energy structures (7) and (8) are consistent with nmr results.[32] Dimethyl-1,4-cyclohexadienes undergo addition of methanol on reaction with $(MeCN)_2PdCl_2$ to give, in the case of the 1,2-dimethyl derivative, the η^3-allyl complex (9). Other derivatives yield isomeric complexes whose structure is dependent on the solution basicity.[33] Reaction of $(PhCN)_2PdCl_2$ with 1,2,6-heptatriene or 1,2,8-nonatriene yields η^3-allyl complexes of structure (10); in the former case, cyclization also occurs to give (11).[34] The species present in solution on addition of PPh_3 to [(allyl)PdCl]$_2$ dimers (allyl = norcamphenyl) have been investigated; in thf, rapidly equilibrating (allyl)PdCl(PPh_3) complexes are present, whereas in CH_2Cl_2, $CHCl_3$ or Me_2CO in the presence of excess PPh_3, an equilibrium between a contact ion pair (allyl)Pd$(PPh_3)_2$Cl and free ion pair [(allyl)Pd$(PPh_3)_2$]Cl is evident, with the latter favoured at low temperature; the cation has been isolated and structurally characterized as its PF_6^- salt. Regardless of solution species present, nucleophilic attack by malonate proceeds to give identical products. Other work also establishes the same product distribution in Pd-catalysed allylic alkylation as in stoichiometric alkylation of [(allyl)PdCl]$_2$ dimers, thus implicating η^3-allyl intermediates in the catalytic process. The stereochemistry of malonate addition is unambiguously <u>exo</u> to the Pd atom in such complexes, though the regiospecificity is sensitive to steric bulk of both the nucleophile and allyl substituent.[35-37] Nmr studies of (allyl)PdCl(PR_3) complexes reveal two distinct fluxional processes, both of which occur by π-σ-π rearrangement.[38] (Allyl)$_2$Ni reacts with PF_3 and a variety of other fluoro- and chlorophosphines to yield NiL_4 complexes,[39] and with $HSiX_3$ (X = Cl, F) in the presence of toluene to give (toluene)Ni$(SiX_3)_2$ derivatives.[40] Mass spectra of [(allyl)NiX]$_2$ (X = Cl, Br, I) and (allyl)Ni(L)Br complexes have been reported.[41]

2. Co, Rh and Ir

The fragment $HCoL_3$, generated by laser flash photolysis of $HCoL_4$ (L = diethylphenylphosphonite) exhibits a bimolecular rate constant of ca 10^8 dm^3 mol^{-1} s^{-1} in combination with 1-hexene.[42] Cocondensation of Co atoms with ethylene yields a labile Co-C_2H_4 complex which reacts with RCHO (R = H, Me) to give the formal product of insertion of C_2H_4 into the aldehydic C-H bond.[43] Protonation

of $Me_5CpCo(C_2H_4)(PR_3)$ (R = Me, Ph, p-tolyl) yields the $[Me_5CpCo(PR_3)C_2H_5]^+$ cation which a crystal structure shows to have a strong β-H-C-M interaction.[44] $Me_5CpCo(C_2H_4)_2$ undergoes oxidative addition with $(SCN)_2$ and $S(CN)_2$ to give $Me_5CpCo(C_2H_4)(NCS)_2$ and $Me_5CpCo(C_2H_4)(NCS)(CN)$ respectively.[45] A crystal structure determination of Me_5CpRh(syn-1,3-dimethylallyl)Cl reveals partial localization of the Rh-Cp bonding.[46] Sterically hindered secondary phosphines such as $HPBu^t_2$ react with (1-methylallyl)M(cod) (M = Rh, Ir) to give trigonal bipyramidal (1-methylallyl)M(cod)L complexes, whereas with smaller phosphines such as $HPCy_2$, cod displacement occurs to give square planar (1-methylallyl)ML_2; both types have been characterized crystallographically.[47] $Rh_2(CO_2CF_3)_4$ forms 1:1 adducts with a variety of olefins; adduct stability is greatest when the olefin possesses π-donor substituents.[48]

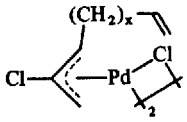
3. Iron, Ruthenium and Osmium

Core electron binding energies[49] and molecular orbital calculations[50] have been reported for $Fe(CO)_4$(olefin) complexes containing electron withdrawing substituents. Calculations indicate that complex stability is primarily a function of the energy of the olefin π^* level. $Fe(CO)_3$(cis-cyclooctene)$_2$ has been prepared; the complex undergoes exchange with 1,3-dienes and reacts with acetylenes to give coupled products under mild conditions.[51] A crystal structure determination shows that olefin coordination in complex (12) is weak and twisted in orientation.[52]

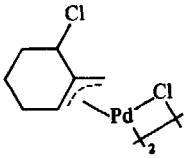
The use of $[CpFe(CO)_2(\eta^2\text{-}H_2C = C(OEt)CO_2Et)]^+$ salts as organic equivalents of the α-acrylic ester cation have been described.[53a] $Me_5CpFe(PMe_3)_2C_2H_5$ exists in equilibrium in solution with the olefin complex $Me_5CpFe(PMe_3)(C_2H_4)H$.[53b]

Further applications of compounds of structure (13) in lactone synthesis have been reported.[54a,b] Complexes of structure (14) exist in equilibrium with the η^2-azadiene tautomer (15); the cyclic tautomer is favoured where R' is bulky whereas branching of the nitrogen substituent favours the azadiene tautomer.[55]

Substitution of (allyl)$Fe(CO)_2NO$ with optically active phosphine (L^*) yields separable (allyl)$Fe(CO)(NO)L^*$ diastereoisomers which are configurationally stable at the Fe atom up to 120 °C.[56] Very basic phosphines undergo addition to the allyl group to give $Fe(\eta^2\text{-}CH_2CHCH_2PR_3)(NO)(CO)_2$ zwitterions.[57] Reaction of $FeCl_2(PMe_3)_2$ with potassium pentadienide yields syn,syn-bis-(η^3-pentadienyl)$Fe(PMe_3)_2$ characterized structurally as having



(10) x = 2, 4



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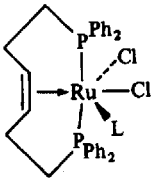

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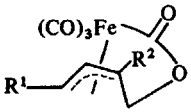

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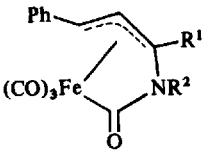

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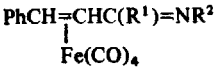

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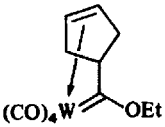

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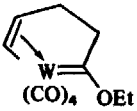

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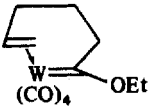

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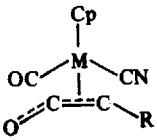

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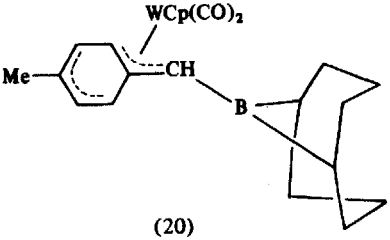


(20)

a staggered configuration of the two allyls.[58]

Allylic halides undergo oxidative addition to $CpRu(CO)_2X$ to give $CpRu(\eta^3\text{-allyl})X_2$ complexes.[59] Reaction of $(\eta^3\text{-allyl})_2(cod)Ru$ with haloacetic acids provides good yields of $[Ru_2(cod)_2(O_2CR)_2\text{-}(\mu\text{-}O_2CR)_2(\mu\text{-}OH)_2]$ dimers (R = CF_3, CCl_3, CH_2Cl).[60]

4. Cr, Mo and W

Cocondensation of Cr atoms with cyclohexenes initially yields Cr-olefin complexes which undergo dehydrogenation to give $(arene)_2Cr$ derivatives.[61] Photolysis of $CpW(CO)_3R$ complexes results in initial loss of CO to give a 16e- $CpW(CO)_2R$ intermediate which, when the R group possesses β-hydrogens, undergoes β-photoelimination to give $CpW(CO)_2(\eta^2\text{-olefin})H$ complexes which are isolated as the trans-isomer. Where β-hydrogens are absent (R = Ph), the 16e- intermediate may be trapped in the presence of C_2H_4 to give $CpW(CO)_2(C_2H_4)Ph$. The olefin in trans-$CpW(CO)_2(C_2H_4)H$ can be replaced thermally and photochemically by other ligands (CO, PMe_3, thf).[62,63] (Cis-cyclooctene)$M(CO)_5$ (M = Cr, W) has been prepared photochemically and acts as an efficient source of the $M(CO)_5$ moiety. Photolysis of $(CO)_5WCPh_2$ in the presence of cis-cyclooctene yields the trans-$W(CO)_4(CPh_2)$(olefin) complex, characterized crystallographically.[64,65] Intramolecularly chelated olefin-carbene complexes (16) to (18) having a cis-geometry have also been prepared; in (18) the carbene and C = C bonds are essentially parallel, and the complex undergoes facile elimination of a cyclopropane.[66,67] Reaction of $CpM(CO)_2CR$ complexes (M = Mo, W) with CN^- yields salts of the η^2-ketenyl anion (19).[68] Reaction of WCl_2L_4 (L = PMe_3, PMe_2Ph, $PMePh_2$) with ethylene yields sequentially $WCl_2L_3(C_2H_4)$ and $WCl_2L_2(C_2H_4)_2$. The latter reacts with $AlMe_3$ to give $[WMe(PMe_3)_2(C_2H_4)_2][ClAlMe_xCl_{3-x}]$, characterized crystallographically as containing cis-ethylenes, trans-phosphines and a weakly coordinated aluminate; conductivity studies suggest the existence of an ion pair in solution formed by loss of aluminate.[69]

The allyl ligand in $CpMo(CO)_2$(2-methylallyl) adopts the endo conformation in the solid state,[70] as do both allyl ligands in the 17e- $CpMo(allyl)_2$.[71] The η^3-benzyl complex (20) formed from reaction of $CpW(CO)_2CC_6H_4Me$-p with 9-borabicyclo[3.3.1]nonane has a similar endo solid state conformation.[72]

$AgBF_4$ reacts with $MoCl(bipy)(CO)_2(allyl)$ to give the dimeric cation $[Mo(bipy)(CO)_2(allyl)(\mu\text{-}Cl)]_2^+$, characterized

crystallographically. The ground state allyl conformation (21) in this and related $L_2X(CO)_2Mo(allyl)$ complexes may be traced to the strong π-bonding character of the carbonyls. Nucleophilic attack is frontier orbital controlled and occurs at the terminal allyl carbon for $L_3(CO)_2M(allyl)$ complexes, but at the central carbon for $Cp_2M(allyl)^+$ derivatives (M = Mo, W).[73,74] Nucleophilic attack on the $[CpMo(CO)(NO)(\eta^3\text{-cyclooctenyl})]^+$ cation is highly regiospecific, occurring cis to NO in both exo and endo conformations; this regiospecificity has been used in an asymmetric synthesis of (-)-cycloocten-3-ol.[75,76] A crystal structure determination of $CpMo(NO)(\eta^3\text{-hexenyl})GePh_3$ exhibits a 57/42 exo/endo population in the solid state.[77]

5. Other Metals

$Pt(PR_3)_2$ complexes catalyse the reaction of $ReH_7(PR_3)_2$ complexes [PR_3 = $PPhPr^i_2$, P(cyclopentyl)$_3$] with C_2H_4 to give $ReH_3(C_2H_4)_2(PR_3)_2$ which affords $ReH_5(C_2H_4)(PR_3)_2$ on treatment with H_2.[78]

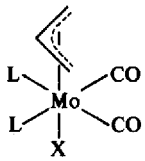
Deprotonation of $Cp_2Zr(COCH_3)CH_3$ yields the $[Cp_2Zr(\eta^2 - H_2C = C = O)CH_3]^-$ anion in which the ketene is π-bonded via the C = O linkage;[79] a similar acetyl deprotonation has been used in the preparation of the anion of structure (22).[80] The complexes $CpTi(allyl)_2$ and $CpV(allyl)_2$ have been prepared by reaction of C_3H_5MgX with $CpTiCl_2$ and $CpVCl_2(PEt_3)_2$ respectively.[81]

Cocondensation of Cu and Au atoms with propene (L) yields both ML and ML_2 complexes; Ag atoms fail to form any detectable complex.[82] A 1:1 π-bonded adduct may be detected at low temperature in the reaction of $LiCuMe_2$ with t-butyl cinnamate.[83] A crystal structure determination of (cyclohexene)Cu[hydrotri-(1-pyrazolyl)borate].CuCl reveals an in-plane coordination of cyclohexene in a trigonal planar metal environment.[84]

C Complexes Derived from Unconjugated Dienes

1. Ni, Pt and Pd

A low temperature crystal structure determination of $(cod)PtCl_2$ shows a completely symmetrical Pt-olefin bonding.[85] Calorimetric measurements on $(cod)PtCl_2$ show that the metal-olefin bond is weaker than Pt-phosphine bonds but stronger than Pt-NR_3 or Pt-pyridine bonds.[86] Pt-C and Pt-H coupling constants have been reported for a variety of $(cod)Pt(C_6H_4X)_2$ complexes (X = H, Me, CF_3, OMe, NMe_2), and used in the assignment of



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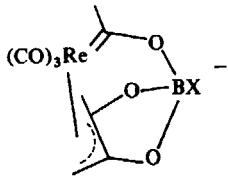
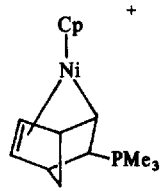


(22) X = Cl, F



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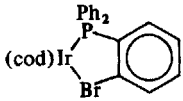

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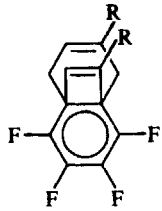
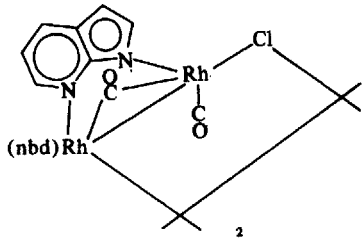


(25) R = H
(26) R = Me

(27) N—N = naphthyridine



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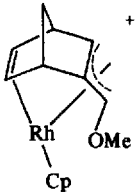

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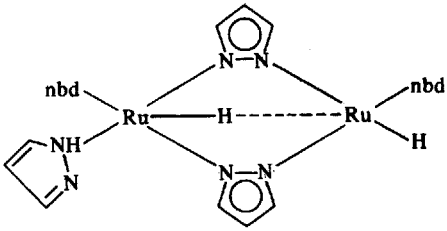


(30)

configuration.[87] (Cod)$PtCl_2$ reacts with $SnCl_2/SnCl_3^-$ to give $[(cod)Pt(SnCl_3)_3]^-$, characterized crystallographically as a distorted square pyramid with cod in the basal plane.[88] The complex $[CpNi(nbd)]^+$ undergoes nucleophilic attack by PMe_3 to give (23).[89]

2. Co, Rh and Ir

A crystal structure determination of trans-(acac)Cl_2Ir(cod) reveals a Cl-Ir-Cl angle of 159° which accommodates the steric requirements of the cod ligand.[90] The rate of diene binding to $[Ir(PPh_3)_2(Me_2CO)_2H_2]^+$ to form $[Ir(PPh_3)(diene)H_2]^+$ is considerably faster for nbd than for cod; isomer interconversion occurs in solution.[91] A series of $[L_2Ir(cod)H_2]^+$ cations (L, L_2 = mono- or bidentate sulphur ligand respectively) has also been prepared.[92] Reaction of ClIr(cod)(o-$BrC_6H_4PPh_2$) with $AgSbF_6$ yields the intramolecularly chelated complex (24) which reacts reversibly with hydrogen to yield $[Ir(cod)(\eta^2\text{-}BrC_6H_4PPh_2)H_2]^+$.[93]

A variety of four and five coordinate neutral and cationic complexes of the stoichiometry $IrX(diene)L_y$ (y = 1,2; X = Cl, $SnCl_3$, $OClO_3$), $[Ir(diene)_2L]^+$, $[Ir(diene)L_2]^+$ and $[Ir(diene)(CO)_3]^+$ have been prepared where the diene is tetrafluorobenzobarrelene (25) and L is a N,P,As,Sb,O or S-donor.[94] Treatment of the $[IrCl(diene)]_2$ derivative [diene = (25) or (26)] with Ag^+ in the presence of arenes yields $[Ir(diene)(arene)]^+$ cations which show a staggered arrangement of the arene and diene moieties.[95] Reaction of 1,8-naphthyridine with $[Rh(diene)(Me_2CO)_x]^+$ yields $[Rh_2(\mu\text{-naphthyridine})_2(diene)_2]^{2+}$ cations (27) [diene = nbd, (25)] characterized crystallographically for the nbd complex.[96] Reaction of RhCl(nbd)(azaindole) with $Rh(acac)(CO)_2$ yields the tetranuclear complex (28).[97]

Crystal structures of several $[(nbd)Rh(P^*\text{-}P^*)]^+$ complexes ($P^*\text{-}P^*$ = chiral bidentate phosphorus ligand) all show the diene twisted in the same sense relative to the chirality at the phosphine, a factor of importance in asymmetric hydrogenation using such complexes.[98] $(F_6acac)Rh(C_2H_4)_2$ reacts with trans,trans-2,5-heptadiene to give an $(F_6acac)Rh(\eta^4\text{-diene})$ complex, whereas cis,cis-2,5-heptadiene yields the $(F_6acac)Rh(\eta^2\text{-diene})_2$ derivative due to severe steric interaction between the terminal substituents of each double bond.[99] Reaction of $CpRh(\eta^4\text{-}C_7H_7\text{-}2\text{-}CHO)$ with MeOH in the presence of HBF_4 yields complex (29).[100]

3. Fe, Ru and Os

A variety of $[RuH(cod)L_3]^+$ complexes (L = phosphorus donor) undergo irreversible conversion on heating to the $[\eta^3$-cyclooctenyl$)RuL_3]^+$ derivative, the ease increasing with the steric bulk of L. Nmr studies show an agostic interaction between the metal and an endo C-H bond adjacent to the allyl group.[101] $[RuH(cod)(NH_2NMe_2)_3]PF_6$ undergoes reaction with pyrazole in basic solution to yield the dimer (30) containing a semibridging hydride.[102] Reaction of $[OsCl_2(cod)]_x$ with hydrazine in the presence of $NaBPh_4$ yields $[Os(cod)(NH_2NH_2)_4](BPh_4)_2$; treatment with $CNBu^t$ in acetone yields $[Os(cod)(CNBu^t)_2(NH_2N = CMe_2)_2](BPh_4)_2$ characterized crystallographically as having trans-hydrazone ligands.[103]

4. Other metals

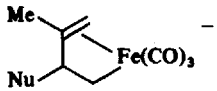
Kinetic studies of the displacement of diene from $(diene)M(CO)_4$ (diene = cod, nbd; M = Cr, Mo, W) by phosphorus ligands reveal a rate law which is first order in ligand; the order of lability is Mo>>W>Cr and nbd>cod.[104]

D. Complexes Derived from Conjugated Dienes

1. Fe, Ru and Os

(a) Acyclic Dienes

$(\eta^4$-enone$)Fe(CO)_2L$ complexes [enone = benzylideneacetone, cinnamaldehyde; L = PPh_xMe_{3-x} (x - 1-3)] exist as interconverting isomers in solution in which L occupies the axial or basal position of a square pyramid. Exchange with chd to give $(chd)Fe(CO)_2L$ involves a stepwise loss of enone, and is slower than for the analogous $(enone)Fe(CO)_3$ complex. Optically active ligands may also be incorporated using this method.[105,106] Nucleophilic attack on $(isoprene)Fe(CO)_3$ proceeds reversibly at -78° to give the kinetic product (31); on warming to 0° the more stable η^3-allyl complex (32) is formed by loss of nucleophile and readdition at terminal carbon. Similar results are obtained with other substituted acyclic $(diene)Fe(CO)_3$ complexes with the exception of the $(2\text{-methoxybutadiene})Fe(CO)_3$ where rearrangement to the more stable η^3-allyl is intramolecular.[107] Reaction of $(2,4\text{-hexadienal})Fe(CO)_3$ with $Ph_3P = CHR$ where R is electron withdrawing yields primarily the trans-isomer (33) which on heating undergoes some isomerization to the cis-isomer and a metal shift to the more stable tautomer (34).[108] Variable temperature circular



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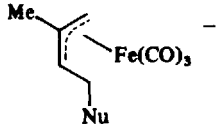

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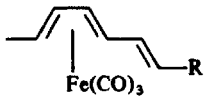
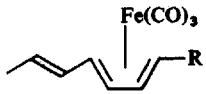


(33) R = CO_2R, COR, CN



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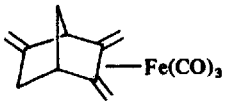

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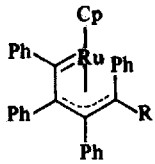
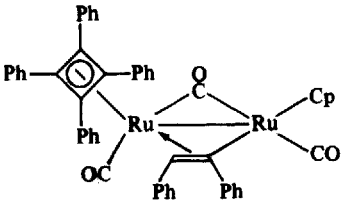


(36) R = H
(37) R = CHO



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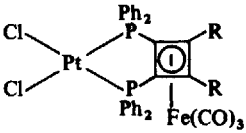

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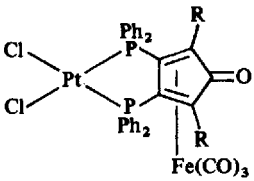


(40)

dichroism studies of complexes such as (35) have been used to support the σ,π-bonding mode for (diene)$Fe(CO)_3$ complexes in solution.[109] Cocondensation of Ru atoms with 2,3-dimethylbutadiene or chd in the presence of CO yields the (η^4-diene)$_2$Ru(CO) complex[110]. A crystal structure determination of (butadiene)$_2$-$Fe(PMe_3)$ has been reported.[111]

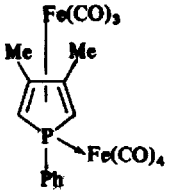
Mössbauer and photoelectron spectra for acyclic (pentadienyl)$_2$Fe complexes have been reported; an increase in electron density at the iron relative to ferrocene is indicated.[112,113]

(b) Cyclic Dienes

Reaction of $[Ph_4cbdFe(CO)(NO)(PPh_3)]^+$ with bidentate anions yields neutral $(Ph_4cbd)Fe(NO)(Z\text{-}Z)$ complexes (Z-Z = NO_3, acac, S_2CNEt_2), characterized crystallographically for the dithiocarbamate derivative.[114] Reaction of PhC ≡ CPh with $Cp_2Ru_2(CO)_4$ in the presence of $AgBF_4$ yields the $[CpRu(CO)(Ph_4cbd)]^+$ cation; the remaining CO is photolabile, undergoing substitution with MeCN to give $[CpRu(MeCN)(Ph_4cbd)]^+$ (characterized crystallographically) and coupling with further PhC ≡ CPh to give [CpRu(hexaphenylbenzene)]$^+$. Photosubstitution with C_2H_4 results in liberation of 1,2,3,4-tetraphenylchd and formation of $[CpRu(C_2H_4)_3]^+$. Reduction of $[CpRu(L)(Ph_4cbd]^+$ (L = MeCN, CO) with $KBHBu_3$ results in ring opening to yield the complexes (36) and (37) respectively; dimer (38) is also formed in the reduction of the CO derivative.[115,116] Reaction of cis-$X_2Pt(Ph_2PC \equiv CR)_2$ complexes (X = halide, R = alkyl, aryl) with $Fe_2(CO)_9$ results in coupling to yield either cbd or cyclopentadienone complexes of structures (39) and (40), both characterized crystallographically.[117]

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ with $LiPR_2$ (R = $SiMe_3$) results in exo-addition to the ring to yield (η^4-$C_5H_5PR_2$)$Fe(CO)_3$ complexes which rearrange at room temperature to the (η^5-C_5H_5)$Fe(CO)_2PR_2$ complex.[118] The $Fe(CO)_4$ group may be easily decomplexed in (41) and the phosphorus can be oxidized, sulfurized or quaternized.[119]

Hydride abstraction from (42) gives mainly (45) but from (43) gives mainly (46); these results are consistent with calculations which show these to be the most stable dienyl complexes. In (45) the π-donor substituent causes a slipping of the metal (confirmed by crystallography) which partially decoordinates C_5, thus rendering it susceptible to nucleophilic attack.[120] Hydride



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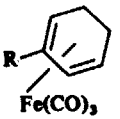
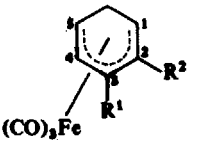
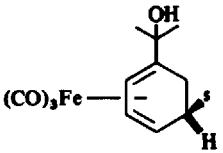


(42) R = OMe
(43) R = CO_2Me
(44) R = $SiMe_3$



(45) R^1 = H, R^2 = OMe
(46) R^1 = CO_2Me, R^2 = H
(47) R^1 = $SiMe_3$, R^2 = H



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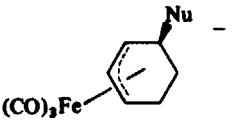

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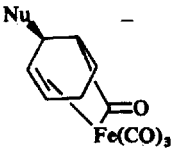

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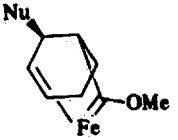

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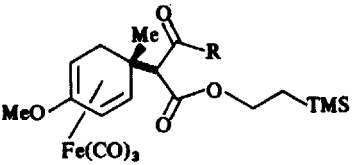

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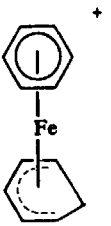

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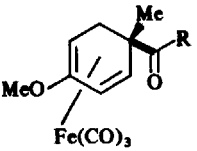


(53)

abstraction from (44) regiospecifically yields (47), consistent with an acceptor character for the $SiMe_3$ group.[121] It has been argued that the much slower rate of nucleophilic attack on [(cycloheptadienyl)$Fe(CO)_3$]$^+$ (as opposed to the six-membered ring analogue) and the formation of products resulting from attack at C-2 are the result of steric inhibition by the methylene (CH_2CH_2) moiety.[122] Reactions of both six- and seven membered ring [(dienyl)$Fe(CO)_3$]$^+$ cations with soft nucleophiles (X = NO_3^-, NCO^-, N_3^-, $R_2NCS_2^-$, NCS^-, $NCSe^-$) result initially in <u>exo</u>-addition, followed in most cases by rapid rearrangement to the <u>endo</u>-isomer or metal/carbonyl attack.[123] Proton elimination from dienols of structure (48) on treatment with acid to yield dienyl salts has been shown to be exclusively <u>endo</u> at C-5.[124] Barriers to dienyl rotation in the six-membered [(cyclohexadienyl)$Fe(CO)_3$]$^+$ series are in the range 40-50 kJ mol^{-1}.[125]

The exchange reaction between (η^4-enone)$Fe(CO)_3$ complexes (where the enone is optically active) and prochiral 1,3-cyclohexadienes yields (chd)$Fe(CO)_3$ complexes with enantiomeric enrichments of up to 40%.[126] The absolute configurations of the [(cyclohexadienyl)$Fe(CO)_3$]$^+$ salts derived from them may be determined from their cd spectra.[127]

Applications of cyclohexadiene complexes in organic synthesis continue. Nucleophilic attack on (chd)$Fe(CO)_3$ proceeds in a similar way to the acyclic derivative, yielding the product of attack at C-2 which rearranges on warming to anion (49). The product of C-2 attack may be trapped as its carbonyl insertion product (50) which undergoes methylation to give the isolated complex (51).[128] Acetylation of (chd)$Fe(CO)_2PPh_3$ proceeds in good yield to give (5-<u>endo</u>-acetylcyclohexadiene)$Fe(CO)_2PPh_3$.[129] Mono-ketone derivatives of structure (53) have been obtained by mild decarboxylation of the diketone (52).[130] Efficient methods are now available for the preparation of (<u>N</u>-alkoxycarbonyl-1,2-dihydropyridine)$Fe(CO)_3$ complexes.[131] The [(benzene)$_2$Fe]$^{2+}$ cation reacts with $NaBH_4$ to yield the monocation (54) which adds Grignard or lithium reagents stereospecifically to give (55) from which the free diene may be liberated by oxidation.[132] The exocyclic methylene group in (56) easily undergoes Michael addition reactions with acrylonitrile or methylacrylate.[133]

The yield and regioselectivity of the reaction of [(cycloheptadienyl)$Fe(CO)_3$]$^+$ with nucleophiles is greatly improved by use of the $Fe(CO)_2L$ complex [L = PPh_3, $P(OPh)_3$]; soft

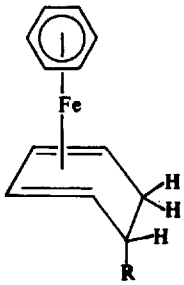
nucleophiles add at C-1 whereas C-2 is preferred for hard nucleophiles.[134] Ketene ($R_2C = C = O$) addition to (η^4-chpt)Fe(CO)$_3$ and (η^4-cot)Fe(CO)$_3$ is 2+2 in nature, as evidenced by a crystal structure determination of (57), obtained from (chpt)Fe(CO)$_3$; isomerization occurs on heating to give the σ,π-allyl complex (58).[135,136] Carbene addition to the uncoordinated double bond of (η^4-chpt)Fe(CO)$_3$ using N_2CHCOOEt occurs in the normal way; use of N_2(Ph)CCOPh (azibenzil) yields instead the furan derivative (59).[137] *In situ* alkylation of (η^4-tropone)Fe(CO)$_3$ yields the oxytropylium cation (60) which undergoes cycloaddition reactions with, for example, CpFe(CO)$_2$(η^1-allyl) to give ketohydroazulene complexes such as (61).[138]

Full details have appeared on the structure of (62), obtained from oxidation of (cot)Fe(CO)$_3$ with $C_7H_7^+$: studies of the Mecot derivative show that both the C_8 and C_7 rings undergo contraction in the formation of (62).[139] Though addition of PBu_3 to (63) [obtained by oxidative dimerization of (cot)Fe(CO)$_3$] occurs in the normal way to the termini of the dienyl moiety, ring opening occurs on reaction with PPh_3 to give (64).[140]

Reaction of $[C_6H_6RuCl(PMe_3)_2]^+$ with PMe_3 in the presence of PF_6^- results in the formation of cation (65); a similar *exo*-addition of nucleophile is observed in the reaction of $[(C_6H_6)MX(PMe_3)_2]^+$ (M = Ru, X = Cl; M = Os, X = I) with Grignard and alkyl lithium reagents to give the products (66) and (67), characterized crystallographically in the case of (67) (R = Bu^n). Restricted dienyl rotation is evident at low temperature.[141,142] Complex (67) reacts smoothly with Ph_3CPF_6 to give $[(RC_6H_5)OsI(PMe_3)_2]PF_6$.[143] Detailed methods have been reported for the synthesis of (η^6-C_6H_6)(η^4-chd)Ru, (cod)(η^6-cotr)Ru and (η^5-cyclohepta-dienyl)$_2$Ru.[144] Protonation of $(C_6Me_6)_2$Ru, followed by hydride reduction, may be used to generate an analogous (η^5-cyclo-hexadienyl)$_2$Ru complex.[145]

2. Cr, Mo and W

Photolysis of Cr(CO)$_4$L$_2$ in the presence of butadiene and its substituted derivatives yields Cr(CO)$_2$L$_2$(η^4-diene) complexes [L = PMe_3, P(OMe)$_3$] which exist in solution and solid state as the *trans*-L$_2$ isomer; ligand interchange probably occurs *via* trigonal prismatic transition states. Essentially the same conclusions apply to the mixed ligand Cr(CO)$_2$LL'(η^4-diene) derivatives (L = PMe_3, L' = P(OMe)$_3$].[146,147] Treatment of



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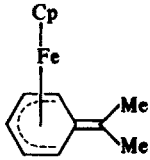

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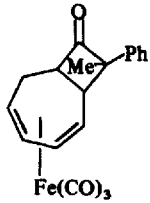

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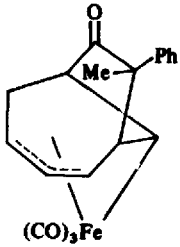

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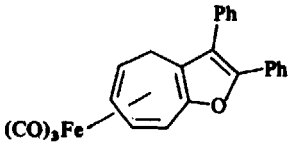

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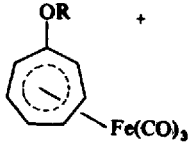

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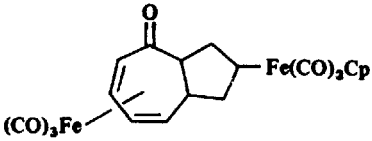

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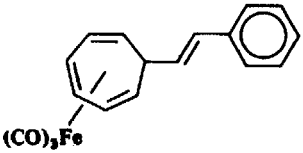

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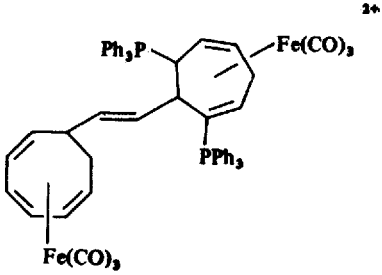

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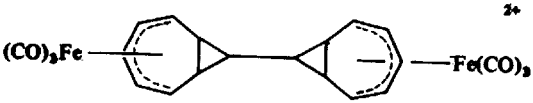


(63)

$W(PMe_3)_4(\eta^2\text{-}H_2C = PMe_2)H$ with ethylene yields $(butadiene)_2W(PMe_3)_2$.[148]

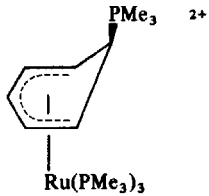
$[(Me_5Cp)Mo(CO)_2(\eta^4\text{-tmm})]BF_4$, obtained by treatment of methylenecyclopropane with $(Me_5Cp)_2Mo_2(CO)_6$ in the presence of $AgBF_4$, shows the predicted solid state syn-configuration. Simple Mo-tmm rotation is predicted to have a high barrier, and the observed room temperature equivalence is attributed to a $\eta^4\text{-}\eta^1\text{-}\eta^4$ interconversion.[149] Easy cleavage of $CpMo(CO)_2(\eta^3$-cyclohexenyl) derivatives occurs on reaction with I_2 to yield either the organic allyl iodide or lactones derived from internal cyclization; these reactions improve the potential of $[CpMo(CO)_2(\eta^4\text{-chd})]^+$ salts as organic synthons.[150,151] The methylenecyclobutenyl complex (68) undergoes facile protonation to give $[CpMo(CO)_2(\eta^4\text{-}Ph_3Mecbd]^+$, characterized crystallographically as its neutral chloride.[152]

$(\eta^6$-8,8-dimethylheptafulvene$)Cr(CO)_3$ undergoes photochemical reaction with dimethylfulvene to yield (69).[153] Intramolecular isomerization of $(C_7H_8)_2Mo$ to give $(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)Mo$ is faster by a factor of 100 than the analogous isomerization of the $17e^-$ $[(C_7H_8)_2Mo]^+$ cation.[154]

3. Co, Rh and Ir

The complexes $(tmm)Ir(CO)(PPh_3)Cl$ and $Os(tmm)(CO)_2(PPh_3)$ have been prepared by treatment of $IrCl(CO)(PPh_3)_2$ and $Os(CO)_2(PPh_3)_3$ with $Me_3SiCH_2C(=CH_2)CH_2X$ (X = Cl, OAc); the barrier to ligand rotation is high (> 90 kJ mol^{-1}), and the Ir-C bond lengths reflect the differing trans-influence of CO, Cl and PPh_3.[155]

Interconversion of the two diastereoisomers (70) and (71) on flash pyrolysis has been taken to indicate direct ring opening to a $CpCo(alkyne)_2$ complex without the intermediacy of a cobaltacyclopentadiene intermediate.[156] Reaction of $[Cp_2Co]Cl$ with a variety of Li, Mg, Al and Zn alkyls results in exo-attack to give $CpCo(\eta^4\text{-}C_5H_5R)$ complexes. Similar reaction of CpCo(allyl)Br with RLi or RMgX gives the CpCo(allyl)R complex which, where R = CH = CH_2, isomerizes by coupling to $CpCo(\eta^4$-penta-1,3-diene).[157] Protonation of the η^4-triene complex (72) yields the allyl olefin cation (73), rather than the expected η^5-dienyl species.[158] Double hydride addition to $[(Me_5Cp)Ir(arene)]^{2+}$ yields sequentially $[(Me_5Cp)Ir(\eta^5\text{-cyclohexadienyl})]^+$ and $Me_5CpIr(\eta^4\text{-chd})$; treatment of the latter with HCl liberates cyclohexene.[159] Photoelectron spectra of a variety of conjugated



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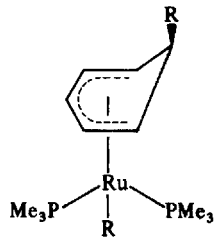
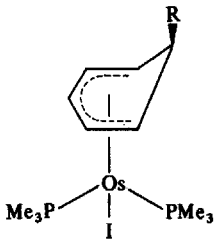


(66) R = Me, Ph



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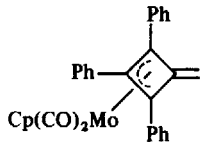

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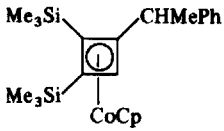

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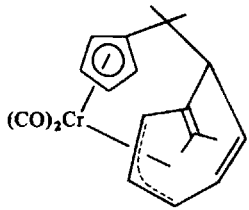

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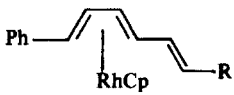
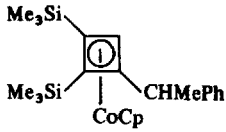


(72) R = H, Ph



(71)

and non-conjugated CpM(diene) complexes (M = Co, Rh, Ir) show that for Co, the HOMO is largely metal d, whereas for Rh and Ir, there is substantial ligand localization.[160]

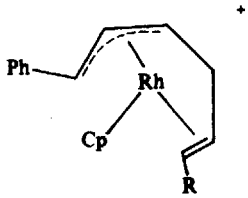
The $[Ir(PPh_3)_2(\eta^3\text{-cyclohexenyl})H]^+$ cation may be generated by addition of $[Ir(PPh_3)_2(Me_2CO)_2H_2]^+$ to chd or to cyclohexane in the presence of $Bu^tCH = CH_2$; nmr studies show an interchange of the endo-hydrogen of the α-CH_2 group via an agostic C--H--M interaction.[161]

Reaction of butadiene with $CoCl_2/PMe_3/Mg$ results in dimerization to yield the allyl complex (74); use of non-conjugated dienes yields $17e^-$ $Co(PMe_3)_2(\eta^4\text{-diene})$ complexes characterized crystallographically as tetrahedral.[162] The allyl complex (75) is isolated from reaction of $ClCo(PMe_3)_3$ with 2,4-dimethylpentadienide ion, and undergoes syn-anti exchange in solution via a π-σ-π mechanism. Reductive reaction of $CoCl_2/PEt_3$ with 2,4-dimethylpentadienide yields (η^5-2,4-dimethylpentadienyl)-$Co(PEt_3)_2$, characterized crystallographically.[163] Simple reaction of $CoCl_2$ with 2,4-dimethylpentadienide initially yields $(2,4\text{-dimethylpentadienyl})_2Co$ which dimerizes on standing to give (76).[164]

4. Mn and Re

Epr studies of $17e^-$ $Mn(butadiene)_2PMe_3$ show that the unpaired electron resides predominantly in an orbital directed along the Mn-P bond.[111,165]

$[(\eta^6\text{-chpt})Mn(CO)_3]^+$ undergoes nucleophilic attack by enolate ions to give substituted (η^5-cycloheptadienyl)$Mn(CO)_3$ complexes from which the ligand can be liberated with concomitant oxygenation.[166] Ring opening occurs on reaction of $CpMn(CO)_3$ with 1,2,3-triphenylcyclopropene to give the η^4-ketene complex (77), characterized crystallographically, and similar products are obtained from reactions using $CpV(CO)_4$ and $CpCo(CO)_2$.[167] (η^5-Pentadienyl)$Mn(CO)_3$ reacts at room temperature with basic phosphines (PMe_3, PMe_2Ph, PBu_3^n) to give (η^3-pentadienyl)-$Mn(CO)_3L$, and (η^3-pentadienyl)$Mn(CO)_4$ is formed on irradiation in a CO matrix. At higher temperatures, loss of CO occurs to give the (η^5-pentadienyl)$Mn(CO)_2L$ complex.[168] The phosphacyclohexadienyl complex (78) has been prepared,[169] and full details of the synthesis and structure of (79) have appeared; bonding of the central Mn is essentially electrostatic, though weak covalent couplings are apparent.[170]



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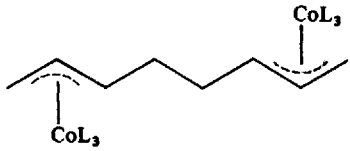
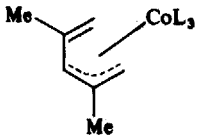
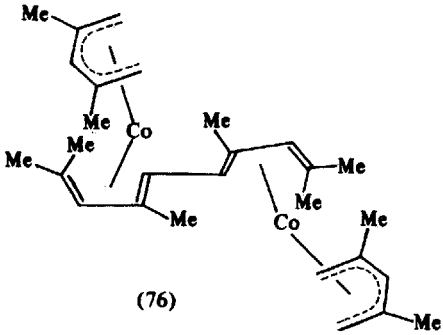


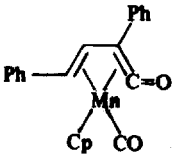
(74) L = PMe_3



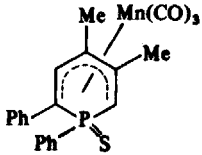
(75) L = PMe_3



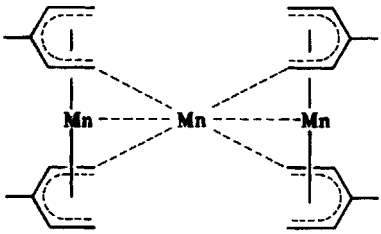
(76)



(77)



(78)



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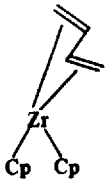

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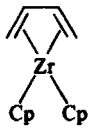
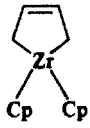


(81)



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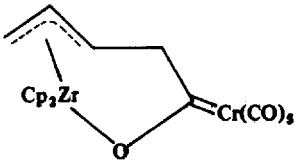

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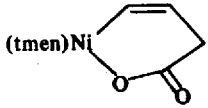

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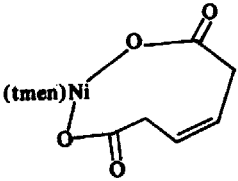

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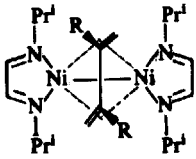
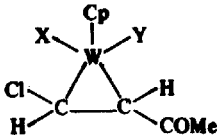
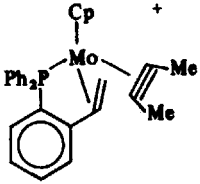


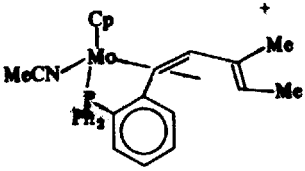
(86) R = CH_2OH, CH_2OR



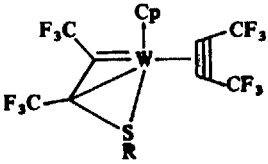
(87) a; X = CO, Y = Cl
b; X = Cl, Y = CO



(88)



(89)



(90)

Crystal structure determinations of $ReH_3(PPh_3)_2$(chd) and (benzene)Re(chd)H show no evidence for agostic C--H--Re interactions; coordination in the former is a distorted pentagonal bipyramid with axial phosphines.[171,172] The latter is prepared from the reaction of Re atoms with benzene and cyclohexene which also yields the mixed valence dimer (benzene)$Re(\mu\text{-}H)_2Re(chd)_2$. The seven coordinate $ReH_3(PPh_3)_2$(diene) complexes (diene = butadiene and its substituted derivatives, chd) are fluxional, showing a lower energy ligand interchange which is accompanied at higher temperature by a reversible migration of hydride to the diene ligand to generate $ReH_2(PPh_3)_2(\eta^3\text{-allyl})$ species.[173]

5. Other Metals

New methods for the synthesis of $Cp_2Zr(\eta^4\text{-diene})$ complexes have been reported. Reaction of Cp_2ZrCl_2 with CH_2 = CHLi yields $Cp_2Zr(\eta^4\text{-butadiene})$,[174] while photolysis of $Cp_2Zr(CH_2Ph)$(CH = CHPh) yields $Cp_2Zr(\eta^4$-trans,trans-1,4-diphenylbutadiene);[175] both reactions appear to proceed via $Cp_2Zr(CH = CHR)_2$ intermediates (R = H, Ph). Reaction of Cp_2ZrHCl with pentadienyl anion yields $Cp_2Zr(\eta^4$-penta-1,3-diene), and alkyl substituted analogues may be prepared using substituted pentadienyl anions.[176] Such complexes exist in an s-trans ⇌ s-cis [(80) ⇌ (81)] equilibrium which is dependent on diene substituent; thus whereas 1,3-pentadiene and 2,4-hexadiene yield approximately equimolar amounts of (80) and (81), 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene and Me_3Si-substituted pentadienes exist solely as the s-cis isomer. Crystal structure determinations of several s-cis complexes show a smooth transition from (η^4-diene) (81) to metallocyclic structure (82) which depends on the substituents on the diene moiety.[177] Cp_2Zr(butadiene) reacts with $Cr(CO)_6$ via its s-trans isomer to give (83), an "inorganic" analogue of its reactions with ketones.[178] Reaction of $CpZrCl_3$ with (3-methylbutenyl)MgCl yields $CpZr(1,1\text{-dimethylallyl})_3$; this complex decomposes at -15 °C to give CpZr(1,1-dimethylallyl)-(η^4-isoprene) which rearranges at room temperature to CpZr(1,2-dimethylallyl)(η^4-isoprene) via a $CpZr(isoprene)_2H$ intermediate.[179] Nmr shifts for ^{91}Zr involve distinctly different ranges for $16e^-$ and $18e^-$ complexes.[180]

Reaction of $(cod)_2Ni$ with 1,3-dienes in the presence of CO_2 and tmen results in insertion to give nickelacarboxylate complexes which may be represented as (84); for substituted complexes,

the regiospecificity is dependent on both temperature and the bidentate ligand employed. With butadiene, the dicarboxylate (85) is also formed.[181,182] Similar insertions occur with olefins, acetylenes, and 1,2-dienes.[183,184]

Reactions of PhC ≡ CMe with $Pt(CO)_2Cl_2$ yields $[(Me_2Ph_2cbd)$-$Pt(\mu\text{-}Cl)_3Pt(Me_2Ph_2cbd)]Pt(CO)Cl_3$ which on treatment with Cl^- yields the neutral $[(Me_2Ph_2cbd)PtCl(\mu\text{-}Cl)]_2$ dimer. A structure determination of monomeric $(Me_2Ph_2cbd)Pt(PPh_3)Cl_2$ obtained by bridge cleavage reveals a cis-methyl configuration on the cbd ring.[185]

E Complexes Derived from Acetylenes

$(Diazadiene)_2Ni$ complexes selectively catalyse the cyclotetramerization of acetylenes of the type RC ≡ CH and RC ≡ CR ($R = CH_2OH$, CH_2OMe, CH_2O-p-tolyl); for disubstituted acetylenes, the reaction proceeds via the intermediacy of the (diazadiene)-Ni(acetylene) complex which can be isolated and structurally characterized where $R = CH_2OH$. For the monosubstituted acetylenes, the intermediate (which can again be isolated) is a dimer of structure (86).[186,187] Similar $(PPh_3)_2Ni$(acetylene) complexes have been prepared by acetylene exchange with $(PPh_3)_2Ni(C_2H_4)$.[188] Acetylenes such as $MeO_2CC \equiv CCO_2Me$ are selectively cyclotrimerized to arenes via (diazadiene)Ni(acetylene) intermediates.[189]

Reaction of CpW(CO)(HC ≡ CH)COMe with NO yields CpW(CO)(NO)(HC ≡ CH) and CpW(CO)(NO)(HC ≡ CCOMe); high barriers (>90 kJ mol^{-1}) are observed for acetylene rotation.[190] Reaction with NOCl yields primarily a diastereoisomeric mixture of the tungstenacyclopropane complex (87), characterized crystallographically.[191] Reaction of Cp_2MoH_2 with PhC ≡ CPh yields $Cp_2Mo(\eta^2$-cis-stilbene) from which the olefin may be displaced to give a variety of $Cp_2Mo(\eta^2$-acetylene) complexes.[192]

Two-dimensional nmr techniques have established acetylene rotational barriers for $[CpMo(CO)(RC \equiv CR)_2]^+$ cations in the range 62-73 kJ mol^{-1}.[193] Reaction of $[CpMo(CO)(MeC \equiv CMe)_2]^+$ with o-diphenylphosphinostyrene yields (88) which on heating in CH_3CN undergoes coupling via C-C bond formation and a hydrogen shift to give (89).[194] Reaction of $[CpMoL_2(MeC \equiv CMe)]^+$ $[L = P(OMe)_3]$ with NaSR yields neutral CpMo(L)(MeC ≡ CMe)SR complexes in which acetylene is oriented along the Mo-P axis; rotational barriers are sensitive to the electronic character of R.[195] Though metathetic reaction of $CpW(CF_3C \equiv CCF_3)_2Cl$ with

TlSR yields simple $CpW(CF_3C \equiv CCF_3)_2SR$ complexes where R = Ph, C_6F_5, p-tolyl, use of more electron donating R groups (Me, Et, Pr^i) yields complexes of structure (90); in solution two geometric isomers exist which interconvert via reversible formation of the $CpW(CF_3C \equiv CCF_3)_2SR$ complex.[196] $CpW(CO)_3SR$ complexes (R = alkyl, aryl, CF_3, CO_2Me) react with $CF_3C \equiv CCF_3$ to give initially (91) which isomerizes on heating to the η^2-vinyl complex (92) and ultimately yields $CpW(CO)(CF_3C \equiv CCF_3)SR$ and the O-bonded ketone complex (93). The reaction of $CpFe(CO)_2SR$ yields a product analogous in structure to (91).[197]

Electronic spectra and reduction potentials for the d^4-complexes $Mo(S_2CNR_2)_2(RC \equiv CR)$ support the dual π-donor/π-acceptor role of the formal $4e^-$ donor acetylene.[198] Reaction of $W(CO)_4(dppe)(thf)$ with terminal acetylenes $RC \equiv CH$ (R = Ph, CO_2Me) yields initially a $W(CO)_4(dppe)(RC \equiv CH)$ intermediate which undergoes migration to give mer-$W(CO)_3(dppe)C = C(H)R$, a reaction attributed to the unfavourable two-centre four-electron interaction in the initially formed d^6 acetylene complex.[199] Reduction of $W(PhC \equiv CPh)_3CO$ yields in situ $[W(PhC \equiv CPh)_3]^{2-}$ which has been structurally characterized by conversion to $[W(PhC \equiv CPh)_3SnPh_3]^-$ on reaction with Ph_3SnCl; acetylene rotation has a barrier of 52 kJ mol^{-1}.[200] Reaction of WCl_4 with $RC \equiv CR$ in ether yields $W(RC \equiv CR)Cl_4.Et_2O$ (R = Me, Et, Ph) which are best regarded as a metallocyclopropenes. Reaction with t-butoxide and chloride yields $W(PhC \equiv CPh)(OBu^t)_3$ and $[W(RC \equiv CR)Cl_5]^-$ respectively; the latter may be alkylated to give $W(RC \equiv CR)R'_3Cl$ (R = Et, Me; R' = Me, CH_2SiMe_3).[201]

Addition to $[CpFe(CO)(L)(\eta^2\text{-alkyne})]^+$ (L = PPh_3, $P(OPh)_3$) complexes occurs in a trans-fashion with a variety of nucleophiles (R^-, CN^-, SPh^-) to give $CpFe(CO)(L)(\eta^1\text{-alkenyl})$ complexes which in the case of the $P(OPh)_3$ complex exist as interconverting rotamers in solution;[202] $CpFe(CO)(L)(\eta^1\text{-alkenyl})$ complexes are also formed by nucleophilic addition to the isomeric $[Cp(CO)(L)Fe = C = CR_2)]^+$ vinylidene cation.[203]

Reaction of $[(cod)IrCl]_2$ with PPr_3^i/ $PhC \equiv CPh$ yields trans-$IrCl(PhC \equiv CPh)(PPr_3^i)_2$ which on reaction with NaCp gives $CpIr(PhC \equiv CPh)(PPr_3^i)$. Protonation with CF_3COOH yields $CpIr[C(Ph) = CHPh](PPr_3^i)X$ (X = O_2CCF_3) which may be converted sequentially into the iodide (X = I) and methyl (X = Me) derivatives. The methyl complex undergoes elimination of CH_4 to regenerate $CpIr(PhC \equiv CPh)(PPr_3^i)$.[204] The complex

$Ir(CH_2OMe)(RC \equiv CR)(PMe_3)_3$ ($R = C_6H_4Me$-p) undergoes reaction with $BrSiMe_3$ to give metallocyclobutene (94) via the intermediacy of an $Ir = CH_2$ complex.[205]

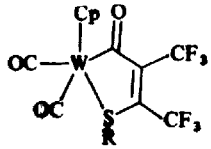
Reaction of trans-$ReCl(N_2)(dppe)_2$ with $PhC \equiv CMe$ yields the η^2-allene complex $ReCl(H_2C = C = CHPh)(dppe)_2$ via a 1,3-hydrogen migration,[206] and a similar intermediate seems likely in the reaction of $(CO)_5ReFBF_3$ with $MeC \equiv CMe$ to give the methylene-cyclobutene complex (95).[207] Reaction of $ReO_2I(PPh_3)_2$ with $MeC \equiv CMe$ yields $ReOI(MeC \equiv CMe)_2$, characterized crystallographically as a distorted tetrahedron (regarding the acetylene mid-points as vertices.)[208] Reaction of $(Cp)(Me_5Cp)Ti(CO)_2$ with $PhC \equiv CPh$ in the presence of PMe_3 yields $(Cp)(Me_5Cp)Ti(PhC \equiv CPh)$ which undergoes coupling with CO_2 to give (96).[209]

Cocondensation of Ag, Au and Cu atoms with terminal and internal acetylenes yields $M(RC \equiv CR)_n$ complexes ($n = 1,2$).[210]

F Polynuclear Complexes

1. Bimetallic Complexes

$^1J(C-C)$ values for acetylenes are decreased substantially on coordination in $Co_2(CO)_6$(μ-acetylene) or $Co_4(CO)_6$(μ-acetylene) complexes, consistent with the rehybridization at carbon.[211] The change in $C \equiv C$ stretching frequency on coordination for $Co_2(CO)_6$(μ-acetylene) complexes may be correlated with the electronic nature of the acetylene substituent, and in combination with CO stretching frequencies, allows a separation of the σ- and π-components of the metal-alkyne bond.[212] Nmr spectra of stabilized cations of the type $[Co_2(CO)_6(\mu\text{-}MeC \equiv CCHMe]^+$ reveal a significant barrier (60 kJ mol^{-1}) for rotation about the C-CHMe bond.[213] Reduction of $Co_2(CO)_{6-x}L_x$(μ-acetylene) complexes yields $19e^-$ $Co(RC \equiv CR)L_x(CO)_{3-x}$ radicals (L = phosphine, phosphite, arsine) which where $x = 2,3$ are long lived at room temperature and are assigned a pseudo-square planar structure.[214] Other M_2L_6(μ-acetylene) complexes characterized structurally this year include $Co_2(CO)_6(\mu\text{-}P \equiv CBu^t)$,[215] $Co_2(CO)_6(\mu\text{-}PhC \equiv CMn(CO)_4PCy_3)$,[216] $Ir_2(CO)_4(PPh_3)_2(\mu\text{-}PhC \equiv CPh)$,[217] and the $Co_2(CO)_6$ complex of the phosphazene (97).[218] Carbon-carbon coupling occurs in the reaction of $Co_2(CO)_4(\mu\text{-}CH_2)_2$(μ-dppm) with acetylenes to give $Co_2(CO)_4$(μ-acetylene)(μ-dppm) and ethylene.[219] A molecular orbital study of the coupling and dismantling of CH_2–CH_2 and CH–CH units bonded to one or two tungsten atoms has been reported.[220] Oxidation of isonitrile in $Cp_2Rh_2(CO)(CNR)(\mu\text{-}CF_3C \equiv CCF_3)$ using Me_3NO results in coupling to give the bridged amide



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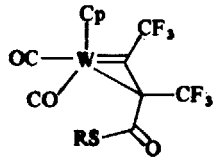

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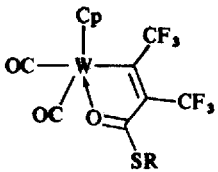

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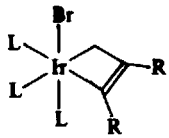
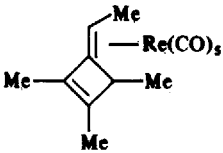


(94) R = *p*-tolyl



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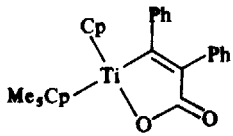

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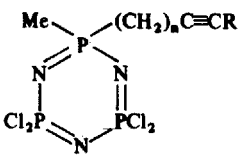
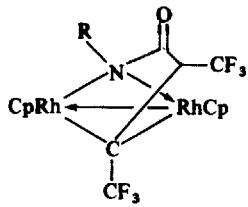


(97) n = 0, R = Me
n = 1, R = H



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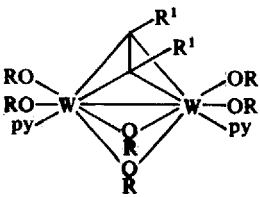
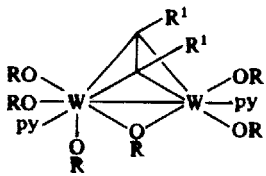


(99) R = Pr^i, R^1 = H

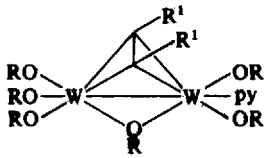


(100) R = CH_2Bu^t; R^1 = Me, H

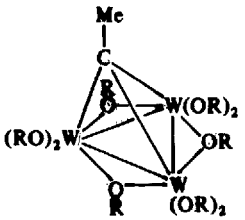
complex (98), characterized crystallographically.[221]

Reaction of $W_2(OR)_6$ with one equivalent of acetylene (R'C ≡ CR') in the presence of py yields one of three structural types [(99) to (101)], depending on steric factors associated with the alkoxy group and acetylene substituent. Crystal structures show that the central core is best regarded as a dimetallatetrahedrane, and solution labelling studies on (101) show that it is in equilibrium with the carbyne complex $(Bu^tO)_3W \equiv CH$.[222] High temperature reaction of $W_2(OBu^t)_6$ with PhC ≡ CPh yields only $(Bu^tO)_3W \equiv CPh$, characterized crystallographically.[223] Reaction of MeC ≡ CMe with $W_2(OPr^i)_6(py)_2$ proceeds to yield the trinuclear complex (102), probably via the intermediacy of $(Pr^iO)_3W \equiv CMe$ which reacts with further $W_2(OPr^i)_6(py)_2$.[224] $Mo_2(OBu^t)_6$ reacts with terminal acetylenes (RC ≡ CH; R = Ph, Pr^n) in the presence of quinuclidine (L) to give $(Bu^tO)_3(L)Mo \equiv CR$ and $(Bu^tO)_3(L)Mo \equiv CH$ complexes, though the use of acetylene itself yields a thermally unstable $Mo_2(OBu^t)_6(\mu\text{-HC} \equiv \text{CH})$ adduct.[225] Reaction of (101) with further acetylene results in coupling without C-C or C-H bond rupture to give (103); reaction of (100)(R = H) proceeds to yield the related complex (105) via the intermediacy of the py adduct (104).[226] Complex (101) undergoes coupling on reaction with PhCN to give (106), which is best formally regarded as the alkylidene-imido complex shown; other W_2(μ-acetylene) complexes yield similar coupled products.[227] Reactions of RC ≡ CR (R = H, Me, Ph) with $(Me_3SiCH_2)_4W_2(\mu\text{-CSiMe}_3)_2$ yields initial η^2-acetylene adducts which undergo insertion to give the η^3-allyl structure (107).[228] Insertion also occurs on reaction of $Cp(CO)_2W(\mu\text{-CR})Co(CO)Me_5Cp$ and $Cp(CO)_2W(\mu\text{-CR})Rh(CO)$(indenyl) (R = p-tolyl) with acetylenes to give complexes of structure (108), and analogous $Fe(CO)_3$ complexes may also be obtained.[229,230] Reduction of $[MeCpMo(NCMe)(MeC \equiv CMe)_2]^+$ with $[CpFe(CO)_2]^-$ results in acetylene coupling to yield (109), characterized crystallographically; protonation yields a monocation containing an agostic Mo--H--C interaction which in solution equilibrates between carbons 1 and 2.[231]

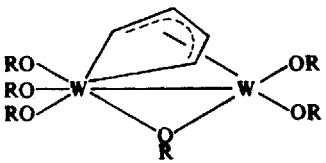
Dihydrofulvalene reacts with $Ru_3(CO)_{12}$ or $M(CO)_3L_3$ (M= Mo, L = CO; M = Cr, W, L = EtCN) to give (η^5:η^5-fulvalene)-$Ru_2(CO)_4$ and (η^5:η^5-fulvalene)$M_2(CO)_6$, characterized crystallographically where M = W.[232,233] The Mo complex undergoes sequential photochemical substitution with PhC ≡ CPh to give



(101) R = Bu^t, R^1 = H

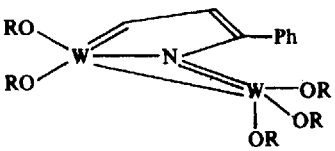


(102) R = Pr^i

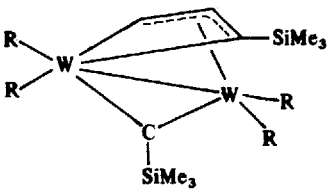


(103) R = Bu^t

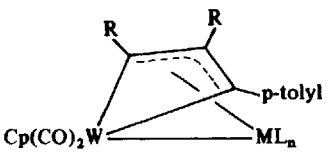
(104) R = CH$_2$Bu^t; L = py
(105) R = CH$_2$Bu^t; L = η^2 − HC ≡ CH



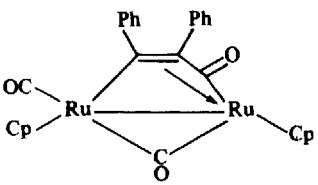
(106) R = Bu^t



(107) R = CH$_2$SiMe$_3$



(108) ML$_n$ = Me$_5$CpCo, (indenyl)Rh, Fe(CO)$_3$



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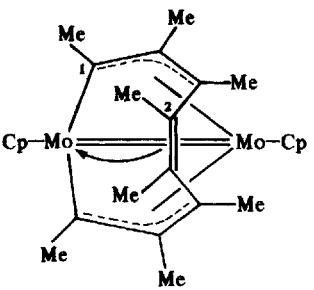

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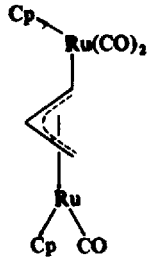

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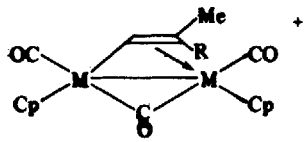
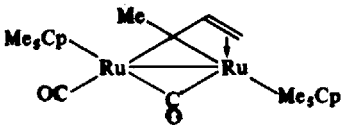


(112) M = Ru, R = H
M = Fe, R = Me



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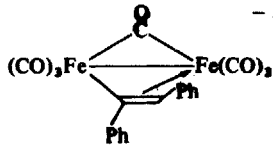

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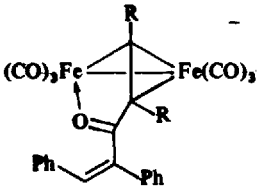
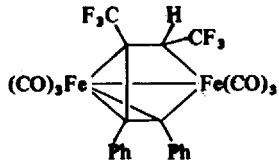


(115) R = CO_2Me



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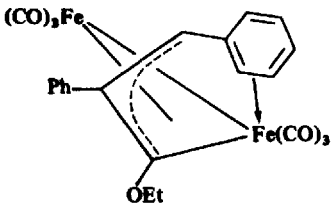

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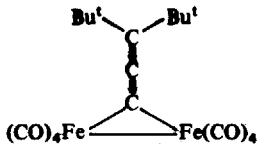
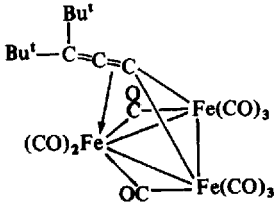


(118)

(η^5:η^5-fulvalene)$Mo_2(CO)_4$(μ-PhC ≡ CPh) and (η^5:η^5-fulvalene)-$Mo_2(CO)_2$(PhC ≡ CPh)(μ-PhC ≡ CPh) in which the terminal acetylene acts as a $4e^-$ donor. The Ru_2 dimer undergoes photochemical reaction with PhC ≡ CPh to give a bridged complex containing "parellel" bonded acetylene,[234] in contrast to the reaction of $Cp_2Ru_2(CO)_4$ which yields (110). Complex (110) reacts with ylids Ph_3P = CHR to give $Cp_2Ru_2(CO)_2$(μ-CO)(μ-CHR) complexes (R = H, Me, Et, Ph). Where R = CH = CH_2, the major product is the allyl complex (111) which on protonation yields the μ-vinyl cation (112); hydride addition to (112) yields $Cp_2Ru_2(CO)_2$-(μ-CO)(μ-CHEt).[235] Protonation of $Cp_2Ru_2(CO)_2$(μ-CO)(μ-CH_2) yields the bridged methyl cation $[Cp_2Ru_2(CO)_2(\mu\text{-CO})(\mu\text{-}CH_3)]^+$; the analogous $[Cp_2Ru_2(\mu\text{-dppm})(\mu\text{-CO})(\mu\text{-}CH_3)]^+$ loses hydrogen to generate the μ-methyne $[Cp_2Ru_2(\mu\text{-dppm})(\mu\text{-CO})(\mu\text{-CH})]^+$ cation.[236] Photolysis of $(Me_5Cp)_2Ru_2(CO)_4$ in the presence of ethylene yields sequentially $(Me_5Cp)_2Ru_2(CO)(C_2H_4)(\mu\text{-CO})_2$, $(Me_5Cp)_2Ru_2(CO)_2$-(μ-CHMe)(μ-CO) and complex (113), which is also formed by photolysis of $(Me_5Cp)_2Ru_2(CO)_2$(μ-C = CH_2)(μ-CO) in the presence of C_2H_4.[237] Mono- and disubstituted ethylenes react with $[Cp_2Fe_2(CO)_2(\mu\text{-CO})$-($\mu$-CH)]$^+$ <u>via</u> a concerted C-H addition to give (in the case of cis-2-butene) $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-CCH(Me)CH}_2\text{Me})]^+$ which equilibrates on standing with the μ-vinyl cation of structure (112).[238]

Anion (114), obtained from reaction of $[HFe_3(CO)_{11}]^-$ and PhC ≡ CPh, undergoes insertion of alkyne and CO into the Fe-C σ-bond on reaction with $MeO_2CC \equiv CCO_2Me$ to give (115), but insertion into the C-H bond on reaction with $CF_3C \equiv CCF_3$ to give (116).[239] The bridging carbonyl of (114) may be alkylated to give $(CO)_3Fe(\mu\text{-COEt})(\mu\text{-C(Ph)} = \text{CHPh})Fe(CO)_3$ which on heating undergoes coupling of carbyne and σ-vinyl group to give (117).[240] The allenylidene complex $(CO)_4Fe = C = C = C(Bu^t)_2$ has been prepared, and undergoes reaction with $Fe_2(CO)_9$ to yield complexes (118) and (119); complex (118) reacts with py to give initially the product of carbonyl substitution which rearranges on heating to give (120).[241,242] The related $M_2(CO)_9[C = C = C(Bu^t)_2]$ complexes (M = Mn, Re) have also been prepared; the Mn complex possesses a $(CO)_3Mn(\mu\text{-CO})_3(\mu\text{-C} = C = CR_2)Mn(CO)_3$ structure, whereas all ligands are terminal in the Re analogue.[243]

Irradiation of $Re_2(CO)_{10}$ with HC ≡ CH yields (121) as the main product;[244] much better yields of the phenyl derivative (122) are obtained from reaction of (123) with HC ≡ CPh.[245] Compounds



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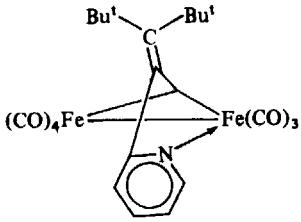

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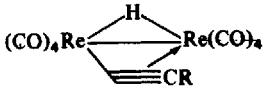
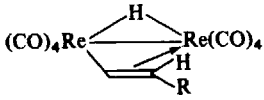
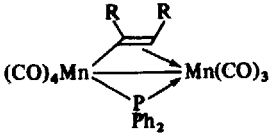


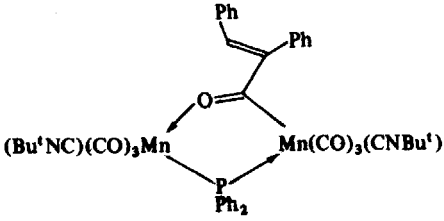
(121) R = H
(122) R = Ph



(123) R = Me
(124) R = H
(125) R = Et



(126) R = H, Ph



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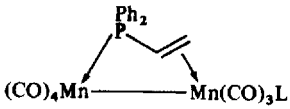

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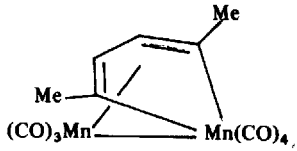

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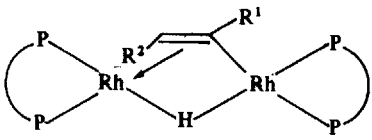
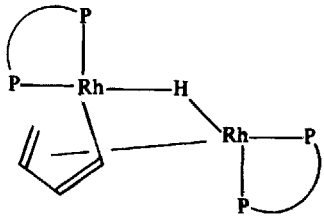


(130) $R^1 = R^2 = H$
(131a) R^1 = alkyl, $R^2 = H$
(131b) $R^1 = H$, R^2 = alkyl



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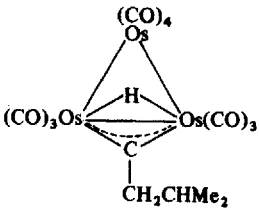
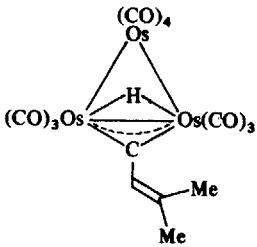
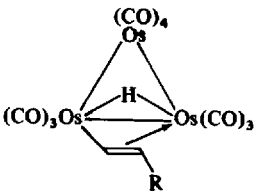


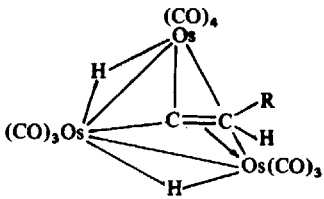
(133)



(134)



(135) $R = CHMe_2$
(137) R = H
(142) R = COMe



(136)

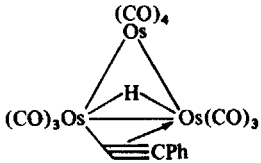
of structure (123) are obtained in high yield by photolysis of $Re_2(CO)_{10}$ in the presence of ethylene, terminal olefins, or 2-butene. In addition to the exchange with acetylenes noted above, elimination of olefin also occurs on reaction of (123) with mono- or bidentate nitrogen or phosphorus donors to give $Re_2(CO)_8L_2$ complexes.[246,247] One exception is PMe_3 which reacts with both (122) and (124) to give products of dipolar addition to the μ-acetylide and μ-vinyl groups respectively. Both the μ-acetylide and μ-vinyl structures undergo a fluxional process which interchanges the σ and π bonds between the Re atoms. Photolysis of (124) in the presence of ethylene results in formal C-H insertion to give (125), though the mechanism involves initial coordination of C_2H_4, followed by insertion into the Re-H-Re bond.[248] Reactions of the μ-vinyl complex (126) with $2e^-$ donors promotes insertion of either CO or PPh_2 into the M-C bond; thus, reaction with Bu^tNC yields (127), whereas treatment with PEt_3 gives (128).[249]

Low temperature photolysis of $Mn_2(CO)_{10}$ in the presence of allene yields $Mn_2(CO)_8[(\mu\text{-}(1,2\text{-}\eta:2,3\text{-}\eta\text{-allene})]$.[250] Photolysis of $Mn_2(CO)_{10}$ with cis,trans-2,4-hexadiene yields mainly $(allyl)Mn(CO)_4$ complexes, though the manganocyclopentadiene complex (129) is also formed in low yield.[251]

The complex $(R_2PCH_2CH_2PR_2)_2Rh_2(\mu\text{-}H)_2$ ($R = Pr^i$) reacts with ethylene with elimination of C_2H_6 to yield the μ-vinyl complex of structure (130); with substituted derivatives of ethylene, isomeric mixtures (131a, b) are obtained. Reaction with butadiene yields a complex of structure (132). The substituted complexes of structure (131) rearrange thermally to yield $(\eta^3\text{-allyl})\text{-}Rh(R_2PCH_2CH_2PR_2)$ derivatives.[252,253]

2. Polymetallic Complexes

Vibrational and ^{13}C spectra of various Os_3 and Ru_2 clusters containing $\eta^2\text{-}C_2H_4$, $\mu_3\text{-}C_2H_2$, μ_3-CMe, μ_2-CMe, μ_2-CHMe and $\mu_3\text{-}C \equiv CH$ ligands have been recorded as an aid to assignment of surface-adsorbed species.[254] Reaction of 3,3-dimethylcyclopropene with $H_2Os_3(CO)_{10}$ yields the bridged carbyne complex (133), together with (134) which is the result of dehydrogenation of 3,3-dimethylcyclopropene by "$Os_3(CO)_{10}$" generated *in situ*. On heating, (133) undergoes sequential isomerization to the σ-vinyl and vinylidene complexes (135) and (136).[255] The addition of $H_2Os_3(CO)_{10}$ to $HC \equiv CH$ to give (137) has been shown



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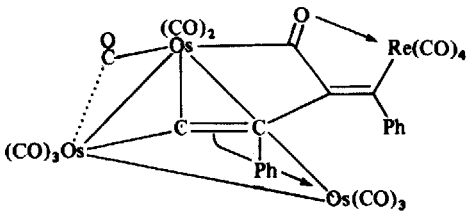

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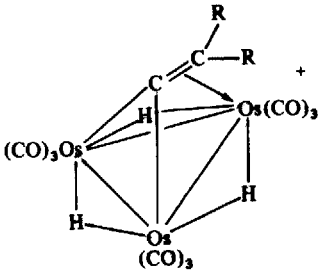

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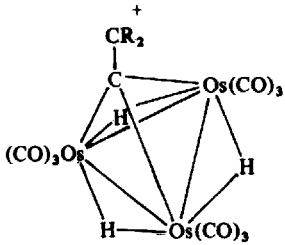

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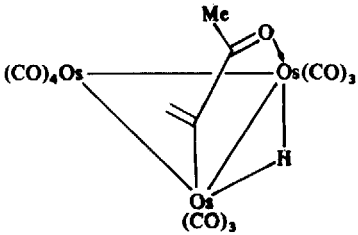

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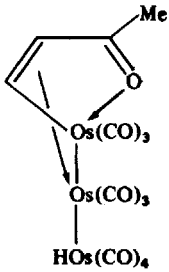

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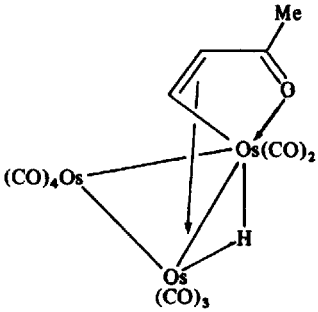

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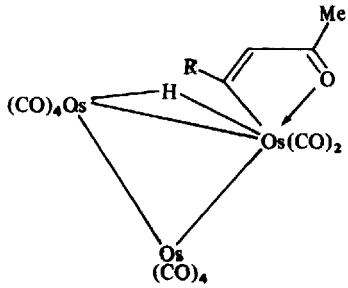
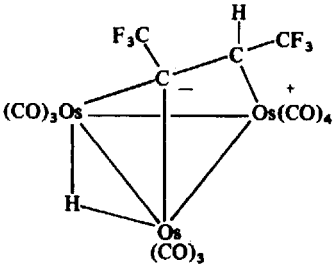


(146) R = Me, Ph



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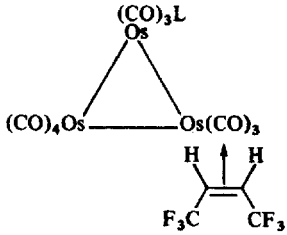
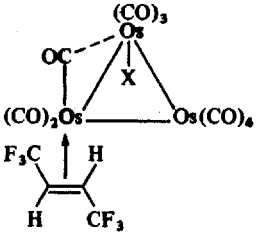
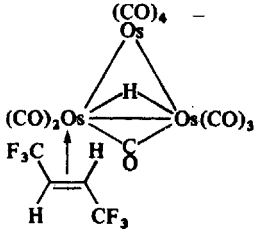


(148) L = CO, PEt_3



(149) X = Cl, Br, I



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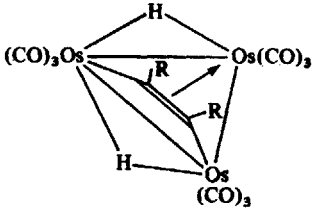

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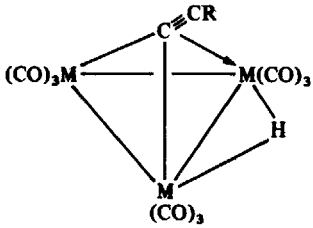
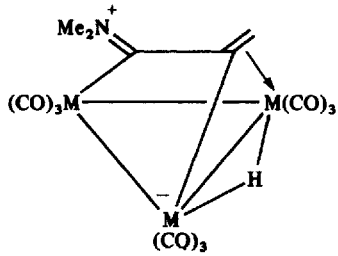


(152) M = Os; R = CF_3
(154) M = Ru, Os; R = CH_2NMe_2



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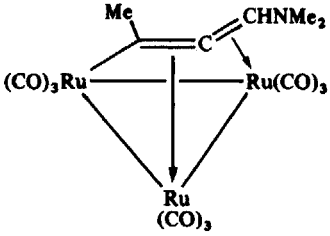

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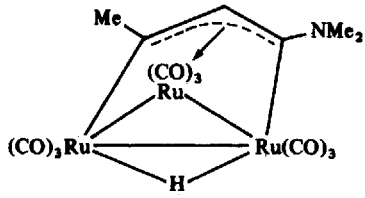

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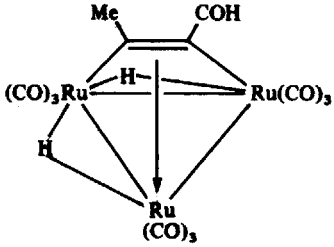

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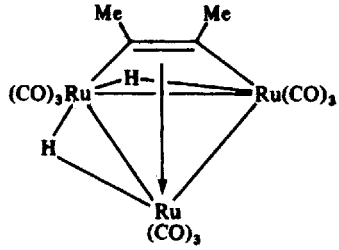

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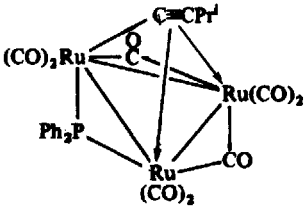

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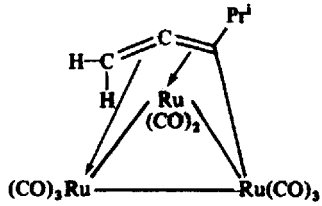
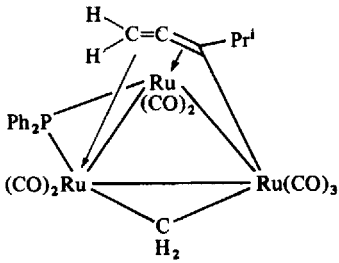


(160)

to be exclusively cis by labelling experiments; cis-trans isomerization about the C = C bond of derivatives of structure (137) is catalysed by pyridine via the intermediacy of the zwitterion $Os_3H(\mu,\eta^1\text{-}CHCH_2py)(CO)_{10}$.[256] Reaction of $(CO)_5MC \equiv CPh$ (M = Mn, Re) with the σ-acetylide (138) results in C-C coupling to give (139), related in structure to (136).[257] Nmr studies show that the cation produced on protonation of complexes of structure (136) has the tilted structure (140) rather than the upright carbenium ion structure (141).[258] Reaction of $H_2Os_3(CO)_{10}$ with $HC \equiv CCOMe$ yields initially a mixture of (142) and its isomeric ketone-bonded complex (143), both of which isomerize on heating to (144) which undergoes decarbonylation to give (145); complex (144) is also obtained by reaction of $Os_3(CO)_{12}$ with $CH_2 = CHCOMe$, though use of substituted enones (RCH = CHCOMe) yields instead complexes of structure (146).[259]

Reaction of $H_2Os_3(CO)_{10}$ with $CF_3C \equiv CCF_3$ yields the μ_3-vinyl complex (147). Reaction with a variety of $2e^-$ ligands induces hydrogen migration; thus, treatment with CO or PEt_3 yields the cis complex (148), whereas Br^-, I^- and Cl^- yield the trans-complex (149). Use of F^- generates (150), the additional hydrogen being derived from water. Attempted alkylation of (150) using Me_3O^+ results in hydride abstraction to regenerate (147) which sequentially eliminates CO and HCF_3 to give (151) and (152).[260,261] Reaction of $M_3(CO)_{12}$ with $HC \equiv CCH_2NMe_2$ yields complexes of structure (153), formed presumably via (154) followed by a 1,3-shift of the NMe_2 group.[262] Use of $MeC \equiv CCH_2NMe_2$ yields (155) which thermally isomerizes to (156); the amine residue of (155) may be eliminated on either hydrolysis or hydrogenolysis to give (157) and (primarily) (158) respectively.[263] Reaction of the acetylide complex (159) with CH_2N_2 results in sequential methylene addition to give (160) and (161); further CH migration to the organic ligand may be induced in (161) to give (162).[264] The bridged phosphide $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ undergoes acetylene and CO insertion on reaction with $PhC \equiv CPh$ to give (163) which undergoes facile decarbonylation of the acyl CO.[265] The unsaturated cluster $HRu_3(CO)_9(\mu\text{-}PPh_2)$ reacts with $PhC \equiv CPh$ without ligand loss to give (164).[266]

The $46e^-$ cluster $Fe_2Ru(CO)_9(PhC \equiv CPh)$ has the acetylene perpendicular to the Fe_2 edge of the metal triangle.[267] In contrast, acetylene is parallel to the metal-metal edge in the



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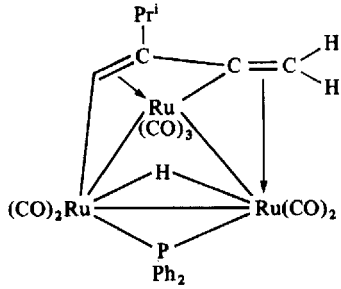

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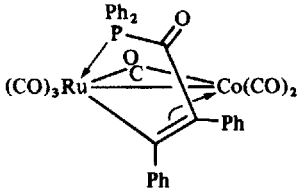

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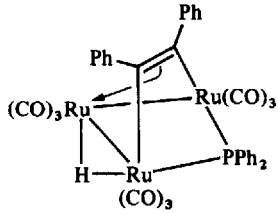

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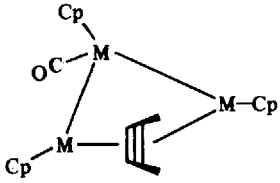

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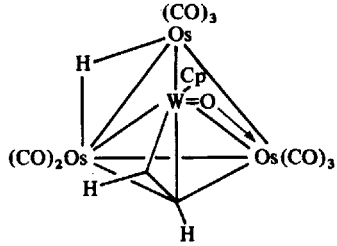
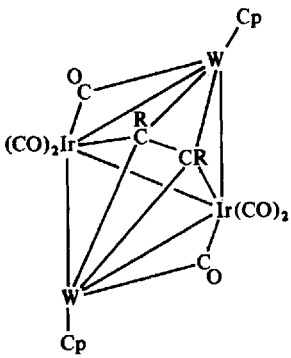


(166)

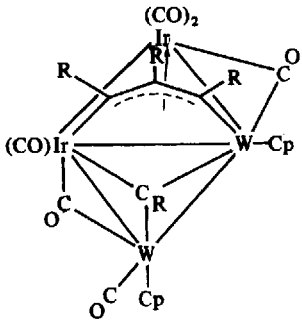
$47e^-$ cluster $[Fe_3(CO)_9(MeC \equiv CO)]^-$, obtained by reductive coupling of carbyne and CO in $[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CMe)]^-$.[268] The $48e^-$ complex $RuCo_2(CO)_9(HC \equiv CBu^t)$ also contains acetylene parallel to one Ru-Co edge; this complex rearranges thermally to the vinyldene derivative $RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C = C(H)Bu^t)$.[269]

$Cp_3M_3(\mu_3\text{-}CO)(\mu_3\text{-}PhC \equiv CPh)$ (M = Rh, Ir) undergo alkyne scission on flash pyrolysis to give $Cp_3M_3(\mu_3\text{-}CPh)_2$ complexes; calculations indicate that the rate determining step is not CO loss but formation of an intermediate of structure (165).[270] Unlike its aryl substituted analogues, $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}HC \equiv CH)H$ does not undergo alkyne scission on decarbonylation with Me_3NO, but yields instead the oxo-acetylene complex (166).[271] A complex of stoichiometry $CpWOs_3(CO)_6(\mu\text{-}O)(\mu_3\text{-}CCH_2C_6H_4Me)$ contains a similar oxo-ligand.[272] Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with $PhC \equiv CPh$ results in coordination <u>via</u> cleavage of the W-W bond to give (167), but fission via cleavage of the W-Ir bond to give (168).[273]

Reaction of $[Ir_4(CO)_{11}Br]^-$ with olefins and dienes in the presence of $AgBF_4$ gives high yields of $Ir_4(CO)_{11}$(olefin) and $Ir_4(CO)_{10}$(diene) complexes.[274]



(167) R = Ph



(168) R = Ph

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14

π-Cyclopentadienyl, π-Arene, and Related Complexes†

BY W. E. WATTS

1 Introduction

The organisation of this Report is similar to that of Volume 13. Cyclopentadienyl and arene complexes that contain metal-metal bonds, carbene, carbyne, or hydrocarbyl ligands, and reactions that involve replacement or elaboration of other ligands present, generally are not included (see Chapters 9-13). Only those metalla-borane and -carbaborane complexes that also incorporate a Cp or arene ligand are described, and crystal-structure determinations are included only where results of particular significance or solutions to structural problems are provided.

2 Studies of General Interest

Review articles that contain material relevant to this Chapter have appeared, dealing with electron-transfer reactions of Cp- and arene-metal complexes,[1] electron-rich half-sandwich complexes that incorporate a Cp or arene ligand ("metal bases par excellence"),[2] inelastic electron tunnelling spectra of cymantrene and benchrotrene complexes,[3] mechanisms of catalysis by organometallic complexes,[4a] polymerisation and co-polymerisation of metal-containing compounds,[4b] chelated complexes of the π,π-type and π,n-type,[4c] and the factors controlling the site of nucleophilic attack on metal-complexed cyclic π-hydrocarbons.[5]

3 Mono-(π-cyclopentadienyl)metal Complexes

Studies of General Interest.- MO calculations have been reported for complexes of the type $CpM(L)_nH$ with a view to understanding the factors responsible for the acidic or hydridic character of the M-H bond.[6] Redistribution reactions that involve exchange of Cp ligands between different $CpM(L)_n$ complexes have been reviewed.[7] A variety of bimetallic μ-fulvalene complexes of Cr, Mo, W, Co, and Ru, including the mixed-metal complex $[(OC)_3Mo\text{-}Ru(CO)_2(\mu\text{-fulvalene})]$,

† Throughout this review, the abbreviations Cp, Cp', Cp^*, and hmb explicitly denote (η^5-C_5H_5), (η^5-C_5H_4Me), (η^5-C_5Me_5), and (η^6-C_6Me_6) ligands, respectively.

[For References see page 364

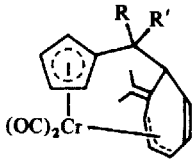
has been synthesised by reactions of dihydrofulvalene with metal carbonyls.[8] Whereas two-electron oxidation of $[CpCr(NO)_2]_2$ affords $[CpCr(NO)_2]^+$ reversibly, further oxidation of $\{[CpFe(CO)_2]_2\}^+$ causes irreversible scission.[9]

Titanium, Zirconium, and Hafnium.- The photoelectron spectra of $CpMX_3$ (M = Ti, Zr, Hf; X = Cl, Br) and some Cp' and Cp* analogues have been analysed.[10] Various rearrangements of the dithiocarbamate ligands in $CpM(Me_2NCS_2)_3$ (M = Ti, Zr, Hf) have been studied with the aid of variable-temperature ^1H n.m.r. spectroscopy.[11] Cyclic voltammetric studies on the sandwich complex $CpTi(\eta^8\text{-cot})$ and its Cp', indenyl, and fluorenyl analogues have been described.[12]

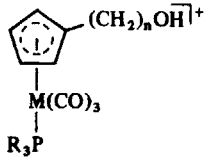
Vanadium, Niobium, and Tantalum.- The ^{51}V n.m.r. spectra of $[CpV(CO)_3EPh_3]^-$ (E = Si, Ge, Sn, Pb)[13] and the ^{31}P n.m.r. spectra of $CpNb(CO)_{4-n}(PR_3)_n$ (R = H, alkyl, aryl, OR, NMe_2, etc.; n = 1,2)[14] have been recorded. The complex $CpV(\eta\text{-allyl})_2$, in contrast with Ti analogues, is an active catalyst for double-bond isomerisation of alkenes.[15] Photochemical reactions of 6,6-disubstituted pentafulvenes with complexes such as $HV(CO)_4(dppe)$ proceed by hydride-transfer to the pentafulvene and formation of η-cyclopentadienyl complexes, e.g. $(\eta\text{-}C_5H_4CHR_2)V(CO)_2(dppe)$.[16] Reduction of $CpM(CO)_4$ (M = Nb, Ta) with Na in liquid NH_3 affords the dianions $[CpM(CO)_3]^{2-}$ which are isolable as cesium salts.[17] The complex $[Cp^*NbCl_2]_2$ has been synthesised and found to react with hex-3-yne to give $Cp^*Nb(\eta\text{-hex-3-yne})Cl_2$.[18]

Chromium, Molybdenum, and Tungsten.- The radical anions $[CpM(CO)_2(NO)]^-$ (M = Cr, Mo) have been prepared by electrochemical reduction of the neutral analogues and their structures have been investigated by the use of e.s.r. spectroscopy.[19] Efficient methods of synthesis of salts of the anions $[CpM(CO)_3]^-$ (M = Cr, Mo, W) and ring-formylated derivatives have been described,[20] and chloride-displacement reactions of hexachlorocyclotriphosphazene with these anions have been investigated.[21] Photochemical reactions of pentafulvenes with $(\eta^6\text{-dimethylheptafulvene})Cr(CO)_3$ have given the unusual products (1).[22] The paramagnetic complex $CpMo(\eta\text{-allyl})_2$ has been synthesised and its crystal structure has been determined.[23]

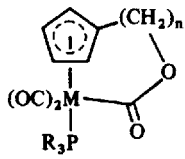
Deprotonation of cations of the type (2; M = Mo, W; n = 1,2) affords the corresponding cyclic ester complexes (3) resulting from intramolecular reaction; the analogues with n = 3 give only products of intermolecular reaction; treatment of the complexes (3; n = 2) with MeOH leads to ring-opening to give the σ-carbomethoxy products (4).[24] Cycloaddition reactions of complexes of the type (5) with


R
R'
(OC)2Cr

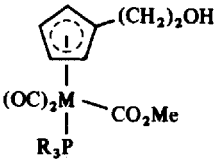
(1)


(CH2)nOH
M(CO)3
R3P

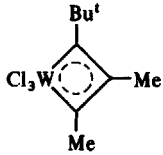
(2)


(CH2)n
O
(OC)2M
O
R3P

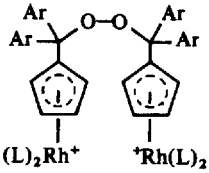
(3)


(CH2)2OH
(OC)2M
CO2Me
R3P

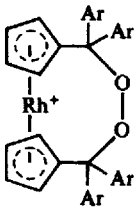
(4)


Bu^t
Cl3W
Me
Me

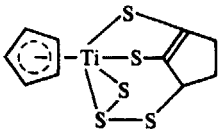
(5)


Ar
O—O
Ar
Ar
Ar
(L)2Rh+
+Rh(L)2

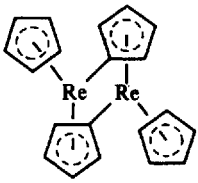
(6)


Ar
Ar
O
Rh+
O
Ar
Ar

(7)


S
Ti
S
S
S
S

(8)


Re
Re

(9)

RC≡CR proceed by insertion of the alkyne into a W-C bond and ligand reorganisation to give ring-peralkylated η-cyclopentadienyl products.[25] An efficient "one-pot" synthesis of $CpW(CO)_3Cl$ has been reported.[26] Interaction of W vapour with a mixture of cyclopentane and PMe_3 affords $CpW(PMe_3)H_5$; with cyclopentene in place of cyclopentane, $CpW(PMe_3)_2$(η-cyclopentene)H and $CpW(PMe_3)_2H_3$ are formed.[27]

Manganese and Rhenium.- An i.r./Raman study[28] and a proton n.m.r. study (in nematic liquid crystal solvents)[29] of $CpM(CO)_3$ (M = Mn, Re) have been reported, and there have been studies of electron-impact reactions of cymantrene and various related complexes.[30] The salt $K^+(C_5X_5)^-$ (X = CO_2Me) reacts with $BrMn(CO)_5$ to give $(\eta\text{-}C_5X_5)Mn(CO)_3$ which has been converted into several other cymantrene derivatives.[31] Reaction of Cp_2Mn with TMED gives $CpMn(\eta^1\text{-}C_5H_5)$(TMED) whose unusual crystal structure has been determined.[32] Ring-lithiated cymantrene (RLi) reacts with CdI_2 to give RCdI and R_2Cd.[33] When $CpMn(CO)_2(SiPh_3)Me$ is treated with PPh_3, one of the products is $Cp'Mn(CO)_2(PPh_3)$ in which migration of the methyl group from the metal atom to the ring has occurred.[34]

Electrophilic substitution of $CpRe(CO)_3$ occurs on reaction with $MeOCH_2Cl$ in the presence of Al_2Cl_6 to give $(\eta\text{-}C_5H_4R)Re(CO)_3$ (R = CH_2Cl) which is readily hydrolysed to the corresponding alcohol (R = CH_2OH).[35] The lithio-derivatives $(\eta\text{-}C_5H_4Li)Re(NO)(PPh_3)COR$ (R = Me, Ph, CH_2Ph) rearrange rapidly, even at -78°C, by metal-to-ring migration of the acyl group to give $[(\eta\text{-}C_5H_4COR)Re(NO)(PPh_3)]^-Li^+$ which can be trapped by reaction with MeI to give the neutral Re-Me product; the lithio-derivatives $(\eta\text{-}C_5H_4Li)Re(NO)(PPh_3)CH_2R$ (R = H, Ph) of the metal-alkyl complexes, on the other hand, are stable to rearrangement and react normally with MeI and Ac_2O to give methyl- and acetyl-cyclopentadienyl products, respectively.[36] The trioxide $Cp^*Re(O)_3$ is readily obtained by photochemical oxidation[37a] of $Cp^*Re(CO)_3$ and by high-pressure oxygenation of $Cp^*Re(CO)_2$(THF).[37b]

Iron and Ruthenium.- A spectroscopic study (i.r., ^1H and ^{13}C n.m.r., ^{57}Fe Mössbauer) of complexes of the type $CpFe(CO)(L)Ar$ has been reported,[38] and there have been extended Hückel calculations of the conformational preferences of the related complexes $CpFe(CO)(PPh_3)R$.[39] The i.r. spectra of the transient species $CpFe(CO)_2$ and $CpFe(\mu\text{-}CO)_3FeCp$, produced by flash photolysis of Fp_2, have been obtained by use of a line-tunable CO laser.[40] Electrochemical reduction of complexes of the type $FpER_3$ (E = Si, Ge, Sn) has been investigated.[41] Contrary to earlier views, the complex FpH has been shown to be not unduly thermally labile and can be

maintained in solution for several hours at room temperature.[42] The mechanism of formation of the related complex $Cp^*Fe(CO)(dppe)H$ by the reaction of $LiAlH_4$ with $[Cp^*Fe(CO)(dppe)]^+$ has been investigated.[43] The cation $[Fp(CO)]^+$ undergoes exo-addition of phosphide anions $R^1R^2P^-$ (R^1,R^2 = $SiMe_3$, Bu^t) to the Cp ligand; at room temperature, the resulting η^4-cyclopentadiene products lose CO with rearrangement to give $FpPR^1R^2$.[44]

The pK_a values of the carboxylic acids $(\eta\text{-}C_5H_4CO_2H)Fe(CO)_2R$ (R = Ph, CH_2Ph, cymantrenyl) have been measured.[45] Reaction of $RuCl_3$ with a mixture of pentamethylcyclopentadiene and PMe_3 affords $Cp^*Ru(PMe_3)_2Cl$ which has been converted into a series of other Cp^*Ru-containing complexes.[46]

Cobalt, Rhodium, and Iridium.- There have been MO calculations of the structures of $CpM(CO)_2$ and $Cp^*M(CO)_2$ (M = Co, Rh)[47] and $CpCo(\eta\text{-}L)$ (L = cyclobutadiene, cyclopentadienone).[48] Photoelectron spectra have been determined for a variety of complexes incorporating CpM and Cp^*M residues (M = Co, Rh, Ir).[49] The electronic structures of radicals produced by electrochemical reduction of $CpCo(RN_4R)$ (R = Me, aryl) have been investigated by use of e.s.r. spectroscopy.[50] The bimetallic complexes $(\eta\text{-}C_5R_5)M(\mu\text{-cot})M(\eta\text{-}C_5R_5)$ (M = Co, R = Me; M = Rh, R = H) undergo reversible two-electron oxidation and the crystal structure of a salt of the dicationic Rh_2 complex has been determined.[51] The dimer $[CpCo(\mu\text{-}NO)]_2$ is cleaved upon reaction with Na-Hg affording $[CpCo(NO)]^-Na^+$ which displaces Cl^- from R_3SnCl to give $CpCo(NO)SnR_3$ (R = Me, Ph).[52] Rates of replacement of a CO ligand of $(\eta^5\text{-}L)Rh(CO)_2$ by PPh_3 are very sensitive to the identity of the ligand L and decrease along the series L = indenyl > Me_7-indenyl > $C_5H_4NO_2$ > $C_5H_4\overset{+}{P}Ph_3$ >> Cp.[53]

A review of [2 + 2 + 2]-cycloadditions mediated by complexes such as $CpCo(CO)_2$ has appeared,[54a] and there have been further examples of the use of such reactions for the synthesis of compounds containing benzene[54b] and pyridine[55] ring systems. The crystal structure of $Cp^*Rh(\eta\text{-}1,3\text{-dimethylallyl})Cl$ at -120°C has revealed an unusual $(\eta^4:\eta^1)$-type of asymmetric bonding of the Cp^* ligand to the metal atom.[56] Reactions of 6,6-diarylpentafulvenes with $[Rh(L)_2]^+$ (L = CO, phosphite, alkene) afford cations of the types $[(\eta\text{-pentafulvene})Rh(L)_2]^+$ and $[(\eta\text{-pentafulvene})_2Rh]^+$ which add O_2 to give peroxy-products of the types (6) and (7), respectively.[57] A series of complexes of the type $[(\eta^5\text{-azulene})M(\eta^4\text{-diene})]^+$ (M = Rh, Ir; diene = cod, nbd, F_4-benzobarrelene, duroquinone) has been prepared and isolated in salts.[58]

Thermolysis of a salt of $[(\eta^4\text{-L})Ir(PAr_3)_2]^+$ (L = 5,5-dimethylcyclopentadiene) gives $[Cp'Ir(PAr_3)_2Me]^+$ by migration of a methyl group from the ligand to the metal atom.[59]

Nickel, Palladium, and Platinum.- The complex CpNi(NO) has been synthesised by electrolysis at a nickel anode of a solution of cyclopentadiene in MeCN or DMSO containing $Et_4N^+Br^-$, followed by treatment with NO.[60] Treatment of $(Me_3P)_2Ni(CH_2Bu^t)Cl$ with CpNa affords $CpNi(PMe_3)CH_2Bu^t$.[61] A series of complexes of the type $(\eta\text{-}C_5Ph_5)Pd(\eta^3\text{-L})$ (L = allylic ligand) has been prepared by reactions of $(C_5Ph_5)^-Na^+$ with $[(\eta^3\text{-L})PdCl]_2$ in THF; the parent Pt analogue $(\eta\text{-}C_5Ph_5)Pt(\eta^3\text{-}C_3H_5)$ has been obtained similarly.[62]

Actinide Elements.- Complexes of general structure $(\eta\text{-}C_5H_4R)M(solv)_xCl_3$ (R = H, Me; M = Th, U; solv = THF, MeCN; x = 2,3) have been obtained from MCl_4 by chloride-displacement reactions.[63]

4 Bis-(π-cyclopentadienyl)metal Complexes

Studies of General Interest.- A review dealing with the obtention of reactive organometallic compounds from metallocenes has appeared.[64] Quantitative estimates of steric strain in Cp_nM molecules (n = 2-4) have been calculated,[65] and methods of evaluation of metal-ligand bond strengths in complexes of the type $Cp_2M(L)_2$ have been discussed.[66] Standard enthalpies of formation of complexes of the latter type (M = Ti, Mo, W; L = thiolate) have been measured by reaction solution calorimetry.[67] State correlation diagrams have been proposed for photochemically-induced dissociations of Cp_2ReH, $Cp_2M(CO)$, and $Cp_2M(R)H$ (M = Mo, W; R = H, Me).[68] Inelastic electron tunnelling spectra of various metallocenes and metallocenium ions (M = Fe, Co, Ni) have been recorded.[69]

Diamines of structure $(\eta\text{-}C_5H_4NMe_2)_2M$ (M = Fe, Co^+, $TiCl_2$) have been prepared by direct synthesis from $(C_5H_4NMe_2)^-Li^+$.[70] Thermally-induced displacements of Cp ligands from Cp_2M (M = Co, Ni) have afforded products of the types $CpCo(\eta^4\text{-diene})$, $CpNi(\eta^3\text{-allylic})$, and $(\eta^4\text{-tetracyclone})_2Ni$.[71] The Se-M-Se bridging chains in the bimetallic complexes $(\eta\text{-}C_5H_4R)_2M[Se(\eta\text{-}C_5H_4)]_2Fe$ (M = Zr, Hf; R = H, Bu^t) do not undergo conformational inversion as is usually found for other [3]ferrocenophane derivatives.[72]

Scandium.- The complex $Cp_2Sc(BH_4)$ has been synthesised and its properties have been compared with those of related complexes such as $Cp_2Zr(BH_4)_2$.[73]

Titanium, Zirconium, and Hafnium.- Carbonylation reactions of zirconocene complexes have been reviewed.[74] There have been

calculations of the electronic configurations of the complexes Cp_2MX_2 (M = Ti, Zr; X = halide).[75] Several spectroscopic studies have been described, viz., the ^{47}Ti and ^{49}Ti n.m.r. spectra of Cp_2TiX_2 and ring-substituted derivatives,[76] the ^{91}Zr n.m.r. spectra of $Cp_2Zr(L)_n$ and related complexes,[77] and the negative-ion mass spectra of $Cp_2Ti(OR)_2$.[78] E.s.r. spectroscopy has been used to investigate the photochemical breakdown of Cp_2ZrX_2 and $Cp^*_2ZrX_2$ (X = Cl, Me),[79] and the radical anion resulting from electrochemical reduction of $Cp_2Ti(NCS)_2$.[80]

A novel rearrangement occurs in the thermolysis of Cp_2TiS_5 which leads to detachment of a Cp ligand from the metal and formation of the unusual product (8) whose crystal structure has been determined.[81] Variable-temperature n.m.r. spectroscopy has been used in a study of the conformational mobility of the polysulphide chains in Cp_2MS_5 and $Cp^*_2MS_3$ (M = Ti, Zr, Hf).[82] Diastereoselectivity in the addition of $Cp_2Ti(CH_2CH{=}CHMe)X$ (X = halide) to RCHO, to give finally $RCH(OH)CH(Me)CH{=}CH_2$, is sharply reversed when the reaction is carried out in the presence of BF_3.[83] A derivative of Cp_2TiCl_2 incorporating an interannular disiloxane bridge, and related polymers, have been prepared.[84]

Vanadium and Niobium.- E.s.r. spectra of Cp_2VX_2 (X = Cl, Br)[85] and $Cp_2M(SR)_2$ (M = V, Nb; R = Me, Ph)[86] have been recorded. The reactivity of the metal atom in Cp^*_2V towards addition of alkenes, alkynes, hetero-analogues, etc., has been explored and a variety of products has thereby been obtained.[87] The reactions of $(\eta\text{-}C_5H_4R)_2V$ (R = H, Me) with 1,1'-dilithioferrocene afford $[(\eta\text{-}C_5H_4R)_2V]_2X$ (X = 1,1'-ferrocenylene); a crystal structure (R = Me) shows that the Cp ligands of the metal-linking ferrocenylene group are severely distorted towards an η^4-bonding interaction.[88] One-electron reduction of Cp_2NbCl_2 affords $[Cp_2Nb(\mu\text{-}Cl)_2Nb(Cl)Cp_2]^-$ which is stable in solution for several hours at low temperatures.[89]

Chromium, Molybdenum, and Tungsten.- Mass spectra of the thiolate complexes $Cp_2M(SR)_2$ (M = Mo, W; R = alkyl) have been recorded.[90] Reaction of $Cl_2Cr(THF)$ with $(C_5Me_4Et)^-Li^+$, followed by CpNa, has given $CpCr(\eta\text{-}C_5Me_4Et)$ in 38% yield.[91] Flash photolysis of Cp_2MoH_2 in THF has given monomeric Cp_2Mo, which has been spectroscopically characterised; this highly reactive metallocene, which has a half-life of only a few μs, is consumed under the experimental conditions by reaction with the precursor to give the bimetallic product $CpMoH_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4)MoHCp_2$ or with added CO to give $Cp_2Mo(CO)$.[92] Reactions of Cp_2MH_2 (M = Mo, W) with SO_2 cause reduction/complexa-

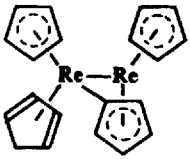
tion giving the S,O-linked chelated thiosulphate products $Cp_2M(S_2O_3)$.[93] U.v. spectroscopy has been used in an investigation of the electron-donor properties of $(\eta\text{-}C_5H_4R)_2WX_2$ (R = alkyl; X = Cl, Br, I) towards strong π-acids; reactions with TCNE, for example, give the radical-anion salts $[(\eta\text{-}C_5H_4R)_2WX_2]^+(TCNE)^-$ in MeCN solutions.[94]

Manganese and Rhenium.- Complexes of the type $(C_5H_5)_2Mn(PR_3)$, $(C_5H_5)_2Mn(dmpe)$, and related (C_5H_4Me) products, have been obtained by additions of the phosphines to $(C_5H_4R)_2Mn$ (R = H, Me); crystal-structure determinations have shown that one of the rings in these products is symmetrically η^5-bonded to the metal atom, while the other planar ring is tilted with respect to the Mn-ring centroid vector, such that the Mn-C distances vary in the range 233-272 pm.[95]

Attempts to prepare monomeric Cp_2Re from Cp_2ReH via Cp_2ReLi have been unsuccessful, but a dimer of proposed structure $Cp_2Re\text{-}ReCp_2$ has been isolated; this complex undergoes thermal and photochemical rearrangements to give the products (9) and (10), respectively.[96] Oxidation of Cp_2ReH with $CuCl_2$ affords $(Cp_2Re)^+(CuCl_2)^-$; in the crystal, the rings in the metallocenium cation are tilted by 30° from a parallel-plane arrangement.[97]

Iron and Ruthenium.- A book on the chemistry of ferrocene has been published.[98] MO calculations on FcH and polychlorinated derivatives have been carried out in an attempt to account for the anomalously large quadrupole splittings found for the latter.[99] Spin-lattice relaxation measurements for FcR (R = H, Bu^t, CMe_2Et) have been carried out[100,101] and activation energies for ring rotation and molecular tumbling have been determined[101] for the alkyl derivatives. Photoelectron spectra of FcCl and 1,1'-dihaloferrocenes,[102] and n.m.r./i.r./Mössbauer spectra of aryl- and aroyl-ferrocenes[103] have been discussed. Bond dissociation energies (for Cp-Fe) for FcH have been obtained from thermal decomposition rates.[104]

There have been further studies of redox reactions of ferrocene derivatives and one-electron oxidation potentials have been correlated with ^{57}Fe Mössbauer quadrupole splittings,[105] ^{13}C n.m.r. chemical shifts,[106] and Hammett σ-constants (for aryl-containing derivatives).[106] Further studies of the oxidation of FcR to $(FcR)^+$ (R = H, Me) have been reported,[107] and the kinetics of electron transfer from FcH to $[Co(dmg)_3(BF)_2]^+$ [108] and to $(FcR)^+$ from NADH[109] and ferrocytochrome c [110] have been measured. Oxidations of $[Cp^*Fe(CO)_2]_2$ by $(FcH)^+$ in donor solvents have afforded salts of the



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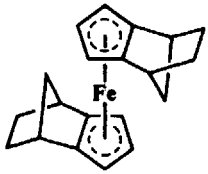

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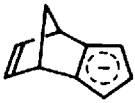

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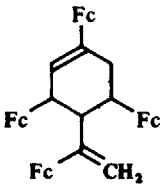

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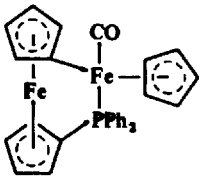

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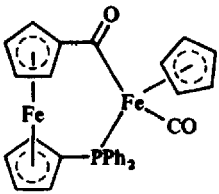

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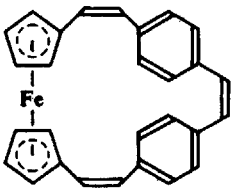

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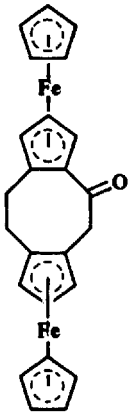

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type $[Cp^*Fe(CO)_2(solv)]^+(PF_6^-)$ (solv = THF, MeCN, py, Me_2CO) which are useful precursors for the preparation of other Cp^*Fe-containing complexes.[111] Various $(FcH)^+X^-$ salts have been found to have anti-neoplastic (tumour-inhibiting) activity in mice.[112]

Reaction of the isodicyclopentadienide anion (11) with Fe^{2+} affords stereoselectively the ferrocene derivative (12) through attachment of the metal atom to the exo-face of the ligand anions; the related dehydro-anion (13) complexes with Fe^{2+} in the same stereochemical sense.[113] Electrophilic substitution of FcH by aldehydes and ketones R^1COR^2 in conc. H_2SO_4 affords reasonable yields (33-55%) of alcohols $FcC(OH)R^1R^2$ and, in some cases, related alkenes resulting from alcohol dehydration, but such reactions are described as "extraordinarily capricious".[114] Photochemically-induced substitution reactions of FcX (X = Cl, Br, I) with alcohols (ROH) give modest-to-good yields of the alkoxyferrocenes FcOR.[115] The first reported synthesis of FcNO has been achieved, the key reaction involving nucleophilic addition of FcLi to an NO ligand of $CpCr(NO)_2Cl$.[116]

Lithiated ferrocenes have been used to effect the introduction of SiH(Ph)Me[117] and $SC(S)NR_2$[118] substituents into the cyclopentadienyl rings. The reactions of FcI and Fc_2Hg with Yb metal have afforded FcYbI and Fc_2Yb, respectively; cymantrenyl analogues react similarly.[119] Thermal reactions of FcH with quinoline, isoquinoline, and imidazole in the presence of $PhSO_2N{=}C(Cl)Ph$ have afforded products of addition of Fc and $C(Ph){=}NSO_2Ph$ groups to these heterocyclic compounds.[120] The properties of inclusion complexes of β- and γ-cyclodextrin with FcH and its acetyl derivatives have been investigated.[121]

Several mechanistic studies in ferrocene chemistry have been reported including the regioselectivity of hydroboration-oxidation reactions of alkenylferrocenes,[122] the kinetics of S_N1 hydrolysis reactions of FcCH(OAc)Ar (Hammett ρ-value = -1.40 against σ^+ aryl substituent constants),[123] and the kinetics of hydrolysis of ferrocenyliminium cations to acylferrocenes.[124] Such cations and ruthenocenyl analogues can be synthesised by ligand-exchange reactions of $[CpFe(\underline{p}\text{-xylene})]^+$ and $[CpRu(NCMe)_3]^+$ with various 6-(dimethylamino)-pentafulvenes.[125] A series of new ferrocenylalkylium salts $(Fc\overset{+}{C}R^1R^2)(BF_4^-)$ has been prepared from acylferrocenes.[126] Comparison of the ^{19}F n.m.r. spectra of $\underline{p}\text{-}FC_6H_4\overset{+}{C}HMc$ (Mc = Fc, ruthenocenyl) indicates that the ruthenocenyl group more effectively delocalises the positive charge.[127] Mössbauer spectra of $Fc\overset{+}{C}HAr$ and $Fc\overset{+}{C}(OH)Ar$

(Ar = aryl, Fc) have been discussed.[128] Treatment of the 1,3-diferrocenyl-1-methylallyl cation with $PhNMe_2$ or py causes cyclodimerisation to give finally the diene (14) and a mechanism for the reaction has been proposed.[129]

The chemistry of bridged ferrocenes (ferrocenophanes) has continued to attract much interest and earlier work has been reviewed.[130] The Mössbauer spectra of [1]ferrocenophanes (PPh and $GePh_2$ interannular bridges) have been discussed in relation to the ring-tilting present in these ferrocene derivatives.[131] The former compound undergoes bridge-cleavage on treatment with PhLi and the resulting 1'-lithioferrocenyldiphenylphosphine reacts with FpI to give the novel [2]- and [3]-ferrocenophanes, (15) and (16), respectively.[132] Spectroscopic evidence (particularly from Mössbauer studies) has been interpreted to indicate the presence of Fe-Hg and Fe-Sn bonds, respectively, in the adducts of [2]ferrocenophanes with HgX_2 and SnX_4.[133a] Similar evidence also suggests the presence of a strong Fe····I interaction in the I_3^- salt resulting from one-electron oxidation of [2]ferrocenophane with I_2; such interaction is absent with corresponding salts obtained from [3]- and [4]-ferrocenophanes.[133b]

Treatment of a series of alkyl-substituted [m]ferrocenophanes (m = 3-5) with HBF_4 has afforded long-lived metal-protonated cations which have been characterised by ^1H n.m.r. spectroscopy.[134] Other work on [3]ferrocenophanes includes studies of i.r. and n.m.r. spectra of bridge-carbonyl derivatives,[135a] the crystal structure of the ring-tilted (by 9.8°) 1,3-dione derivative,[135b] and the electrochemical reduction of the β-formyl derivative and other acylferrocenes.[136] Syntheses of new derivatives of [3]ferrocenophan-1-one[137] and [5]ferrocenophane-1,5-dione[138] and of the unusual ferrocenophanes (17)[139] and (18)[140] have been reported. A variety of [m]ferrocenophanes and [m]ruthenocenophanes incorporating sulphur and/or oxygen atoms in the bridging chains has been synthesised[141] and their use for solvent extraction of metal cations has been assessed. The stereo-dynamics of conformational motion of the bridging chains in ferrocenophanes incorporating interannular S(R)-M(X_2)-S(R) linkages (M = Pd, Pt) have been studied by use of variable-temperature n.m.r. spectroscopy.[142] Polarisation-transfer sequences (INEPT and DEPT) in conjunction with ^2H n.m.r. spectroscopy have been used to assign signals in the ^{13}C n.m.r. spectra of novel ferrocene derivatives containing bridging cryptand groups.[143]

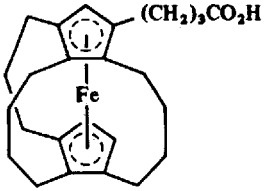
Several new multi-bridged ferrocenophanes[144,145] and ruthenocenophanes[146] incorporating up to four interannular carbon bridges have been synthesised and their structures established. Examples of novel hetero- to homo-annular bridge rearrangements of multi-bridge ferrocenes have been discovered; e.g. Friedel-Crafts cyclisation of the acid (19) affords the rearranged ketone (20).[144b] The Mössbauer spectra of a wide range of ferrocenophan-es and -ones incorporating one to four bridging chains have been discussed.[147]

The mechanism of liberation of H_2 which occurs when [1.1]ferrocenophanes are treated with protic acids has been investigated[148] and polymer-bound systems have been incorporated into photoelectrochemical devices for H_2 production.[148b] The properties of derivatives of [1.1]ferrocenophane containing an additional three-carbon chain linking the rings of one of the ferrocene residues have been studied.[149] Further detailed investigations (see Volume 13, refs. 115,155) of the properties and structures of the mixed-valence cations resulting from one-electron oxidation of [m.m]ferrocenophanes (m = 0-2) and biferrocenyls have been reported.[150] Reaction of the 2,1'-dilithio-derivative of $FcCH_2NMe_2$ with $HgCl_2$ affords a [1.1]ferrocenophane with two Hg-atom bridges which can be oxidised selectively to both mono- and di-cationic species.[151]

Methods of synthesis of salts of $(Cp_2RuX)^+$ (X = Cl, Br, I) have been described;[152,153] these react with water to give Cp_2Ru and, surprisingly, $CpRu(\eta^4\text{-cyclopentadienone})X$.[152] It has also been established that the photochemical reaction of Cp_2Ru with CCl_4 gives $(Cp_2RuCl)^+$ and not Cp_2Ru^+ as previously claimed.[153]

Cobalt.- The spin-density distribution in Cp_2Co has been investigated in a single-crystal proton ENDOR study of the metallocene dissolved in a cymantrene host lattice.[154] A review of the chemistry of Cp_2Co^+ has appeared.[155] Reactions of this cation with a variety of organometallic reagents RM (R = alkyl, benzyl, allyl; M = Li, MgX, ZnR, AlR_nCl_{2-n}) have given the corresponding exo-addition products $CpCo(\eta^4\text{-}C_5H_5R)$.[156]

Nickel.- There has been an e.s.r. spectroscopic study of (Cp_2Ni^+)-(BF_4^-), doped with ^{61}Ni, dissolved in several diamagnetic host lattices.[157] The short-lived anion Cp_2Ni^-, obtained by electrochemical reduction of Cp_2Ni, fragments by loss of a cyclopentadienyl anion to give CpNi which can be trapped with CO.[158] Further examples of displacements of one Cp ligand from Cp_2Ni have been reported to give products of the types $CpNi(\eta\text{-ene})R$,[159] $CpNi(ER_3)I$ and $[CpNi(ER_3)]^+I^-$ (E = P, As, Sb),[160] $[CpNi(B_6H_6)]^-(Bu_4N^+)$,[161] and



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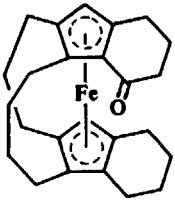

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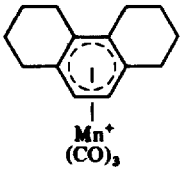

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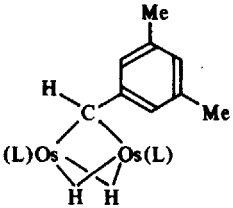

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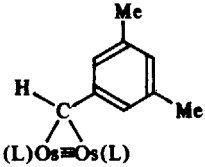

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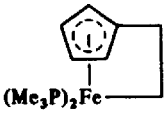

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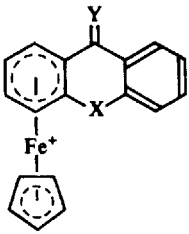

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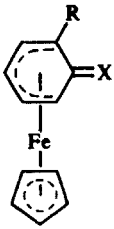

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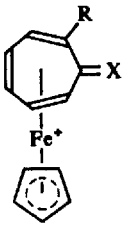

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CpNi(η^3-cycloalkenyl).[162]

Lanthanide and Actinide Elements.- The chemistry of organo-lanthanide compounds, including Cp and indenyl complexes, has been reviewed.[163] The molecular and electronic structures of such complexes of Pr, Nd, Yb, and U have been investigated by use of variable-temperature ^{1}H n.m.r. spectroscopy.[164] The first example of a lanthanide metallocene unsupported by additional ligands, viz. Cp^*_2Sm, has been obtained by the reaction of Sm vapour with C_5HMe_5; the Cp^* rings in the crystal are tilted by 40° from a parallel-plane arrangement.[165] New syntheses of a variety of Cp_2, Cp^*_2, and Cp_3 complexes of lanthanide elements have been described by various groups.[166,167] The THF adducts of Cp^*_2Yb and Cp^*_2YbCl exhibit chemiluminescence on reaction with O_2^- or O_2.[167]

An MO study of the structures of complexes of the type Cp_3UR has been reported.[168] Thermal decomposition of such complexes and their reactions with CO and CO_2 have been investigated.[169] A derivative of Cp_2ThR_2 has been synthesised in which the cyclopentadienyl rings are linked by an $SiMe_2$ bridge.[170] Complexes of the types $Cp^*_2M(OMe)(\mu\text{-}PH)M(OMe)Cp^*_2$ (M = Th, U),[171] $Cp^*_2Th(R)X$,[172] and $(\eta^5\text{-}L)_2U(\mu\text{-}F)_2(\mu\text{-}BF_4)_2U(\eta^5\text{-}L)_2$ [L = 1,3-bis(trimethylsilyl)cyclopentadienyl][173] have also been prepared.

5 Mono-(π-arene)metal Complexes

Studies of General Interest.- Dicationic benzene-metal complexes such as $[Cp^*M(\eta\text{-}PhH)]^{2+}$ (M = Rh, Ir) and $[(hmb)Ru(\eta\text{-}PhH)]^{2+}$ add two hydride ions (from $NaBH_4$) successively to give finally neutral products from which cyclohexene can be liberated by treatment with protic acid (i.e., overall benzene + $2H^-$ + $2H^+$ → cyclohexene); similar reactions occur with MeLi and MeONa in place of $NaBH_4$.[174]

Vanadium.- MO calculations on the triple-decker sandwich complexes CpV(arene)VCp (arene = PhH, mesitylene) have been correlated with photoelectron spectroscopic data.[175]

Chromium and Molybdenum.- New $Cr(CO)_3$ complexes of arenes have been synthesised by reactions of $Cr(CO)_6$ with a series of di- and tri-substituted benzenes,[176] 2-phenylindolizine,[177] chroman-4-one,[178] and benzoxazocine.[179] MO calculations on the bonding of $Cr(CO)_3$ to bi- and tri-phenylene have been reported.[180] There have been rate and equilibrium measurements of arene-exchange reactions of $(\eta\text{-arene})Cr(CO)_3$ with alternative arenes; such reactions are catalysed by I_2, cyclohexanone, and $(hmb)Cr(CO)_3$ and the mechanisms of exchange have been discussed.[181] Thermochemical mearurements on

benchrotrene and a series of ring-substituted derivatives have been carried out.[182] Electrochemical one-electron oxidations of a variety of ring-substituted benchrotrenes and (hmb)$W(CO)_3$ have been studied,[183,184] and the kinetics of breakdown of the resulting radical cations have been measured.[184]

The electronic spectra and photo-reactivities of slurries of various benchrotrene derivatives adsorbed on to silica gel have been studied.[185] In solution in CCl_4, several benchrotrenes have been found to be active photo-initiators of polymerisation of alkenes such as styrene.[186] Such reactions probably involve the production of $Cl_3C^{\bullet}$ radicals and, indeed, it has been shown that free-radical addition of CCl_4 to alkenes such as oct-1-ene is initiated in the presence of (η^6-naphthalene)$Cr(CO)_3$.[187]

The electronic[188] and mechanical[189] spectra of complexes of the type (η-PhH)$Cr(CO)_2$(L) (L = CO, CS, CSe, PPh_3) have been discussed. The ^{13}C (and ^{31}P) n.m.r. spectra of a range of such complexes have been recorded,[190] and variable-temperature ^1H n.m.r. spectroscopy has been used to investigate the conformational mobility of (η-C_6Et_6)$Cr(CO)_2$(L) (L = CS, PMe_3),[191] several ring-disubstituted derivatives of benchrotrene,[192] and the $Cr(CO)_2(PPh_3)$ complexes of 2,6-di-t-butylanisole and 2,6-di-t-butyl-4-methylanisole.[193] The stereochemical features of chiral complexes of the benchrotrene type and methods for their optical resolution have been discussed.[194] Stereo-controlled reactions of an optically-active $Cr(CO)_3$ complex of o-tolualdehyde, followed by metal decomplexation, have been used to achieve the asymmetric syntheses of benzenoid compounds.[195]

It is well established that the benchrotrenyl group (Bt) exerts a strong acidifying effect upon neighbouring benzylic C-H bonds. This effect is well illustrated by kinetic data[196] on the rates of benzylic deprotonation (with KH in THF) of uncomplexed and metal-complexed substrates; e.g. the relative rates for Ph_2CHR and $(OC)_3Cr(\eta$-Ph)CH(R)Ph are 1:460 (R = H) and 1:240 (R = Ph), respectively. In contrast with the properties of uncomplexed substrates, rates of deprotonation of the benchrotrenyl analogues do not vary appreciably with structure; e.g., whereas the kinetic acidity of fluorene is ca. 220 times greater than that of Ph_2CH_2, the corresponding difference in reactivity between their $Cr(CO)_3$ complexes is a factor of only ca. 5.[196]

The enhanced stability of Bt-substituted carbanions, and the stereo-controlled exo-addition of electrophiles to such species,

can be put to synthetic use. Many examples of such an approach have been reported by French chemists,[197] e.g. for the stereospecific 6-alkylation of oestradiol complexes,[197a] and for the synthesis of ethyl phenylpyruvates.[197c] Bt-stabilised carbanions are also more easily oxidised than are the corresponding uncomplexed benzylic anions; this property has been exploited in the O_2 oxidation of the $Cr(CO)_3$ complexes of toluene[198] and fluorene[199] to benzoic acid and fluorenone, respectively. There has been a further study (see Volume 11, ref. 279; Volume 12, refs. 269,295) of the influence of ligand structure and solvent on the $\eta^6 \rightleftharpoons \eta^5$ ligand-slip rearrangements of carbanions derived by benzylic deprotonation of the $Cr(CO)_3$ complexes of indene, fluorene, and fluoradene.[200]

It has also been established (see Volume 12, refs. 285-288; Volume 13, refs. 200-206) that the orientation of lithiation of the arene ligand ring in substituted benchrotrenes is strongly influenced by the nature of the substituent groups already attached to the ring. The regioselectivity of such reactions has been utilised in the directed syntheses of acyl-, aryl-, vinyl-, and allyl-arenes,[201] and 11-deoxydaunomycinone.[202] The distribution of isomeric products obtained following addition of $Me_2\bar{C}(CN)$ to the arene ring of the $Cr(CO)_3$ complex of N-methyltetrahydroquinoline has been found to be dependent on the temperature and duration of the reaction.[203] The rates of nucleophilic substitution of fluoride by methoxide in substituted fluorobenchrotrenes $(\eta\text{-}FC_6H_4X)Cr(CO)_3$ are sensitive to the identity of X and decrease through the series X = H > m-Me > p-Me > o-Me > p-OMe.[204] The ease of H/D exchange of arene ligand protons in reactions of the complexes $(\eta\text{-arene})Cr(CO)_2(L)$ (arene = PhH, mesitylene; L = CO, maleic anhydride) with CF_3CO_2D has been studied; the identity of the ligand L has little effect on the reactivity of the ring in these exchanges.[205]

Complexes of the type $(Ph_2PMe)_3Mo(\eta\text{-}Ph)P(Me)Ph$ bind both N_2 and H_2, reversibly.[206]

Manganese and Rhenium.- Reactions of Mn and Re vapours with benzene in conjunction with PMe_3, cyclohexene, or an alkane, have afforded a variety of new complexes including $(\eta\text{-PhH})Mn(PMe_3)_2H$, $(\eta\text{-PhH})Re(PMe_3)_2Ph$, $[(\eta\text{-PhH})Re(PMe_3)_2]_2$, $(\eta\text{-PhH})Re(\eta\text{-cyclohexa-1,3-diene})H$, and $[(\eta\text{-PhH})Re]_2(\mu\text{-H})_2(\mu\text{-}CR_2)$.[207] A series of salts of the type $[(\eta\text{-arene})M(CO)_3]^+X^-$ (M = Mn, Re) has been synthesised by reactions of $XM(CO)_5$ (X = Cl, Br) with arenes.[208,209] Hydride addition to $[(\eta\text{-mesitylene})Re(CO)_3]^+$ affords the corresponding neutral (η-cyclohexadienyl) product.[209] In reactions of $BrMn(CO)_5$ with

naphthalene and anthracene in the presence of Al_2Cl_6, complexation is accompanied by ligand reduction and the cations $[(\eta\text{-tetralin})\text{-}Mn(CO)_3]^+$ and $[(\eta\text{-9,10-dihydroanthracene})Mn(CO)_3]^+$, respectively, are formed; a similar reaction with tetralin itself gave not only the expected former cation, but also the cation (21) resulting from prior Al_2Cl_6-induced "dismutation" of tetralin.[210] Rate constants and activation energies have been obtained for the $\eta^6 \rightarrow \eta^5$ ligand-slip rearrangements of $(L)(OC)_2Mn^+$ complexes (L = CO, PBu^n_3) of fluorenyl carbanions.[211]

Reactions of salts of $[(\eta\text{-arene})Mn(CO)_3]^+$ (arene = hmb, mesitylene) with NaX under photochemical initiation and with $NaBH_4$ have afforded $(\eta\text{-arene})Mn(CO)_2X$ (X = Cl, Br, I) and $(hmb)Mn(CO)_2H$, respectively.[212] Various $[(\eta\text{-arene})Mn(CO)_3]^+$ salts have been converted finally into substituted cyclohexa-1,3-dienes by a four-step reaction sequence.[213]

Iron, Ruthenium, and Osmium.- Co-condensations of Fe vapour with PMe_3/benzene,[214] pentaborane(9)/but-2-yne,[215a] and decaborane(14)/arene,[215b] give the products $(\eta\text{-PhH})Fe(PMe_3)_2$, $(hmb)Fe[(MeC)_m(BH)_n]$ (m = 2, n = 4; m = 4, n = 3), and $(\eta\text{-arene})Fe(B_mH_n)$ (m = 9, n = 9, 13; m = n = 10), respectively. A similar reaction of Os vapour with benzene gives $(PhH)_2Os$ in which one ring is η^6-bonded and the other η^4-bonded; with mesitylene, the products (22) and (23) [L = (η-mesitylene)] result.[216] The benzene ligand of $(\eta\text{-PhH})Fe(PMe_3)_2$ is readily displaced by C_5HR_5 (R = H, Me) giving $(\eta\text{-}C_5R_5)Fe(PMe_3)_2H$; with spiro[2.4]hepta-4,6-diene, the metal-ring bridged product (24) is formed.[214]

Mössbauer parameters and crystallographic data for CpFe(hmb) and the corresponding 18-electron cation have been compared.[217] Ligand-replacement reactions of Cp_2Fe with xanthene and thioxanthene afford the corresponding cations (25; X = O, S; Y = H_2) which can be oxidised with $KMnO_4$ to the products (25; X = O, S, SO_2; Y = O); the γ-pyrone ring in the cation (25; X = Y = O) undergoes ring-opening in reactions with carbanions $X\bar{C}H_2$ (X = CN, NO_2) and amines to give 2,2'-disubstituted derivatives of $[CpFe(\eta^6\text{-benzophenone})]^+$.[218] The cot ligand in $(\eta\text{-cod})Ru(\eta^6\text{-cot})$ can be replaced by naphthalene; the naphthalene ligand in the resulting product $(\eta\text{-cod})Ru(\eta^6\text{-}C_{10}H_8)$ is readily exchanged for other arenes.[219a] Such $(\eta\text{-cod})Ru(\eta\text{-arene})$ complexes (arene = PhH, p-xylene, mesitylene) are active catalytic precursors for the homogeneous hydrogenation of alkenes and cycloalkenes under mild conditions.[219b]

Under photochemical conditions, the cationic cyclobutadiene

complex $[CpRu(\eta\text{-}C_4Ph_4)(CO)]^+$ undergoes cycloaddition of alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2 = Ph$, Me, CO_2Me; $R^1 = Ph$, $R^2 = Me$) accompanied by decarbonylation to give the arene sandwich cations $[CpRu(\eta\text{-}C_6Ph_4\text{-}R^1R^2)]^+$, isolable as BF_4^- salts.[220] The cations $[CpFe(\eta\text{-arene})]^+$ (arene = PhH, p-xylene, durene, naphthalene) react with hexamethylbicyclo[2.2.0]hexa-2,5-diene (a Dewar benzene) under visible-light irradiation to give $[CpFe(hmb)]^+$ with liberation of the original bound arene ligand.[221] There has been a study of photochemically-induced displacements, in a variety of solvents, of the arene ligand in salts of the cation $[CpFe(\eta\text{-}p\text{-xylene})]^+$ with various counterions; quantum yields ranged from 0.81 (in H_2O) to 0.084 (in CH_2Cl_2).[222] In a related study of photochemical displacements of the arene and Cp ligands of $[CpM(\eta\text{-arene})]^+$ (M = Fe, Ru) by phen to give $[Fe(phen)_3]^{2+}$, Hammett correlations of $\log[\phi/(1-\phi)]$ with arene σ_p substituent constants were found (ρ = 1.03 in CH_2Cl_2, 0.53 in MeCN).[223]

One-electron reduction of $[(\eta\text{-}C_5H_4CO_2H)Fe(hmb)]^+$ with Na-Hg affords the corresponding unstable 19-electron neutral acid which is then more slowly converted into a more stable carboxylate radical anion.[224] There has also been a study of stepwise electrochemical reductions of salts of cations of the types $[CpFe(\eta^6\text{-cyclophane})]^+$ and $[(CpFe)_2(\eta^6{:}\eta^6\text{-cyclophane})]^{2+}$ incorporating a variety of cyclophane ligands including [2.2]meta- and [2.2]para-cyclophanes and [2.2.2.2](1,2,4,5)-, [2.2.2.2.2]-, and [2.2.2.2.2.2]-cyclophanes.[225] The reactivities of $[CpRu(\eta\text{-PhX})]^+$ towards nucleophilic substitution of halide (X = F, Cl) have been investigated and found to be very similar to those of the Fe analogues [226]

Nucleophilic additions of PR_3 and R^- (from RLi; R = Me, Ph) to $[(\eta\text{-PhH})Ru(PMe_3)_2Cl]^+$ give (η-cyclohexadienyl) products in which replacement of chloride by the nucleophile has also occurred;[227a,b] the cation $[(\eta\text{-PhH})Os(PMe_3)_2I]^+$ undergoes exo-addition of R^- to give $(\eta^5\text{-}C_6H_6R)Os(PMe_3)_2I$[227b] which reacts with Ph_3C^+ to give $[(\eta\text{-PhR})Os(PMe_3)_2I]^+$; a mechanism for this latter reaction, which does not involve direct abstraction by Ph_3C^+ of the 6-endo-hydrogen atom, has been suggested.[227c] Complexes of the type (26; R = H, X = CH_2, CMe_2, etc.) react with electrophilic alkenes $CH_2{=}CHR$ (R = CN, CO_2Me) to give, following protonation, cationic adducts of the type $[CpFe(\eta\text{-Ph})XCH_2CH_2R]^+$, isolable in salts.[228] Reactions of the related complexes (26; R = H, X = O, S; R = Cl, X = O) with CH_2N_2 lead to ring-expansion, affording products of the type (27), isolated as PF_6^- salts.[229]

Photochemical reactions of PF_6^- salts of $[CpFe(\eta\text{-PhMe})]^+$ and $[Fp(CO)]^+$ with donors (L) in MeCN have afforded the salts $[CpFe(L)(NCMe)_2]^+(PF_6^-)$ (L = CO, PPh_3, cyclohexene, etc.).[230] A variety of new arene complexes of Ru has been synthesised, including $\{[(hmb)Ru(PPh_3)]_2(\mu\text{-Cl})_2\}^{2+}(PF_6^-)_2$,[231] $\{[(hmb)Ru]_2(\mu\text{-Cl})_3\}^+(PF_6^-)$,[231] $[(\eta\text{-PhH})RuBr]_2(\mu\text{-H})(\mu\text{-Br})$,[232] $\{[(\eta\text{-PhH})Ru]_2(\mu\text{-H})(\mu\text{-Cl})_2\}^+(PF_6^-)$,[232] and $(\eta\text{-}p\text{-cymene})Ru(PR_3)Cl_2$.[233]

Cobalt, Rhodium, and Iridium.- Dications of the type $[Cp^*Co(\eta\text{-arene})]^{2+}$ (arene = PhH, mesitylene, hmb, etc.) have been synthesised; electrochemical reduction of these complexes is reversible and can be controlled to give either the corresponding monocations or neutral complexes.[234] A full account has been published of the metal-assisted conversions of 3-(o-fluorophenyl)propan-1-ols into chromans (see Volume 10, ref. 350).[235] The cationic comples of 2-ethylnaphthalene with a $(Ph_3P)_2Ir^+$ residue has been synthesised; in this complex, the ligand is probably attached to the metal atom in an η^4-bonding mode and, in solution, it has been found that an equilibrium is established between the stereoisomers with the metal attached to the alternative naphthalene rings.[236] Complexes of the type $[(\eta\text{-arene})Ir(\eta^4\text{-L})]^+$ (L = trimethyltetrafluorobenzobarrelene; arene = p-xylene, Ph_3N) have been prepared and the crystal structures of salts have been determined; whereas the p-xylene ligand is η^6-bonded, the metal-complexed phenyl ring of the Ph_3N ligand is η^5-bonded with an uncomplexed exocyclic $C{=}NPh_2$ double bond.[237] Stepwise addition of two hydride ions to $[Cp^*Ir(\eta\text{-arene})]^{2+}$ can be achieved to give finally $Cp^*Ir(\eta\text{-cyclohexa-1,3-diene})$ products.[238]

Nickel.- Co-condensation of Ni vapour with PhMe affords a highly labile complex (PhMe)Ni in which the weakly bound ligand is possibly attached to the metal atom by η^2-bonding.[239] Reactions of $(\eta^3\text{-2-methylallyl})_2Ni$ with PhMe $HSiX_3$ (X = F, Cl) have yielded labile $(\eta\text{-PhMe})Ni(SiX_3)_2$ products.[240]

6 Bis-(π-arene)metal Complexes

Studies of General Interest.- Publication of a review of thermal decomposition reactions of bis(arene) complexes of V, Cr, and Mo has been announced.[241]

Titanium.- Metallic K effects one-electron reduction of $(\eta\text{-PhR})_2Ti$ (R = H, Me) to give $[(\eta\text{-PhR})_2Ti]^-K^+$ which can be isolated in a crystalline state.[242]

Vanadium.- Bis(germyl)mercury compounds oxidise $(\eta\text{-PhEt})_2V$; e.g.

reaction with $(Ar_3Ge)_2Hg$ affords $[(\eta\text{-PhH})_2V]^+[Hg(GeAr_3)_2]^-$ (Ar = C_6F_5).[243]

Chromium.- Co-condensations of Cr vapour with [10]paracyclophane[244] and anthracene[245] have given the corresponding $(\eta\text{-arene})_2Cr$ products; in the anthracene complex, the metal atom is bonded to the terminal ring of each ligand. When mixtures of two arenes are used in such reactions (e.g. PhCN together with PhMe, PhOMe, or PhAc), all three possible bis(arene) complexes result.[246a] Cyclohexene is oxidised to benzene on reaction with Cr vapour and bis(arene) complexes are formed, together with hydrocarbon products, when the reaction is conducted in the presence of an arene; e.g. reaction with cyclohexene and PhMe affords a mixture of $(\eta\text{-PhH})_2Cr$, $(\eta\text{-PhMe})_2Cr$, and $(\eta\text{-PhH})Cr(\eta\text{-PhMe})$.[246b] A series of semiconducting materials has been produced by reactions of $(\eta\text{-PhH})_2Cr$ with lamellar $FePS_3$.[247] One-electron reduction of $(\eta\text{-PhH})_2Cr$ with metallic K in DME in the presence of a crown ether affords a radical anion $[(PhH)_2Cr]^-$; spectroscopic evidence suggests that one benzene ring in this species is η^6-bonded, while the other is attached to the metal atom as a rapidly fluxional η^4-C_6H_6 ligand.[248]

Ion cyclotron resonance spectroscopy has been used to measure the gas-phase acidities of the methyl groups in the complexes $(\eta\text{-arene})Cr(\eta\text{-}C_6F_6)$ (arene = PhMe, m- and p-xylene); the results show that π-attachment of a $Cr(\eta\text{-}C_6F_6)$ residue to a methylarene ring raises the acidity of the methyl group by a factor similar to that produced by a p-NO_2 substituent.[249] Mono- and 1,1'-dilithio derivatives of $(\eta\text{-PhH})_2Cr$ have been converted into the ketones $(\eta\text{-PhCOAr})Cr(\eta\text{-PhX})$ (X = H, COAr) which can be chemically (K) or electrochemically reduced to the corresponding radical anions.[250] Rates of nucleophilic substitution by methoxide of chloride in $[(\eta\text{-PhCl})Cr(\eta\text{-PhR})]^+$ are sensitive to the identity of R, increasing as the electron-withdrawing power of R increases.[251]

Iron and Ruthenium.- Benzene reacts with Fe vapour to give a mixture of products including the 18-electron complex $(\eta\text{-PhH})Fe(\eta^4\text{-}C_6H_6)$ and the 20-electron complex $(\eta\text{-PhH})_2Fe$.[252] The extensive chemistry of $(hmb)_2Fe$ has been explored with particular reference to electron-transfer reactions and to the strategic role of this complex in C-H bond activation and C-C bond formation.[253a] Hydride reduction (with $NaBH_4$) of $[(\eta\text{-}C_6R_6)_2Fe]^{2+}$ (R = H, Me) affords the corresponding monocations $[(\eta\text{-}C_6R_6)Fe(\eta^5\text{-}C_6HR_6)]^+$; whereas the unmethylated cation further adds hydride or carbanionic reagents to give neutral (η^4-cyclohexa-1,3-diene) complexes, the Me_{12}-cation

affords instead bis(η^5-cyclohexadienyl) products.[253b]

A variety of cyclophane complexes of the type [(η-[2.2]para-cyclophane)Ru(η-arene)]$^{2+}$ (arene = hmb, [2.2]meta- and [2.2]para-cyclophane) has been prepared and isolated in salts.[254] The hmb complex undergoes two-electron reduction (with Al/NaOH) and the resulting 20-electron complex can be protonated to give the cation (28); a similar protonation of $(hmb)_2Fe$ can be effected and the resulting cation adds hydride (from Red-Al) to give the product (29).[254b] Two-electron reduction (with Na-Hg) of dications of the type [(η-arene)Ru(η^6-naphthalene)]$^{2+}$ affords (η-arene)Ru(η^4-naphthalene) and the crystal structure of a representative example (arene = hmb) has been determined.[255]

Cobalt.- One of the hmb ligands of $[(hmb)_2Co]^+$ can be replaced by a diene (cod, nbd) to give [(hmb)Co(η^4-diene)]$^+$ which undergoes reversible one-electron reduction.[256]

7 Complexes with Related Ligands

Boracyclopentadienyl Complexes.- A series of 1-phenyl(η^5-boracyclopentadienyl) (≡ L) complexes has been synthesised from 1-phenyl-2,5-dihydroborole, *viz*. (L)Ru$(CO)_3$, (L)Ru(η-PhH), and the bimetallic complexes $(OC)_3$Mn(L)Mn$(CO)_3$ and (L)Rh(L)Rh(L) in which both faces of the central ligand ring are metal-complexed.[257]

Pyrrolyl Complex.- A review of the chemistry of (η^5-pyrrolyl)Mn$(CO)_3$ (*i.e*. azacymantrene) has appeared.[258]

Phosphacyclopentadienyl Complexes.- A ^{1}H n.m.r. spectroscopic study (in nematic solvents) of the structure and conformation of 3-methyl-(η^5-phosphacyclopentadienyl)Mn$(CO)_3$ (*i.e*. 3-methylphosphacymantrene) has been reported.[259] Photoelectron spectroscopy has been used to investigate the electronic structure of (η^5-phosphacyclopentadienyl)$_2$Fe (*i.e*. 1,1'-diphosphaferrocene) and the results have been interpreted in the light of MO calculations.[260] There has been an electrochemical study of the redox properties of phospha- and 1,1'-diphospha-ferrocene and their 3,3',4,4'-Me_4 derivatives.[261] The P atoms of Me_4-1,1'-diphosphaferrocene can function as two-electron donors; complexes with $M(CO)_5$ (M = Cr, Mo, W) and $Mn_2(CO)_9$ have thereby been prepared, and the novel bridged species (30) has also been synthesised.[262]

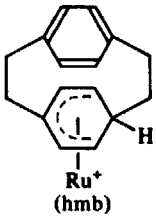
Thiophene Complex.- Treatment of $(OC)_5MnOSO_2CF_3$ with boiling thiophene gives an isolable salt [(η^5-thiophene)Mn$(CO)_3$]$^+$($CF_3SO_3^-$) which adds nucleophiles such as hydride and cyanide (Nu^-) to give products of the type (31; *cis*- and *trans*-stereoisomers).[263]

Diboracyclopentadienyl Complexes.- Complexes of the types CpM(L) (M = Pd, Pt) and $(L)_2Pt$ (L = Et_5-η^5-1,3-diboracyclopentadienyl) have been synthesised; the latter Pt complex undergoes reduction (with metallic K) to a mono- and then a di-anion.[264]

Azaboracyclopentadienyl Complexes.- The chemistry of complexes of the type $(L)_2M$ (M = Fe, Ru, Co; L = 1,2-disubstituted-η^5-1-aza-2-boracyclopentadienyl) has been studied.[265]

Borabenzene Complexes.- The syntheses and properties of $(L)_2V$ and $(L)V(CO)_4$ (L = 1-phenyl-η^6-borabenzene) have been described; the latter complex reacts with chpt to give the tropylium complex $(L)V(\eta\text{-}C_7H_7)$.[266]

Pyridine Complexes.- Reactions of $Cr(CO)_6$ with 2,6-di-t-butyl- and 2,4,6-tri-t-butyl-pyridine (≡ L) have afforded complexes of the type $(L)Cr(CO)_3$; the crystal structure of the dibutyl derivative has shown that the pyridine ligand ring is planar and η^6-bonded to the metal atom.[267]



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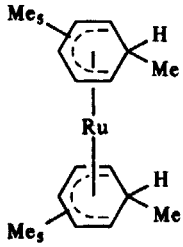

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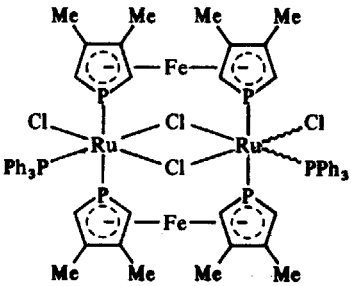

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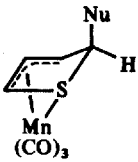

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15

Homogeneous Catalysis by Transition-metal Complexes

BY M. E. FAKLEY

1 Introduction and General Reviews

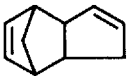
A book surveys the catalysis of industrially significant reactions[1] and another the chemistry of metal carbene complexes with reference to their intermediacy in catalytic reactions[2]. General discussions of transition metal catalysed processes have appeared[3-6], and mechanistic aspects of the literature covering the period mid-1982 to end-1983 have been reviewed[7]. Applications of transition metals in hydroformulation, reduction and oxidation published during 1982 have been surveyed[8]. Reviews cover catalysis by complexes under phase transfer conditions[9], asymmetric catalysis[10], and catalysis with metallacarboranes[11]. Molecular orbital calculations show similarities and differences between the breaking of the H-H bond in H_2 and a C-H bond in CH_4 on both discrete complexes and Ni or Ti surfaces[12]. The chemistry of cis-alkyl and cis-acylrhodium and iridium hydrides as model intermediates has been reviewed[13]. The oxidative addition reaction of ClCOEt to $[RhCl(PPh_3)_3]$ to give cis- and trans-$[RhCl_2(COEt)(PPh_3)_3]$ is promoted 5-10 fold by through space interactions of linear polyethers $R(CH_2CH_2O)_{10}C_{16}H_{33}$ (R = MeO, Ph_2P) [14].

2 Hydrogenation

The role of transition metal hydrides has been reviewed[15] and a comparison between gas-phase, liquid-phase and electrochemical hydrogenation has appeared[16]. Laser radiation of $Fe(CO)_5$ photocatalyses the gas phase hydrogenation of ethylene(10-70°C, 1-2.4 atm) with quantum yields up to 170[17]. Selective hydrogenation of dicyclopentadiene (1) to (2) without formation of (3) is achieved via the $[RhCl(PPh_3)_3]$ catalysed reduction of complex (4)[18]. The new hydride $[ThH_2(Me_2SiR_2)]_x$ (R = Bu,

[For References see page 405

CH_2CMe_3, CH_2SiMe_3, CH_2Ph, Ph) catalyses hex-1-ene and hex-2-ene hydrogenation at turnover frequencies 13 and 21 times greater than $[ThH_2Cp^*_2]$ (Cp^* = pentamethylcyclopentadienyl), respectively[19]. Photolysis of cis-$[MnH(CO)_4(PPh_3)]$ in the presence of H_2 and an alk-1-ene results in both hydrogenation and isomerisation of both cis- and trans-alkenes[20]. N-benzylideneaniline, PhN=CHPh is hydrogenated to $PhNHCH_2Ph$ with $Fe(CO)_5$ as catalyst precursor in alcohol solution at 150°C and 100 atm H_2 pressure[21]. The first examples of the hydrogenation of α,β-unsaturated aldehydes by Ru complexes (high selectivity for C=C bond reduction) and Os complexes (selective reduction of C-O bond) have appeared (reaction 1)[22]. A kinetic study of cyclohexene hydrogenation by $[RuCl_2(PPh_3)_3]$ in benzene-ethanol (1:1) suggests dimerisation of the catalyst at high concentration; inhibition by added PPh_3; and promotion by Et_3N with an activation energy of 11.97 kcal mol^{-1} [23]. Hydrido(phosphine)ruthenates, (5), $K_2^+[Ru_2H_4(PPh_2)(PPh_3)]^{2-}$ and $K^+[RuH_3(PPh_3)_3]_2^-$ are very active catalysts for the reduction of polar compounds (ketones, aldehydes, nitriles, esters), for example CF_3CO_2Me was hydrogenated with (5) at 90°C and 620 kPa of H_2 to CF_3CH_2OH and MeOH[24]. Regioselective hydrogenation of unsymmetrical substituted cyclic anhydrides (6) (R = $CHMe_2$, Ph, R' = H, n = 1; R = Me, R' = H, Me, n = 1, 2) catalysed by Ru(II) complexes produced the isomeric lactones where regioselectivity was directed by the steric bulk of both substrate and the phosphine ligands[25]. $[Ru(\eta^6\text{-arene})(1,5\text{-cod})]$ (arene = benzene, p-xylene, mesitylene) catalyses hydrogenation of α- and cyclic olefins under mild conditions (room temperature, 1-20 atm H_2)[26]. The unusual diphosphine ruthenium complexes (7, n = 3, 4) have been prepared and (7, n = 4) is claimed to be a superior hydrogenation catalyst for cyclohexene and norbornenone[27]. $RC_6H_4NO_2$ (R = H, 2-Me, 2-MeO, 2-Cl, 4-Me, 4-MeO, 4-Cl) were reduced to $RC_6H_4NH_2$ in high yields by formic acid with $[RuCl_2(PPh_3)_3]$ as catalyst[28]. Heterocyclic compounds such as quinoline, indole and quinoxaline are similarly hydrogenated. During a study of Group VIII alkoxides relevant to the catalytic hydrogenation of ketones, the reduction of F_3CCOPh by $[Ru_2H_2(PPh_3)_4]$ and by $[RhH(PPh_3)_4]$ was observed[29]. $[Co_2(CO)_6(PBu_3)_2]$ and $[HCo(CO)_2(PBu_3)_2]$ are good catalysts for the hydrogenation of terpenes (α-terpinene, α-phellandrene and limonene) in Δ^1 and Δ^3-methenes[30]. Micellar-promoted



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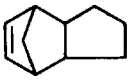

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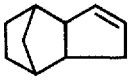

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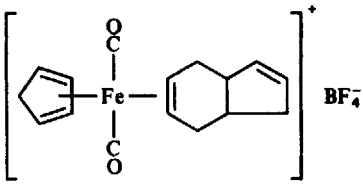

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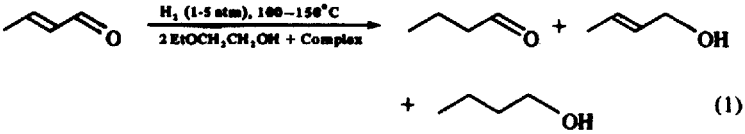
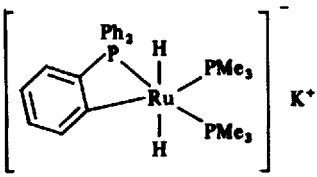


(1)

Complexes: [RuHCl(CO)(PPh$_3$)$_3$]
[OsHBr(CO)(PPh$_3$)$_3$]
[RuCl(OCOCH$_3$)(CO)(PPh$_3$)$_2$]
[OsBr(OCOCH$_3$)(CO)(PPh$_3$)$_2$]
[RuH(OCOCF$_3$)(CO)(PPh$_3$)$_2$]



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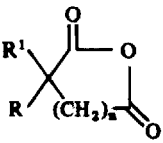
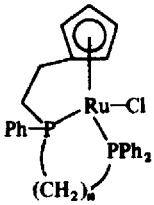


(6)

$K_3[HCo(CN)_5]$ catalyses hydrogenation of atropic acid and its esters $CH_2=C(Ph)CO_2R$ (R = H, Me, Et, Pr^n, and Bu^n) with neutral or ionic surfactants at 25°C and 1 atm H_2 [31]. Stopped flow nmr studies of the rates of coordination of cod and nbd to $[IrH_2(PPh_3)_2(OCMe_2)_2]^+$ show initial formation of $[IrH_2(diene)(PPh_3)_2]^+$ either by H_2 elimination or by hydrogenation of coordinated nbd to norbornene[32]. Further examples of hydroxy-directed stereochemical control occur in cyclic and acyclic systems catalysed by $[Ir(cod)(py)(PCy_3)]PF_6$ and $[Rh(nbd)(dppb)]BF_4$ unless steric conjestion overrides[33]. However, 3-methylene cyclohexanol gives trans-3-methylcyclohexanol with 98% selectivity but low selectivity is observed for 2-methylenecyclohexanol[34].

Magnetisation transfer experiments in ^1H and ^{31}P nmr suggest that in the catalytic cycle of hydrogenation by Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, a cis-$(PPh_3)_2Rh$ conformation occurs at key stages[35]. Wilkinson's catalyst hydrogenates allyl alcohol with an activation energy of 19.7 kcal mol^{-1} but under certain conditions is deactivated to $[RhCl(CO)(PPh_3)_2]$[36]; catalyses selective reduction of heteroaromatic nitrogen and sulphur compounds such as quinoline, 5,6-benzoquinoline, 7,8-benzoquinoline, acridine, phenanthridine and benzothiophene under mild conditions (85°C, 310 psi H_2)[37]; and stereoselective hydrogenation of tetrahydronaphthalenones (±)-(8), (R = H, OAc, R' = Me; R = OH, OAc, R' = CO_2Me) to the decahydro derivatives (±)-(9) (R = H, R' = Me; R = OH, R' = CO_2Me)[38]. Solvent polarity exerts considerable influence over hydrogenations catalysed by $[RhCl(m\text{-}SPPh_2)_3]$ ($m\text{-}SPPh_2$ = m-sulphophenyldiphenyl phosphine)[39]. The new complexes $[MCl(HN\{CH_2CH_2PPh_2\}_2)]$ (M = Rh and Ir) catalyse cyclohexene hydrogenation, possibly via dihydrido intermediates[40]. Addition of a suitable base, eg Et_3N to rhodium phosphine catalyst systems alters the ratio of Rh(III) and Rh(I) hydrides which in turn determines the stereoselectivity in cyclic ketone hydrogenation[41]. The proposal of Halpern (1981) of a dihydride-type intermediate in alkene hydrogenation is supported by EHT MO calculations on the model compound $[Rh(PH_3)(CO)(H_2)(C_2H_4)]^+$ [42]. A number of alkenes, dienes and α,β-unsaturated carbonyl compounds, eg p-$MeOC_6H_4CH=CH_2$, 1,4-octadiene, cot, and PhCH=CHCHO can be hydrogenated at room temperature and atmosphere pressure using [RhCl(1,5-hexadiene)] in a two phase system[43].



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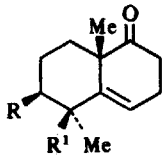

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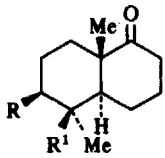

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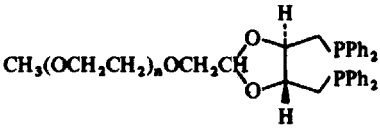
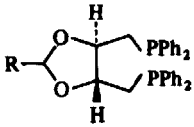
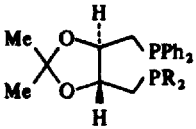


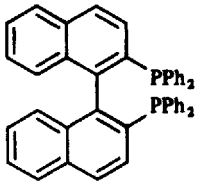
(11) n = 5, 16



(12) R = 2-naphthyl, 1-pyrenyl



(13) R = *p*-tolyl, C_6H_4OMe-*p*, 1- or 2-naphthyl



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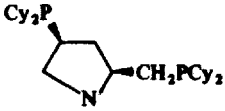

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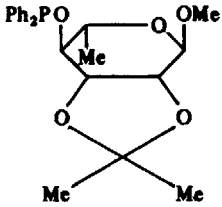


(16)

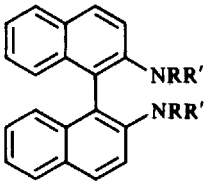
Kinetics of 1-butyl acrylate hydrogention by catalysts derived from rhodacarboranes [closo-3,3-$(PPh_3)_2$-3-H-3,1,2-RhC_2B_9H] and [closo-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] show slow equilibration in initial hydrido metallation reactions which accounts for the lengthy induction period[44]. Similar studies of 3-methyl-3-phenyl-but-1- ene hydrogenation and isomerisation are reported[45]. Reductions of nitroarenes, alkenes and benzaldehyde catalysed by trans-$[Pd_2Cl_2Az_2]$ and trans-$[PdCl_2(AzH)_2]$ (AzH=azobenzene) give anilines or hydroxylamines, alkanes and 2-alkenes and benzyl alcohol respectively[46].

2.1 Asymmetric Hydrogenation.- Hydrogenation of prochiral unsaturated esters (eg ethyl α-methyl-crotonate) by $[MCl_2\{(-)$-DIOP$\}]$ (M = Co, Ni) (and for comparison by $[Rh_2Cl_2\{(-)$-DIOP$\}]$, $[Ru_2Cl_4\{(-)$-DIOP$\}]$) complexes with and without Et_3N give small (0.8-11.7%) enantiomeric excesses of the (R)-isomer[47]. Asymmetric induction occurs in hydrogenations catalysed by $[Co(\text{achiral base})(dmg)_2]^{2+}$/chiral cocatalyst systems, for example, N,N'-dimethyl-5-benzylidenehydantoin was hydrogenated with e.e. of 79.1% in the presence of (S)-N-[(R)-1-phenylethyl]-2-quincludinecarboxamide[48].

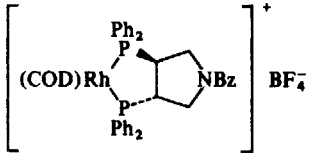
A discussion of asymmetric hydrogenation and hydrosilylation catalysed by Rh complexes highlights the effects of H_2 pressure on the stereoselectivity and efficiency of typical chiral diphosphine ligands[49]. Dehydropeptides Ac-ΔTyr(Ac)-(S)-Ala-Gly-OMe, Ac-ΔTyr(Ac)-(R)-Ala-Gly-(S)-Phe-OMe, Ac-ΔPhe-NHCHRCH_2OCH_2Ph (R = CH_2Ph, CH_2CHMe_2, $CHMe_2$, CH_2CH_2SMe), HCO-ΔPhe-(S)-Leu-OMe, R'-X-ΔPhe-X'-OMe (10; R' = Me_2CO_2C, $PhCH_2O_2C$, CF_3CO; X,X'-α-amino acid residue) and Boc-X-ΔPhe-X'-NHR^2 (R^2 = H, Boc-X-ΔPhe-X'-NH, NHPh) are hydrogenated to the corresponding chiral oligopeptides in high selectivity in the presence of $[RhL(nbd)]ClO_4$ (L = chiral diphosphine)[50]. Rhodium cationic complexes of the asymmetric water-soluble diphosphine ligands (11) are active catalysts for the reduction of prochiral esters $R'CH{=}C(CO_2R^2)NHCOCH_3$ (R' = R^2 = H; R' = Ph, R^2 = H; R' = Ph, R^2 = Me) with modest enantioselectivity (e.e. up to 69%)[51]. Modification of the dioxolane ring in DIOP ligands (12) has a small effect on the asymmetric induction in the hydrogenation of dehydroamino acids and dehydropeptides, whereas modification at the phosphine group (13) affected the stereochemical control such

that (13; R' = 2-naphthyl) gives higher optical yields than (-)DIOP[52]. The new atropisomeric ligand 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (14, BINAP) can be resolved by complexation with Pd and (S)-[Rh(BINAP)]ClO_4 catalyses hydrogenation of 2-(acylamino)acrylic acids to give chiral alanines with 92-99% yields and 67-100% e.e[53]. New chiral peralkyldiphosphines (15) containing a pyrollidine ring are prepared[54] by a new method widely applicable to the transformation of known chiral diphosphines into the corresponding cyclohexyl analogues[55]. Asymmetric hydrogenation of α-dicarbonyl compounds by Rh complexes of (15) proceeds under mild conditions (1 atm H_2, 35°C) and with moderate induction (e.e. 35-66%)[54]. The influence of the heterocyclic ring on the asymmetric synthesis of β-hetarylalnines using neutral of cationic Rh-DIOP systems has been reported[56]. Hydrogenation of prochiral alkenes with $[Rh_2Cl_2(C_8H_{12})_2]$ in the presence of a chiral phosphinite derivative of L-rhamnose (16) and Et_3N gives products in high optical yield eg α-benzoylaminocinnamic acid gave N-benzoyl-(R)-phenylalanine in 100% chemical and 80% optical yield[57]. The effect of introducing a dimethylamino group into chiral diphosphinite ligands has been studied[58] and double asymmetric induction in dehydropeptide hydrogenation catalysed by Rh(I) complexes has been observed[59].

The axially unsymmetrical bis(aminophosphine) ligands (17) have been prepared and resolved; hydrogenation of α-acylamidoacrylic acids and esters, such as (Z)-PhCH=C(CO_2H)NHAc catalysed by $[Rh(cod)(L)]^+BF_4^-$ (L = (R)-(17), R' = H) or $[RhCl(olefin)]_2$ (olefin = cod or cot) plus (R) or (S)-(17) gives the corresponding amino acids with up to 95% optical purity of the same sign of centro-chirality as the axial chirality of the ligand[60]. The novel rhodium complex (18)[61] and rhodium complexes of the new optically active ligands (19-21) catalyse the asymmetric hydrogenation of (Z)-α-acetylamidocinnamic acids[62]. A direct relationship between structure of the chiral environment of the catalyst centre and the enantiomeric composition of the hydrogenation products is claimed for a number of isomerically related bis-(aminophosphine) rhodium complexes[63], whilst different trans-labilizing effects and solvent polarity are responsible for the enantiomeric selectivities observed using chiral O,N-bis(diphenylphosphino)aminoalkanol ligands (22-23)[64].



(17) R = PPh_2, R′ = H, Me



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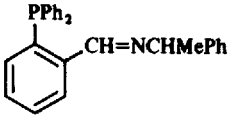

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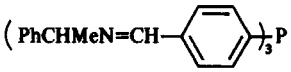

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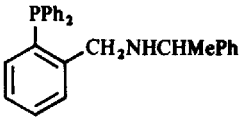

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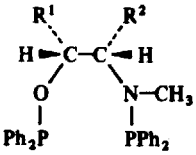
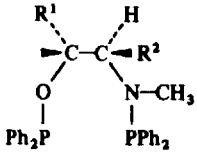


(22) R^1 = Ph, R^2 = Me (1R; 2S)
R^1 = Ph, R^2 = H (1R)



(23) R^1 = Ph, R^2 = Me (1R; 2R)
R^1 = H, R^2 = Ph (2R)

$$C_6H_5CH{=}CHCOCH_3 \xrightarrow[\text{[Ir(TMphen)(1,5-hexadiene)]}^+]{(CH_3)_2CHOH,\ \text{aq. KOH}} C_6H_5CH_2CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_3 + 2(CH_3)_2CO \qquad (2)$$

(TMphen = 3,4,7,8-tetramethylphenanthroline)

2.2 Heterogenised Catalysts.- The surface chemistry and catalytic activity of a number of organometallic complexes supported on Al_2O_3 have been described with particular attention to the effect of surface hydroxyl concentration[65]. $[M(CH_3)_2(Cp')_2]$, (M = Th, U) and $[ThH_2(Cp')_2]$ ($Cp'=C_5Me_5$) on Al_2O_3 produce very active catalysts for the hydrogenation of propylene at -63°C[65], $[RhCl_3(m\text{-}SPPh_2)_5]$ and $[RuCl_2(m\text{-}SPPh_2)_2]$ (m-$SPPh_2$ = m-sulphophenyldiphenylphosphine) immobilised on strongly basic anion exchange resins catalyse hydrogenation of various olefins both in solution and gas phase at 60°C and 120°C respectively[66]. An oxygen stable supported analogue of $[Ru_3O(O_2CMe)_6(H_2O)_3]^+$, prepared by reacting $RuCl_3.3H_2O$ with a carboxylate polymer, catalyses cyclooctene hydrogenation at a rate α $[Ru][H_2][olefin]/(1 + [olefin])$[67]. A mathemetical model developed to investigate the influence of substrate intraparticle mass transport limitations on the hydrogenation rate of cyclohexene and cyclooctene at 25-50°C, 1 atm H_2 over $[RhCl(PPh_3)_3]$ bound to polystyrene-(divinylbenzene) polymer beads shows negligable limitations within 200-400 mesh, 1,2 and 3% DVB[68].

A study of unsaturated ester hydrogenation by homogeneous and heterogeneous palladium catalysts reveals enhanced selectivity in serbate reduction catalysted by $Pd(acac)_2$ compared with Pd/C[69].

Polystyrylbipyridine supported $Pd(acetate)_2$ catalyses the hydrogenation of mono alkenes at atmospheric pressure with selectivity determined by steric hindrance at the double bond and rate decreasing hex-1-ene < oct-1-ene < cyclohexene < cyclooctene[70].

3 Hydrogen-Transfer and Dehydrogenation Reactions

Hydrogen transfer from secondary alcohols catalysed by $[RuH_2(PPh_3)_4]$ regiospecifically occurs at one terminal anthracene ring[71]. A kinetic study of the $[Ru_2Cl_4L_3]$ (L = (-)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) catalysed transfer hydrogenation of unsaturated acids and esters by alcohols indicates that the active $[RuCl_2L]$ complex generated by disproportionation affords chiral products *via* the reaction of a H-acceptor-$[RuCl_2L]$ (H donor) complex and a H-donor-$[RuCl_2L]$ (H acceptor) complex[72]. Saturated aldehydes and ketones are hydrogenated by $NaHCO_2$ under phase transfer catalysis in the presence of Aliquat-336; $[RuCl_2(PPh_3)_3]$ and $[RhCl(PPh_3)_3]/PPh_3$

(1:10) being the best catalysts respectively[73]. Irradiation of $[CoH\{PPh(OEt)_2\}_4]$ generates the unsaturated hydrido species $CoH\{PPh(OEt)_2\}_3$ which catalyses hydrogen transfer from secondary alcohols to ketones[74]. The stereoselectivity of transfer hydrogenation of 2-and 4-alkylcyclohexanones (alkyl = Me, Me_3C) by propan-2-ol catalysed by $[RhCl(cod)]_2$ and Ph_3P or BuP_3 depends on both phosphine basicity and bulk and position of alkyl-substituent in the substrate[75]. Efficient photocatalytic dehydrogenation of propan-2-ol is observed in the presence of rhodium complexes[76], [RhCl(TPP)][77] and $RhCl_3/PPh_3O$ or PPh_3[76], and a quantum chemical interpretation of the process has appeared[78]. In the presence of the soluble catalysts, $[\{MCp'\}_2Cl_4]$ (M = Rh, Ir) $[\{RhCp'\}_2(OH)_3]Cl$, $[OsHBr(CO)(PPh_3)_3]$ and $[RuCl_2(PPh_3)_3]$, methanol functions as a hydrogen donor to hydrogenate ketones eg cyclohexanone, EtCOMe, and activated alkenes eg 3-buten-2-one; with concommitant formation of HCO_2Me[79]. Selectivity in the iridium catalysed transfer hydrogenation of both functions of unsaturated ketones, α,β-unsaturated aldehydes and in particular benzylidene acetone (reaction 1) depends upon substrate hydrogen donor and catalyst[80]. The catalyst formed <u>in situ</u> from $[IrCl(cod)]_2/P(o\text{-}MeOC_6H_4)_3$ promotes selective hydrogenation of the carbonyl group in 5-hexen-2-one and benzylidene acetone particularly at high phosphine/Ir ratios[81]. Similarly, reduction of cyclic ketones by hydrogen transfer is catalysed by a series of iridium complexes $[Ir(cod)L_2]^+$ with KOH (L_2 = PPh_3, P(<u>p</u>-tolyl)$_3$ > P (<u>p</u>-anisyl)$_3$ >> $PMePh_2$, dppe) whose activities decrease with increasing ligand basicity as shown[82]. The hydrogenolysis of aryl bromides by benzyl alcohol is catalysed by a Pd(II) complex under phase transfer conditions (reaction 2)[83].

<u>3.1 Heterogenised Catalysts</u>.- Trichloromethyl compounds Cl_3CR (R = CHPhOH, CO_2CHMe_2, Bz) are hydrogenolysed to Cl_2CHR by $HOCHMe_2$ in the presence of $[RhCl(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$ coordinated to phosphinated polystyrene[84]. The latter catalyst promotes hydrogen transfers from HCO_2H to alkenes[85].

4 Alkane Activation

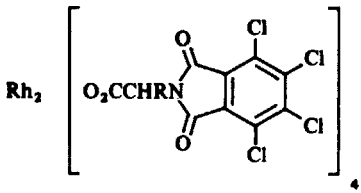
A book describes the activation of saturated hydrocarbons by transition metal complexes[86] and C-H bond activation in actinide phosphine/phosphite coordination chemistry has been reviewed[87]. Catalytic dehydrohalogenation of 2-chloro-2-methylbutane, 1-chloroheptane, 2-bromobutane, t-butylchloride and bromide occurs with double bond migration in the presence of (listed in order of decreasing activity) $[Mo(toluene)(CO)_3]$, $[Mo(mesitylene)(CO)_3]$, $[Mo(CO)_6]$ and $[Mo(CH_3CN)_3(CO)_3]$[88]. Insertion of carbalkoxy carbenes into the C-H bond of normal and branched alkanes is catalysed by Rh(II) carboxylates (eg 24)[89]. Cyclooctane is dehydrogenated by $[IrH(Me_2CO)_2(PPh_3)_2]^+SbF_6^-$ to give $[Ir(cod)(PPh_3)_2]^+SbF_6^-$ but addition of base liberates cyclooctene instead; cyclohexenes are catalytically aromatised[90]. In related studies, cycooctane is catalytically dehydrogenated to cycooctene by Ir and Ru polyhydrides eg $[IrH_5(PR_3)_2]$ ($R=Me_2CH$, $\underline{p}$-FC_6H_4) and $[RuH_4\{P(\underline{p}\text{-}FC_6H_4)_3\}_3]$ at 150°C in the presence of an olefin as the H_2 acceptor[91]. Aromatic C-H bonds in nitro-4-bromobenzene are cleaved in the $[Pd(PPh_3)_4]$ catalysed reaction with norbornene to give (25) and (26) in 23% and 11% yields respectively[92].

5 Carbonylation and Hydroformylation and Hydrocarbonylation reactions

Carbonylation and decarbonylation reactions of alkyl complexes in catalytic cycles have been reviewed[93]. A full account of the carbonylation and homologation of formic and other carboxylic acid esters catalysed by Ru/CO/I systems at 200°C and 150-200 atm CO/H_2 has appeared[94]. In a novel reaction, cyclobutanones are converted to disiloxycyclopentenes with hydrosilane and CO in the presence of cobalt carbonyl (reaction 4)[95]. The oxidative addition of MeI to $[Rh(CO)_2I_2]^-$ in aprotic solvents (MeOH, $CHCl_3$, THF, MeOAc), the rate determining step in carbonylation of methyl acetate and methyl halides, is promoted by iodides, such as $Bu_4N^+I^-$, and bases (eg 1-methylimidazole)[96]. A further kinetic study of rhodium catalysed methanol carbonylation has appeared[97]. The carbonylation of methanol by catalysts prepared by deposition of Rh complexes on silica alumina or zeolites is comparable with the homogeneous analogue[98].

$$ArBr + PhCH_2OH + NaOH \xrightarrow[PTC]{[PdCl_2(PPh_3)_2]/PPh_3} ArH + PhCHO + NaBr + H_2O \quad (3)$$

(ArBr = 4-bromotoluene, 4-bromoanisole, 2-bromoanisole, 2-bromonaphthalene)



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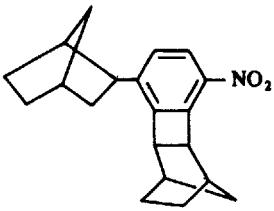

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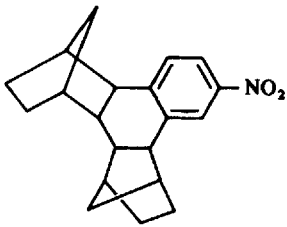

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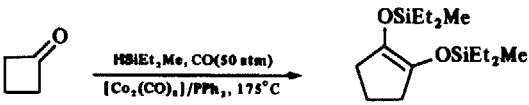

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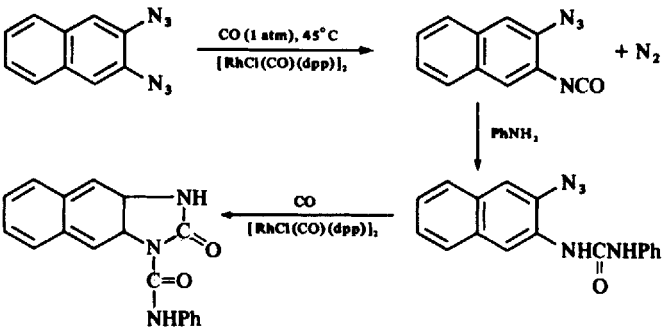
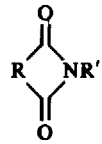


Scheme 5

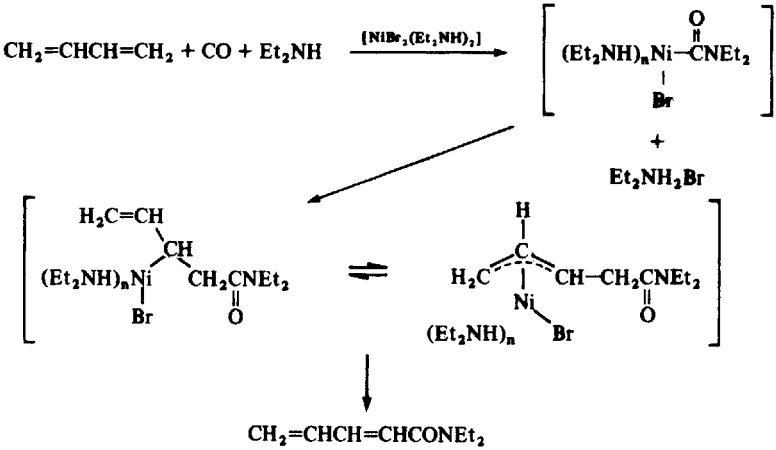
Carbonylation kinetics of ethanol to propionic acid using Rh/HI catalyst is 0, 0.828 and 0.664 order with respect to dissolved [CO], [HI], [ethanol] and [Rh] respectively[99]. A spectroscopic study of the $RhCl_3/MeI/PPh_3$ catalysed carbonylation of MeOAc to acetic anhydride reveals initial formation of $[Rh(CO)_2I_2)^-$ which enters an equilibrium with $[RhI(CO)(PPh_3)_2]$, both complexes can act as starting compounds in catalytic cycles[100]. A catalytic procedure for the preparation of ^{13}CO-labelled aroyl chlorides ($Ph^{13}COCl$, $2\text{-}ClC_6H_4{}^{13}COCl$, $3\text{-}O_2NC_6H_4{}^{13}COCl$ etc) employs $[RhCl(CO)(PPh_3)_2]$[101]. A new synthesis of heterocycles from 2,3-diazidonaphthalene is catalysed by Rh(I) complexes (Scheme 5)[102]. The regioselective conversion of α-lactams (27) to azetidine-2,4-diones (28) is catalysed by $[RhCl(CO)_2]_2$ under CO, whilst the reaction in the presence of $[Co_2(CO)_8]$ is non-catalytic and inhibited by CO[103]. 1,3-dienes such as but-1,3-diene, isoprene or piperylene reaction with CO and secondary amines in the presence of Ni(II) salts to form amides of 2,4-diene carboxylacids (Scheme 6)[104]. 2-butyne reacts with secondary amines and CO in similar systems either stoichiometrically or catalytically depending on temperature and pressure[105]. Unactivated alkyl, vinyl, aryl and benzyl bromides are carbonylated at 1 atm CO and esterified in situ by [RhCl(1,5-hexadiene]$_2$ and $[Pd(PPh_3)_4]$ in conjunction with Lewis acids such as $Al(OR)_3$ (R = Et, $CHMe_2$, CHMeEt)[106] or $B(OR)_3$[107]. The palladium catalysed carbonylative coupling of vinyl triflates with alkyl-, vinyl- and arylstannanes gives good yields of the cross coupled ketone products with useful maintenance of the vinylstannane E and Z geometry[108]. The asymmetric hydrocarboalkoxylation of 2-phenylpropene catalysed by Pd/chiral diphosphine catalysts has been examined in detail[109]. Evidence against the consecutive insertion of CO in the palladium catalysed double carbonylation of organic halides to α-keto amides arises from studies of trans-$[PdCl(COCOR)(PMePh_2)_2]$ (R = Me, Ph)[110]. The $[PtCl_2(PR_3)_2]$/N-ethylpiperidine system catalyses the carbonylation of methanol to afford methyl formate with high selectivity, dimethylcarbonate and dimethyloxalate are minor products[111]. The syntheses of antibiotics (29-30) containing the benzodiazepine unit are facilitated by $Pd(OAc)_2/PPh_3$ catalysed insertion of CO (at 5 atm) into o-bromoprolylaniline precursors.[112,113]. Et_2Zn is claimed to catalyse carbonylation of aliphatic and aromatic amines (RR'NH; R=R'=Et, Me_2CHCH_2; R-R' = $(CH_2)_5$; R = H, R' = Bu; R = Ph, R' = Me, Et) to the

(27)

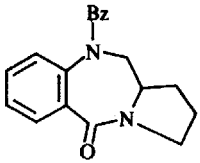


(28)

(R = R′ = Me_3C, 1-adamantyl; R = Me_3C, R′ = 1-adamantyl; R = 1-adamantyl, R′ = Me_3C)



Scheme 6



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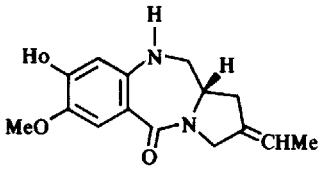


[SEN 215]

(30)

corresponding formamides in good yield[114].

5.1 Reductive Carbonylation.- Quinoline is reduced regiospecifically in the N-containing ring by $[Fe(CO)_5]$ at 150-300°C in the presence of CO, H_2O, base and a phase transfer catalyst (particularly 18-crown-6, 87 turnovers)[115]. Aromatic nitro compounds are reduced under mild conditions in a genuine bimetallic phase transfer catalysed reaction (reaction 7)[116], or by a $[PtCl_2(PPh_3)_2]/SnCl_4/Et_3N$ system under more forcing conditions[117].

A number of studies of the important (non-phosgene) route to aryl isocyanates *via* carbonylation of nitro compounds have appeared[118-120]. In a comparative study of Rh(I), Ir(I), Pd(I) and Pd(II) catalysts, $Bu_4N^+[RhX_2(CO)_2]^-$ (X = Cl, Br, I) was most effective giving 83-89% PhNCO with 100% $PhNO_2$ conversion at 125°C under 80 atm CO pressure[118]. The kinetics of carbonylation by $[PdCl_2py_2]$ at 170-230°C and 23-94 atm CO pressure are first order in p[CO] and catalyst and zero order in $PhNO_2$[119]. The reductive N-carbonylation of nitroarenes to the carbamates is catalysed by $[PtCl_2(PPh_3)_2]$ in ethanol, promoted by Lewis acids ($SnCl_4$, $FeCl_3$, $AlCl_3$ and $TiCl_4$) and Et_3N (reaction 8)[120]. Similarly, performing the reaction in carboxylic acids gives the corresponding N-substituted amides in moderate to good yield[121].

5.2 Oxidative Carbonylation.- The kinetics and mechanism of the catalytic production of dimethyl oxalate by oxidative carbonylation of methanol with the $[PdCl(CO)]_n/LiCl/$*p*-benzoquinone have been investigated[122]. The hydroesterification of alkenes[123] and alkynes[124] is catalysed by Pd $Cl_2/CuCl_2$ catalysts under mild conditions (reaction 9). Allene undergoes alkoxy-oxy-carbonylation in a similar reaction to give methyl 2-methoxymethylacrylate in good yield[125]; 1,1-disubstituted allenes react regiospecifically but in lower yields.

5.3 Hydroformylation.- A review of hydroformylation catalysis has appeared[126]. The stability of the P-C bond in aryl substituted phosphines in hydroformylation by Co[127,128], Rh[128,129] and Ru[128] catalysts depends on the metal and the tendency of the ligand to undergo oxidative addition. Infra-red and ^1H NMR studies of propene and pent-1-ene hydroformylation in the presence of $[Fe(Cp)_2(CO)_2]$ reveal the presence of "$FeH(Cp)(CO)_2$" [130]. High

$$RNO_2 \xrightarrow[\text{5N NaOH, } C_6H_6\text{, R.T., CO (1 atm).}]{[Co_2(Co)_8]/[RhCl(1,5\text{-hexadiene})]_2\text{, DTAC}} RNH_2 \quad (7)$$

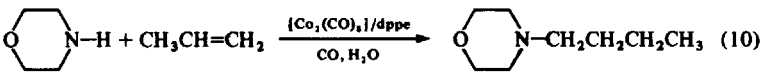
(DTAC = dodecyltrimethylammonium chloride,
R = Ph, *p*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, 2,4,6-$(CH_3)_3C_6H_2$, *p*-ClC_6H_4, *p*-$PhCOC_6H_4$, *p*-$PhCH{=}CHC_6H_4$, *p*-$PhCH_2OC_6H_4$, 1-naphthyl)

$$RNO_2 \xrightarrow[\text{EtOH, 180°C, CO (60 atm)}]{[PtCl_2(PPh_3)_2]/SnCl_4/Et_3N} RNHCO_2Et \quad (8)$$

(R = Ph, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4, 2,5-$(CH_3)_2C_6H_3$)

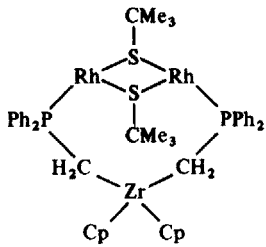
$$CH_2{=}CH(CH_2)_4CH{=}CH_2 \xrightarrow[\text{HCl, MeOH, 25–35°C.}]{PdCl_2/CuCl_2\text{, CO, } O_2 \text{ (1 atm)}} MeO_2CHMe(CH_2)_4CHMeCO_2Me \quad (9)$$

(Other substrates: propene, dec-1-ene, allenes)



(10)

(89% yield, n/(n + iso) = 66%)



(31)

pressure infra-red and ultra-violet spectroscopic studies of $[Co_2(CO)_8]$ catalysed hydroformylation of mono-olefins confirm the Heck/Breslow mechanism in which $[HCo(CO)_4]$ is formed chiefly via the reaction of acylcobalt tetracarbonyl with H_2[132]. Similar studies with butadiene under 95 bar Co/H_2 and 80°C show formation of "$Co(\eta^3-C_4H_7)(CO)_3$" and "$Co_2(\eta^4-C_4H_6)_2(CO)_4$"[132]. Formation of formate during $[Co_2(CO)_8]/PR_3$ catalysed reactions depends upon the cone angle of the ligand[133]. $[Co_2(CO)_8]$/dppe catalysts for hydroformylation under CO/H_2 and CO/H_2O are most active at a ratio of 1:1 and are more active than monophosphine catalysts[134]. The same system catalyses the aminomethylation of propene by secondary amines (reaction 10). A comparative study of Ph_3N, PPh_3, $AsPh_3$, $SbPh_3$ and $BiPh_3$ as ligands in rhodium-catalysed hydroformylation of dodec-1-ene has appeared[135]. Excess phosphite or phosphine improved both yield and selectivity in hydroformylation of hex-1-ene catalysed by $[RhL(CO)(PPh_3)]$ or $[RhL(P\{OPh\}_3)_2]$ (L = β-diketonate or 8-hydroxyquinolate)[136]. Unreactive olefins (2-methyl-hex-1-ene, limonene, cyclohexene, methylenecyclohexene) are hydroformylated under mild conditions (90°C, 10 bar CO/H_2) with Rh catalysts modified by phosphites which stabilise unsaturated species (eg $P(O^tBu)_3$, $P(O^iC_3F_7)_3$)[137]. The ability of α,ω-bis(diphenylphosphine)alkanes to promote the otherwise sluggish reaction of substituted terminal olefins in the presence of excess PPh_3 is explained by the formation of a three phosphine coordinated trigonal pyramidal intermediate which readily loses phosphine to ligate CO[138]. The novel heterobimetallic complex (31) is claimed to be a better catalyst for the hydroformylation of hex-1-ene than the $Ph_2P(CH_2)_4PPh_2$ analogue. Cocondensation of Rh atoms with cycloocta- and cyclohexa-dienes at liquid N_2 temperature yields Rh complexes which catalyse selective hydroformylation of cyclodienes to cycloalkenecarboxyaldehydes[140]. An infra-red study (under 18 atm CO/H_2, 2:3) of $[RhH(CO)(PPh_3)_3]$ bound to phosphinated gel-form polystyrene/divinylbenzene beads shows predominantly two species -a bis(phosphine)dicarbonyl and a dimer[141]. Dialkyl ketones are formed under mild conditions (30-70°C, 1 atm) from ethylene or propylene in acidic aqueous solutions of Pd(II) salts (reaction 11)[142].

5.4 Hydrocarbonylation.- The mechanism and kinetics of methanol homologation catalysed by metal carbonyls in the presence of

amines reveals the intermediacy of methylammonium formate[143]. The cobalt catalysed homologation of methanol continues to attract attention; chelating solvents (eg tetraglyme) are claimed to increase both conversion and selectivity to acetaldehyde (80%) with minimal solvent degradation[144]. Ruthenium promoted Co/I systems in glymes or cyclic ethers produce some of the best selectivities to ethanol (>80%)[145] but novel basic co-ligands (32-34) do not improve yields[146]. A mixture of cobalt and platinum complexes is claimed increase the homologatin rate by a factor of 3; the platinum reduces cobalt salts to $[Co(CO)_4]^-$ (reaction 12)[147]. Gas phase homologation with a supported liquid-phase catalyst $CoI_2/[RuCl_2(CO)_2(PPh_3)_2]/NaI/PR_3$ gives high selectivities for ethanol and propanol without formation of ethers[148].

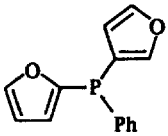
Pyridine reacts with synthesis gas at 212°C and 1150 psi in the presence of Co(0) catlaysts to produce N-formyl-, N-methyl-, N-ethyl-, and N-propylpiperidine[149]. THe hydrocarbonylation of β-substituted N-vinylphthalimides by Rh or Pd complexes is strongly affected by the substituent[150]. A palladium catalysed synthesis of β,γ-unsaturated aldehydes from chloride or bromide precursors is reported (eg reaction 13)[151].

6 Carbon Monoxide Reduction, The Water Gas Shift Reaction and Reactions of Carbon Dioxide

6.1 Carbon Monoxide Reduction.- Books describe the catalytic conversions of synthesis gas and alcohols to chemicals[152], and the chemistry of the catalysed hydrogenation of carbon monoxide[153]. The role of metal hydrides in the catalytic reduction of CO *via* both intra- and intermolecular hydride transfer pathways has been discussed[154]. The activation of CO by reaction with a secondary amine and subsequent reduction to the methylamine is catalysed by Group VIII carbonyls albeit at very low rates[155].

6.2 The Water Gas Shift Reaction.- A review of transition metal carbonyls as precursors for water gas shift catalysts has appeared[156]. $[HRu_3(CO)_{11}]^-$ anchored to silica via ammonium or pyridinium groups is active at low temperatures 100-150°C[157] and $[Rh_6(CO)_{16}]$ chemisorbed on η-Al_2O_3 or $[RhCl(CO)_2]_2$ chemisorbed on η-Al_2O_3, NaY zeolite and HY zeolite are active between 25-100°C[158].

$$2C_nH_{2n} + CO + H_2 \xrightarrow[F_3CCO_2H/H_2O,\ 30-70^\circ C]{Pd(II)/PPh_3,\ CO/H_2\ (1\ atm)} (C_nH_{2n+1})_2CO \quad (n = 2, 3) \qquad (11)$$



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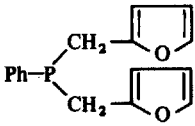

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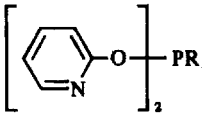
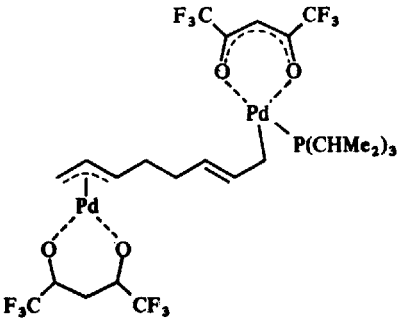


(R = Me, CMe_3)

(34)

$$MeOH + CO + H_2 \xrightarrow[4000\ psi,\ 130^\circ C,\ 6\ h]{Co(OAc)_2 \cdot 4H_2O/PtCl_2/LiI} CH_3CHO + H_2O \qquad (12)$$

$$RCMe{=}CHCH_2X \xrightarrow[CO/H_2,\ 1:1\ (80\ atm),\ 100^\circ C]{[PdBr_2(PPh_3)_2]/Et_3N} RCMe{=}CHCH_2CHO \qquad (13)$$



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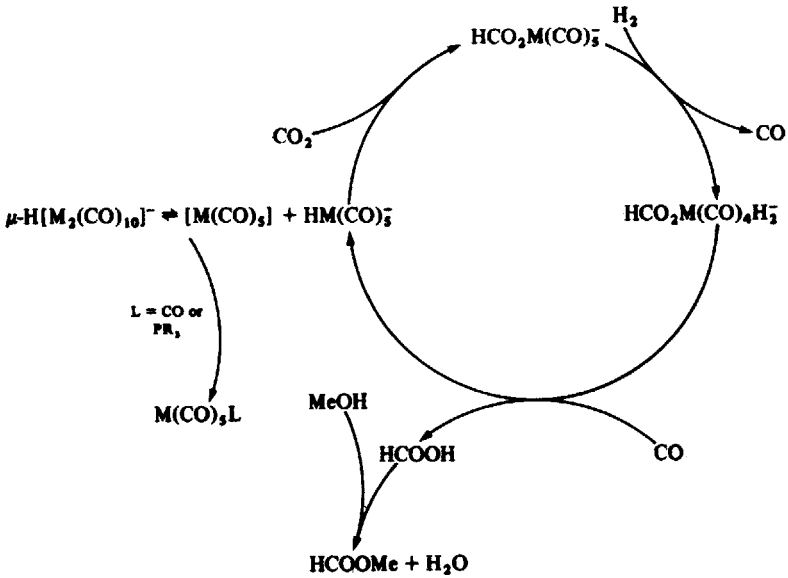
6.3 Reactions of Carbon Dioxide.- The anionic species $[HM(CO)_5]^-$ (M=Cr, W; derived from $[(\mu\text{-}H)\{M_2(CO)_{10}\}]^-$) and their CO_2 insertion products $[M(HCO_2)(CO)_5]^-$ slowly catalyse the hydrogenation of carbon dioxide in alcohols under mild conditions (125°C, 250 psi CO_2 + 250 psi H_2) to yield alkyl formates (Scheme 14)[159]. $[ReCl(bipy)(CO)_3]$ is an efficient catalyst for the selective and sustained electrochemical reduction of CO_2 to CO at low potential[160]. Aromatic compounds (C_6H_6, PhOMe, PhCl) are slowly carboxylated by Pd(II) catalysts at 70 or 150°C and 1 or 30 atm CO_2 pressure to give the corresponding benzoic acids[161]. The Pd(II) catalysed cleavage of C-Sb or C-P bonds of $SbPh_3$ or PPh_3 gives benzoic acid in the presence of CO_2[162]. The reactions of CO_2 with a bimetallic octadienyl-bridged palladium compound (35) is discussed in relation to the mechanism of the Pd catalysed reaction between butadiene and carbon dioxide[163].

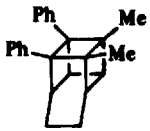
7 Alkene Isomerisation and Skeletal Rearrangements

A comprehensive review of the catalysis of the Cope and Claisen rearrangements includes catalysis by transition metal complexes[164].

The mechanism of hydrogen transfer and double bond migration catalysed by trans-$[Mo(N_2)_2(dppe)_2]$ is reported[165]. The reaction of the phenylated bishomocubane (36) with Fe(III) gives the [2+2] cycloreversion product (37) exclusively whereas that with Ag(I) gives both (37) and the skeletal rearranged snoutene derivative (38)[166]. Photoreaction of $[Fe(CO)_5]$ with cis-cyclooctene in alkane solvent at -40°C gives $[Fe(\eta^2\text{-cyclooctene})_2(CO)_3]$ which catalyses the thermal isomerisation of pent-1-ene with turnover numbers up to 2000[167]. The role of the cobalt ion in vicinal interchange reactions catalysed by Coenzyme B_{12} is suggested to occur via the activation of alkyl groups by π-bonding[168]. Cycloreversion of trishomocubanones (39; R = Me, Ph) and (40; H, Me, Ph) catalysed by $[RhCl(CO)_2]_2$ gives (41) and (42) (same R) respectively[169]. Products of value for terpene synthesis are accessible via highly enantioselective isomerisation of prochiral allylamines catalysed by chiral diphosphine Rh(I) complexes[170]. Optically active 3,4-disubstituted pentenals $H_2C{=}CRCHR'CH_2CHO$ (R = Me, CH_2OAc, OBz, CH_2Cl; R'=CH_2CH_2COMe, $CH_2CH_2CHMeOH$) undergo cyclization in the presence of $[RhCl(PPh_3)_3]$ to give cis-3,4-



Scheme 14



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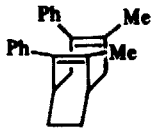

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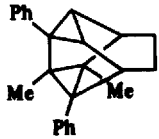

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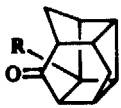

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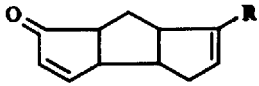
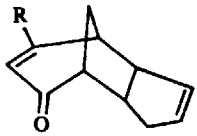


(41)

disubstituted cyclopentanones (43) in 53-80% yield[171]. Treatment of $PhCMe(CHO)CH_2CH{=}CH_2$ with $[RhL_2]Cl$ (L = 2S, 3S-bis(diphenylphosphinobutane) at 160°C gives 40-50% cyclopentanone (44) in 52% e.e.[172]. Rearrangement of dienols eg $RR'C(OH)CH{=}CHC(SMe){=}CMe_2$ (RR' $(CH_2)_{11}$) are effected by $NiCl_2$ in aqueous Me_3COH to give vicinally-substituted dienols eg $RR'C{-}CHCH{=}C(SMe)CMe_2OH$[173]. The palladium promoted cyclization of alkylated 1-arylazonaphthalenes (45; R,R'=H, Me) to 2-arylbenzo[g]indazoles (46) is reported[174]. Rearrangement of allylic esters in the presence of $[PdCl_2(MeCN)_2]$[175,176] and isomerisation of allyl alcohol by $[PdCl_4]^{2-}$ have been studied[177]. 1,6-, 1,7- and 1,8-dienes are cyclized to cyclopentenes and methylenecyclopentenes by Pd and Rh catalysts[178]. An ^{17}O nmr study of the rearrangements of (E,Z)-4-acetyl[^{17}O]oxy-hept-2,5-diene catalysed by Pd(O) reveals an intermediate coordinated pentadienyl species and acetate [^{17}O], whilst the Pd(II) catalysed reaction proceeds via an intermediate acetoxonium ion[179]. The [3,3]-sigmatropic type rearrangement of propargyl thionophosphates eg $(EtO)_2P(S)OCH_2C{\equiv}CH$, to provide allenyl thiolophosphates eg $(EtO)_2P(O)SCH{=}C{=}CH_2$ is catalysed specifically by Pd(II)[180]. Methyl (R)-3-oxo-7-(methoxycarbonyloxy)-8-nonenoate (47) undergoes intramolecular allylation catalysed by $Pd(OAc)_2/P_2H_6$ to give racemic cyclohexanone derivative (48) but similar cyclization of the sodium salt of (47) gives an optically active product[181]. The isomerisation of trans-stilbene to its cis form is catalysed by $[Cu(CH_3CN)_4]^+$/LL systems (LL = 2,2'-bipyridyl, o-phenanthroline and derivatives) upon irradiation with visible light (>390 nm)[182]. Copper(I) trifluoromethane sulphonate catalyses photobicyclisation of myrcene to afford 6,6-dimethyl-2-methylenebicyclo[3.2.0]heptane[183] and of ethyl N, N-diallycarbamates to afford bicyclic pyrrolidines[184].

8 Alkene and Alkyne Metathesis

Acetylenes are metathesised by Mo(VI) alkylidyne complexes ligated by electron-withdrawing ligands eg $[Mo(CCMe_3)\{OCMe_2(CF_3)\}_3)$[185]. The essential role of $\{Mo^0Cl(NO)\}$ containing intermediates in olefin metathesis catalysed by nitrosylmolybdenum complexes has been established[186]. The triphenoxytungstenacyclobutadiene complex (48) catalyses the



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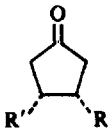

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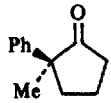

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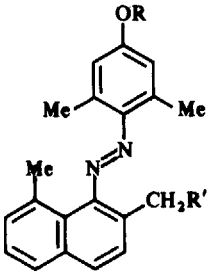

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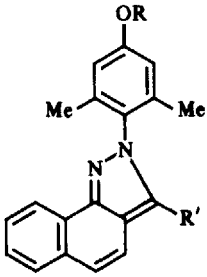

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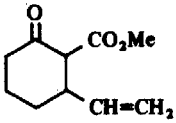

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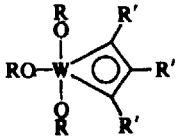
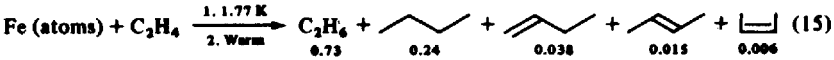


(48) R = $(CHMe_2)_2C_6H_3$-, R' = Et, Pr
(49) R = $(CF_3)_2CH$; R' = Et

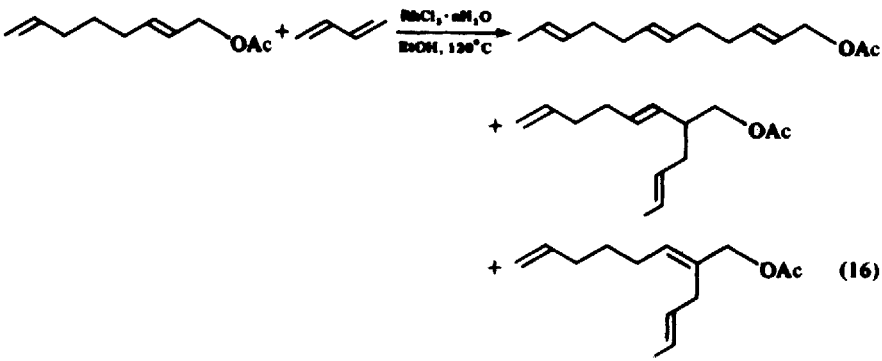


(15)

methathesis of hept-3-yne or non-4-yne[187] and the related complex (49) the rapid methathesis of acetylenes by a dissociative mechanism which is solvent assisted[188]. A new catalytic system for methathesis of functionalised olefins employs WCl_6 or $WOCl_4$ in conjunction with organosilanes (especially Ph_2SiH_2) and is directly comparable with WCl_6/SnR_4 systems[189]. A mechanism has been proposed for metathesis of pent-2-ene catalysed by the photosensitive system $W(CO)_6/CCl_4$ under photolysis[190]. Methathesis of $(RO)_3SiCH{=}CH_2$ (R=Me, Et) catalysed by $RuCl_3$, $[RuCl_2(PPh_3)_3]$, $[RuHCl(PPh_3)_3]$, etc., proceeds at ~120°C in air to give 38-83% (Z) and (E)-$(RO)_3(SiCH{=}CHSi(OR)_3$[191].

9 Oligomerisation and Polymerisation of Alkenes and Alkynes

9.1 Alkenes.- Hexa-2,4-dienes are formed in the catalytic codimerisation of butadiene with ethylene in the presence of $[Ti(\eta^3\text{-1-methallyl})Cp_2]$, with >99% regioselectivity[192]. The Ziegler catalyst $TiCl_4/Et_2AlCl$ and the Ti(II) complex $[Ti(\eta^6\text{-}C_6H_6](AlCl_4)_2]$ both induce [6+2] cycloaddition reactions of cycloheptatriene with dienes and acetylenes[193]. $[Mo(allyl)_4]$ reacts with HCl to give $[Mo_2(\mu\text{-}Cl)_2(allyl)_6]$ which catalyses the polymerisation of buta-1,3-diene[194]. The cocondensation of Fe atoms and C_2H_4 brings about the reduction, dimerisation and reductive dimerisation of ethylene (reaction 15)[195]. The codimerisation of non-conjugated olefins such as 1-acetoxy-oct-2,7-diene with buta-1,3-diene catalysed by phosphine-free (Rh(III) complexes gives linear and branched dodecatrienyl derivates (reaction 16)[196,197]. The reaction is promoted by allylic chlorides and hydrated $CrCl_3$ which regenerate the active catalyst[197]. UV photolysis of $[Rh_2(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_8]$ and C_2H_4 gives but-1-ene whilst the thermal reaction of the μ-butenyl intermediate with ethylene gives trans-hex-3-ene[198]. $[Ni(\sigma\text{-}C_2H_5)(PPh_3)(Ph_2PCHCOPh)]$ (50) and (51) heterogenised on SiO_2 and SiO_2/Al_2O_3 yield active catalysts for the oligomerisation of ethylene[200]; binding (50) via the phosphine or the P-O-chelate to polystyrene results in a catalyst producing 99% linear α-olefins at >1080 moles C_2H_4/mol Ni/Hr[200]. A theoretical study of nickel catalysed olefin oligomerisation suggests a rearrangement involving rotation of the olefin around its bond to the metal is



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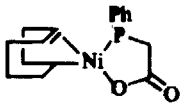

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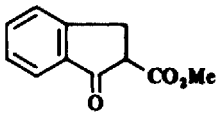

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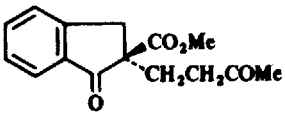

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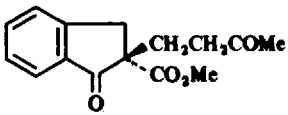

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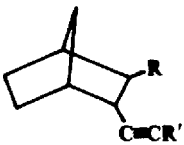

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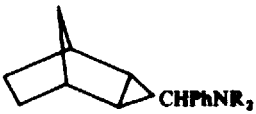

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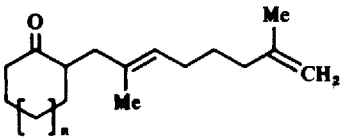


(57)

required before the reaction will occur[201]. The catalytic activity and selectivity of $[Ni(\eta-C_3H_5)L_2]PF_6$ (L = monodentate neutral ligand) for the 1,4-polymerisation of buta-1,3-diene increases as the Ni-L bond strength (measured by electron-impulse induced decomposition) decreases[202]. Selective dimerisation of $H_2C{=}CHCO_2Me$ to (E)-$MeO_2CCH{=}CHCH_2CH_2CO_2Me$ with 82-96% selectivity and 23-58% conversion is catalysed by [Pd(methallyl)(cod)]BF_4/0.5-1 equiv PBu_3[203]. Pd(0) phosphine complexes in the presence of water catalyse the co-oligomerisation of buta-1,3-diene and cyclic ketones to yield α-octadienyl derivatives[204].

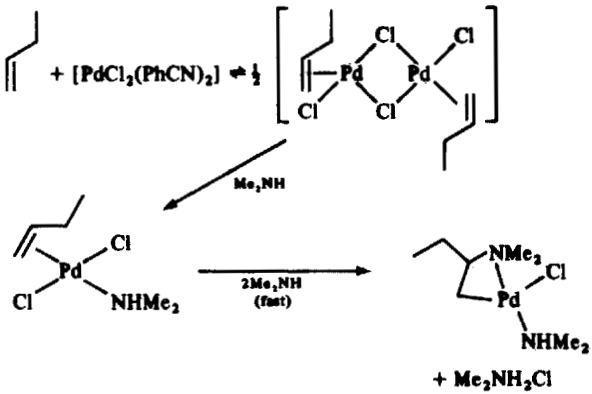
9.2 Alkynes.- The polymerisation of substituted acetylenes by Mo and W based catalysts is reviewed with evidence for the mediation of carbenes[205]. A mechanism of catalytic cyclotrimerisation of hex-3-yne *via* a cyclobutadienenickel complex is proposed[206]. Examples of alkyne coupling[207], cyclotetramerisation of $HC{\equiv}CCH_2OC_6H_4Me$-4[208] and cyclotrimerisation of $RC{\equiv}CCO_2R'$ (R=Me, Ph, MeO_2C, EtO_2C, Me_2CHO_2C, Me_3CO_2C; R'= Me, Et, $CHMe_2$, CMe_3)[209] by diazadiene modified Ni catalysts are reported.

10 Catalysed Additions to Alkenes, Alkynes and Telomerisation Reactions

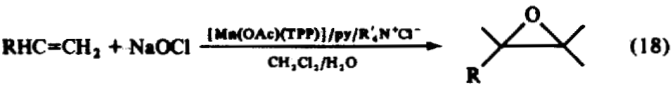
Acetophenone oxime is produced by the regioselective hydronitrosation of styrene catalysed by [CoCl(DMGH)py] (DMGH = monoanion of dimethylglyoxime[210]. Nitroenones are formed by the reaction of π-allyl cobalt complexes from the acylation of 1,3-dienes by $[Co(CH_3CO)(CO)_4]$[211]. Enantiomeric Michael additions of $H_2C{=}CHCOMe$ to indancarboxylate (52) giving the addition products (53) and (54) are catalysed by [Co(acac)(LL)] (LL = (+) or (-)-$H_2NCHPhCHPhNH_2$)[212]. Fe, Co and Ru carbonyls catalyse the addition of polyfluoroalkyl halides R_fX (eg $CF_3CF_2CF_2I$ and $BrCFClCF_2Br$) to $R'CH{=}CH_2$ (eg R'=Me_3Si, C_4Ha, H) and $R^2C{\equiv}CH$ (eg $R^2{\equiv}Me_3SiCH_2$, Ph, $HOCH_2CH_2$) to give adducts $R_fCH_2CHR'X$ and $R_fCH{=}CR^2X$ respectively[213]. A correlation is observed between ^{13}C and ^{59}Co NMR data and catalytic activity of organocobalt complexes [Co(Cp')(cod)] in pyridine synthesis from $MeC{\equiv}CH$ and $EtCN$[214]. N-substituted aziridines are formed by [Fe(TPP)Cl] or [Mn(TPP)Cl] catalysed reactions of PhI=NR (R = tosyl or $COCF_3$) with alkenes[215]; the stereochemical characteristics being very

different from the analogous epoxidation reactions with PhI=O. The kinetics and mechanism of nickel-catalysed olefin hydrocyanation have been reported[216], and the addition of DCN to cyclohexa-1,3-diene catalysed by $[Ni(P\{OPh\}_3)_4]$ is found to occur with cis-stereochemistry indicating cis-migration of coordinated cyanide in the intermediate π-allyl complex[217]. The reactions of various organic bromides RBr (R = Ph, PhCH=CH, allyl, $MeCH=CHCH_2$) with a mixture of bicycloheptene or bicycloheptadiene and alkynes R'C≡CH (R'=Ph, hexyl, etc) catalysed by Ni(0) or Pd(0) complexes produce bicyclic compounds such as (55)[218]. PhCH=CHBr reacts with bicyclo [2.2.1]hept-2-ene and R_2NH ($R_2=(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$; R = Me) in the presence of $[Pd(PPh_3)_4]$ to give the cyclopropane derivative[219]. A novel reaction between allene and water catalysed by $[Pd(dba)_2]/PPh_3$ in the presence of CO_2 yields 3-methyl-2-methylene-3-buten-1-ol, selectively[220]. Telomerisation of formamide with buta-1,3-diene with a catalyst derived from $Pd^{2+}/PPh_3/Et_3Al/CF_3CO_2H$ gives 16.8% $CH_2=CH(CH_2)_3CH=CHCH_2NHCHO$ and $CH_2=CH(CH_2)_3CH(NHCHO)CH=CH_2$ (83:17)[221]. Telomerisation of isoprene with cyclopentanone or cyclohexanone in the presence of H_2O and $Pd(0)/PR_3$ complexes gives the tail-to-tail products (57; n = 0, 1)[222]. The arylation of activated alkenes with aryl chlorides catalysed by $Pd(OAc)_2/PR_3$ (R = Ph, p-MeC_6H_4) is accelerated by electron-withdrawing substituents in the aryl chloride[223].

$Pd(PPh_3)_4$ catalyses the addition of Sn_2Me_6 to $RR'C=C=CHR^2$ (R=H, Ph, MeO, Me_3Sn; R^1,R^2=H, Me)[224] and the alkylation of chiral sulphones with retention of configuration[225]. Regioselective aminophenylation or aminoalkenylation of $H_2C=C=CHR$ (R = Bu, CHPhOH, CMe_2CH_2OAc, $CH(OMe)CH_2CHMe_2$), PhI, PhCH=CHBr or $PhCBr=CH_2$ with R^1R^2NH ($R^1=R^2$=Et, $R^1R^2=(CH_2)_4$) to give allylic amines $R^1R^2NCH_2CR^3=CHR$ (R^3=Ph, CH=CHPh, $CPh=CH_2$) is catalysed by $Pd(OAc)_2$/dppe or $P(C_6H_4Me\text{-}o)_3$[226]. Unsaturated γ-lactones arise from the Pd/PPh_3 complex catalysed codimerisation of methylenecyclopropane with CO_2[227]. The mechanism of Pd-assisted amination of olefins has been studied by low temperatures NMR and UV spectroscopy etc[228], the specific sequence of steps depending on the nature of the amine (Scheme 17). CuCl-catalysed photochemical addition of CH_2Cl_2 to electron-deficient olefins (eg $CH_2=CHCN$) gives 1,3-dichloro compounds[229]. The stereochemistry of the $[Ni(OPPh_3)_4]$ catalysed addition of HCN to alkynes $RC=CR^1$

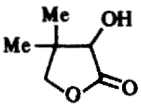


Scheme 17



(18)

(R = Ph, Yield = 80%)



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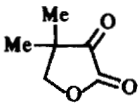

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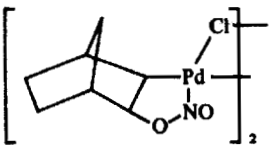

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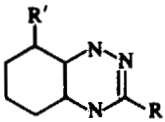

(61)

($R=R^1=Ph$, CO_2Me; $R=CMe_3$, Ph; $R^1=Me$, H) and $R^2C{\equiv}CH$ ($R^2=Pr$, Bu, hexyl) has been examined[230]. A new synthesis of trisubstituted alkenes by the $Pd(OAc)_2/PPh_3$ catalysed arylation of mono- and di-substituted acetylenes is observed in the presence of formic acid and a tertiary amine[231]. Cyclopropanation of olefins is catalysed by a number of complexes of late transition metals[232] and the electronic effects of the metal provide the stereochemical and regiochemical control[233].

11 Oxidation Reactions

Recent advances in homogeneous oxidation catalysed by transition metals[234], transition-metal peroxides as reactive intermediates[235] and synthetic applications of Pd-catalysed oxidation of olefins to ketones[236] have been reviewed. A MO model of bonding in peroxo-complexes has been developed[237] and applied to the mechanism of catalytic epoxidation. Amide autoxidation catalysed by Fe(II), Co(II) and Cu(II) bipyridyl compounds proceeds *via* peroxy radicals[238]. The rates of oxidation of 2,6-di-t-butylphenol by O_2 in DMF decrease in the order Co(TPP)>>Fe(TPP)Cl>Mn(TPP)Cl>VO(TPP) whilst selectivity for quinone formation relative to coupling is Co(TPP)>>VO(TPP) >Fe(TPP)Cl>Mn(TPP)Cl[239]. Olefin oxidation by iodosobenzene is catalysed by Cu ions[240] and Fe-, Mn- or Cr-tetraarylporphyrins[241]. Ti-tartrate catalysed asymmetric epoxidation with Me_3COOH has been studied in detail[242]. The epoxidation of isoprene by alkyl hydroperoxides is catalysed by [Ti(O)(TPP)][243]. A new catalytic route for olefin epoxidation uses NaOCl and Mn porphyrin complexes[244] (reaction 18). A two-phase system using a Mn porphyrin as a catalyst and sodium ascorbate as a reducing agent activates oxygen; oxidises olefins selectively to epoxides, and alkanes to alcohols or ketones[245]. Stereospecific epoxidation of both *cis*- and *trans*-alkenes by $NaIO_4$ is catalysed by $RuCl_3.xH_2O$/bipy[246]. Pantolactone (58) is air oxidised to the tetrahydrofurandione (59) in the presence of $[RuCl_2(PPh_3)_3]$ and $[RuH(OAc)(PPh_3)_3]$[247]. The rate and selectivity of oxidation of hindered phenols (eg 2, 4, 6-$(Me_3C)_3C_6H_2OH$) by O_2 catalysed by monomeric and polymeric Co-Schiff base complexes, Co and Mn porphyrins, and pyridinecobaloxime are very dependent on catalyst and solvent[248]. The kinetics of oxidation of benzoin to benzil,

benzaldehyde and benzoic acid catalysed by nickel acetate and cobalt acetate in MeOH and EtOH are second-order overall[249]. The oxidation of aliphatic, alicyclic and substituted benzyl alcohols to carbonyl compounds by MeCOOOH in HOAc containing $Co(OAc)_3$ is accelerated by NaBr addition[250]. Rh and Ru complexes as catalysts for the PTC Wacker oxidation of terminal olefins give ketones and internal olefins with less selectivity than the analogous Pd-catalysed reaction[251]. Mechanistic studies of the $RhCl_3.3H_2O/Cu(NO_3)_2(HMPT)_2$ catalysed oxidation of oct-1-ene to octan-2-one in ethanol reveal H-exchange with solvent[252]. [^{2}H] labelling studies show that conversion of cis-cyclooctene into cycloocto-2-en-1-ol at a Rh carbon involves oxygen attack at a vinylic carbon and double bond migration[253]. Rh complexes are also reported to catalyse: oxidation of oct-1-ene by Me_3COOH to yield the same products as O_2 oxidation [254]; selective oxidation of secondary alcohols $RCHR^1OH$ (R=Me, R^1=Bu, hexyl, octyl; $RR^1=(CH_2)_5$) to $RCOR^1$ with 87-99.5% conversion and 74-96% selectivity[255]; stereoselective dehydrogenation of cis- and trans-methylcyclohexanols[256]; and autoxidation of hydrocarbons[257]. Terminal olefins $H_2C=CHR$ ($R=(CH_2)_nCH_3$ (n=2, 3, 8, 10), cyclohexyl) and terminal diolefins $H_2C=CH(CH_2)_mCH=CH_2$ (m=3, 5) are oxidised by O_2 to 22-73% MeCOR and 77-78% $MeCO(CH_2)_mCOMe$ using a system containing $PdCl_2$ or Pd(O), $CuCl_2$, H_2O, benzene and a phase transfer catalyst[258]. A new catalytic air oxidation of alkenes is found in the presence of cis-$[PdCl(NO_2)(MeCN)_2]$; monosubstituted terminal olefins and trans-cyclooctene yield the corresponding ketone; cyclo-pentene and -hexene the allyl alcohol; and bicyclic alkenes the epoxide, etc[259]. The epoxidation of norbornene by O_2 catalysed by the same Pd complex reveals an intermediate (60) with a Pd-C bond[260]. $Pd(OAc)_2$ containing catalysts catalyse the selective oxidation of 1,3-dienes to give 1,4-diacetoxy-2-alkenes[261]; the oxidative dimerisation of activated thiophenes and furans[262]; and the catalytic preparation of allyl acetates from mono-olefins[263]. $[Pt(OH)(CF_3)(depe)]$ catalyses the selective epoxidation of simple terminal alkenes with dilute H_2O_2[264].

12 Synthesis

A book dealing with selective reactions includes those of

diene-metal complexes and asymmetric epoxidation[265]. The systematic replacement of atoms as an experimental strategy, and target-orientated system enlargement, in metal-catalysed organic synthesis are reviewed[266]. A survey of transition metals in synthesis covering the 1982 literature has appeared[267]. New Pd-cataysed reactions of allylic compounds has been reviewed[268].

Alkylation to form substrates which undergo intramolecular Diels-Alder reaction is controlled by choice of metal (Pd, Mo, W) template[269]. $[MoCp(cyclohexadiene)(CO)_2]^+$ may be used to control functionalisation of the 6-membered ring; in particular a novel stereocontrolled lactone synthesis[270]. The effects of m- or p-electron withdrawing groups on benzylic functionalisation of $[Cr(arene)(CO)_3]$ complexes are described[271] and steroespecific 6-alkylation of oestradiol derivatives achieved[272]. Repeated deprotonation and alkylation of $[Fe(=COCH_2CH_2CH_2)Cp(CO)(PPh_3)]^+$ allows stereoselective synthesis of quaternary carbon centres[273]. $[Fe(4\text{-methoxycyclohexadienyl})(CO)_3]PF_6$ is a synthetic equivalent to the p-anisyl cation for synthesis of (±)-o-methyljoubertiamine[274]. A new synthesis of fused 1, 2, 4-triazines (61) requires RCN, adiponitriles $NC(CH_2)_3CHR^1CN$, and $Fe_2(CO)_9$[275]. The preparation of 2(1H)-pyridinones and 2,3-dihydro-5(1H)-indolizinones via cocyclization of two acetylenes with an isocyanate is achieved using $[Co(Cp)(CO)_2]$ and $[Ni(cod)_2]$ catalysts[276]. A Ni(O) catalysed synthesis of imines from isocyanates and aldehydes is reported[277]. α-diazoketones cyclize to bicyclo [5.3.0]-decatrienones or 2-tetralones in the presence of $Rh(OAc)_2$[278]. Pd(II) catalysts are found for cyclisation of o-ethenylaniline p-toluenesulphonamide for efficient synthesis of 4-bromo-1-tosylindole[279]; ortho-alkylation of acetanilide using alkyl halides[280]; a high yield synthesis of γ, δ-unsaturated esters from ketene acetals with allylic alcohols[281]; and facile synthesis of bicyclo [3.3.1] nonadienones[282]. Regioselectivity in metal promoted C-C coupling reactions is reviewed[283] and a MO model of allylic alkylation developed[284]. The effect of metal catalyst on cross-coupling is described[285,286]. Numerous examples are catalysed by Ni[287-293], Fe[294,295], Pd[292,293,296-323], Cu[324-328].

12.1 Asymmetric Synthesis.- A general strategy for chiral, bidentate ligands for use in asymmetric synthesis is based upon

optically active 2,2'-dihalo-1,1'-binaphthyls[329]. Chiral Cu(II) Schiff base complexes catalyse the asymmetric synthesis of cyclopropanecarboxylates[330].

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16

Structures of Organometallic Compounds determined by Diffraction Methods

BY D. R. RUSSELL

1 Introduction

This Chapter is arranged in the same format used in Volume 13, and consists of a comprehensive list of organometallic compounds whose structures have been determined by X-ray, neutron or electron diffraction methods and reported during 1984. The definition of metals remains the same, and the ordering of formulae in the Main Table is based on the modified Hill system as before. Under the Structure heading the line formula is an attempt to describe the structural identity of the compound. The less familiar abbreviations used are listed at the end of the Main Table. Mixed metal compounds appear only once in the Main Table. The Metals Cross Reference Table can be used to locate mixed metal compounds in the Main Table which appear alphabetically under another metal.

The growth in numbers of structure determinations shows no sign of abating. The Main Table contains 1564 entries (874 is not allocated), which is an eleven per cent increase over 1983. The most frequently occurring metal is Si, found in 181 compounds, with Fe(173), Rh(133), W(125), and Ru(111) appearing in more than 100 compounds. Compounds 44, 87 and 88 contain four different metal atoms, and 87 has the largest number (9) of different elements present in one molecule.

[For References see page 472

2 Main Table

No.	Formula	Structure	Details	Ref.
1	$[AgC_{11}H_{16}]^+$	$[Ag\{\eta^4\text{-}2,6\text{-}(CH_2)_2bicyclo[3.3.1]C_9H_{12}\}][NO_3]$	153	1
2	$AgAuC_{16}H_8F_{10}S$	$[\{Au(C_6F_5)_2\}_2\{\mu\text{-}Ag(SC_4H_8)\}_2]_n\text{-}(\underline{Au}\text{-}\underline{Au})$		2
3	$AgAuC_{18}H_6F_{10}$	$[\{Au(C_6F_5)_2\}_2\{\mu\text{-}Ag(\eta^2\text{-}C_6H_6)\}_2]_n\text{-}(\underline{Au}\text{-}\underline{Au})$		2
4	$[AgOsC_6H_{20}O_{20}]^-$	$[PPN][Ag\{Os_3(\mu\text{-}H)(CO)_{10}\}_2]$		3
5	$AgRu_3C_{60}H_{44}F_3P_4$	$Ru_3(CO)_8(\mu\text{-dppm})_2(\mu\text{-}AgO_2CCF_3).0.5CH_2Cl_2$	140	4
6	$[AgSi_4C_{20}H_{54}]^-$	$[Li(THF)_4][Ag\{C(SiMe_3)_3\}_2]$		5
7	$[Ag_2Pt_2C_{24}Cl_4F_{20}]^{2-}$	$[NBu_4]_2[Ag_2Pt_2(C_6F_5)_4(\mu\text{-}Cl)_4]$		6
8	$Ag_2Si_4C_{24}H_{44}N_2$	$Ag_2\{\mu\text{-}\eta^1\text{:N-}2\text{-}(Me_3Si)_2CC_5H_4N\}_2$		7
9	$Ag_4Co_4C_{16}O_{16}$	$[AgCo(CO)_4]_4$		8
10	$Ag_6Fe_3C_{49}H_{31}O_{12}P_3$	$Ag_6\{Fe(CO)_4\}_3\{(Ph_2P)_3CH\}$		9
11	$[AlC_3H_9NO_3]^-$	$[K(\text{dibenzo-18-crown-6})][AlMe_3NO_3].0.5PhH$		10
12	$AlC_{24}H_{27}N_4$	$EtAl\{(NCMeCHCMeNC_6H_4\text{-}\underline{o})_2\}.0.5PhH$		11
13	$AlLiC_{14}H_{38}N_2P_2$	$(TMEDA)Li(PMe_2CH_2)_2AlMe_2$	233	12
14	$AlMgC_{30}H_{45}O_3$	$(THF)_3Mg(\mu\text{-}H)(\mu\text{-}9,10\text{-dihydroanthrylene})AlEt_2$		13
15	$AlReC_{28}H_{38}P_2$	$Me_2Al(\mu\text{-}H)_2ReH_4(PMePh_2)_2$	109	14
16	$AlReC_{41}H_{49}P_3$	$Me_2Al(\mu\text{-}H)_2ReH_2(PMePh_2)_3$	111	14
17	$AlSiC_{41}H_{37}O_4$	$Al(acac)(OSiPh_3)_2$		15
18	$AlTiC_{14}H_{22}Cl_2O$	$(Cp)_2Ti(\mu\text{-}H)_2AlCl_2(OEt_2)$		16
19	$AlWC_{12}H_{18}$	$(Cp)_2W(\mu\text{-}H)_2AlMe_3$	107	17
20	$AlWC_{13}H_{35}Cl_2P_2$	$WMe(PMe_3)_2(\eta\text{-}C_2H_4)_2(ClAlMe_xCl_{3-x})$		18
21	$AlZrC_{37}H_{53}O_2$	$Me_2Al(\mu\text{-}O\text{:}\eta^2CO\text{-}OCCHCH_2Bu^t)_2[\{Zr(Cp)_2\}_2(\mu\text{-}Me)]$		19
22	$[Al_2C_6H_{18}Cl]^-$	$[K(\text{dibenzo-18-crown-6})][Al_2Me_6(\mu\text{-}Cl)].2PhH$		20
23	$Al_2RhC_{15}H_{35}Cl_2$	$Rh(PMe_3)_2(Cp)\{AlMe_2(\mu\text{-}Cl)AlClMe_2\}$	173	21
24	$Al_2Si_4C_{12}H_{18}Cl_2N_4$	$\{ClAlNMeSiMe_2SiMe_2NMe\}_2$		22
25	$Al_2Si_4C_{22}H_{50}O_8$	$(Me_3SiO)_2Al(\mu\text{-}OSiMe_3)_2Al(acac)_2$		15
26	$Al_2Ti_2C_{26}H_{44}N_2$	$\{(Cp)_2Ti(\mu\text{-}H)_2AlH_2\}_2(\mu\text{-TMEDA}).PhH$		23
27	$Al_2Y_2C_{24}H_{38}O$	$Y_2(Cp)_4(\mu\text{-}H_2AlH_2)\{\mu\text{-}H_2AlH(OEt_2)\}(\mu_3\text{-}H)$		24
28	$Al_2Y_2C_{28}H_{44}O_2$	$\{(Cp)_2Y(\mu\text{-}H)AlH_2(THF)(\mu_3\text{-}H)\}_2$		25
29	$Al_2Y_2C_{32}H_{58}N_2$	$\{(Cp)_2Y(\mu\text{-}H)(\mu_3\text{-}H)AlH_2NEt_3\}_2$		24

No.	Formula	Structure	Details	Ref.
30	$[Al_3C_9H_{27}O_4S]^{2-}$	$[Cs_2(18\text{-crown-}6)][(Me_3AlO)_3SO]$		26
31	$Al_3C_{29}H_{51}O_6$	(dibenzo-18-crown-6)$(AlMe_3)_3$		27
32	$[Al_4C_{12}H_{36}O_4S]^{2-}$	$[K]_2[S(OAlMe_3)_4]$		28
33	$Al_4C_{32}H_{60}O_6$	(dibenzo-18-crown-6)$(AlMe_3)_4$		27
34	$[AsC_{12}H_{10}]^-$	$[Li(12\text{-crown-}4)_2][AsPh_2]$.THF		29
35	$AsC_{12}H_{19}S$	$AsPhPr^i_2S$		30
36	$AsC_{13}H_{12}NO$	$[N(\underline{o}\text{-}C_6H_4)_2As(O)Me][TCNQF_4]$.MeCN		31
37	$AsC_{18}H_{12}Cl_3O$	$OAs(\underline{p}\text{-}ClC_6H_4)_3$		32
38	$AsC_{18}H_{12}Cl_3S$	$SAs(\underline{p}\text{-}ClC_6H_4)_3$		32
39	$AsC_{18}H_{15}O$	$NiBr_2.4Ph_3AsO.8H_2O$ and $.H_2O.1.5PhMe$		33
40	$AsC_{24}H_{18}F_5O_3$	$Ph_3AsC(CO_2Me)C(O)C_2F_5$		34
41	$[AsC_{24}H_{20}]^+$	$[AsPh_4]^+$		35-50
42	$[AsC_{25}H_{24}]^+$	(<u>R</u>)-$[AsMe(CH_2Ph)(pTol)(naphth)][Br]$ and $[PF_6]$		51
43	$AsCoC_{20}H_{25}ClN_4O_5$	$CoCl(dmgH)_2(AsPh_2(OH))$		52
44	$AsCo_2FeMoC_{17}H_{11}O_{10}$	$(Cp)(OC)_2MoFeCo_2(CO)_{10}(\mu\text{-}AsMe_2)(\mu_3\text{-}S)$		53
45	$AsCr_2C_{14}H_9O_{10}$	$(Cr(CO)_5)_2(\mu\text{-}AsBu^t)$		54
46	$AsMn_2C_{24}H_{31}O_4$	$\{(\eta\text{-}C_5Me_5)(OC)_2Mn\}_2(\mu\text{-}AsH)$		55
47	$AsNaC_{16}H_{18}O_2$	$[\{O(CH_2CH_2)_2O\}NaAsPh_2]_n$ -(<u>Na</u>-<u>As</u>)		56
48	$AsNiC_{44}H_{36}OP$	$NiPh(AsPh_2CHCPhO)(PPh_3)$		57
49	$AsPdC_{20}H_{21}Cl_2N_2S$	<u>cis</u>-$PdCl_2(SNNMe_2)(AsPh_3)$		58
50	$AsPtC_{37}H_{33}ClP$	<u>trans</u>-$PtClMe(PEt_3)(AsPh_3)$		59
51	$AsSi_2C_{25}H_{48}P$	$(2,4,6\text{-}Bu^t_3C_6H_2)P{=}AsCH(SiMe_3)_2$		60
52	$AsTi_2C_{15}H_{21}OS_3$	$(\eta\text{-}C_5H_4Me)_2Ti(\mu\text{-}O)(\mu\text{-}AsS_3)Ti(\eta\text{-}C_5H_4Me)$		61
53	$As_2C_2H_2Cl_2F_6O_4$	$\{(As(CF_3)Cl(OH)(\mu\text{-}O)\}_2$		62
54	$As_2C_4H_2F_{12}O_4$	$\{(As(CF_3)_2(OH)(\mu\text{-}O)\}_2$		62
55	$As_2C_8H_{18}N_4S_2$	$Bu^t_2As_2(\mu\text{-}NSN)_2$		63
56	$As_2C_{24}H_{20}N_2S$	$(Ph_2AsN)_2S$		63
57	$As_2C_{43}H_{35}P$	$Ph_3PC(AsPh_2)_2$	238	64
58	$As_2CrC_{30}H_{24}O_4$	$(OC)_4Cr(CH_2AsPh_2CH_2AsPh_2)$		65
59	$As_2CrSi_2C_{30}H_{48}O_5$	$Cr(CO)_5[As\{CH(SiMe_3)_2\}{=}As(Mes)]$		66

No.	Formula	Structure	Details	Ref.
60	$As_2Cr_2PdC_{28}H_{28}O_{16}P_2$	$\{(MeO)_3P\}_2Pd[\eta^2\text{-}As_2Ph_2\{Cr(CO)_5\}_2]$		67
61	$As_2Cr_2PdC_{32}H_{18}N_2O_{10}$	$(bipy)Pd[\eta^2\text{-}As_2Ph_2\{Cr(CO)_5\}_2].CH_2Cl_2$		67
62	$As_2Cr_3C_{29}H_{19}O_{17}P$	$\{(MeO)_3P\}(OC)_4Cr[\eta^2\text{-}As_2Ph_2\{Cr(CO)_5\}_2]$		67
63	$As_2Mn_2C_{24}H_{30}O_4$	$\{(\eta\text{-}C_5Me_5)(OC)_2Mn\}_2(\mu\text{-}\eta^2\text{-}As_2)$		55
64	$As_2Mn_2C_{30}H_{20}Br_2O_6$	$Mn_2(CO)_6(\mu\text{-}As_2Ph_4)(\mu\text{-}Br)_2$		68
65	$As_2NiSi_2C_{47}H_{51}NO_2P_2$	$Ph_2As_2Ni\{(PPh_2)_2C_4(OSiMe_3)_2NMe\}$	180	69
66	$As_2PtRhC_{51}H_{44}Cl_3OP_2$	<u>trans</u>-$RhCl(CO)(\mu\text{-}Ph_2AsCH_2PPh_2)$-<u>cis</u>-$PtCl_2.CH_2Cl_2$		70
67	$As_2Ru_3C_{33}H_{22}N_2O_8$	$Ru_3(\mu\text{-}H)(CO)_8(\mu\text{-}\underline{o}\text{-}C_6H_4NN)(\mu_3\text{-}\overline{AsPhCH_2AsPh_2})$		71
68	$As_2Ru_3C_{50}H_{23}O_7$	$Ru_3(CO)_7(AsPh_3)_2(\mu\text{-}H)_3(\mu_3\text{-}CPh)$		72
69	$As_2Si_2C_{25}H_{48}$	$(2,4,6\text{-}Bu^t{}_3C_6H_2)As{=}AsCH(SiMe_3)_2$		60
70	$As_2SnC_6H_{18}S_4$	$Me_2Sn\{SAs(S)Me_2\}_2$		73
71	$As_2TiC_{18}H_{34}Cl_2S_2$	$TiCl_2(SBu^t)_2(diars)$		74
72	$As_3C_{19}H_{29}O_8$	$MeC(CH_2As)_3\{\mu\text{-}C(CO_2Et)_2\}_2$		75
73	$As_3Co_2C_{24}H_{23}F_6O_3$	$(OC)_3Co_2(ttas)\{\mu\text{-}\eta^2\text{-}C_2(CF_3)_2\}$		76
74	$As_3MoC_{12}H_{15}O_2$	$Mo(CO)_2(\eta^3\text{-}As_3)(\mu\text{-}C_5Me_5)$		77
75	$As_3RhC_{29}H_{30}O$	$Rh(AsPhAsPhAsPh)(CO)(\eta\text{-}C_5Me_5)$	125	78
76	$As_3Se_2C_5H_9$	$MeC(CH_2As)_3Se_2$		75
77	$As_4C_6H_2F_{18}O_8$	$As_4(CF_3)_6O_6(OH)_2$		62
78	$As_4CrC_{20}H_{36}Cl_2O_4$	$(OC)_4CrAsClBu^tAsBu^tAsBu^tAsClBu^t$		54
79	$AuC_{10}H_9N_2O$	$Au(CN)(\overline{COCH_2CHPhNH})$		79
80	$AuC_{14}H_{26}P$	$Au(PPr^i{}_3)(\eta^1\text{-}C_5H_5)$	153	80
81	$AuC_{20}H_{15}Cl_2NP$	$Ph_3PAuCCl_2CN$		81
82	$[AuC_{24}H_{18}N_4]^+$	$[\overline{Au(C_6H_4NN}Ph\text{-}\underline{o})_2][AuCl_4]$		82
83	$AuC_{26}H_{15}F_5P$	$Au(C{\equiv}C_6F_5)(PPh_3)$		83
84	$[AuC_{30}H_{32}N_4]^+$	$[Au(C\{NH(pTol)\}_2)_2][BF_4]$		84
85	$AuC_{34}H_{21}F_{10}N_4$	$\overline{Au\{C(pTol){=}NNPhCN}(pTol)\}(C_6F_5)_2$		85
86	$AuB_9WC_{32}H_{37}O_2P$	$Ph_3PAuW\{\mu\text{-}C(pTol)\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2).CH_2Cl_2$		86
87	$AuCoFeRuC_{27}H_{15}O_9PS$	$CoFeRu(CO)_9(\mu\text{-}AuPP\mu_3)(\eta_3\text{-}S)$		87
88	$AuCoFeRuC_{28}H_{18}O_9P_2$	$CoFeRu(CO)_9(\mu\text{-}AuPPh_3)(\mu_3\text{-}PMe)$		87
89	$AuCoRu_3C_{31}H_{15}O_{13}P$	$Ph_3PAuCoRu_3(CO)_{10}(\mu\text{-}CO)_3$		88

No.	Formula	Structure	Details	Ref.
90	$AuCrC_{23}H_{16}O_5P$	$(Ph_3P)AuCr(\mu\text{-}H)(CO)_5$	210	89
91	$[AuCr_2C_{16}H_{10}O_6]^-$	$[NBu_4][Au\{Cr(CO)_2(Cp)\}_2]$		90
92	$AuMn_2C_{28}H_{21}O_8P_2$	$Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8$		91
93	$AuNiOs_3C_{32}H_{22}O_9P$	$(Cp)NiOs_3(\mu\text{-}H)_2(\mu\text{-}AuPPh_3)(CO)_9$		92
94	$[AuPtWC_{24}H_{39}O_2P_3]^+$	$[(Cp)(OC)_2WAuPt(PMe_3)_3\{\mu_3\text{-}C(pTol)\}][PF_6]$		93
95	$[AuPt_3C_{75}H_{132}O_3P_4]^+$	$[(PCy_3)AuPt_3(PCy_3)_3(\mu\text{-}CO)_3][PF_6]$		94
96	$AuRu_3C_{23}H_{17}O_9P_2$	$Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}AuPMe_2Ph)(\mu_3\text{-}PPh)$		95
97	$AuRu_3C_{28}H_{15}ClO_{10}P$	$Ru_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)$	118	96
98	$AuRu_4C_{19}H_{15}IO_{12}P$	$Ru_4C(CO)_{12}(\mu\text{-}I)(AuPEt_3)$		97
99	$AuRu_4C_{31}H_{16}O_{12}P$	$Ru_4C(CO)_{12}(\mu\text{-}H)(AuPPh_3)$		97
100	$AuRu_5C_{35}H_{19}O_{15}P$	$Ru_5C(CO)_{14}(\mu\text{-}AuPPh_3)(\mu\text{-}\eta^2\text{-}MeCO)$		98
101	$AuRu_5C_{37}H_{20}O_{13}P$	$Ru_5C(CO)_{13}(Cp)(\mu\text{-}AuPPh_3)$		98
102	$AuWC_{33}H_{28}O_2P$	$Ph_3PAuW(CO)_2(Cp)\{\mu\text{-}CH(pTol)\}.CH_2Cl_2$	200	93
103	$[AuW_2C_{30}H_{24}O_4]^+$	$[AuW_2(CO)_4(Cp)_2\{\mu\text{-}C(pTol)_2\}][PF_6]$	200	99
104	$Au_2C_8H_{24}N_2$	$\{Me_2Au(\mu\text{-}NMe_2)\}_2$		100
105	$Au_2C_{26}H_{28}I_2P_2S_2$	$Au_2I_2\{\mu\text{-}C{:}S\text{-}CH_2P(S)Ph_2\}_2$		101
106	$Au_2C_{26}H_{28}I_2P_2S_2$	$AuI_2(CH_2PPh_2S)_2Au$		101
107	$Au_2C_{26}H_{28}P_2S_2$	$Au_2\{\mu\text{-}C{:}S\text{-}CH_2P(S)Ph_2\}_2$		101
108	$Au_2C_{29}H_{30}ClIP_2$	$IAuAu(CH_2Cl)\{\mu\text{-}(CH_2)_2PPh_2\}_2$		102
109	$Au_2C_{43}H_{21}F_{15}P_2$	$(C_6F_5)_2\overline{Au(PPh_2CH(AuC_6F_5)}PPh_2)$		103
110	$Au_2C_{43}H_{39}NO_6P_2$	$Au_2(OCOPh)_2\{\mu\text{-}CHNO_2\}\{\mu\text{-}\eta^1{:}\eta^1\text{-}(CH_2)_2PPh_2\}_2$		104
111	$Au_2CoRu_3C_{48}H_{31}O_{12}P_2$	$(Ph_3P)_2Au_2CoRu_3(\mu\text{-}H)(CO)_{12}.0.5CH_2Cl_2$		88
112	$Au_2Li_2C_{36}H_{48}N_4$	$Au_2Li_2(\mu\text{-}\mu C{:}N\text{-}\underline{o}\text{-}C_6H_4CH_2NMe_2)_4$		105
113	$Au_2OsC_{40}H_{30}O_4P_2$	$(Ph_3P)_2Au_2Os(CO)_4$		106
114	$Au_2PdC_{74}H_{44}F_{20}P_4$	$\underline{trans}\text{-}Pd(C_6F_5)_2\{(\mu\text{-}dppm)Au(C_6F_5)\}_2$		107
115	$[Au_2Pt_2C_{108}H_{96}N_4P_4]^{2+}$	$[(XyNC)_4Pt_2Au_2(PPh_3)_4][PF_6]_2$		108
116	$Au_2Ru_4C_{29}H_{22}O_{12}P_2$	$Ru_4C(CO)_{12}(\mu\text{-}AuPMe_2Ph)_2$		97
117	$Au_2Ru_5WC_{30}H_{30}O_{17}P_2$	$Ru_5WC(CO)_{17}(AuPEt_3)_2$		109
118	$Au_2Ru_6C_{43}H_{26}O_{16}P_2$	$Ru_6C(CO)_{16}(AuPMePh_2)_2$		109
119	$[Au_3C_{74}H_{42}F_{20}P_4]^+$	$[\{(C_6F_5)_2\overline{AuPPh_2CH(PPh_2)}\}_2Au][ClO_4].xCHCl_3$		103

No.	Formula	Structure	Details	Ref.
120	$Au_3Ru_3C_{74}H_{60}O_8P_3$	$(Ph_3P)_3Au_3Ru_3(CO)_8(\mu_3\text{-}\eta^1:\eta^3:\eta^1\text{-}C_{12}H_{15})$		110
121	$Au_3Ru_4C_{66}H_{46}O_{12}P_3$	$(Ph_3P)_3Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}$		111
122	$BC_6H_{13}N_2O_2$	$Me_2\overline{BNMeC(O)C(NHMe)O}$		112
123	$[BC_6H_{18}N_2O_2]^+$	$[Me_2\overline{BOC(NHEt)C(NHEt)O}]Br$		112
124	$BC_8H_{18}N$	Bu^tBNBu^t	188	113
125	$[BC_8H_{20}]^-$	$[Pt_3S_2(PMe_2Ph)_6][BEt_4]_2$		114
126	$BC_{16}H_{17}N_2O_2$	$Me_2\overline{BNPhC(O)C(NHPh)O}$		112
127	$BC_{17}H_{22}NO_2$	$Ph_2\overline{BOCMe_2NMe_2O}$		115
128	$[BC_{19}H_{15}N]^-$	$[Fe_2Hg_2C_{26}H_{32}N_2][Ph_3BCN]_2$	153	116
129	$BC_{19}H_{16}NO_2$	$Ph_2\overline{BN(OH)CH(\underline{o}\text{-}C_6H_4O)}$		117
130	$[BC_{24}H_{20}]^-$	$[BPh_4]^-$		118-136
131	$BC_{30}H_{21}$	$B(naphth)_3.PhH$		137
132	$BCoC_{30}H_{38}P_2$	$Co(PMe_3)_2(\eta^6\text{-}C_6H_5BPh_3)$		138
133	$BCu_2C_{15}H_{20}ClN_6$	$Cu(HBpz_3)(\eta^2\text{-}C_6H_{10}).CuCl$	173	139
134	$BFeC_{29}H_{25}$	$Fe(Cp)(\eta^6\text{-}C_6H_5BPh_3)$		140
135	$BFeWC_{22}H_{17}N_6O_5$	$(OC)_3FeW(CO)_2(HBpz_3)\{\mu\text{-}C(pTol)\}$	190	141
136	$BFe_3C_9H_5O_9$	$Fe_3(\mu\text{-}H)(\mu_3\text{-}BH_4)(CO)_9$		142
137	$BLiSi_3C_{37}H_{60}O_3$	$(THF)_3Li(\mu\text{-}H)_3BC(SiMe_2Ph)_3$		143
138	$BMoC_{13}H_{20}NO_2$	$Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}Me\overline{BCHCHCHNBu^t})$		144
139	$[BMoC_{15}H_{16}N_6O_3]^-$	$[NEt_4][Mo(CO)_3\{HB(mpz)_3\}]$		145
140	$BMoC_{24}H_{26}N_7O_4S$	$Mo(CSC_6H_4NO_2\text{-}\underline{p})(CO)_2\{HB(dmpz)_3\}$		146
141	$BReC_{14}H_{12}ClNO_5$	$\underline{cis}\text{-}(OC)_4\overline{Re\{CMeNHBClPhOCMe\}}$		147
142	$BSi_3C_{18}H_{39}$	$B\{C(SiMe_3)=CHMe\}_3$		148
143	$BSi_3C_{18}H_{42}FO_4$	$Me_2Si(O_2SiBu^t_2)_2BF$		149
144	$BSi_3C_{22}H_{37}$	$Ph_2BC(SiMe_3)_3$		150
145	$BSnC_{12}H_{19}N_6$	$SnMe_3(HBpz_3)$		151
146	$BTaC_{12}H_{19}ClN_6$	$TaMe_3Cl\{HB(pz)_3\}$	123	152
147	$BVC_{10}H_8O_4$	$V(CO)_4(\eta^6\text{-}C_5H_5BMe)$		153
148	$[BWC_{13}H_{14}N_6S]^+$	$[W(CO)_2(HBpz_3)(\eta^2\text{-}CHSMe)][CF_3SO_3]$	233	154
149	$BWC_{22}H_{19}N_8O_2$	$W\{C(pTol)\}(CO)_2(Bpz_4)$	190	141

No.	Formula	Structure	Details	Ref.
150	$BWC_{23}H_{27}O_2$	$W(CO)_2(Cp)\{\eta^3\text{-}CH(BC_8H_{14})(pTol)\}$		155
151	$BW_2C_{18}H_{19}O_4$	$EtB(\mu\text{-}H)W_2(CO)_4(Cp)_2(\mu_3\text{-}CMe)$		155
152	$B_2C_8H_{18}N_2O_2$	$Me_2BNMeCOBMe_2NMeCO$		112
153	$B_2C_{14}H_{30}N_2$	$Bu^tCB(NMe_2)CBu^tBNMe_2$		156
154	$B_2C_{15}H_{18}N_2O_3$	$PhBOBPhONMeCH_2NMeO$		157
155	$B_2C_{16}H_{36}N_2$	$Bu^t_2B_2N_2Bu^t_2$	193	113
156	$B_2C_{20}H_{21}NO_2$	$Ph_2BOBPhONMe_2$		115
157	$B_2C_{26}H_{23}NO_3$	$PhBONMe(\underline{o}\text{-}CHPhC_6H_4O)BPhO$		158
158	$B_2C_{28}H_{40}O_4P_2$	$\{1,5\text{-}C_8H_{14}BOPHPh(\mu\text{-}O)\}_2$		159
159	$B_2C_{32}H_{40}O_4P_2$	$\{Et_2BOPPh_2(\mu\text{-}O)\}_2$		159
160	$B_2NiC_{16}H_{30}N_2$	$Ni(\eta^3\text{-}CHCHCHBMeNBu^t)_2$		160
161	$B_2RuC_{16}H_{30}N_2$	$Ru(\eta^5\text{-}MeBCHCHCHNBu^t)_2$		161
162	$B_2Si_6U_2C_{44}H_{84}F_{10}$	$[U\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}F)(\mu\text{-}BF_4)]_2$		162
163	$B_3C_{21}H_{48}N_3$	$(Pr^iBNBu^t)_3$		163
164	$B_3FeC_{20}H_{33}$	$1\text{-}(\eta\text{-}C_6Me_6)Fe\text{-}4,5,7,8\text{-}Me_4C_4B_3H_3$		164
165	$B_3Os_9C_{30}H_9O_{33}$	$[Os_3(\mu\text{-}H)_3(CO)_9\{\mu_3\text{-}COB(\mu\text{-}O)\}]_3$	123	165
166	$B_3UC_{15}H_{50}P_4$	$U(BH_3Me)_3(dmpe)_2$		166
167	$B_4C_{10}H_{28}N_4$	$H_2C\{B(NMe_2)B(NMe_2)\}_2CH_2$		167
168	$B_4CoC_5H_{13}$	$2\text{-}\{(Cp)Co\}B_4H_8$		168
169	$B_4CrC_{13}H_{21}$	$Cr(\eta^5\text{-}Et_2C_2B_4H_4)(\eta^7\text{-}C_7H_7)$		169
170	$B_4IrC_{17}H_{31}OP_2$	$Ir(\eta^4\text{-}B_4H_8)(CO)(PMe_2Ph)_2$	111	170
171	$B_4SiSnC_6H_{16}$	$2\text{-}SiMe_3\text{-}1,2,3\text{-}SnC_2B_4H_4$		171
172	$B_4TiC_{14}H_{22}$	$Ti(\eta^5\text{-}Et_2C_2B_4H_4)(\eta^8\text{-}C_8H_8)$		169
173	$B_4UC_{10}H_{40}P_2$	$U(BH_3Me)_4(dmpe)$		166
174	$B_4VC_{14}H_{22}$	$V(\eta^5\text{-}Et_2C_2B_4H_4)(\eta^8\text{-}C_8H_8)$		169
175	$B_5FeC_{15}H_{25}$	$2\text{-}(\eta\text{-}C_6H_5Me)Fe\text{-}6,7,9,10\text{-}Me_4C_4B_5H_5$		164
176	$B_6Si_6C_{21}H_{63}N_7S_3$	$B_6N_7(SMe)_3(SiMe_3)_6$		172
177	$B_8C_{12}H_{28}$	<u>closo</u>$\text{-}2,3,7,8\text{-}Et_4C_4B_8H_8$		173
178	$[B_8CoC_6H_{14}]^-$	$[NMe_4][1,2\text{-}(Cp)CoCB_8H_9]$		174
179	$B_8FeC_9H_{22}O$	$2\text{-}(\eta^6\text{-}Mes)Fe\text{-}6\text{-}OB_8H_{10}$		175

No.	Formula	Structure	Details	Ref.
180	$B_8IrC_7H_{29}OP_2$	2-$(Me_3P)_2$(OC)-2-<u>nido</u>-IrB_8H_{11}		176
181	$B_8IrC_7H_{30}ClOP_2$	1-Cl-4-(OC)$(Me_3P)_2$H-4-<u>arachno</u>-IrB_8H_{11}		177
182	$B_8Ni_2C_{29}H_{57}$	$\{(\eta^5\text{-}Et_2HC_3B_3Me_3)Ni\}_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}\overline{BMeCEtCEtBMeCH})$		178
183	$B_8RhC_{38}H_{41}P_2$	9,9-$(PPh_3)_2$-<u>nido</u>-9,7,8-$RhC_2B_8H_{11}$		179
184	$B_9C_4H_{17}OS$	5-Me_2SO-<u>nido</u>-7,8-$C_2B_9H_{11}$		180
185	$B_9C_4H_{17}S$	8-SMe_2-<u>nido</u>-7,9-$C_2B_9H_{11}$		181
186	$B_9FeC_9H_{25}$	5-(η^6-Mes)FeB_9H_{13}		175
187	$B_9IrC_{44}H_{46}P_2$	<u>closo</u>-2,1,8-$\{(Ph_3P)_2HIr\}C(PhC)B_9H_{10}.0.5CH_2Cl_2$		182
188	$B_9RhC_{20}H_{26}ClP$	<u>closo</u>-2,1,7-$\{(PPh_3)ClRh\}C_2B_9H_{11}$.PhH	119	183
189	$B_9RhC_{21}H_{48}P_2$	<u>closo</u>-2,1,8-$\{(Et_3P)_2HRh\}(MeC)(PhC)B_9H_9$		184
190	$B_9RhC_{28}H_{41}O_2P$	<u>closo</u>-3,1,2-$\{(Ph_3P)(CH_2CH_2COOBu)Rh\}(MeC)CB_9H_{10}$		183
191	$B_9RhC_{45}H_{48}P_2$	<u>exo</u>-<u>nido</u>-4,9-$\{(Ph_3P)_2Rh(\mu\text{-}H)_2\}$-7,8-(MeC)(PhC)$B_9H_8$		184
192	$B_9RhC_{46}H_{48}P_2$	<u>closo</u>-3,1,2-$\{(PPh_3)_2HRh\}[(\mu\text{-}\underline{o}\text{-}(CH_2)_2C_6H_4)C_2]B_9H_9$		184
193	$B_9RhC_{46}H_{66}P_2$	<u>exo</u>-<u>nido</u>-6,10-$\{(Ph_3P)(Cy_3P)Rh(\mu\text{-}H)_2\}$-7,8-$[(\mu\text{-}\underline{o}\text{-}(CH_2)_2C_6H_4)C_2]B_9H_8$.1.5PhH		184
194	$B_9RhC_{48}H_{58}O_2P_2$	<u>exo</u>-<u>nido</u>-$(Ph_3P)_2(\mu\text{-}H)_2Rh$-10-$\{CH_2CH_2C(O)Bu\}$-7,8-$\{\mu\text{-}(CH_2)_3C_2\}B_9H_9$	133	185
195	$B_9RhWC_{50}H_{52}O_2P_2$	$(Ph_3P)_2Rh(\mu\text{-}CO)\{\mu\text{-}C(pTol)\}W(CO)(\eta^5\text{-}C_2B_9H_9Me_2)$		86
196	$B_9RhWC_{57}H_{60}O_2P_2$	$(Ph_3P)_2Rh(\mu\text{-}CO)\{\mu\text{-}C(pTol)\}W(CO)\text{-}\{\eta^5\text{-}C_2B_9H_8Me_2(C_7H_9)\}.0.5CH_2Cl_2$		86
197	$B_9Rh_2C_{20}H_{38}ClS$	7-Cl-2,3-$(\eta\text{-}C_5Me_5)_2$-<u>closo</u>-1,2,3-$SRh_2B_9H_8$		186
198	$B_9SnC_{14}H_{23}N_2$	1-bipy-2,3-Me_2-1,2,3-$SnC_2B_9H_9$		171
199	$B_{10}LiC_{12}H_{36}N_3$	<u>closo</u>-1,2-$\{MeN(CH_2CH_2NMe_2)_2\}Li(MeC)CB_{10}H_{10}$		187
200	$[B_{18}C_4H_{20}S_4]^{2-}$	$[NHMe_3]_2[7,8\text{-}S_2C_2B_9H_{10})_2\text{-}(\underline{S}\text{-}\underline{S})]$		188
201	$B_{18}NiC_6H_{26}O_2$	$Ni\{8\text{-}MeO\text{-}1,2\text{-}C_2B_9H_{10}\}_2$		189
202	$[B_{19}C_4H_{22}]^-$	$[Rh(PPh_3)_3][$<u>nido</u>-7-(1′-<u>closo</u>-1′,2′-$C_2B_{10}H_{11})$-7,8-$C_2B_9H_{11}].CH_2Cl_2$		184
203	$B_{30}C_{33}H_{54}$	1,3,5-$C_6H_3(\underline{p}\text{-}C_6H_4CH_2C_2B_{10}H_{11})_3$		190
204	$BeC_{10}H_{10}$	$Be(C_5H_5)_2$	128	191
205	$Be_2C_{18}H_{30}N_2$	$\{Be(C{\equiv}CMe)(NMe_3)\}_2(\mu\text{-}CCMe)_2$		192

No.	Formula	Structure	Details	Ref.
206	$[BiC_{16}H_{10}F_6O_4]^-$	$[BiPh_4][BiPh_2(OTFAc)_2]$		193
207	$[BiC_{24}H_{20}]^+$	$[BiPh_4][(pTol)SO_3]$		193
208	$BiC_{27}H_{21}ClNO$	$BiClPh_3$(oxine)		193
209	$BiCoC_{33}H_{25}O_3P$	$Ph_2BiCo(CO)_3(PPh_3)$		194
210	$[BiFe_3C_{10}O_{10}]^-$	$[NEt_4][BiFe_3(CO)_9(\mu_3\text{-}CO)]$		195
211	$BiLiSi_2C_{10}H_{28}O_2$	$(DME)LiBi(SiMe_3)_2$	183	196
212	$Bi_2C_{24}H_{20}$	Bi_2Ph_4		197
213	$Bi_2Si_4C_{12}H_{36}$	$\{(Me_3Si)_2Bi\}_2$		196
214	$[CoC_4O_4]^-$	[Cs] and $[Tl][Co(CO)_4]$	117,295	198
	$[CoC_4O_4]^-$	$[NEt_4]_3[Co_9Si(CO)_{21}][Co(CO)_4]$		199
215	$[CoC_6H_7NO]^-$	$[PPN][Co(NO)(\eta\text{-}C_5H_4Me)]$		200
216	$CoC_8H_{18}N_3O_2P_2$	$Co(N_3)(CO)_2(PMe_3)_2$		201
217	$CoC_{11}H_{14}NS_3$	$Co(S_2CS)(CNBu^t)(Cp)$		202
218	$CoC_{11}H_{21}P_2$	$Co(PEt_3)_2(\eta^5\text{-}CH_2CMeCHCMeCH_2)$		203
219	$CoC_{11}H_{33}N_3P_3$	<u>mer</u>-$CoMe_2(N_3)(PMe_3)_3$		201
220	$CoC_{12}H_{21}N_6O_4$	$CoMe(dmgH)_2$(imid)		204
221	$CoC_{16}H_{19}O_2$	$Co(\underline{o}\text{-}O_2C_6H_4)(\eta\text{-}C_5Me_5)$		205
222	$CoC_{16}H_{38}P_3$	$Co(PMe_3)_3$(<u>anti</u>-$\eta^3\text{-}CH_2CMeCHCMeCH_2$)		203
223	$CoC_{17}H_{24}N_5O_6$	$Co\{(\underline{R})\text{-}CHMeCO_2Me\}(dmgH)_2(py).MeOH$	223	206
224	$CoC_{17}H_{27}N_6O_5$	$CoEt(dmgH)_2\{4\text{-}NC_5H_4C(NH)OMe\}$		207
225	$[CoC_{19}H_{35}PS]^+$	$[Co(\eta^2CS\text{-}MeSCCBu^t{}_2)(PMe_3)(Cp)][I]$		208
226	$CoC_{21}H_{33}N_5O_4P$	$Co\{CHMeCN\}(dmgH)_2(PEt_2Ph)$		209
227	$CoC_{22}H_{35}N_6O_4$	<u>trans</u>-Co(adamantyl)$(dmgH)_2$(1-Meimid)		210
228	$CoC_{25}H_{33}N_5O_4P$	$Co\{CHMeCN\}(dmgH)_2(PEtPh_2)$		209
229	$CoC_{27}H_{21}N_4O_2$	$Co(CH_2CN)(py)\{\underline{o}\text{-}C_6H_4(NCHC_6H_4O\text{-}\underline{o})_2\}.H_2O$		211
230	$CoC_{27}H_{21}O$	$Co(\eta^4\text{-}PhCHCPhCPhCO)(Cp)$		212
231	$CoC_{27}H_{24}N_3O_2$	$CoEt(py)\{\underline{o}\text{-}C_6H_4(NCHC_6H_4O\text{-}\underline{o})_2\}.H_2O$		211
232	$CoC_{27}H_{24}P$	$Co(CHCHCHCH)(PPh_3)(Cp)$		213
233	$CoC_{29}H_{26}O_2P$	$Co(CHCHCHCH)(PPh_3)(\eta\text{-}C_5H_4CO_2Me)$		213
234	$[CoC_{33}H_{41}P]^+$	$[Co(\eta^2CH\text{-}Et)\{P(pTol)_3\}(\eta\text{-}C_5Me_5)][BF_4].PhMe$	200	214

No.	Formula	Structure	Details	Ref.
235	$[CoC_{43}H_{42}NP_3S]^+$	$[Co(CS)(np_3)][BPh_4]$		131
236	$CoC_{46}H_{31}N_4O$	$Co(CH_2CHO)(Ph_4porph)$		215
237	$CoC_{49}H_{47}N_2P_3S$	$Co(\eta^2\text{-}SCNPh)(np_3).1.3BuOH$		216
238	$CoC_{55}H_{46}OP_3$	$CoH(CO)(PPh_3)_3.Et_2O$		217
239	$CoCrC_{19}H_{36}O_5P_3$	$(Me_3P)(OC)CoCr(CO)_3(PMe_3)(\mu\text{-}CO)(\mu\text{-}PBu^t_2)$		218
240	$CoCr_2C_{18}H_{23}O_2S_3$	$(OC)_2Co(\mu_3\text{-}S)_2Cr_2(\mu\text{-}SBu^t)(\eta\text{-}C_5H_4Me)_2$		219
241	$CoCr_3C_{18}H_{15}O_4S_3$	$(Cp)_3Cr_3Co(CO)_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3.Bu^tCO_2H$	153	220
242	$CoCr_4C_{28}H_{38}S_6$	$\{(Cp)_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2\}_2Co$	153	220
243	$CoFeC_{12}H_{11}O_4S_2$	$(OC)_2Co(\mu\text{-}CO)(\mu\text{-}\eta^2:\eta^1\text{-}MeSCSMe)Fe(CO)(Cp)$		221
244	$CoFeC_{19}H_{36}O_5P_3$	$(Me_3P)(OC)_2CoFe(CO)_3(PMe_3)(\mu\text{-}PBu^t_2)$		218
245	$[CoFe_2C_{11}O_{10}]^-$	$[PPN][Fe_2Co(CO)_9(\mu_3\text{-}CCO)]$		222
246	$CoMnC_{13}H_{19}N_2O_2P$	$(Cp)CoMn(PMe_3)(\mu\text{-}NO)_2(Cp)$		200
247	$CoPd_2C_{23}H_{26}Cl_3N_2O_4$	$(OC)_2Co(\mu\text{-}CO)_2\{Pd(\underline{o}\text{-}C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Cl)$		223
248	$CoPt_2C_{69}H_{55}O_3P_4$	$(Ph_3P)(OC)Co(\mu\text{-}CO)_2Pt_2(PPh_3)_2(\mu\text{-}PPh_2)$		224
249	$[CoRh_6C_{15}NO_{15}]^{2-}$	$[PPh_4]_2[CoRh_6N(CO)_{10}(\mu\text{-}CO)_4(\mu_3\text{-}CO)]$		225
250	$[CoRuC_{18}H_{11}O_6P]^-$	$[NEt_4][(OC)_3CoRuH(CO)_3(\mu\text{-}PPh_2)]$		226
251	$CoRuC_{33}H_{20}O_7P$	$RuCo(CO)_5(\mu\text{-}CO)(\mu\text{-}P,\eta^1:\eta^2\text{-}PPh_2C(O)CPh{=}CPh)$		227
252	$CoSi_2C_{14}H_{36}OP_2$	$Co\{(\eta^2\text{-}CH_2CHSiMe_2)_2O\}(PMe_3)_2$		228
253	$[CoWC_{29}H_{34}O_2]^+$	$[(\eta\text{-}C_5Me_5)CoW(CO)_2(Cp)\{\mu\text{-}\eta^1:\eta^3\text{-}CHMeCMeC(pTol)\}]\text{-}[BF_4]$		229
254	$Co_2C_{10}F_6O_6$	$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}C_4F_6)$	100	230
255	$Co_2C_{10}H_2O_{10}$	$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}C_2(CO_2H)_2)$		230
256	$Co_2C_{10}H_6Cl_4N_3O_6P_3$	$Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}HCCCH_2\overline{PMeNPCl_2NPCl_2N}\}$		231
257	$Co_2C_{10}H_6Cl_4N_3O_6P_3$	$Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}MeCC\overline{PMeNPCl_2NPCl_2N}\}$		231
258	$Co_2C_{10}H_6O_8$	$Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}C_2(CH_2OH)_2\}.H_2O$		230
259	$Co_2C_{12}H_8Cl_4N_3O_6P_3$	$Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}HCCCH_2\overline{P(C_3H_5)NPCl_2NPCl_2N}\}$		231
260	$Co_2C_{14}F_6O_6$	$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}C_8F_6)$	163	232
261	$Co_2C_{14}H_{12}O_2$	$\{(Cp)(OC)Co\}_2(\mu\text{-}C{=}CH_2)$		233
262	$Co_2C_{24}H_{34}O_2$	$Co_2(\mu\text{-}CO)_2(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2$		234
263	$Co_2C_{26}H_{36}O_4S_2$	$Co_2(CO)_4\{\mu\text{-}S:\eta^2CS\text{-}S{=}C{=}CCMe_2CH_2CH_2CH_2CMe_2\}_2$		208

No.	Formula	Structure	Details	Ref.
264	$Co_2C_{28}H_{44}$	$\{Co(\eta^5\text{-}CH_2CMeCHCMeCH_2)\}_2\{\mu\text{-}\eta^4:\eta^4\text{-}(Me_2CCHCMeCH)_2\}$		235
265	$Co_2C_{32}H_{46}S_2$	$Co_2(Cp)_2\{\mu\text{-}S:\eta^2CS\text{-}S{=}C{=}CCMe_2CH_2CH_2CH_2CMe_2\}_2$		208
266	$Co_2C_{34}H_{31}O_4P$	$(\eta\text{-}C_5H_4CO_2Me)_2Co_2(\mu\text{-}P,\eta^1:\eta^3\text{-}PPh_2C_6H_4CMe\text{-}o)$		213
267	$Co_2C_{48}H_{30}F_6O_4P_2$	$Co_2(CO)_4(PPh_3)_2(\mu\text{-}\eta^2\text{-}C_8F_6)$	163	232
268	$Co_2MnC_{36}H_{38}O_{10}P$	$Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}PhCCMn(CO)_4(PCy_3)\}.0.5EtOH$		236
269	$Co_2RuC_{15}H_{10}O_9$	$Co_2Ru(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}HCCBu^t)$		237
270	$Co_2RuC_{15}H_{10}O_9$	$Co_2Ru(CO)_9(\mu_3\text{-}\eta^2:\mu\eta^1\text{-}CCHBu^t)$		237
271	$Co_2RuC_{32}H_{20}O_8P_2$	$Co_2Ru(CO)_8(\mu\text{-}PPh_2)_2$		238
272	$Co_2Si_8C_{24}H_{72}N_4$	$Co_2\{N(SiMe_3)_2\}_2(\mu\text{-}N(SiMe_3)_2)_2$	140	239
273	$Co_3C_{12}H_5O_{10}$	$Co_3(CO)_9(\mu_3\text{-}COEt)$		240
274	$Co_3C_{15}H_{14}NO_9P$	$Co_3(CO)_9(\mu_3\text{-}PNPr^i_2)$		241
275	$Co_3C_{20}H_{15}F_6O$	$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_4F_6)$		242
276	$Co_3FeC_{46}H_{31}O_{10}P_2$	$FeCo_3(\mu\text{-}H)(CO)_7(\mu\text{-}CO)_3(PPh_3)_2$		243
277	$[Co_3HgC_{12}O_{12}]^-$	$[NMe_4][Hg\{Co(CO)_4\}_3]$		244
278	$[Co_3Ni_9C_{21}O_{20}]^{3-}$	$[NEt_4]_3[Co_3Ni_9C(CO)_4(\mu\text{-}CO)_{16}]$		245
279	$Co_3Si_2Yb_2C_{60}H_{86}O_4$	$\{Yb(\eta\text{-}C_5Me_5)_2\}_2\{Co(\eta\text{-}C_5H_4SiMe_3)\}_2Co(\mu_3\text{-}O:\mu_2C\text{-}CO)_4$		246
280	$Co_4C_{46}H_{31}O_9P_3$	$Co_4(CO)_6(\mu\text{-}CO)_3\{\mu_3\text{-}HC(PPh_2)_3\}$		247
281	$Co_4Cu_4C_{16}O_{16}$	$\{CuCo(CO)_4\}_4$		248
282	$Co_4HgRuC_{16}O_{16}$	$RuCo_3(CO)_{12}\{\mu_3\text{-}HgCo(CO)_4\}$		249
283	$[Co_5Sn_2C_{19}Cl_2O_{19}]^-$	$[Co(HBpz_3)_2][Co(CO)_3(SnCl\{Co(CO)_4\}_2)_2]$		250
284	$Co_6C_6O_6S_8$	$Co_6(CO)_6(\mu_3\text{-}S)_6.3S_8$		251
285	$Co_6C_{16}O_{14}S$	$Co_6(\mu_6\text{-}C_2)(CO)_8(\mu\text{-}CO)_6(\mu_4\text{-}S)$		252
286	$Co_6C_{18}O_{16}S_3$	$(OC)_9Co_3CSCSCo_3(CO)_7(\mu_3\text{-}S)$		253
287	$[Co_6Ni_2C_{18}O_{16}]^{2-}$	$[NEt_4]_2[Co_6Ni_2C_2(CO)_8(\mu\text{-}CO)_8]$		254
288	$[Co_9SiC_{21}O_{21}]^{2-}$	$[NEt_4]_3[Co_9Si(CO)_{21}][Co(CO)_4]$		199
289	$CrC_8H_5Cl_5N_3O_3P_3$	$Cr(\overline{PClNPCl_2NPCl_2N})(CO)_3(Cp)$		255
290	$[CrC_9H_5O_4]^-$	$[PPh_4][Cr(CO)_3(\eta\text{-}C_5H_4CHO)]$		256
291	$CrC_{10}H_5NO_5$	$Cr(CO)_5(py)$		257
292	$[CrC_{11}H_9O_4]^+$	$[Cr(CO)_3(\eta^7\text{-}C_7H_6OMe)][BF_4]$		258
293	$CrC_{11}H_{10}O_6$	$(OC)_5Cr\{C(OMe)CMe{=}CHMe\}$		259

No.	Formula	Structure	Details	Ref.
294	$CrC_{12}H_8O_5$	$Cr(CO)_3(\eta\text{-}C_6H_4OCH_2CH_2CO\text{-}1,2)$		260
295	$CrC_{12}H_{12}O_5S_3$	$Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}$		261
296	$CrC_{12}H_{14}O_2S_2$	$Cr(CO)_2\{S(CH_2)_3SCH_2\}(\eta\text{-}C_6H_6)$		262
297	$CrC_{12}H_{23}O_4P_3$	$(OC)_4CrCH_2PMe_2C(PMe_2)MePMe_2$		263
298	$CrC_{13}H_{10}O_6$	$(OC)_4Cr\{C(OMe)C_6H_4OMe\text{-}o\}$		264
299	$CrC_{13}H_{14}O_5$	$Cr(CO)_3\{\eta^6\text{-}C_6H_5C(Me)(CH_2OH)_2\}$		265
300	$CrC_{13}H_{26}O_2P_2$	$Cr(CO)_2(PMe_3)_2(\eta^4\text{-}CH_2CHCHCHMe)$	173	266
301	$CrC_{14}H_{10}N_2O_4$	<u>cis</u>-$Cr(CO)_4(py)_2$		257
302	$CrC_{14}H_{12}O_6$	$Cr(CO)_3\{\eta^6\text{-}C_6H_5CH{=}C(OH)CO_2Et\}$		267
303	$CrC_{14}H_{16}O_4S_2$	$Cr(CO)_2\{S(CH_2)_3SCH_2\}(\eta\text{-}C_6H_5CO_2Me)$		262
304	$CrC_{14}H_{22}$	$Cr(\eta^5\text{-}CH_2CMeCHCMeCH_2)_2$		268
305	$CrC_{14}H_{28}O_2P_2$	$Cr(CO)_2(PMe_3)_2(\eta^4\text{-}MeCHCHCHCHMe)$		266
306	$CrC_{15}H_8O_3$	$Cr(CO)_3(\eta^6\text{-biphenylene})$		269
307	$CrC_{15}H_{11}NO_8$	$Cr(CO)_3\{\eta^6\text{-}o\text{-}C_6H_4NHC_6H_6O_5\}$		270
308	$CrC_{16}H_{12}NO_4P$	$Cr(CO)_4\{4,5\text{-}Me_2\text{-}2\text{-}(2\text{-pyridyl})\text{phosphorin}\}$		271
309	$CrC_{16}H_{21}NO_3$	$Cr(CO)_3(\eta^6\text{-}2,6\text{-}Bu^t{}_2C_5H_3N)$	200	272
310	$CrC_{17}H_{27}O_5P_3$	$Cr(CO)_5(PBu^tPBu^tPBu^t)$		273
311	$CrC_{19}H_{15}NO_2$	$Cr(CPh_2)(CO)(NO)(Cp)$		274
312	$CrC_{21}H_{12}O_3$	$Cr(CO)_3(\eta^6\text{-triphenylene})$		269
313	$CrC_{23}H_{39}O_2P$	$Cr(CO)_2(PMe_3)(\eta\text{-}C_6Et_6)$		275
314	$CrC_{24}H_{34}N_2O_6$	$(OC)_4Cr\{NCy{=}CC(OMe)MeCMe(OMe)C{=}NCy\}$		276
315	$CrC_{25}H_{16}NO_5P$	$(OC)_5Cr(NCCH{=}PPh_3)$		277
316	$CrC_{35}H_{39}O_3P$	$Cr(CO)_2(PPh_3)(\eta\text{-}C_6H_3OMe\{Bu^t{}_2\text{-}2,6\})$		278
317	$[CrC_{42}H_{30}N_6]^+$	$[Cr(CNPh)_6][CF_3SO_3]$		279
318	$[CrC_{42}H_{30}N_6]^{2+}$	$[Cr(CNPh)_6][PF_6]_2$		279
319	$[CrC_{42}H_{30}N_6]^{3+}$	$[Cr(CNPh)_6][SbCl_6]_3.CH_2Cl_2$		279
320	$[CrFe_3C_{14}O_{14}]^{2-}$	$[PPN]_2[Fe_3Cr(CO)_{12}(\mu\text{-}CO)_2]$		280
321	$[CrGeC_5H_3O_5]^-$	$[PPh_4][Cr(CO)_5GeH_3]$		281
322	$CrNiC_{18}H_{36}ClO_4P_3$	$(Me_3P)(OC)_4CrNiCl(PMe_3)(\mu\text{-}PBu^t{}_2)$		282
323	$CrPtC_{28}H_{41}O_4P_3$	$(OC)_4Cr(\mu\text{-}H)(\mu\text{-}PPh_2)Pt(PEt_3)_2$		283

No.	Formula	Structure	Details	Ref.
324	$CrRhC_{19}H_{36}O_5P_3$	$(Me_3P)(OC)_4CrRh(CO)(PMe_3)(\mu\text{-}PBu^t{}_2)$		282
325	$CrRhC_{21}H_{30}O_5P$	$(OC)_5CrRh(cod)(\mu\text{-}PBu^t{}_2)$		218
326	$CrSiC_{23}H_{18}O_5$	$(OC)_3Cr\{\eta\text{-}C_6H_5SiPh_2(CO_2Me)\}$		284
327	$CrSi_2C_{19}H_{20}O_3$	$Cr(CO)_3\{\eta^6\text{-}\underline{o}\text{-}C_6H_4(SiMe_2)_2(\underline{o}\text{-}C_6H_4)\}$		285
328	$[CrSn_3C_{58}H_{45}O_4]^-$	$[NEt_4][(Ph_3Sn)_3Cr(CO)_4]$		286
329	$CrZrC_{20}H_{16}O_6$	$(OC)_5Cr\{\mu\text{-}\eta^1:\eta^3,O\text{-}C(O)CH_2CHCHCH_2\}Zr(Cp)_2$		287
330	$[Cr_2C_{10}HO_{10}]^-$	$[K(phen)_3][Cr_2(CO)_{10}(\mu\text{-}H)]$		288
331	$Cr_2C_{14}H_9O_{10}$	$\{Cr(CO)_5\}_2PBu^t$		289
332	$Cr_2C_{30}H_{20}O_4$	<u>trans</u>-$C_2Ph_2\{CCr(CO)_2(Cp)\}_2$	153	290
333	$Cr_2MnC_{17}H_{19}O_3S_3$	$(OC)_3Mn(\mu_3\text{-}S)_2Cr_2(\mu\text{-}SBu^t)(Cp)_2$	153	219
334	$Cr_2PdC_{38}H_{47}$	$(Ph_3P)Pd(\mu\text{-}SBu^t)_2\{CrCl(\eta\text{-}C_5H_4Me)\}_2(\mu_3\text{-}S)$	153	291
335	$Cr_2Pt_2C_{28}H_{40}O_6P_2$	$(Cp)_2Cr_2Pt_2(PEt_3)_2(\mu\text{-}CO)_4(\mu_3\text{-}CO)_2$		292
336	$Cr_2Si_2C_{22}H_{20}O_6$	<u>cis</u> & <u>trans</u> $\{(OC)_3Cr(\eta^6\text{-}\underline{o}\text{-}C_6H_4)\}_2(SiMe_2)_2$		285
337	$Cr_2TeC_{16}H_{10}O_6$	$\{Cr(CO)_3(Cp)\}_2Te$		293
338	$[Cr_4C_{16}H_{12}O_{16}]^{4-}$	$[NMe_4]_4[Cr(CO)_3(\mu_3\text{-}OMe)\}_4]$		294
339	$Cr_4FeC_{32}H_{46}S_6$	$\{(\eta\text{-}C_5H_4Me)_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)\}_2Fe$		295
340	$Cr_4MnC_{28}H_{38}S_6$	$\{(Cp)_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2\}_2Mn$	153	296
341	$Cr_4MnC_{32}H_{46}S_6$	$\{(\eta\text{-}C_5H_4Me)_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)\}_2Mn$		295
342	$Cr_5C_{28}H_{38}S_6$	$\{(Cp)_2Cr_2(\mu\text{-}SBu^t)(\mu_3\text{-}S)_2\}_2Cr$	173	297
343	CuC_3H_5ClNO	$CuCl(\eta^2\text{-}CH_2{=}CHCONH_2)$		298
344	CuC_3H_6ClO	$CuCl(\eta^2\text{-}CH_2CHCH_2OH)$		299
345	$CuC_7H_{10}F_3O_3S$	$\{Cu(\eta^2\text{-}C_6H_{10})(\mu_3\text{-}O_3SCF_3)\}_n$		300
346	$[CuC_{11}H_9N_3O]^+$	$[Cu(CO)\{(2\text{-}NC_5H_4)_2NH\}][ClO_4]$	173	301
347	$[CuC_{12}H_{11}N_3]^+$	$[Cu(\eta\text{-}C_2H_2)\{(2\text{-}NC_5H_4)_2NH\}][BF_4]$	173	301
348	$[CuC_{12}H_{13}N_3]^+$	$[Cu(\eta\text{-}C_2H_4)\{(2\text{-}NC_5H_4)_2NH\}][ClO_4]$	173	301
349	$CuC_{30}H_{35}N_2O$	$Cu(2,6\text{-}Bu^t{}_2C_6H_3O)\{CN(pTol)\}_2$		302
350	$CuC_{47}H_{44}P_3$	CuPh(triphos)		303
351	$CuOs_3C_{28}H_{18}O_{10}P$	$(OC)_{10}Os_3Cu(\mu\text{-}H)_3(PPh_3)$		304
352	$CuPtWC_{31}H_{45}O_2P_2$	$(\eta\text{-}C_5Me_5)CuW(CO)_2(Cp)Pt(PMe_3)_2\{\mu_3\text{-}C(pTol)\}$		305
353	$CuRh_2C_{32}H_{45}O_2$	$CuRh_2(\eta\text{-}C_5Me_5)_3(\mu\text{-}CO)_2$		305

No.	Formula	Structure	Details	Ref.
354	$CuSb_3C_{54}H_{45}Cl$	$CuCl(SbPh_3)_3.CHCl_3$		306
355	$[CuSi_6C_{19}H_{54}]^-$	$[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$		307
356	$CuWC_{44}H_{35}O_3P_2$	$(Ph_3P)_2CuW(CO)_3(Cp)$		308
357	$Cu_2C_{10}H_{10}Cl_2N_2$	Cu_2Cl_2(<u>trans</u>-NCCH=CHCH=CH_2)$_2$		309
358	$Cu_2Re_2C_{20}H_{22}I_2$	$\{(Cp)_2HRe\}_2Cu_2(\mu\text{-}I)_2$		310
359	$Cu_2Ru_6C_{30}H_{16}O_{18}$	$(\eta^2\text{-PhMe})_2Cu_2Ru_6(CO)_{18}$		311
360	$[Cu_3Li_2C_{36}H_{30}]^-$	$[Li_4Cl_2(Et_2O)_{10}][Li_2Cu_3(\mu\text{-Ph})_6]_2$	140	312
361	$EuNaSi_6C_{18}H_{54}N_3$	$NaEu\{N(SiMe_3)_2\}_3$		313
362	$Eu_2C_{52}H_{72}O_4$	$Eu_2(THF)_4(\eta\text{-}C_5Me_5)_2(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2$		314
363	$[FeC_4HO_4]^-$	$[Fe(Etimid)_6][FeH(CO)_4]_2$	225	315
364	$[FeC_7H_5O_6]^-$	$[PPN][Fe(CH_2CO_2Me)(CO)_4]$		316
365	$FeC_{10}H_4Cl_8N_6P_6$	$Fe(\eta\text{-}C_5H_4PNPCl_2NPCl_2N)_2$ (<u>P</u>-<u>P</u>)		317
366	$FeC_{10}H_6Cl_4$	$Fe(\eta\text{-}C_5H_3Cl_2\text{-}1,2)_2$		318,319
367	$FeC_{10}H_9Cl_{11}N_7P_7$	$(Fc)P(NPCl_2)_2NPCl(NPCl_2)_3N$		320
368	$FeC_{10}H_9F_5N_3P_3$	$Fe(Cp)(\eta\text{-}C_5H_4PFNPF_2NPF_2N)$		317
369	$[FeC_{10}H_9O_4]^+$	$[Fe(CO)_3\{\eta^5\text{-}C_6H_6OMe\}][PF_6]$		321
370	$[FeC_{10}H_{10}]^+$	$[Fe(Cp)_2]_2[(FeCl_3)_2(\mu\text{-}O)]$		322
371	$FeC_{10}H_{10}F_7O_3PS$	$Fe(C_3F_7)(CO)_3(\eta^2\text{-}SPEt_2)$	173	323
372	$[FeC_{11}H_{11}O_4]^+$	$[Fe(CO)_3\{\eta^5\text{-}C_6H_6Me(OMe)\text{-}1,4\}][PF_6]$		321
373	$FeC_{11}H_{21}P$	$Fe(PMe_3)(\eta^4\text{-}C_4H_6)_2$		324
374	$FeC_{12}H_{12}O$	$Fe(Cp)(\eta\text{-}C_5H_4COMe)$		325
375	$FeC_{12}H_{14}O_2S_4$	<u>cis</u>-$Fe(SacSac)_2(CO)_2$		326
376	$[FeC_{12}H_{30}N_2O_4P]^{\bullet}$	$[Fe(CO)_4P(NEt_2)_2][AlCl_4]$	165	327
377	$FeC_{13}H_{10}O_2$	$Fe(\eta\text{-}C_5H_4)_2C(O)CH_2CO$		328
378	$[FeC_{13}H_{18}N]^+$	$(Cp)Fe(\eta\text{-}C_5H_4NHMe_2)]_2[B_{12}H_{12}]$		329
379	$FeC_{13}H_{19}NO_5$	$Fe\{C(OEt)NPr^i_2\}(CO)_4$	243	330
380	$FeC_{13}H_{19}NO_5$	$Fe\{C(NPr^i_2)OCEtO\}(CO)_3$	243	330
381	$FeC_{14}H_{16}O_4$	$Fe(CO)_3\{\eta^3\text{-}CHCMeCHC(O)CMeCH_2CMe_2\}$		331
382	$FeC_{16}H_{27}O_6P_2S_2$	$Fe\{\eta^2CS\text{-}MeSCC(O)C(CO_2Me)C(CO_2Me)S\}(CO)(PMe_3)_2$		332
383	$FeC_{16}H_{32}P_2$	<u>syn</u>-<u>syn</u>-$Fe(\eta^3\text{-}CH_2CHCHCHCH_2)_2(PMe_3)_2$		333

No.	Formula	Structure	Details	Ref.
384	$FeC_{17}H_{14}O$	$Fe(Cp)(\eta\text{-}C_5H_4COPh)$		334
385	$FeC_{17}H_{14}O_5$	$(OC)_3Fe\{2\text{-}5\eta\text{-}1,1\text{-}C_6H_6(Ph)(CO_2Me)\}$		335
386	$FeC_{17}H_{18}O_7$	$(OC)_4FeC{=}C{=}COC(O)OCBu^t{}_2$	223	336
387	$FeC_{18}H_{14}O_3$	$Fe(CO)_3\{\eta^4\text{-}C_7H_7CHCHPh\}$		337
388	$FeC_{18}H_{16}O_6$	$Fe(CO)_3\{\eta^4\text{-}C(OEt)CMeCMeCPhC(O)O\}$		338
389	$FeC_{18}H_{16}O_6$	$Fe(CO)_3\{\eta^4\text{-}CMeCMeCPhC(OEt)OCO\}$		338
390	$FeC_{18}H_{16}O_6$	$Fe(CO)_3\{\eta^4\text{-}C(OEt)CEtCHCPhC(O)O\}$		338
391	$FeC_{18}H_{22}$	$Fe[(\eta^5\text{-}C_5H_3\text{-}1,2)_2\{(CH_2)_4\}_2]$		339
392	$FeC_{19}H_{16}O_4$	$Fe(CO)_3\{\eta^4\text{-}CH(CH)_3CH_2CHC(O)CMePhCH\}$		340
393	$FeC_{20}H_{18}$	$Fe\{\eta^5\text{-tricyclo[5.2.1.0}^{2,6}\text{]deca-2,5,8-triene}\}_2$		341
394	$FeC_{20}H_{20}$	$(Cp)Fe\{\eta\text{-}1,3\text{-}C_5H_3(CH_2CH_2)_2C_6H_4\}$ (1′,3′ and 1′4′ isomers)		342
395	$FeC_{20}H_{28}O_2S_2$	meso-$Fe\{\eta\text{-}C_5H_4CH(Me)SCH_2CH_2OCH_2\text{-}\}_2$		343
396	$FeC_{21}H_{19}BrN_2O$	$Fe(Cp)\{\eta\text{-}C_5H_4CNNAcCH(p\text{-}C_6H_4Br)CH_2\}$		344
397	$FeC_{21}H_{19}BrN_2O$	$Fe(Cp)\{\eta\text{-}C_5H_4CHNAcNC(p\text{-}C_6H_4Br)CH_2\}$		344
398	$FeC_{22}H_{28}$	$Fe[(\eta^5\text{-}C_5H_2\text{-}1,2,4)_2\{(CH_2)_4\}_3]$		339
399	$FeC_{23}H_{17}O_4P$	$Fe(CH_2PPh_3)(CO)_4$		345
400	$FeC_{23}H_{19}O_3P$	$Fe(CO)_3(PPh_3)(\eta\text{-}C_2H_4)$	193	346
401	$[FeC_{23}H_{43}N_2O_2P_2]^+$	$[Fe(CO)_2(PMe_3)\{C(=CH_2)NCyC{=}NHCy\}][BPh_4]$		130
402	$FeC_{24}H_{16}O_4$	$(OC)_3Fe(5\text{-}8\eta^4\text{-}2,3\text{-}Ph_2\text{-}4H\text{-cyclohepta[b]furan})$		347
403	$FeC_{24}H_{23}OP$	$Fe(Cp)\{\eta^5\text{-}CHCMeCMeCHCPhP(O)Ph\}$		348
404	$FeC_{24}H_{25}N_2O_2P$	$Fe(CO)(NO)(PPh_2NHCHMePh)(\eta^3\text{-}C_3H_5)$		349
405	$FeC_{24}H_{30}$	[4][3][4][3]-(1,2,3,4)-ferrocenophane		350
406	$FeC_{25}H_{23}O_3P$	$Fe(CH_2CH_2CH_2CH_2)(CO)_3(PPh_3)$	183	346
407	$FeC_{25}H_{27}N_2O_2P$	$Fe(CO)(NO)(PPh_2NMeCHMePh)(\eta^3\text{-}C_3H_5)$		349
408	$FeC_{25}H_{34}$	$Fe[(\eta^5\text{-}C_5H_2\text{-}1,2,4)_2\{(CH_2)_5\}_3]$		339
409	$FeC_{26}H_{32}F_7O_7PS$	$Fe\{C(CO_2Cy){=}C(CO_2Cy)PEt_2S\}(C_3F_7)(CO)_3$	193	323
410	$FeC_{27}H_{20}O_6P_2$	$Fe_2(CO)_6\{\mu\text{-}P{:}C,\mu P\text{-}MePhPCHC_6H_4CH_2PPh\text{-}o\}$		351
411	$FeC_{28}H_{27}O_2P$	(Z)-$Fe(COMe{=}CHMe)(CO)(PPh_3)(Cp)$		352
412	$[FeC_{28}H_{29}NO_3P]^+$	$[Fe(CNPr^i{}_2)(CO)_3(PPh_3)][BCl_4].CH_2Cl_2$	233	353

No.	Formula	Structure	Details	Ref.
413	$FeC_{33}H_{30}N_2OS_2$	$Fe(detc)(NO)(\eta^4\text{-}C_4Ph_4)$		354
414	$FeC_{35}H_{24}O_3$	$Fe(CO)_3(\eta^4\text{-}MePh_3fluorene)$		355
415	$[FeC_{37}H_{33}OP_2]^+$	(-)-$[Fe(CO)(Cp)\{(Ph_2P)_2norbornene\}][PF_6].PhH$		356
416	$FeC_{40}H_{31}O_3P_3$	$Fe(CO)_3(\eta^2\text{-triphos})$		357
417	$FeC_{40}H_{58}O_4P_2$	$Fe(CO)_4\{(Mes)P{=}P(Mes)\}$		66
418	$FeC_{50}H_{33}N_4$	FePh(<u>meso</u>-Ph_4porph).C_5H_{12}		358
419	$FeHgC_{25}H_{28}Cl_2O_6P_2S_2$	$Cl_2HgFe\{CSC(CO_2Me)C(CO_2Me)S\}(CO)_2(PMe_2Ph)_2$		359
420	$FeMnC_{15}H_9O_5$	$Mn(CO)_3\{\eta^5\text{-}C_5H_4Fe(CO)_2(Cp)\}$		360
421	$FeMnC_{16}H_{21}N_2O_6$	$FeMn(CO)_6(\mu\text{-}\eta^3\text{:N:N-}Bu^tNCHCHNHBu^t)$		361
422	$FeMnC_{22}H_{16}O_5P$	$(OC)_4MnFe(\mu\text{-}H)(CO)(Cp)(\mu\text{-}PPh_2)$		362
423	$FeMnC_{24}H_{18}O_6P$	$(OC)_4Mn(\mu\text{-}PPh_2)(\mu\text{-C:O-OCMe})Fe(CO)(Cp)$		362
424	$FeMnC_{32}H_{24}O_4P$	$Mn(CO)_3\{\eta^5\text{-}C_5H_4Fe(CO)(PPh_3)(Cp)\}$		360
425	$FeMnSiC_{27}H_{23}O_3$	$Mn(CO)_3(\eta\text{-}C_5H_4SiMePhCH{=}CH(Fc)$		363
426	$FeMoC_{33}H_{20}O_{10}P_2$	$(OC)_5MoPPh_2OPPh_2Fe(CO)_4$		364
427	$FeNaC_{19}H_{14}NO_5S$	$Fe\{(\eta^5\text{-}C_5H_4OCH_2CH_2OCH_2CH_2)_2O\}.NaSCN$		365
428	$[FeOs_3C_{13}HO_{13}]^-$	$[PPN][FeOs_3(\mu\text{-}H)(CO)_{13}]$		366
429	$FePdC_{34}H_{28}Cl_2P_2$	$Fe(\eta\text{-}C_5H_4PPh_2)_2PdCl_2$		367
430	$FePtC_{39}H_{38}Cl_2O_3P_2$	$(OC)_3Fe\{\eta^4\text{-}C_4Bu^t_2(PPh_2)_2PtCl_2\}.2CHCl_3.0.5CH_2Cl_2$		368
431	$FePtC_{44}H_{30}Cl_2O_4P_2$	$(OC)_3Fe\{\eta^4\text{-}C_5OPh_2(PPh_2)_2PtCl_2\}.3CHCl_3.0.5PhH$		368
432	$FeRhC_{36}H_{31}O_3P_2$	$(OC)_3Fe(\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7)Rh(dppe)$		369
433	$[FeRhC_{42}H_{31}O_5P_3]^+$	$[(OC)_3FeRh(CO)_2\{PPh_2CH(PPh_2)_2\}][RhCl_2(CO)_2]$		357
434	$[FeRh_5C_{16}O_{16}]^-$	$[NEt_4][Rh_5Fe(CO)_{12}(\mu_3\text{-}CO)_4]$	153	370
435	$FeRuC_{14}H_{10}O_4$	<u>trans</u>-$FeRu(CO)_2(\mu\text{-}CO)_2(Cp)_2$		371
436	$FeRu_2C_{12}O_{12}$	$FeRu_2(CO)_{12}$		372
437	$FeRu_2C_{29}H_{15}O_{11}P$	$(OC)_4FeRu_2(CO)_9(PPh_3)$		372
438	$FeRu_2C_{46}H_{30}O_{10}P_2$	$(OC)_2Fe(\mu\text{-}CO)_2Ru_2(CO)_6(PPh_3)_2$		372
439	$FeRu_3C_{13}H_2O_{13}$	$(OC)_4FeRu_3(\mu\text{-}H)_2(CO)_9$		373
440	$FeSb_2Si_4C_{18}H_{38}O_4$	$Sb_2\{CH(SiMe_3)_2\}_2\{\mu\text{-}Fe(CO)_4\}$		374
441	$FeSiC_7H_5Cl_3O_2$	$Fe(SiCl_3)(CO)_2(Cp)$	193	375
442	$FeSiC_{19}H_{15}FO_2$	$Fe(SiFPh_2)(CO)_2(Cp)$		375

No.	Formula	Structure	Details	Ref.
443	$FeSiC_{32}H_{43}O_4P$	$Fe(CO)_4P(=CPhSiMe_3)(2,4,6\text{-}C_6H_2Bu^t_3)$		376
444	$FeSi_4C_{17}H_{36}NO_4P$	$Fe(CO)_4P\{N(SiMe_3)_2\}=C(SiMe_3)_2$		377
445	$FeSnC_{40}H_{44}N_4O_4$	$(OC)_4FeSn(Et_8porph)$		378
446	$FeV_2C_{34}H_{36}$	$Fe\{\eta\text{-}C_5H_4V(\eta\text{-}C_5H_4Me)_2\}_2$		379
447	$[FeWC_9HO_9]^-$	$[PPN][(OC)_4Fe(\mu\text{-}H)W(CO)_5]$	170	380
448	$FeWC_{22}H_{18}O_5$	$(OC)_3Fe\{\eta^3\text{-}CMeCMeC(pTol)\}W(CO)_2(Cp)$	220	381
449	$Fe_2C_7O_7S_2$	$Fe_2(CO)_6\{\mu\text{-}S)_2CO\}$		382
450	$Fe_2C_8Cl_4N_3O_8P_3$	$Fe_2(CO)_8(\mu\text{-}PNPCl_2NPCl_2N)$		383
451	$Fe_2C_{10}H_{12}O_6P_4$	$Fe_2(CO)_6\{(\mu\text{-}PMe)PMePMe(\mu\text{-}PMe)\}$		384
452	$Fe_2C_{12}H_{10}O_6$	$\{Fe(CO)_3(\eta^3\text{-}C_3H_5)\}_2$		385
453	$Fe_2C_{12}H_{12}O_8S_2$	$Fe_2(CO)_6(\mu\text{-}S{:}\eta^2CS\text{-}SCHOEt)_2$		386
454	$Fe_2C_{16}H_{14}O_3$	$Fe_2(CO)_2(Cp)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2)$		387
455	$Fe_2C_{16}H_{20}N_2O_8P_2$	$(OC)_4FePHNBu^tPHNBu^tFe(CO)_4$		388
456	$[Fe_2C_{16}H_{20}O_2S_2]^+$	$[\{(Cp)Fe(CO)\}_2(\mu\text{-}SEt)_2][ClO_3].THF$		389
457	$Fe_2C_{17}H_{13}NO_7$	$Fe_2(CO)_6(\mu\text{-}NCMe_2)(\mu\text{-}C{:}O\text{-}OCCH_2Ph)$		390
458	$Fe_2C_{17}H_{17}N_2O_2S$	<u>cis</u>-$(Cp)(OC)Fe(\mu\text{-}CO)(\mu\text{-}CS)Fe(CNPr^i)(Cp)$		391
459	$Fe_2C_{18}H_{12}O_{10}$	$Fe_2(CO)_6\{\mu\text{-}\eta^3{:}\eta^1,\eta^2\text{-}CH(CH)_4CH_2CHRCR\}$ R=CO_2Me		392
460	$Fe_2C_{18}H_{16}N_2O_6$	$(Cp)(OC)_2FeC(O)NHCH_2CH_2NHC(O)Fe(CO)_2(Cp)$		393
461	$Fe_2C_{19}H_{11}NO_6$	$Fe_2(CO)_6(\mu\text{-}\eta^2{:}\eta^1,\mu N\text{-}\underline{o}\text{-}C_6H_4CH_2NPh)$		394
462	$Fe_2C_{20}H_{18}Cl_6N_4P_4$	$NPCl_2NPCl_2NPClNPCl(Fc)_2$		320
463	$Fe_2C_{20}H_{26}N_2O_6$	$Fe_2(CO)_6\{\mu\text{-}\eta^1,\eta^1{:}\eta^4\text{-}CMeC(NEt_2)C(NEt_2)CMe\}$		395
464	$Fe_2C_{23}H_{16}O_7$	$Fe_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(OEt)CPhCHPh\}$		396
465	$Fe_2C_{23}H_{23}NO_7$	$Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}N{:}\mu C\text{-}CHC(C_5H_4N)CBu^t_2\}$	213	397
466	$[Fe_2C_{24}H_{11}F_6O_6]^-$	$[PPh_4][Fe_2(CO)_6\{\mu\text{-}\eta^1,\eta^1{:}\eta^3\text{-}CPhCPhC(CF_3)CHCF_3\}]$		398
467	$Fe_2C_{24}H_{24}$	<u>trans</u>-[2.2](1,2)-ferrocenophane		399
468	$[Fe_2C_{24}H_{24}]^+$	$[\{Fe(\eta\text{-}C_5H_4)_2\}_2(CHMe)_2][I_3]$		400
469	$Fe_2C_{25}H_{24}$	trimethylene[1.1]ferrocenophane (2,2′and 3,3′)		401
470	$Fe_2C_{26}H_{18}O_6P_2$	$Fe_2(CO)_6\{\underline{o}\text{-}(\mu\text{-}PhPCH_2)_2C_6H_4\}$		351
471	$[Fe_2C_{27}H_{17}O_4]^-$	$[PPh_4][Fe_2(CO)_6\{\mu\text{-}\eta^1,O{:}\eta^2\text{-}CRCRC(O)CPhCHPh\}]$-.0.5CH2Cl2 R=$CO_2Me$		398

No.	Formula	Structure	Details	Ref.
472	$Fe_2C_{28}H_{23}OP$	$\{\eta^5\text{-}C_5H_4Fe(CO)(Cp)\}Fe(\eta^5\text{-}C_5H_4PPh_2)$		402
473	$Fe_2C_{28}H_{24}N_2O_4$	$Fe(CO)_3\{\eta^4\text{-}PhCHCHCHCHCCH_2CH(Fc)N(Ac)N\}$	(2 isomers)	403
474	$Fe_2C_{30}H_{20}O_6P_4$	$Fe_2(CO)_6\{(\mu\text{-}PPh)PPhPPh(\mu\text{-}PPh)\}$		384
475	$Fe_2C_{35}H_{30}O_5P_2$	$(\eta^3\text{-}C_3H_5)Fe_2(CO)_5\{PPh_2(CH_2CHCH2)\}(\mu\text{-}PPh_2)$		404
476	$Fe_2C_{44}H_{51}O_4PS_2$	$(Ph_3P)(OC)_2Fe\{(\mu\text{-}S)_2R\}Fe(CO)_2(CR)$		
		$R=CCMe_2(CH_2)_3CMe_2$		405
477	$[Fe_2C_{58}H_{46}O_6P_2]^{2+}$	$[\{Fe(CO)_3\}_2\{\eta^4:\eta^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2.0.5PhMe$		406
478	$Fe_2Hg_2C_{26}H_{30}N_2$	$Fe_2\{\mu\text{-}\eta^5:\eta^5\text{-}C_5H_3(CH_2NMe_2)HgC_5H_4\}_2$	153	407
479	$[Fe_2Hg_2C_{26}H_{32}N_2]^{2+}$	$[\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3CH_2NMe_2\text{-}2)\}_2Hg_2][Ph_3BCN]_2$	153	116
480	$Fe_2MnC_{14}H_7O_2S$	$(\eta\text{-}C_5H_4Me)MnFe_2(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}S)$		408
481	$Fe_2MnTeC_{18}H_{15}O_8$	$(\eta\text{-}C_5Me_5)MnFe_2(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}Te)$		409
482	$Fe_2Ni_2C_{21}H_{16}O_6$	$(OC)_6Fe_2Ni_2(Cp)_2(\mu_4\text{-}\mu_3\eta^1:\eta^4\text{-}CCHCMeCH_2)$		410
483	$Fe_2PtC_{37}H_{33}O_6P_3$	$(OC)_6Fe_2Pt(dppe)(\mu_3\text{-}P:\mu\eta^2\text{-}PCBu^t)$		411
484	$[Fe_2Rh_2C_{52}H_{93}P_4]^+$	$[\{Fe(\eta\text{-}C_5H_4PBu^t_2)_2RhH\}_2(\mu\text{-}H)_3][ClO_4]$		412
485	$[Fe_2Rh_2C_{60}H_{77}P_4]^+$	$[\{Fe(\eta\text{-}C_5H_4PPhBu^t)_2RhH\}_2(\mu\text{-}H)_3][ClO_4].EtOH$		412
486	$Fe_2RuC_9Cl_4N_3O_9P_3$	$Fe_2Ru(CO)_8(\mu\text{-}CO)(\mu\text{-}PNPCl_2NPCl_2N)$		383
487	$Fe_2RuC_{14}H_9O_{14}P$	$\{(MeO)_3P\}(OC)_3RuFe_2(CO)_6(\mu\text{-}CO)_2$		372
488	$Fe_2RuC_{23}H_{10}O_9$	$Fe_2Ru(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^1\text{-}C_2Ph_2)$		413
489	$Fe_2RuC_{29}H_{15}O_{11}P$	$(Ph_3P)(OC)_3RuFe_2(CO)_6(\mu\text{-}CO)_2$		372
490	$Fe_2Ru_2C_{60}H_{62}Cl_4P_6$	$\{RuCl(PPh_3)(\mu\text{-}Cl)\}_2\{\mu\text{-}P:P\text{-}Fe(\eta^5\text{-}Me_2C_4H_2P)_2\}_2$		414
491	$Fe_2SbSiC_{15}H_{19}O_8$	$Fe_2(CO)_6\{\mu\text{-}SbCH(SiMe_3)_2\}$		374
492	$Fe_2SiWC_{28}H_{30}O_7$	$Fe_2W(CO)_7(Cp)\{\mu\text{-}\eta^2\text{-}C_2(SiMe_3)_2\}(\mu_3\text{-}C(pTol))$		381
493	$Fe_2WC_{21}H_{10}O_8$	$(Cp)(OC)_2WFe_2(CO)_6(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_2Ph)$		415
494	$Fe_3C_9Cl_4N_3O_9P_3$	$Fe_3(CO)_8(\mu\text{-}CO)(\mu\text{-}PNPCl_2NPCl_2N)$		383
495	$[Fe_3C_{12}H_3O_{10}]^{2-}$	$[PPh_4]_2[Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}MeCCO)]$		416
496	$Fe_3C_{12}H_4O_9S_3$	$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}S:\mu C\text{-}SCH_2CH_2SC)$		417
497	$Fe_3C_{13}F_3NO_{11}$	$Fe_3(CO)_{11}(\mu\text{-}CNCF_3)$		418
498	$Fe_3C_{16}H_5NO_9$	$Fe_3(CO)_9(\mu_3\text{-}N:\eta^2:\eta^2\text{-}NCPh)$		419
499	$Fe_3C_{16}H_7O_9PS$	$Fe_3(CO)_9\{\mu_3\text{-}P(pTol)\}(\mu_3\text{-}S)$		420
500	$[Fe_3C_{16}H_8O_{10}P]^-$	$[NBu_4][Fe_3(\mu\text{-}H)(CO)_3(\mu_3\text{-}PC_6H_4OMe\text{-}p)]$		421

No.	Formula	Structure	Details	Ref.
501	$Fe_3C_{18}H_9O_{11}P$	$Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\mu P{:}\eta^2 PC\text{-}CH_2PC_6H_4OMe\text{-}\underline{p})$		421
502	$Fe_3C_{19}H_{24}O_9P_2$	$Fe_3(\mu\text{-}H)(CO)_9(\mu\text{-}P{:}\mu P\text{-}Pr^i{}_2PCH_2PPr^i{}_2)$		422
503	$Fe_3C_{21}H_{10}N_2O_9$	$Fe_3(CO)_9(\mu_3\text{-}NPh)_2$		423
504	$[Fe_3C_{22}H_{15}O_5S_3]^+$	$[(Cp)(OC)FeSC\{Fe(CO)_2(Cp)\}SCS\{Fe(CO)_2(Cp)\}][SO_3CF_3]$		424
505	$Fe_3C_{23}H_{15}O_{10}P$	$Fe_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}\mu P{:}C\text{-}P(\underline{p}\text{-}C_6H_4OMe)CH_2Ph\}$		421
506	$Fe_3C_{24}H_{13}O_{10}P$	$Fe_3(CO)_9\{\mu\text{-}P(\underline{p}\text{-}C_6H_4OMe)\}\{\mu\text{-}\eta^1{:}\eta^1\text{-}CHCPh\}$		425
507	$Fe_3C_{25}H_{13}O_{11}P$	$Fe_3(CO)_{10}\{\mu_3\text{-}P{:}\eta^3 PCC{:}\eta^1\text{-}P(\underline{p}\text{-}C_6H_4OMe)CHCPh\}$		425
508	$Fe_3C_{32}H_{22}O_8P_2$	$Fe_3(\mu\text{-}H)_2(\mu\text{-}Ph_2)_2(CO)_8.0.5PhMe$		426
509	$Fe_3C_{42}H_{30}O_6S_6$	$\{(OC)_3Fe(\mu\text{-}SPh)_3\}_2Fe.2Me_2CO$	193	427
510	$[Fe_3NiC_{12}HO_{12}]^-$	$[NMe_3CH_2Ph][Fe_3Ni(\mu_3\text{-}H)(CO)_8(\mu\text{-}CO)_4]$		428
511	$[Fe_4C_{12}O_{12}S_4]^{2-}$	$[AsPh_4]_2[\{Fe_2(CO)_6(\mu\text{-}S)\}_2(\mu\text{-}S_2)]$		36
512	$Fe_4C_{14}H_4O_{12}$	$Fe_4(\mu\text{-}H)(CO)_{12}(\mu_3\text{-}CMe)$		429
513	$Fe_4C_{16}H_{12}O_{12}P_4$	$\{Fe_2(CO)_6(\mu_4\text{-}\mu P{:}\mu P\text{-}P_2Me_2)\}_2$		430
514	$Fe_4C_{19}H_5NO_{12}$	$Fe_4(CO)_{12}(\mu_4\text{-}N{:}N{:}\eta^2{:}\eta^1\text{-}NCPh)$		419
515	$[Fe_4C_{20}H_{20}S_5]^+$	$[(Cp)_4Fe_4(\mu_3\text{-}S)_3(\mu_3\text{-}S_2)][MoOCl_4(THF)]$		431
516	$Fe_4C_{40}H_{40}N_4O_{20}P_4$	$[NCH{=}CBu^tOP(Fe(CO)_4)]_4\text{-}(\underline{P}\text{-}\underline{N})$	153	432
517	$[Fe_5RhC_{17}O_{16}]^-$	$[NEt_4][RhFe_5C(CO)_{16}]$	153	370
518	$[GaC_{12}H_{18}]^+$	$[Ga(\eta\text{-}C_6Me_6)][GaCl_4]$	233	433
519	$[GaC_{18}H_{24}]^+$	$[Ga(\eta^6\text{-}Mes)_2][GaCl_4]$	233	434
520	$GaReC_{14}H_{19}N_3O_4$	$Me_2Ga(\mu\text{-}dmpz)(\mu\text{-}OCH_2C_5H_4N\text{-}2)Re(CO)_3$		435
521	$GaRhC_{16}H_{24}N_4$	$Rh\{(pz)_2GaMe_2\}(cod)$		436
522	$Ga_2C_{16}H_{24}N_2O_2$	$\{Me_2Ga(NC_5H_4CH_2\text{-}2)(\mu_3\text{-}O)\}_2$		435
523	$Ga_2C_{18}H_{22}O_4$	$\{Me_2Ga(\mu\text{-tropolonate})\}_2$		437
524	$Ga_2C_{28}H_{30}S_2$	$Ga_2Ph_4(\mu\text{-}SEt)_2$	173	438
525	$Ga_2NiC_8H_{16}N_4O_4$	$Ni\{N(O)CHCHNO\}_2(\mu\text{-}GaMe_2)_2$		439
526	$Ga_2PtC_{12}H_{24}N_4O_4$	$Pt(dmg)_2(\mu\text{-}GaMe_2)_2$		439
527	$Ga_2Rh_2C_{29}H_{30}N_{12}O_3$	$\{MeGa(pz)_3\}_2Rh_2(\mu\text{-}CO)_3$		440
528	$GeC_5H_{12}ClNS_2$	$GeClMe_2(dmtc)$		441
529	$GeC_9H_{18}N_2O_4$	$N(CH_2CH_2O)_3GeCH_2CH_2CONH_2$		442
530	$GeC_{10}H_{10}$	$Ge(Cp)_2$	173	443

No.	Formula	Structure	Details	Ref.
531	$GeC_{10}H_{15}Cl$	$GeCl(\eta\text{-}C_5Me_5)$	E	444
532	$GeC_{10}H_{21}NO_3$	$Bu^tGe(OCH_2CH_2)_3N$		442
533	$GeC_{12}H_{28}P_2$	$Et_2GeP(Bu^t)PBu^t$	113	445
534	$GeC_{13}H_{19}NO_6$	$Ge\{CCHCHC(CO_2Et)O\}\{N(CH_2CH_2O)_3\}$		446
535	$GeC_{18}H_{34}S$	$GeCy_3(SH)$		447
536	$GeC_{19}H_{18}S$	Ph_3GeSMe		448
537	$GeC_{20}H_{30}$	$Ge(\eta\text{-}C_5Me_5)_2$	E	444
538	$GeC_{28}H_{28}$	$Ge(oTol)_4$		449
539	$GeC_{36}H_{28}$	$Ge(\eta^1\text{-ind})_4$		450
540	$GeIrC_{40}H_{41}OP_2$	$IrH_2(GeMe_3)(CO)(PPh_3)_2.0.5PhH$		451
541	$GeMn_3C_{21}H_{15}O_6$	$Mn_2(CO)_4(Cp)_2\{\mu\text{-}GeMn(CO)_2(Cp)\}$		452
542	$GeMoC_{29}H_{31}NO$	$Mo(GePh_3)(NO)(\eta^3\text{-}C_3H_4Pr)(Cp)$		453
543	$GeNiC_{23}H_{20}Cl_3P$	$Ni(GeCl_3)(PMe_3)(Cp).0.5PhH$		454
544	$GePbC_{36}H_{30}$	$Ph_3GePbPh_3$	223	455
545	$GeSiC_{16}H_{20}$	$Me_2Ge(\mu\text{-}o\text{-}C_6H_4)_2SiMe_2$		456
546	$GeSi_4C_{14}H_{38}$	$Ge\{CH(SiMe_3)_2\}_2$	E	457
547	$Ge_2C_{10}H_{16}Cl_4S$	$Cl_2GeGeCl_2C{=}CMeCH_2SCH_2CMe_2$	223	458
548	$Ge_2C_{13}H_{26}N_2O_6$	$\{N(CH_2CH_2O)_3Ge\}_2CH_2$		442
549	$Ge_2C_{28}H_{20}Cl_6O_4$	$Ge_2Ph_4(\mu\text{-}O_2CCCl_3)_2$		459
550	$Ge_2C_{32}H_{38}P_2$	$(Bu^tP)_2(GePh_2)_2$		460
551	$Ge_2C_{36}H_{66}S_3$	$(Cy_3Ge)_2S_3$		461
552	$Ge_2C_{40}H_{52}$	$Ge_2(o\text{-}C_6H_4Et_2)_4$		462
553	$Ge_2HgPt_2C_{78}H_{60}F_{18}P_4$	$Hg[Pt(Ge(CF_3)_3)(PPh_3)_2]_2.PhMe$		463
554	$Ge_2MgC_{14}H_{38}O_4$	$Mg(GeMe_3)_2(DME)_2$		464
555	$Ge_2Ni_2C_{22}H_{36}O_{10}$	$((OC)_3NiGe(OBu^t)(\mu\text{-}OBu^t))_2$	173	443
556	$Ge_2Si_2C_{28}H_{32}O_4$	$Me_2GeOSiPh_2OGeMe_2OSiPh_2O$		465
557	$Ge_2Si_2C_{48}H_{40}O_4$	$Ph_2GeOSiPh_2OGePh_2OSiPh_2O$		465
558	$Ge_2Si_8C_{28}H_{76}$	$Ge_2\{CH(SiMe_3)_2\}_4$		466
559	$Ge_3C_{27}H_{44}O$	$(p\text{-}PhOC_6H_4)(Me_3Ge)C\{CH_2CH(GeMe_3)\}_2CH_2$		467
560	$Ge_3Si_3C_{30}H_{72}Cl_3N_6P$	$P\{GeCl(NBu^t)_2SiMe_2\}_3$		468

No.	Formula	Structure	Details	Ref.
561	$Ge_4C_{48}H_{40}O_4$	$\{GePh_2(\mu\text{-}O)\}_4$		469
562	$Ge_5C_{48}H_{40}O_6$	$PhGe(OGePh_2O)_3GePh.0.5Me_2CO$		470
563	$Ge_5C_{60}H_{50}$	$(Ph_2Ge)_5\text{-}(\underline{Ge}\text{-}\underline{Ge}).PhH$	248	471
564	$HfC_{18}H_{18}$	$Hf\{\underline{o}\text{-}(CH_2)_2C_6H_4\}(Cp)_2$		472
565	$HfC_{18}H_{18}N_2$	$Hf(\eta^1\text{-}NC_4H_4)_2(Cp)_2$		473
566	$HgC_8H_5F_3O_2$	HgPh(OTFAc)		474
567	$HgC_8H_8O_2$	HgPh(OAc)		474
568	$HgC_8H_{10}N_4O_2$	MeHg(theophyllinate).H_2O		475
569	$HgC_{10}H_{14}N_4O_3$	$Hg(CH_2CH_2OMe)$(theophyllinate)		476
570	$HgC_{15}H_{11}NS$	HgPh(quinoline-8-thiolate)	153	477
571	$HgC_{15}H_{16}N_6O_4$	$MeHg\{NC_5H_4\text{-}2\text{-}COH(Meimid)_2\}$		478
572	$HgC_{15}H_{25}BrN_2O$	$HgBr\overbrace{CCHCMe_2N(O)CMe_2CHCH_2}NC_5H_{10}$		479
573	$HgC_{18}H_{14}N_2O_4S$	$HgPhN(SO_2Ph)(\underline{o}\text{-}C_6H_4NO_2)$	153	480
574	$HgPt_2C_{64}H_{64}Cl_6P_4$	$Hg\{Pt(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2\}_2$		481
575	$HgRh_2C_{36}H_{32}Cl_2OP_2$	$Rh_2(Cp)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)$		482
576	$HgRh_2C_{44}H_{36}Cl_2N_4O_2P_2$	$(Ph_3P)(OC)Rh(\mu\text{-}HgCl)(\mu\text{-}pz)_2RhCl(CO)(PPh_3)$		483
577	$HgRh_2C_{54}H_{51}ClN_2O_{10}P_4$	$Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}HgCl)[\mu\text{-}EtN\{P(OPh)_2\}_2]_2$		484
578	$HgRu_2C_{26}H_{78}P_8$	$\{\underline{cis}\text{-}RuMe(PMe_3)_4\}_2Hg.THF$		485
579	$HgRu_6C_{20}N_2O_{22}$	$Hg\{Ru_3(CO)_{10}(\mu\text{-}NO)\}_2$		486
580	$Hg_3C_2HCl_3O_2$	$(ClHg)_3CCO_2H.DMSO$		487
581	$[Hg_3C_8H_{11}N_4O_2]^+$	$[(MeHg)_3(xanthH)][NO_3].H_2O$		488
582	$Hg_3Os_9C_{33}O_{33}$	$\{Os_3(CO)_{11}Hg\}_3$		489
583	$[Hg_4C_9H_{13}N_4O_2]^+$	$[(MeHg)_4(xanth)][NO_3]$		488
584	$Hg_4Re_4C_{28}H_{20}O_8$	$\{HgRe(CO)_2(Cp)\}_4$		490
585	$HoLi_3C_{24}H_{66}N_6$	$Ho\{(\mu\text{-}Me)_2Li(TMEDA)\}_3$	160	491
586	$InC_5H_{14}Cl_2N$	$InCl_2Me(NH_2Bu^t)$		492
587	$[InC_{18}H_{24}]^+$	$[In(\eta\text{-}MesH)_2][InBr_4]$	233	493
588	$In_2Nb_3C_{36}H_{45}Cl_2$	$\{(\eta\text{-}C_5H_4Me)_2HNb\}_2In_2(\mu\text{-}Cl)_2\{\mu\text{-}NbH(\eta\text{-}C_5H_4Me)_2\}$		494
589	$[IrC_{12}N_8O_2]^-$	$[NEt_4][Ir(CO)_2(Tcbiim)]$		495
590	$IrC_{13}H_{19}Cl_2O_2$	$IrCl_2(acac)(cod)$	133	496

No.	Formula	Structure	Details	Ref.
591	$IrC_{13}H_{30}Cl_4OP_3$	trans-$IrCl_2(PCl_2)(CO)(PEt_3)_2$		497
592	$IrC_{13}H_{30}Cl_4O_2P$	trans-$IrCl_2(PCl_2O)(CO)(PEt_3)_2$		497
593	$[IrC_{15}H_{42}NOP_4]^{2+}$	$[Ir(CH_2OC(CD_3)=NH)(PMe_3)_4][HPMe_3][PF_6][BF_4]_2$		498
594	$[IrC_{17}H_{23}NO_2]^+$	$[Ir(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_6H_6CH_2NO_2)][BF_4]$		499
595	$IrC_{20}H_{38}P$	$Ir(\eta^3\text{-}2\text{-}C_3H_4Me)(PHBu^t_2)(cod)$	140	500
596	$IrC_{23}H_{21}ClOP$	$IrCl(CO)(PPh_3)(\eta^4\text{-}C(CH_2)_3)$		501
597	$[IrC_{23}H_{22}F_4]^+$	$[Ir(\eta^4\text{-}Me_3tfb)(\eta\text{-}C_6H_4Me_2\text{-}1,4)][ClO_4]$		502
598	$IrC_{25}H_{50}ClOP_2$	$IrCl(CH=CMeCH_2)PBu^t_2)(CO)(PBu^t_2(CH_2cyp)$	122	503
599	$[IrC_{26}H_{26}BrP]^+$	$[Ir(PPh_2C_6H_4Br\text{-}o)(cod)][SbF_6]$		504
600	$IrC_{26}H_{43}BrP_3$	fac-$IrBr(CH_2C(pTol)=C(pTol))(PMe_3)_3.CH_2Cl_2$	173	505
601	$IrC_{27}H_{46}OP_3$	$Ir(CH_2OMe)(PMe_3)_3(\eta\text{-}C_2(pTol)_2)$	173	505
602	$[IrC_{29}H_{30}OP_2S_2]^+$	$[IrH(Ph_2PCH_2CH_2S)(Ph_2PCH_2CH_2SH)(CO)]Cl$		506
603	$[IrC_{30}H_{21}F_4N]^+$	$[Ir(\eta^4\text{-}tfb)(\eta\text{-}C_6H_5NPh_2)][BF_4].CH_2Cl_2$		502
604	$[IrC_{30}H_{24}N_6]^{3+}$	$[Ir(bipy)_2(\eta^2CN\text{-}bipy)][ClO_4]_3.H_2O$		507
605	$IrC_{30}H_{31}Cl_2OP_2$	$IrCl_2(cyp)(CO)(PMePh_2)_2$		508
606	$[IrC_{36}H_{27}N_8P]^-$	$[NEt_4][Ir(cod)(Tcbiim)].CH_2Cl_2$		495
607	$IrC_{37}H_{32}ClOP_2S$	$IrHCl(SH)(CO)(PPh_3)_2$		509
608	$IrC_{38}H_{32}IOP_2$	$IrHI(CH_2PPh_2C_6H_4\text{-}o)(CO)(PPh_3)_2$		510
609	$IrC_{42}H_{31}F_6N_2OP_2$	trans-$Ir(3,5\text{-}(CF_3)_2pz)(CO)(PPh_3)_2$		511
610	$IrC_{45}H_{34}ClOP_2$	$IrCl(CO)(c\text{-benzophenanthrene-}2,11\text{-}(CH_2PPh_2)_2)$		512
611	$IrC_{45}H_{34}Cl_3OP_2$	$IrCl_3(CO)(c\text{-benzophenanthrene-}2,11\text{-}(CH_2PPh_2)_2)$		512
612	$IrC_{47}H_{30}Cl_5OP_2S_4$	$IrCl(CO)(PPh_3)_2(TCTTN)$		513
613	$IrC_{47}H_{31}Cl_4OP_2S_4$	$IrH(CO)(PPh_3)_2(TCTTN)$		513
614	$[IrC_{53}H_{42}N_2OP_2]^+$	$[Ir(CO)(C(o\text{-}C_6H_4PPh_2)=N(3\text{-}MeC_6H_3\text{-}2))_2][BPh_4]$		134
615	$IrOs_3C_{29}H_{18}O_{11}P$	$Os_3Ir(\mu\text{-}H)_3(CO)_{11}(PPh_3)$		304
616	$[IrPtC_{26}H_{68}P_4]^+$	$[(Et_3P)_3HIr(\mu\text{-}H)_2PtEt(PEt_3)][BPh_4]$		128
617	$[IrPtC_{30}H_{68}P_4]^+$	$[(Et_3P)_3HIr(\mu\text{-}H)_2PtPh(PEt_3)][BPh_4]$		128
618	$[IrRh_6C_{15}NO_{15}]^{2-}$	$[PPh_4]_2[IrRh_6N(CO)_{10}(\mu\text{-}CO)_4(\mu_3\text{-}CO)].THF$		225
619	$IrWC_{47}H_{36}O_5P_3$	$(Ph_3P)(OC)HIrW(CO)_4(\mu\text{-}PPh_2)_2$		514
620	$IrWC_{53}H_{44}O_5P_3$	$(Ph_3P)(OC)HIrW(CO)_3(CPhOMe)(\mu\text{-}PPh_2)_2$		514

No.	Formula	Structure	Details	Ref.
621	$Ir_2C_{28}H_{27}N_9$	$Ir_2(cod)_2(MeCN)(\mu\text{-Tcbiim}).MeCN$		515
622	$Ir_2C_{43}H_{48}N_2P_2$	$Ir_2(cod)(1,4,5\eta^3\text{-codH})(\mu\text{-PPh}_2)_2(\mu\text{-pz}).0.5Et_2O$		516
623	$Ir_2C_{44}H_{36}Cl_2N_4O_2P_2$	$\{IrCl(CO)(PPh_3)(\mu\text{-pz})\}_2.2CH_2Cl_2$		517
624	$Ir_2C_{44}H_{36}N_4O_2P_2$	trans-$\{Ir(CO)(PPh_3)(\mu\text{-pz})\}_2$		517
625	$Ir_2C_{53}H_{44}Cl_2O_3P_4$	$Ir_2Cl_2(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2.3THF$	233	518
626	$Ir_2C_{54}H_{40}O_4P_2$	$\{Ir(CO)_2PPh_3\}_2(\mu\text{-}\eta^2\text{-}C_2Ph_2).PhH$		519
627	$Ir_2C_{58}H_{50}Cl_2O_6P_4$	$IrCl_2(CO)_2(\mu\text{-}\eta^1:\eta^1\text{-DMAD})(\mu\text{-dppm})_2.2CH_2Cl_2$		520
628	$[Ir_2C_{59}H_{50}ClO_7P_4]^+$	$[Ir_2Cl(CO)_3(\mu\text{-}\eta^1:\eta^1\text{-DMAD})(\mu\text{-dppm})_2]$-$[PF_6].MeCN$	100	521
629	$Ir_2Pt_2C_{61}H_{45}O_7P_3$	$Pt_2Ir_2(CO)_4(\mu\text{-CO})_3(PPh_3)_3$		522
630	$Ir_2W_2C_{44}H_{30}O_6$	$(Cp)_2W_2Ir_2(CO)_6(\mu_3\text{-CPh})(\mu_3\text{-}\eta^1:\eta^3:\eta^1\text{-}C_3Ph_3)$		523
631	$Ir_3C_{24}H_{36}F_6O_8PS_3$	$Ir_3(CO)_4(\mu\text{-CO})\{P(OMe)_3\}(\mu\text{-SBu}^t)_3(\mu\text{-}\eta^1:\eta^1\text{-}C_4F_6)$		524
632	$Ir_3C_{25}H_{27}F_{12}O_5S_3$	$Ir_2(CO)_4(\mu\text{-}\eta^1:\eta^1\text{-}C_4F_6)$-$(\mu\text{-SBu}^t)_2(\mu_3\text{-SBu}^t)Ir(CO)(\eta^2\text{-}C_4F_6)$		524
633	$Ir_3Pt_3C_{36}H_{45}O_6$	$(\eta\text{-}C_5Me_5)_3(OC)_3Ir_3Pt_3(\mu\text{-CO})_3$		525
634	$[Ir_4C_{11}HO_{11}]^-$	$[PPh_3(CH_2Ph][Ir_4(\mu\text{-H})(CO)_{11}]$	X, N 80	526
635	$Ir_4C_{46}H_{31}O_9P_3$	$Ir_4(CO)_9\{\mu_3\text{-}(PPh_2)_3CH\}$		527
636	$Ir_4C_{52}H_{56}O_8P_4$	$Ir_4(CO)_8(PMe_2Ph)_4.2PhH$		528
637	$Ir_4C_{58}H_{44}O_8P_4$	$Ir_4(CO)_5(\mu\text{-dppm})_2$		529
638	$Ir_6C_{16}O_{16}$	$Ir_6(CO)_{12}(\mu_3\text{-CO})_4$ and $Ir_6(CO)_{12}(\mu\text{-CO})_4$		530
639	$KMoC_{22}H_{35}O_6$	$(18\text{-crown-6})K(\mu\text{-H})Mo(Cp)_2$		531
640	$LaMo_3C_{44}H_{55}O_{14}$	$(THF)_5La\{\mu\text{-O:C-OCMo(CO)}_2(Cp)\}_3$	153	532
641	$LiC_8H_{15}N_2$	$\{LiC_6H_9NNMe_2\}_n$		533
642	$LiC_{13}H_{23}N_2S$	$(TMEDA)LiCH_2SPh$	95	534
643	$[LiMgC_{34}H_{44}N_2]^-$	$[Li(TMEDA)_2][(TMEDA)Li(\mu\text{-Bz})_2MgBz_2]$		535
644	$LiMnSi_2C_{30}H_{72}NO_2$	$Li(\mu\text{-OCBu}^t{}_3)_2MnN(SiMe_3)_2$	140	536
645	$LiMnSi_6C_{22}H_{62}N_3O$	$(Me_3Si)_2NMn\{\mu\text{-N(SiMe}_3)_2\}_2Li(THF)$	140	239
646	$LiSiC_{14}H_{29}N_2$	$Li(TMEDA)(\eta^5\text{-}C_5H_4SiMe_3)$		537
647	$LiSi_2C_7H_{19}$	$Li\{CH(SiMe_3)_2\}$	E,X	538
648	$LiSi_2C_{14}H_{34}NO_4$	$(12\text{-crown-4})LiN(SiMe_3)_2$		539

No.	Formula	Structure	Details	Ref.
649	$LiSi_2C_{18}H_{38}N_3$	$(TMEDA)Li\{\eta^3\text{-}2\text{-}(Me_3Si)_2CC_5H_4N\}$		540
650	$LiSi_4C_{24}H_{45}N_2$	$Li\{2\text{-}(Me_3Si)_2CHNC_5H_4\}\{\eta^3\text{-}2\text{-}(Me_3Si)_2CC_5H_4N\}$		540
651	$Li_2C_{16}H_{42}N_4S_2$	$\{(TMEDA)Li(\mu\text{-}CH_2SMe)\}_2$	113	534
652	$Li_2C_{18}H_{48}N_4P_2$	$\{Li(TMEDA)\}_2\{\mu\text{-}P{:}C\text{-}PMe_2CH_2\}_2$		541
653	$Li_2C_{22}H_{52}O_2P_6$	$[(THF)Li\{C(PMe_2)_3\}]_2$	233	263,542
654	$Li_2C_{24}H_{46}N_4$	$Li_2\{\mu\text{-}\eta^1\text{-}C_6H_8NMe(CH_2)_3NMe_2\}_2$		543
655	$Li_2C_{26}H_{28}N_4$	$\{(TMEDA)LiCH_2C_6H_4\text{-}\underline{o}\}_2$		544
656	$Li_2C_{27}H_{46}N_4O$	$\{(TMEDA)Li\}_2\{(PhCH_2)_2CO\}$	117	545
657	$Li_2C_{32}H_{48}N_4$	$\{Li(TMEDA)\}_2\{\underline{o}\text{-}C_6H_4(CHPh)_2\}$	113	546
658	$Li_2C_{34}H_{50}N_4$	$(TMEDA)_2Li_2\{C(CHPh)_3\}$		547
659	$Li_2Mg_2C_{60}H_{62}N_4$	$\{LiMg(C{\equiv}CPh)_3(TMEDA)\}_2$		535
660	$Li_2Pt_2C_{52}H_{68}P_2$	$Pt_2Bu_2(C{\equiv}CPh)_4(PEt_3)_2(\mu\text{-}Li)_2$		548
661	$Li_2Si_2C_{26}H_{48}N_2O_2$	$(Et_2O)_2Li_2\{\eta^3\text{-}2\text{-}(Me_3Si)CHC_5H_4N\}_2$		540
662	$Li_2Si_2C_{26}H_{56}N_4$	$\underline{p}\text{-}C_6H_4\{CH(SiMe_3)Li(TMEDA)\}_2$		549
663	$Li_2Si_2C_{29}H_{54}N_4$	$\{Li(TMEDA)\}_2(CHSiMe_2C(SiMe_3)C_{10}H_6)$		550
664	$Li_2Si_2C_{32}H_{60}N_4$	$\{(TMEDA)LiCH(SiMe_3)C_6H_4\text{-}\underline{o}\}_2$		544
665	$Li_2Si_4C_{12}H_{36}N_2$	$[Li(\mu\text{-}N(SiMe_3)_2)]_2$	E	551
666	$Li_2Si_8C_{28}H_{76}P_2$	$Li_2[\mu\text{-}P\{CH(SiMe_3)_2\}_2]_2$		552
667	$Li_3C_{42}H_{42}N_3$	$\{(PhCH_2)_2NLi\}_3$		553
668	$Li_3LuC_{18}H_{48}O_6$	$Lu\{(\mu\text{-}Me)_2Li(DME)\}_3$	173	554
669	$Li_3ThC_{25}H_{69}N_6$	$MeTh(\mu\text{-}Me)_6Li_3(TMEDA)_3.TMEDA$	163	555
670	$Li_4C_{20}H_{44}O_4$	$[Li(\mu_3\text{-}CMeCH_2CH_2OMe)]_4$		556
671	$Li_4Si_4C_{32}H_{88}N_4O_4$	$[LiOSiBu^t{}_2NH_2]_4$		557
672	$Li_6C_{48}H_{90}$	$\{Li(CH_2CCMe_2CMe_2)\}_6$		558
673	$[LuC_{13}H_{24}]^-$	$[Li(TMEDA)_2][LuMe_3(\eta\text{-}C_5Me_5)]$	173	559
674	$LuC_{24}H_{40}P$	$Lu(CH_2PMe_2CH_2)(\eta\text{-}C_5Me_5)_2$	133	560
675	$LuC_{27}H_{36}N_3$	$Lu(\underline{o}\text{-}C_6H_4CH_2NMe_2)_3$		561
676	$MgW_2C_{48}H_{64}O_6$	$\{W(\underline{o}\text{-}CH_2C_6H_4CH_2)_2O\}_2Mg(THF)_4$		562
677	$MnC_8H_4NO_3S$	$Mn(CO)_3(\eta^4SC_3\text{-}SCHCHCHCHCN)$		563
678	$MnC_{11}H_4O_8P$	$Mn(CO)_5P(O)(\underline{o}\text{-}OC_6H_4O)$		564

No.	Formula	Structure	Details	Ref.
679	$MnC_{11}H_{16}O_3P$	$Mn(CO)_3(PMe_3)(\eta^3\text{-}CH_2CHCHCHCH_2)$		565
680	$MnC_{13}H_{17}N_2O_2$	$Mn\{N(=CMe_2)N=CMe_2\}(CO)_2(Cp)$		566
681	$MnC_{13}H_{19}P$	$Mn(PMe_3)(Cp)_2$		567
682	$MnC_{16}H_{24}O_2S$	$Mn(SBu^t)(CO)_2(\eta\text{-}C_5Me_5)$	233	568
683	$MnC_{16}H_{26}N_2$	$Mn(\eta^1\text{-}C_5H_5)(Cp)(TMEDA)$		569
684	$MnC_{16}H_{26}P_2$	$Mn(dmpe)(Cp)_2$		567
685	$MnC_{17}H_{10}O_{10}P$	$Mn(CO)_5P(O)(\underline{o}\text{-}OC_6H_4OH)_2$	165	570
686	$MnC_{18}H_{21}O_3$	$Mn(CO)_3\{\eta^5\text{-}(9\text{-}\underline{exo}\text{-}Me)C_{14}H_{18}\}$		571
687	$MnC_{20}H_{15}O_2$	$Mn(CPh_2)(CO)_2(Cp)$	113	274
688	$MnC_{22}H_{16}O_2$	$[Mn(CCH{=}CPh_2)(CO)_2(Cp)][BF_4]$	153	572
689	$MnC_{22}H_{17}O_2$	$(Cp)(OC)_2MnC(\underline{o}\text{-}C_6H_4CH_2CH_2C_6H_4\text{-}\underline{o})$		573
690	$MnC_{23}H_{23}P$	$Mn(PMePh_2)(Cp)_2$		567
691	$MnC_{24}H_{19}O_3$	$(\eta\text{-}C_5H_4Me)(OC)_2Mn\{\eta^2\text{-}OC{=}C(\underline{o}\text{-}C_6H_4CH_2CH_2C_6H_4\text{-}\underline{o})\}$		573
692	$MnC_{28}H_{21}O_2$	$Mn(CO)(\eta^4\text{-}PhCHCPhCPhCO)(Cp)$		212
693	$MnC_{28}H_{21}O_6P_2$	$Mn(CO)_4\{(PPh_2O)_2H\}$		574
694	$MnC_{40}H_{30}O_2P$	$(Cp)(OC)_2Mn\{C(Ph){=}C{=}CPh_2\}.CH_2Cl_2$	153	575
695	$MnC_{57}H_{46}O_{12}P_3$	$Mn(CHO)(CO)_2\{P(OPh)_3\}_3$	213	576
696	$MnNbC_{18}H_{16}O_3$	$(Cp)_2(OC)Nb(\mu\text{-}H)Mn(CO)_2(Cp)$		577
697	$MnOs_3C_{25}H_{12}O_{12}$	$(Cp)(CO)Mn(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CHPh)Os_3(CO)_{10}$		578
698	$MnPdC_{53}H_{44}BrO_3P_4$	$(OC)_3MnPdBr(\mu\text{-}dppm)_2$		579
699	$MnSiC_{25}H_{23}O_2$	$\underline{S}\text{-}(-)\text{-}Mn(SiMePh(naphth))(CO)_2(\eta\text{-}C_5H_4Me)$	243	580
700	$MnSi_4C_{21}H_{41}N_3O_4$	$(OC)_3\overline{Mn\{N(SiMe_3)P(NSiMe_3)}(OPh)N(SiMe_3)_2\}$		581
701	$MnTeC_5F_5O_6$	$Mn(CO)_5(OTeF_5)$		582
702	$MnUC_{32}H_{32}O_3P$	$(Cp)(OC)_2MnC(CHPMe_2Ph)OU(Cp)_3$		583
703	$MnYbC_{25}H_{30}O_5$	$\{(\eta\text{-}C_5Me_5)Yb(\mu\text{-}O{:}C\text{-}OC)_2Mn(CO)_3\}_n$		584
704	$Mn_2C_8H_4O_8P_2$	$\{Mn(CO)_4(\mu\text{-}PH_2)\}_2$		585
705	$Mn_2C_{10}H_3O_9PS$	$Mn_2(CO)_9(\mu\text{-}P{:}\eta^2PS\text{-}SPMe)$		586
706	$Mn_2C_{13}H_8O_7$	$(OC)_3Mn\{\eta\text{-}\overline{CMeCHCHCMeMn}(CO)_4\}$		587
707	$Mn_2C_{17}H_{17}NO_6P_2S_3$	$Mn_2(CO)_6(\mu\text{-}P{:}S\text{-}Me_2PS)(\mu\text{-}PhNC(S)SPMe_2)$	163	588
708	$Mn_2C_{18}H_{18}N_2O_8$	$\underline{cis}\text{-}1,1\text{-}Mn_2(CO)_8(CNBu^t)_2$		589

No.	Formula	Structure	Details	Ref.
709	$[Mn_2C_{20}H_{10}O_8P]^-$	$[PPN][Mn_2(\mu\text{-}PPh_2)(CO)_8]$		91
710	$Mn_2C_{20}H_{11}O_8P$	$Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8$		91
711	$Mn_2C_{20}H_{18}O_9$	$Mn_2(CO)_8(\mu\text{-}CO)(\mu\text{-}\eta^1\text{-}C{=}C{=}CBu^t{}_2)$	233	590
712	$Mn_2C_{20}H_{29}N_2O_6P$	$Mn_2(CO)_8(\mu\text{-}H)\{\mu\text{-}P(NPr^i{}_2)_2\}$		241
713	$Mn_2C_{20}H_{40}Br_2O_{10}P_4$	$Mn_2(\mu\text{-}Br)_2(CO)_4(\mu\text{-tedip})_2$		591
714	$Mn_2C_{20}H_{41}BrO_{10}P_4$	$Mn_2(\mu\text{-}H)(\mu\text{-}Br)(CO)_4(\mu\text{-tedip})_2$		591
715	$Mn_2C_{23}H_{30}O_3$	$Mn_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)_3$		592
716	$Mn_2C_{24}H_{44}Cl_2P_2$	$\{Mn(PEt_3)(\eta\text{-}C_5H_4Me)(\mu\text{-}Cl)\}_2$		593
717	$Mn_2C_{27}H_{28}O_7P_2$	$Mn_2(CO)_7(PEt_3)(\mu\text{-}P{:}\eta^2\text{-}PPh_2CH{=}CH_2)$		594
718	$Mn_2C_{30}H_{20}Br_2O_6P_2$	$Mn_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}P_2Ph_4)$		68
719	$Mn_2C_{30}H_{20}I_2O_6P_2$	$Mn_2(CO)_6(\mu\text{-}I)_2(\mu\text{-}P_2Ph_4)$		68
720	$Mn_2C_{31}H_{20}O_7P_2$	$Mn_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2$		595
721	$[Mn_2C_{33}H_{22}O_7P]^-$	$[PPN][Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C{:}O\text{-}OCCPh{=}CHPh)]$		594
722	$Mn_2C_{43}H_{39}N_2O_7P$	$Mn_2(CO)_6(CNBu^t)_2(\mu\text{-}PPh_2)\{\mu\text{-}C{:}O\text{-}OCCPh{=}CHPh\}$		594
723	$Mn_2C_{50}H_{44}N_2O_8P_2$	$\{Mn(CO)_4(PPh_2NMeCHMePh)\}_2$		596
724	$Mn_2PtC_{12}O_{12}$	<u>trans</u>-$(OC)_2Pt\{Mn(CO)_5\}_2$		597
725	$Mn_2SbC_{16}H_{14}BrO_4$	$\{(\eta\text{-}C_5H_4Me)(OC)_2Mn\}_2SbBr$	245	598
726	$Mn_2Si_8C_{24}H_{72}N_4$	$Mn_2\{N(SiMe_3)_2\}_2(\mu\text{-}N(SiMe_3)_2\}_2$	140	239
727	$Mn_2TeC_{24}H_{30}O_4$	$\{Mn(CO)_2(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}Te)$		599
728	$Mn_3C_{12}H_6O_{12}P_3$	$\{Mn(CO)_4(\mu\text{-}PH_2)\}_3$		585
729	$Mn_3SbC_{24}H_{12}Br_2O_9$	$\{(OC)_3Mn(\eta\text{-}C_5H_4)\}_3SbBr_2$		600
730	MoC_6O_6	$Mo(CO)_6$		601
731	$[MoC_9H_{15}BrN_3O_3]^+$	$MoBr(CO)_3\{N(CH_2)_2N(CH_2)_2NCH_2CH_2)$		602
732	$MoC_{10}H_{10}O_3S_2$	$Mo(S_2O_3)(Cp)_2$	178	603
733	$MoC_{11}H_{12}N_4O_5$	$Mo(CO)_5N_4(CH_2)_6$		604
734	$MoC_{11}H_{12}O_2$	$Mo(CO)_2(\eta^3\text{-}C_3H_4Me)(Cp)$	188	605
735	$MoC_{11}H_{15}$	$Mo(\eta^3\text{-}C_3H_5)_2(Cp)$		606
736	$MoC_{12}H_{27}NO_2P_2S_2$	$Mo(\eta^3C_2H\text{-}COMe)(dmtc)(CO)(PMe_3)_2$		607
737	$[MoC_{12}H_{27}N_4O_3P_4]^+$	$[Mo(CO)_3\{MeP(NMePMe)_2NMePMe_2NMe\}]I.MeCN$		608
738	$MoC_{13}H_{10}Cl_4N_3O_3P_3$	$Mo\{P(C_5H_5)NPCl_2NPCl_2N\}(CO)_3(Cp)$		255

No.	Formula	Structure	Details	Ref.
739	$MoC_{13}H_{16}O_2S_2$	$Mo(S_2CCH_2Bu^t)(CO)_2(Cp)$		609
740	$MoC_{13}H_{18}NO_3P$	$Mo(CO)_2(POCH_2CH_2NBu^t)(Cp)$		610
741	$MoC_{14}H_{17}NO_2$	$Mo(CO)(NO)(\eta^2\text{-}1,3\text{-}C_8H_{12})(Cp)$		611
742	$MoC_{14}H_{19}NO_3$	$Mo(CO)(NO)\{\eta^2\text{-}C_8H_{13}OH\text{-}3)\}(Cp)$		611
743	$MoC_{15}H_{34}NO_4P_3$	trans-mer-$Mo(\eta^2\text{-}CO_2)_2(CNPr^i)(PMe_3)_3$		612
744	$[MoC_{16}H_{21}O_2]^+$	$[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$	268	613
745	$MoC_{16}H_{24}NO_5PS$	$Mo(SC_6H_4NO_2\text{-}p)\{P(OMe)_3\}(\eta^2\text{-}C_2Me_2)(Cp)$	200	614
746	$MoC_{18}H_{28}S_2$	$Mo(SBu^t)_2(Cp)_2$		615
747	$MoC_{20}H_{17}O_2P$	$Mo(CO)_2(Cp)(\eta^2\text{-}Ph_2P{=}CH_2)$		616
748	$MoC_{22}H_{16}O_2$	$Mo(CO)_2(bipy)_2$	111	617
749	$MoC_{22}H_{20}OS_2$	$Mo(SC_6H_4SPh\text{-}o)(CO)(\eta^2\text{-}C_2Me_2)(Cp)$		614
750	$MoC_{23}H_{36}BrNO$	$MoBr(NO)(\eta^3\text{-}C_8H_{13})\{\eta\text{-}C_5H_4(neomenthyl)\}$		618
751	$MoC_{26}H_{20}NO_2PS_2$	$Mo(CO)_2\{NPhC(S)PPh_2S\}(Cp)$		619
752	$MoC_{28}H_{20}O_4P_2S$	$Mo(CO)_4(PPh_2)_2S$		620
753	$MoC_{29}H_{23}ClO$	$MoCl(CO)(\eta^4\text{-}C_4Ph_3Me)(Cp)$		621
754	$[MoC_{29}H_{28}P]^+$	$[Mo(\eta^2\text{-}o\text{-}CH_2CHC_6H_4PPh_2)(\eta^2\text{-}C_2Me_2)(Cp)][BF_4]$		622
755	$[MoC_{31}H_{31}NP]^+$	$[Mo(NCMe)(\eta^4\text{-}o\text{-}MeCHCMeCHCHC_6H_4PPh_2)(Cp)][BF_4]$		622
756	$MoC_{32}H_{33}NO_7P_2$	$Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2NMe_2)$		620
757	$MoC_{36}H_{41}NO_6P_2$	$Mo(CO)_4\{(PPh_2O)_2H\}.0.37CH_2Cl_2$		620
758	$MoC_{40}H_{38}O_8P_2$	$Mo(CPh(OH))(CO)_3(Ph_2POC_2H_4OCH_2\text{-})_2$		623
759	$MoC_{44}H_{35}O_2P_3S_2$	$Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2).CH_2Cl_2$		619
760	$MoC_{44}H_{48}NP_3$	$Mo(CNBu^t)(PMePh_2)_2(\eta^6\text{-}PhPMePh)$		624
761	$MoC_{50}H_{36}N_4O_2$	cis-$Mo(CO)_2\{(pTol)_4porphyrin\}$		625
762	$MoPd_2C_{26}H_{29}ClN_2O_3$	$(Cp)Mo(\mu\text{-}CO)_2(\mu_3\text{-}CO)\{Pd(o\text{-}C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Cl)$		223
763	$[MoPd_3C_{38}H_{29}ClN_3O_3]^+$	$[(Cp)Mo(\mu_3\text{-}Cl)(\mu_3\text{-}CO)_3(Pd(8\text{-}mq))_3][BF_4]$		626
764	$[MoPtC_{58}H_{51}O_2P_4]^+$	$[(\eta\text{-}C_5H_4Me)(OC)_2Mo(\mu\text{-}dppm)Pt(dppm)]_2[Mo_2O_7]$		627
765	$MoPtRhC_{61}H_{50}O_2P_3$	$(Cp)MoRhPt(PPh_3)_2(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_5)$		628
766	$MoRhC_{44}H_{35}O_3P_2$	$(Cp)(OC)MoRh(PPh_3)_2(\mu\text{-}CO)_2$		308
767	$MoRh_2C_{27}H_{30}O_7$	$(OC)_5MoRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)$	200	629
768	$MoRh_3C_{65}H_{50}O_6P_3$	$(Cp)MoRh_3(CO)_3(\mu_3\text{-}CO)_3(PPh_3)_3.CH_2Cl_2$		628

No.	Formula	Structure	Details	Ref.
769	$MoRuC_{26}H_{18}O_3$	$(OC)_2RuMoO(\eta^2\text{-}C_2Ph_2)(\mu\text{-}\eta^5:\eta^5\text{-fulv})$		630
770	$MoSiC_{14}H_{20}$	$Mo(CH_2SiMe_2CH_2)(Cp)_2$		631
771	$MoSiC_{15}H_{38}ClO_2P_3$	$MoCl(\eta^2\text{-}O{=}CCH_2SiMe_3)(CO)(PMe_3)_3$		607
772	$MoSi_2C_{14}H_{23}O_2P$	$Mo\{P{=}C(SiMe_3)_2\}(CO)_2(Cp)$		632
773	$MoSi_6C_{21}H_{36}O_6$	$(OC)_3Mo\{\eta^6\text{-}C_6(Si_2Me_4O)_3\}$		633
774	$MoSnC_2H_6O_4$	$\{Me_2SnMoO_4\}_n$		634
775	$MoSnC_{10}H_{11}Cl_3$	$MoH(SnCl_3)(Cp)_2$		635
776	$MoWC_{19}H_{16}O_6$	$(Cp)(OC)_3MoW(CO)_2(CCH_2CH_2CH_2O)(Cp)$		636
777	$MoW_2C_{32}H_{24}O_6$	$\{(Cp)(OC)_2W\}_2Mo(CO)_2\{\mu\text{-}C(pTol)\}_2$	210	99
778	$Mo_2C_6H_{10}ClF_{12}N_3O_3P_6$	$Mo_2(CO)_3(PF_2NHMe)(\mu\text{-}Cl)(\mu\text{-}PF_2)\{\mu\text{-}(PF_2)_2NMe)\}_2$		637
779	$Mo_2C_{14}H_{10}O_4P_2$	$Mo_2(CO)_4(Cp)_2(\mu\text{-}P_2)$		638
780	$Mo_2C_{16}H_{14}O_5$	$Mo_2(CO)_4(\mu\text{-}O:\eta^2CO\text{-}MeCHO)(Cp)_2$		639
781	$Mo_2C_{16}H_{19}O_6P$	$Mo_2(CO)_3\{P(OMe)_3\}(Cp)_2$		640
782	$Mo_2C_{18}H_{10}F_6N_2O_4$	$Mo_2(CO)_4(Cp)_2(\mu\text{-}N,N:\eta^2\text{-}F_3CNCCNCF_3)$		641
783	$Mo_2C_{20}H_{18}O_6$	$(Cp)(OC)_3(CH_2)_4Mo(CO)_3(Cp)$		636
784	$Mo_2C_{21}H_{15}NO_4$	$Mo_2(CO)_4(Cp)_2(\mu\text{-}\eta^1:\eta^2\text{-}CNPh)$		642
785	$Mo_2C_{24}H_{15}N_9O_6$	$Mo_2(CO)_6(\mu\text{-benzotriazole})_3.7THF$	153	643
786	$Mo_2C_{24}H_{23}NO_5P$	$Mo_2(CO)_3\{PPh(OCH_2CH_2)_2NH\}(Cp)_2$		640
787	$Mo_2C_{25}H_{20}O_{11}$	$Mo_2(CO)_3(\eta^2\text{-}C_2R_2)(\mu\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}\eta^5:\eta^5\text{-fulv})$		
		$R{=}CO_2Me$		630
788	$Mo_2C_{26}H_{34}$	$Mo_2(Cp)_2(\mu\text{-}\eta^3,\eta^3:\eta^1,\eta^2,\eta^1\text{-}C_8Me_8)$		644
789	$[Mo_2C_{26}H_{35}]^+$	$[Mo_2(Cp)_2(\mu\text{-}\eta^3,\eta^3:\eta^2CH,\eta^2,\eta^1\text{-}C_8HMe_8][(TFAcO)_2H]$		644
790	$Mo_2C_{29}H_{24}OP_2$	$(Cp)_2Mo_2(\mu\text{-}CO)\{(\mu\text{-}PhP)_2C_6H_4\text{-}o\}$		645
791	$Mo_2C_{29}H_{51}O_4P$	$(Pr^iO)_3Mo_2(CH_2Ph)_2(OPr^i)(PMe_3)$	114	646
792	$Mo_2C_{30}H_{20}O_4$	$Mo_2(CO)_4(Cp)_2(\mu\text{-}\eta^2\text{-}PhCCCCPh)$	153	647
793	$Mo_2C_{30}H_{25}O_3P_2$	$(Cp)_2Mo_2(CO)_3(\mu\text{-}H)(\mu\text{-}P{:}\mu P\text{-}PhHPC_6H_4PPh\text{-}o)$		645
794	$[Mo_2C_{30}H_{26}ClN_4O_4]^+$	$[\{Mo(CO)_2(bipy)(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}Cl)][BF_4]$		648
795	$Mo_2C_{32}H_{24}F_3O_4P_2$	$(Cp)_2(OC)_2Mo_2(\mu\text{-}O_2CCF_3)\{(\mu\text{-}PhP)_2C_6H_4\text{-}o\}$		645
796	$[Mo_2C_{33}H_{23}O_8P_2]^-$	$[PPh_4][Mo_2(CO)_8(\mu\text{-}H)(\mu\text{-dppm})]$		649
797	$[Mo_2C_{36}H_{29}O_8P_2]^-$	$[NEt_4][Mo_2(CO)_8(\mu\text{-}H)(\mu\text{-dppb})]$		649

No.	Formula	Structure	Details	Ref.
798	$Mo_2C_{40}H_{74}N_2O_8$	$Mo_2(acac)_2(OCH_2Bu^t)_2(CNBu^t)_2(\mu\text{-}OCH_2Bu^t)_2$		650
799	$[Mo_2C_{52}H_{30}N_8O_6P_2]^{2-}$	$[NEt_4]_2[\{(Ph_3P)(OC)_3Mo\}_2(\mu\text{-Tcbiim})].CH_3CN$		651
800	$Mo_2C_{60}H_{52}N_4O_4P_4S_4$	$[Mo(CO)_2\{PPh_2C(S)NMe\}\{\mu\text{-N,S:P-PPh}_2\text{C(S)NMe}\}]_2$		652
801	$Mo_2C_{82}H_{78}N_2P_4$	$\{Mo(CNBu)(PPh_3)(\mu\text{-P:}\eta^6\text{-PPh}_3)\}_2$		653
802	$Mo_2Os_3C_{30}H_{19}O_{15}P$	$Mo_2(CO)_4(Cp)_2\{\mu\text{-}\eta^2\text{PC-Bu}^t\text{C}\equiv\text{POs}_3(CO)_{11}\}$		654
803	$Mo_2PbC_{24}H_{28}O_4$	$\{(Cp)_2MoH\}_2Pb(OAc)_2$		655
804	$Mo_2Pt_2C_{28}H_{40}O_6P_2$	$(Cp)_2Mo_2Pt_2(PEt_3)_2(\mu\text{-CO})_4(\mu_3\text{-CO})_2$		292
805	$Mo_2Re_2C_{20}H_{10}Br_2O_{10}P_2$	$Re_2(CO)_6(\mu\text{-Br})_2\{\mu\text{-P:P-P}_2Mo_2(CO)_4(Cp)_2\}$		656
806	$Mo_2Si_8C_{26}H_{78}N_4$	$Mo_2\{Si(SiMe_3)_3\}_2(NMe_2)_4$	108	657
807	$Mo_2Sn_8C_{26}H_{78}N_4$	$Mo_2\{Sn(SnMe_3)_3\}_2(NMe_2)_4$	111	657
808	$Mo_2Ti_2C_{38}H_{34}O_6$	$\{(\eta\text{-}C_5H_4Me)Mo(CO)(\mu\text{-O:C-CO})_2Ti(Cp)_2\}_2$		658
809	$Mo_4Re_2C_{34}H_{20}Br_2O_{14}P_4$	$[ReBr(CO)_3\{\mu\text{-P:P-P}_2Mo_2(CO)_4(Cp)_2\}]_2$		656
810	$Mo_4Zr_2C_{56}H_{82}N_6O_{12}$	$\{(Cp)(OC)_2MoCOZr(NEt_2)_2(NEt_2H)\}_2$- $\{\mu\text{-OCMo(CO)(Cp)CO}\}_2$		659
811	$NaSi_6YbC_{18}H_{54}N_3$	$NaYb\{N(SiMe_3)_2\}_3$		313
812	$[NbC_{25}H_{41}ClN_4]^+$	$[NbCl(CNBu^t)_4(Cp)][NbOCl_4(THF)].THF$		660
813	$NbSiC_{14}H_{20}$	$Nb(CH_2SiMe_2CH_2)(Cp)_2$		631
814	$NbSi_2C_{24}H_{30}$	$Nb\{o\text{-}(CH_2)_2C_6H_4\}\{\eta\text{-}C_5H_4(SiMe_3)\}_2$		472
815	$NbSnC_{13}H_{14}Cl_3O$	$Nb(SnCl_3)(CO)(\eta\text{-}C_5H_4Me)_2$		661
816	$[NbSnC_{26}H_{20}O_3]^-$	$[NEt_4][Nb(SnPh_3)(CO)_3(Cp)].2THF$		662
817	$NbSnC_{29}H_{25}O$	$Nb(SnPh_3)(CO)(Cp)_2$		661
818	$NbVC_{19}H_{16}O_4$	$(Cp)_2(OC)Nb(\mu\text{-H})V(CO)_3(Cp)$		663
819	$NbZnC_{15}H_{17}$	$(Cp)_2NbH_2\{Zn(Cp)\}$		664
820	$Nb_2C_{19}H_{16}O_4$	$(Cp)_2(OC)Nb(\mu\text{-H})Nb(CO)_3(Cp)$		663
821	$Nb_2C_{20}H_{20}S_2$	$\{(Cp)_2Nb(\mu\text{-S})\}_2$	153	665
822	$Nb_2C_{30}H_{54}Cl_6N_6$	$(Bu^tNC)_4Cl_2Nb(\mu\text{-}\eta^2\text{:N,N-C}_2(NBu^t)_2)NbCl_4$		666
823	$Nb_2C_{36}H_{36}Cl_6S_2$	$\{NbCl_2\{S(CH_2)_3CH_2\}(\eta\text{-C}_2Ph_2)(\mu\text{-Cl})\}_2$		667
824	$[Nb_2RhW_4C_{10}H_{15}O_{19}]^{2-}$	$[NBu_4]_2[(\eta\text{-C}_5Me_5)Rh(Nb_2W_4O_{19})]$		668
825	$Nb_4C_{56}H_{40}Cl_{12}$	$[\{NbCl(\eta^2\text{-C}_2Ph_2)(\mu\text{-Cl})\}_2(\mu_3\text{-Cl})]_2$		669
826	$NdC_{19}H_{23}O$	$Nd(THF)(Cp)_3$		670

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827	$NiC_7H_{18}Cl_2OP_2$	$NiCl_2(CO)(PMe_3)_2$		671
828	$NiC_{13}H_{20}N_2O_2$	$Ni\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OCHO)$		672
829	$NiC_{16}H_{18}N_2O$	$Ni(bipy)\{\eta^3\text{-}CH(O)CMeCHEt\}.0.5H_2O$		673
830	$NiC_{17}H_{28}N_2O_6$	$(TMEDA)Ni\{C(CO_2Me)=C(CO_2Me)CMe=CMeC(O)O\}$		674
831	$NiC_{18}H_{22}O_4S$	$Ni\{\eta^2\text{-}\underline{trans}\text{-}C_2H_2(CO_2Me)(SO_2Ph)\}(cod)$		675
832	$NiC_{18}H_{36}ClP$	$NiCl\{PMeBu^t(menthyl)\}(\eta^3\text{-}C_3H_5)$		676
833	$NiC_{20}H_{22}Cl_6P_2$	$\underline{trans}\text{-}Ni(CCl=CCl_2)_2(PMe_2Ph)_2$		677
834	$NiC_{21}H_{20}N_2O_2$	$(bipy)NiCHCH(C_8H_{10})C(O)O$		678
835	$NiC_{22}H_{32}Br_4O_4P_2$	$\underline{trans}\text{-}Ni\{C_6HBr_2(OMe)_2\text{-}3,5,2,6\}_2(PMe_3)_2$		679
836	$NiC_{22}H_{36}O_4P_2$	$\underline{trans}\text{-}Ni\{C_6H_3(OMe)_2\text{-}2,6\}_2(PMe_3)_2$		679
837	$NiC_{25}H_{37}ClOP_2$	$NiCl(PMe_3)\{\eta^2\text{-}(Me_3P)PhC=CHC(O)CH_2CMe_2Ph\}$		680
838	$NiC_{26}H_{35}P_3$	$Ni(PPh_3)(dmpe)(\eta\text{-}C_2H_4)$		681
839	$NiC_{30}H_{42}N_2O_2$	$Ni\{RNCHCHNR\}\{\eta^2\text{-}C_2(CH_2OH)_2\}$ R=2,6-$Pr^iC_6H_4$		682
840	$NiC_{32}H_{36}Br_4O_4P_2$	$\underline{trans}\text{-}Ni\{C_6HBr_2(OMe)_2\text{-}3,5,2,6\}_2(PMe_2Ph)_2$		679
841	$NiC_{32}H_{40}O_4P_2$	$\underline{trans}\text{-}Ni\{C_6H_3(OMe)_2\text{-}2,6\}_2(PMe_2Ph)_2$		679
842	$NiC_{42}H_{39}P_3S_2$	$Ni(\eta^2\text{-}CS_2)(triphos)$		216
843	$[NiC_{43}H_{43}NOP_3]^+$	$[Ni(CO)\{NH(CH_2CH_2PPh_2)_3\}][BPh_4].0.5THF$		126
844	$[NiC_{44}H_{45}NP_3S_2]^+$	$[Ni\{\eta^2CS\text{-}SCSMe\}\{PPh_2CH_2CH_2N(CH_2CH_2PPh_2)_2\}][BPh_4]$		127
845	$NiC_{48}H_{44}NP_3S$	$Ni(\eta^2\text{-}SCNPh)(triphos).0.5CH_2Cl_2$		216
846	$[NiSe_2C_8N_4S_2]^{2-}$	$[NEt_4]_2[Ni\{Se_2C=C(CN)_2\}\{S_2C_2(CN)_2\}]$		683
847	$NiSiC_{19}H_{35}ClOP_2$	$\underline{trans}\text{-}(\underline{Z})\text{-}NiCl\{CPh=CHC(O)\}CH_2SiMe_3)(PMe_3)_2$		680
848	$NiSi_2C_{14}H_{40}$	$\underline{trans}\text{-}Ni(CH_2SiMe_3)_2(PMe_3)_2$		684
849	$NiSi_2C_{34}H_{39}NO_2P_2$	$Ni(CO)\{\eta^2\text{-}H_2CCHC(NSiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2\}$		685
850	$NiSi_2C_{47}H_{51}NO_2P_4$	$Ph_2P_2Ni\{(PPh_2)_2C_4(OSiMe_3)_2NMe\}$	180	69
851	$NiSi_4C_{20}H_{55}P_3$	$Ni\{\eta^2PC\text{-}(Me_3Si)_2CPCH(SiMe_3)_2\}(PMe_3)_2$		686
852	$NiZr_2C_{32}H_{52}P_4$	$Ni\{(Me_2PCH_2)_2Zr(Cp)_2\}_2.THF$		687
853	$Ni_2C_{42}H_{44}N_4$	$Ni_2\{\mu\text{-}\eta^2\text{:}N,N\text{-}PhCHCHCHN(CH_2)_3NCHCHCHPh\}_2$		688
854	$Ni_2C_{60}H_{84}N_4O_2$	$\{Ni(NRCHCHNR)\}_2\{\mu\text{-}1,4\text{-}CHC(CH_2OMe)C(CH_2OMe)CH\}$ R=2,6-$Pr^iC_6H_3$		689
855	$Ni_2Ru_3C_{32}H_{20}O_8$	$(Cp)_2Ni_2Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C_2Ph_2)$		690

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856	$Ni_3C_{15}H_{21}P_3$	$\{Ni(Cp)(\mu\text{-}PH_2)\}_3$		585
857	$Ni_5Si_8C_{30}H_{76}ClO_6P_4$	$Ni_5Cl(CO)_4(\mu_3\text{-}CO)_2[\mu_4\text{-}\eta^2\text{-}P_2(CH(SiMe_3)_2)_2]_2$	140	691
858	$[OsC_3Cl_3O_3]^-$	$[Os_3C_{14}H_7N_2O_{10}][\underline{fac}\text{-}OsCl_3(CO)_3]$		692
859	$OsC_{16}H_{33}IP_2$	$OsI(PMe_3)_2(\eta^5\text{-}C_6H_6Bu)$		693
860	$OsC_{20}H_{36}Br_2N_4$	$\underline{trans}\text{-}OsBr_2(CNBu^t)_4.2CH_2Cl_2$		694
861	$[OsC_{24}H_{46}N_6]^{2+}$	$[Os(CNBu^t)_2(NH_2NCMe_2)_2(cod)][BPh_4].2Me_2CO$		119
862	$OsC_{25}H_{22}BrP$	$OsBr(\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2\text{-}\underline{o})(Cp)$		695
863	$OsC_{37}H_{32}ClNO_3P_2S$	$Os\{CH_2S(O)O\}Cl(NO)(PPh_3)_2$		696
864	$OsC_{39}H_{28}ClO_2P_2$	$OsCl(\underline{o}\text{-}PPh_2C_6H_4CHC_6H_4PPh_2\text{-}\underline{o})(CO)_2$		697
865	$OsC_{40}H_{34}ClINO_3P_2$	$OsClI(\underline{o}\text{-}PPh_2C_6H_4CHCO_2Et)(NO)(PPh_3)$		698
866	$OsC_{44}H_{36}O_2P_3$	$OsCl(PHPh)(CO)_2(PPh_3)_2.EtOH$		699
867	$OsC_{45}H_{35}Cl_2O_2P_2$	$OsCl(\underline{o}\text{-}PPh_2C_6H_4CHCl)(CO)_2(PPh_3)$		697
868	$OsC_{45}H_{39}O_3P_3$	$Os(CO)_2\{PH(OMe)Ph\}(PPh_3)_2$		699
869	$OsSiC_{16}H_{46}P_4$	$Os\{CH_2SiMe_2CH_2\}(PMe_3)_4$		700
870	$OsWC_{12}H_9O_9P$	$(OC)_5WOs(CO)_4(PMe_3)$		701
871	$OsWC_{45}H_{37}O_7P_3$	$(OC)_4WOs(CO)_2(PMePh_2)(\mu\text{-}PPh_2)(\mu\text{-}P{:}C\text{-}PPh_2CHOMe)$		702
872	$OsZrC_{34}H_{46}ClP_3$	$(Cp)_2ClZrOs(\mu\text{-}H)_3(PMe_2Ph)_3$	111	703
873	$Os_2C_{27}H_{34}$	$Os_2(\eta\text{-}MesH)_2(\mu\text{-}CHC_6H_3Me_2\text{-}3,5)$		704
875	$Os_2C_{40}H_{34}Cl_2O_4P_2$	$Os_2Cl_2(\mu\text{-}\underline{o}\text{-}C_6H_4PPh_2)_2(\mu\text{-}OAc)_2.MeCO_2H$		705,706
876	$Os_2C_{42}H_{38}Cl_2O_4P_2$	$Os_2Cl_2(\mu\text{-}\underline{o}\text{-}C_6H_4PPh_2)_2(\mu\text{-}O_2CEt)_2$		706
877	$Os_2RhC_{14}H_5O_9$	$(Cp)RhOs_2(CO)_9$		707
878	$Os_3C_8H_2O_8S_2$	$Os_3(\mu\text{-}H)_2(CO)_8(\mu_3\text{-}S)_2$		708
879	$[Os_3C_{10}NO_{11}]^-$	$[PPN][Os_3(CO)_{10}(\mu\text{-}NO)]$		709
880	$Os_3C_{10}O_{10}S$	$Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$		710
881	$Os_3C_{10}H_2O_{12}S$	$Os_3(\mu\text{-}H)_2(CO)_{10}(\mu\text{-}SO_2)$	203	711
882	$Os_3C_{10}H_4O_9$	$Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$	X 200,N 11	712
883	$Os_3C_{10}H_6F_3NO_8$	$Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8$		713
884	$Os_3C_{11}H_4F_3NO_9$	$Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9$		713
885	$Os_3C_{12}HF_3O_9$	$Os_3H(\mu_3\text{-}\eta^1{:}\eta^2\text{-}CCF_3)(CO)_9$		714
886	$Os_3C_{12}H_4F_3NO_{10}$	$Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}$		713

No.	Formula	Structure	Details	Ref.
887	$Os_3C_{14}H_2O_{13}$	$Os_3(CO)_{12}(\mu\text{-}\eta^1:\eta^1\text{-}CH_2CO)$		715
888	$Os_3C_{14}H_6N_2O_{14}$	$Os_3(CO)_{10}(\mu\text{-}N,O:N,O\text{-}MeO_2CNNCO_2Me)$		716
889	$[Os_3C_{14}H_7N_2O_{10}]^+$	$[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][OsCl_3(CO)_3]$		692
890	$Os_3C_{14}H_8N_2O_{12}$	$Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}C(OCONHMe)=NMe\}$	115	717
891	$Os_3C_{14}H_{10}O_{11}$	$Os_3(CO)_9\{CMe(OMe)\}(\mu\text{-}H)(\mu\text{-}C:O\text{-}MeCO)$	115	718
892	$Os_3C_{15}H_8O_{11}$	$Os_3(\mu\text{-}H)(CO)_{10}(MeC{=}CHCOMe)$		719
893	$Os_3C_{15}H_{10}O_{10}$	$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)$		720
894	$Os_3C_{16}H_6N_2O_{10}$	$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}N:N\text{-}N_2Ph)$		721
895	$Os_3C_{16}H_6N_2O_{16}$	$Os_3(CO)_{12}(\mu\text{-}N:N\text{-}MeO_2CNNCO_2Me)$		716
896	$Os_3C_{17}H_{13}O_{10}P$	$Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_9(PMe_2Ph)$		719
897	$Os_3C_{33}H_{22}O_8P_2$	$Os_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}P:P:\mu C\text{-}o\text{-}C_6H_4PPh_2CH_2PPh_2)$		722
898	$Os_3PtC_{26}H_{22}O_{10}P_2S$	$(PhMe_2P)_2PtOs_3(CO)_{10}(\mu_3\text{-}S)$		723
899	$Os_3PtC_{28}H_{15}O_{10}PS_2$	$(Ph_3P)(OC)PtOs_3(CO)_9(\mu_3\text{-}S)_2$		724
900	$Os_3PtC_{31}H_{33}O_7P_3S$	$(PhMe_2P)(OC)PtOs_3(CO)_6(\mu\text{-}H)(\mu\text{-}o\text{-}C_6H_4PPh_2)(\mu_3\text{-}S)$		723
901	$Os_3PtC_{32}H_{33}O_8P_3S$	$(PhMe_2P)_2PtOs_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)$		723,725
902	$Os_3PtC_{33}H_{33}O_9P_3S$	$(PhMe_2P)_2PtOs_3(CO)_9(PMe_2Ph)(\mu_3\text{-}S)$		723
903	$Os_3PtC_{45}H_{30}O_9P_2S_2$	$(Ph_3P)(OC)PtOs_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$		724
904	$Os_3ReC_{30}H_{11}O_{14}$	$(OC)_9Os_3(\mu\text{-}H)\{\mu_3\text{-}\mu\eta^1:\eta^2\text{-}CCPhC(CO)CCPh\}Re(CO)_4$	153	726
905	$Os_3Si_4SnC_{24}H_{40}O_{10}$	$Os_3Sn(\mu\text{-}H)_2(CO)_{10}\{CH(SiMe_3)_2\}_2$		727
906	$[Os_3WC_{14}HO_{14}]^-$	$[PPN][Os_3W(\mu\text{-}H)(CO)_{13}(\mu\text{-}CO)]$		728
907	$Os_3WC_{15}H_8O_9$	$(Cp)WOs_3(\mu\text{-}H)(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2H_2)$		729
908	$Os_3WC_{16}H_6O_{11}S$	$(Cp)(OC)_2WOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}S)$		730
909	$Os_3WC_{20}H_{11}O_{12}PS_2$	$(PhMe_2P)(OC)_3WOs(CO)_9(\mu_3\text{-}S)_2$		731
910	$Os_3WC_{23}H_{14}O_{10}$	$(Cp)WOs_3(CO)_6(\mu\text{-}O)\{\mu_3\text{-}CCH_2(pTol)\}$		732
911	$Os_3WC_{27}H_{22}O_{11}P_2S$	$(PhMe_2P)(OC)_3WOs_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)$		725
912	$Os_3WC_{27}H_{22}O_{11}P_2S_2$	$(PhMe_2P)_2(OC)_2WOs_3(CO)_9(\mu_3\text{-}S)_2$		731
913	$Os_3WC_{28}H_{22}O_{12}P_2S_2$	$(PhMe_2P)_2(OC)_2WOs_3(CO)_{10}(\mu_3\text{-}S)_2$		731
914	$Os_3WC_{30}H_{20}O_9$	$(Cp)HWOs_3(CO)_9\{\mu\text{-}C(pTol)\}_2$		733
915	$Os_3WC_{31}H_{20}O_{10}$	$(Cp)W(\mu\text{-}CO)Os_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}C(pTol)\}_2$		733
916	$Os_3W_2C_{31}H_{22}O_{15}P_2S_2$	$(PhMe_2P)_2(OC)_4(\mu\text{-}CO)W_2Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)$		731

No.	Formula	Structure	Details	Ref.
917	$Os_4C_{16}H_9NO_{11}S_2$	$Os_4(CO)_{11}(CNBu^t)(\mu_3\text{-}S)_2$		734
918	$Os_4C_{17}H_9NO_{12}S_2$	$Os_4(CO)_{12}(CNBu^t)(\mu_3\text{-}S)_2$		734
919	$Os_4C_{19}H_{11}O_{11}PS_2$	$Os_4(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)_2$		734
920	$Os_4C_{20}H_{11}O_{12}PS_2$	$Os_4(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$		734
921	$[Os_4C_{24}H_{28}O_5]^{2+}$	$[\{(\eta\text{-}C_6H_6)_2Os_2(\mu\text{-}OH)_2\}_2(\mu_4\text{-}O)][BPh_4]_2.2Me_2CO$		123
922	$Os_4Se_2C_{12}O_{12}$	$Os_4(CO)_{12}(\mu_3\text{-}Se)_2$		735
923	$Os_5C_{17}H_3IO_{16}$	$Os_5C(CO)_{14}(\mu\text{-}CO_2Me)(\mu\text{-}I)$		736
924	$Os_5C_{18}H_6O_{16}$	$Os_5C(CO)_{14}(\mu\text{-}H)(\mu\text{-}CO_2Et)$		736
925	$Os_6C_{16}O_{16}S_4$	$\{Os_3(CO)_8(\mu_3\text{-}S)_2\}_2$		708
926	$Os_6C_{17}O_{17}S$	$Os_6(CO)_{17}(\mu_4\text{-}S)$		737
927	$Os_6C_{19}O_{19}S$	$Os_6(CO)_{19}(\mu_3\text{-}S)$		737
928	$Os_6C_{27}H_{10}N_2O_{17}$	$Os_5(CO)_{14}(\mu_4\text{-}\mu_3C{:}O\text{-}CO)Os(CO)_2(py)_2$		738
929	$Os_6C_{38}H_{20}O_{14}P_2S_4$	$Os_6(CO)_{14}(\mu\text{-}PPh_2)(\mu_3\text{-}S)_3(\mu_4\text{-}S)$		739
930	$Os_6Pt_2C_{33}H_{24}O_{17}$	$(cod)_2Pt_2Os_6(CO)_{17}$		740
931	$Os_6Pt_2C_{52}H_{30}O_{16}P_2S_4$	$(\overline{PtOs_3(\underline{o}\text{-}C_6H_4)PPh_2})(CO)_8(\mu\text{-}H)(\mu_3\text{-}S)(\mu_4\text{-}S))_2$		741
932	$Os_8C_{22}HIO_{22}$	$Os_8(CO)_{22}(\mu\text{-}H)(\mu\text{-}I).H_2O$		742
933	$[Os_8C_{22}HO_{22}]^-$	$[PMePh_3][Os_8(\mu\text{-}H)(CO)_{22}]$		742
934	$Os_{10}C_{23}O_{23}S_2$	$Os_{10}(CO)_{23}(\mu_4\text{-}S)_2$		743
935	$[Os_{10}C_{24}NO_{24}]^-$	$[PPN][Os_{10}C(CO)_{23}(NO)]$		744
936	$[Os_{10}C_{25}NO_{25}]^-$	$[PPN][Os_{10}C(CO)_{24}(\mu\text{-}NO)]$		744
937	$PbC_{19}H_{18}S$	Ph_3PbSMe		448
938	$[PbSe_3C_{18}H_{15}]^-$	$[AsPh_4][Pb(SePh)_3]$		40
939	$PbSnC_{36}H_{30}$	$Ph_3PbSnPh_3$	233	455
940	$Pb_2C_{36}H_{30}$	$Si_2Ph_6.Pb_2Ph_6$		455
941	$PdC_9H_{19}Cl_2N$	$Cl(ClH_2C)\overline{Pd(\eta^2\text{-}H_2C{=}CHCMe_2CH_2NMe_2)}$		745
942	$PdC_{20}H_{23}BrN_2O_6$	$PdBr\{CH(CO_2Et)_2\}\{(NC_5H_4\text{-}2)_2CO_2Et\}$		746
943	$PdC_{23}H_{19}N_3O_3$	$\overline{Pd(C_6H_3(5\text{-}OMe)(2\text{-}NNC_6H_4OMe\text{-}\underline{p}))}(oxine)$		747
944	$[PdC_{25}H_{45}F_5P_3S_2]^+$	$\underline{trans}\text{-}[Pd(C_6F_5)(PEt_3)_2(S_2CPEt_3)][ClO_4].CHCl_3$		748
945	$PdC_{26}H_{25}BrNO_2$	$Pd(8\text{-}mq)(Ph_2PCH_2CO_2Et).H_2O$		626
946	$PdC_{27}H_{34}N_2O_{10}$	$Pd\{CH(CO_2Et)_2\}_2\{(NC_5H_4\text{-}2)_2CO_2Et\}$		746

No.	Formula	Structure	Details	Ref.
947	$PdC_{36}H_{54}P_2$	$Pd(CHCMe_2CH)_4(PMe_2Ph)_2$		749
948	$[PdC_{44}H_{41}P_2]^+$	$[Pd(PPh_3)_2\{\eta^3\text{-}CH_2CCHCH(CH_2)_2CH_2CH_2CH_2\}][PF_6]$		750
949	$PdWC_{48}H_{34}O_{10}P_4$	$Pd[(\underline{E})\text{-}PhP{=}PPh\{W(CO)_5\}_2](dppe).C_6D_6$		751
950	$Pd_2C_8H_{12}I_4N_4$	$Pd_2I_4(CNMe)_4.CH_2Cl_2$	140	752
951	$Pd_2C_{11}H_{28}Cl_2OP_4$	$Pd_2Cl_2(\mu\text{-}CO)(\mu\text{-}dmpm)_2$		753
952	$Pd_2C_{16}H_{34}Cl_4N_2$	$\{PdCl(CH_2CH_2NEt_2)(\mu\text{-}Cl)\}_2$		754
953	$Pd_2C_{20}H_{24}Cl_2N_2O_4$	$[Pd\{CHCH(C_8H_9)ONO\}(\mu\text{-}Cl)]_2$	120	755
954	$Pd_2C_{24}H_{36}I_4N_4$	$Pd_2I_4\{\mu\text{-}CNCMe(CH_2CH_2)_2CHCMe_2NC\}_2$		756
955	$[Pd_2C_{28}H_{44}Cl_2O_{16}]^{2-}$	$Na_2K_2[Pd_2\{CH(CO_2Et)_2\}_2(\mu\text{-}Cl)_2]\text{-}$		
		$[Pd_2\{CH(CO_2Et)_2\}_2(\mu\text{-}C_2O_4)].4H_2O$		757
956	$[Pd_2C_{30}H_{44}O_{20}]^{2-}$	$Na_2K_2[Pd_2\{CH(CO_2Et)_2\}_2(\mu\text{-}Cl)_2]\text{-}$		
		$[Pd_2\{CH(CO_2Et)_2\}_2(\mu\text{-}C_2O_4)].4H_2O$		757
957	$Pd_2C_{30}H_{46}P_4S_2$	$(Pd(PPhBu^t_2))_2(\mu\text{-}S{:}\eta^2CS\text{-}CS_2)_2$		758
958	$Pd_2C_{33}H_{29}Cl_2N_3O_2P_2$	$(MeCN)_2Pd\{\eta^2\text{-}C(O)NMeC(O)C(PPh_2){=}CPPh_2\}PdCl_2)$		759
959	$Pd_2C_{42}H_{40}I_2$	$[Pd\{\underline{o}\text{-}CH_2C_6H_4\}P(oTol)_2\}(\mu\text{-}I)]_2$		760
960	$Pd_2SiC_{29}H_{32}F_{12}N_2$	$\underline{o}\text{-}NMe_2CH_2C_6H_4Pd(\mu\text{-}RC{=}CRCR{=}CR)\text{-}$		
		$Pd\{CH(SiMe_3)C_6H_4NMe_2\}$ R=CF_3		761
961	$Pd_3C_{42}H_{66}N_6$	$Pd_3(CNCy)_3(\mu\text{-}CNCy)_3$		762
962	$[Pd_3C_{46}H_{41}N_3O_3P]^+$	$[\{Pd(8\text{-}mq)\}_3(\mu_3\text{-}OH)(\mu_3\text{-}P{:}C{:}O\text{-}Ph_2PCHCO_2Et)][PF_6]$		626
963	$PtC_8H_{12}Cl_2$	$PtCl_2(cod)$	110	763
964	$PtC_8H_{18}Cl_2N_4$	$PtCl_2\{N(NMe_2)CHCHNNMe_2\}(\eta\text{-}C_2H_4)$		764
965	$PtC_{14}H_{25}IN_4$	$PtIMe_3\{(dmpz)_2CH_2\}$		765
966	$PtC_{15}H_{23}Cl_2NO$	$\underline{cis}\text{-}PtCl_2\{(\underline{S})\text{-}NH_2CHMePh\}\{\eta^2\text{-}CH_2CHCH(CH_2)_4O\}$		766
967	$PtC_{15}H_{26}ClNOP_2$	$\underline{Z}\text{-}PtMe\{C(OMe){=}NC_6H_4Cl\text{-}\underline{p}\}(dmpe)$		767
968	$PtC_{17}H_{20}Cl_3NO_3$	$PtCl_3(\eta^2\text{-morphinium}).0.5H_2O.Me_2CO$		768
969	$[PtC_{24}Cl_{20}]^{2-}$	$[NBu_4]_2[Pt(C_6Cl_5)_4].2CH_2Cl_2$		769
970	$[PtC_{24}Cl_{20}]^-$	$[NBu_4][Pt(C_6Cl_5)_4]$		769
971	$[PtC_{26}H_{30}P]^+$	$(\underline{Z})$ & $(\underline{E})\text{-}[Pt(PPh_3)(\eta\text{-}CHMeCHMe)(\eta^3\text{-}CH_2CMeCH_2)]\text{-}$		
		$[PF_6]$		770
972	$PtC_{28}H_{30}OP_2$	$PtMe(OMe)(dppe)$		771

No.	Formula	Structure	Details	Ref.
973	$PtC_{30}H_{30}F_4OP_2$	$PtMe(CF_2CF_2OMe)(dppe)$		771
974	$PtC_{36}H_{31}Cl_2P$	$PtCl_2(PPh_3)(\eta^4\text{-}C_4Me_2Ph_2)$		772
975	$PtC_{41}H_{37}ClOP_2$	trans-$PtCl\{C{\equiv}CC(OH)Me_2\}(PPh_3)_2.0.5PhMe$		773
976	$PtC_{42}H_{35}ClP_2$	trans-$PtClPh(PPh_3)_2$		774
977	$PtC_{42}H_{39}ClOP_2$	trans-$PtCl\{C{\equiv}CC(OH)MeEt\}(PPh_3)_2.Me_2CO$		773
978	$PtC_{43}H_{38}Br_2P_2$	$PtBr\{C{=}CBrCH(CH_2)CH_2CH_2CH\}$		775
979	$PtC_{43}H_{38}O_5P_2$	$Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2.H_2O$		776
980	$PtC_{46}H_{44}O_2P_2$	cis-$Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2.H_2O$		773
981	$PtC_{48}H_{38}N_2O_4P_2$	$Pt(o\text{-}O_2NC_6H_4)_2(PPh_3)_2$		777
982	$PtC_{50}H_{38}N_2O_2P_2$	$Pt(o\text{-}C_6H_4CONC_6H_4PPh_2\text{-}o)(Ph_2PC_6H_4NHCOPh\text{-}o)$		778
983	$PtC_{53}H_{30}F_{10}O$	$(C_6F_5)_2Pt\{Ph_2PCCPhC(O)CPhCPPh_2\}.CHCl_3$		368
984	$PtC_{54}H_{52}O_6P_2$	trans-$Pt\{2,4,6\text{-}(MeO)_3C_6H_2\}_2(PPh_3)_2$		779
985	$PtRe_2C_{12}O_{12}$	$\{(OC)_5Re\}_2Pt(CO)_2$		780
986	$[PtRhC_{49}H_{43}ClN_2O_3]^+$	$[(Ph_3P)_2PtCl\{C(=NC_6H_4OMe\text{-}p)CMe{=}NMeRh(CO)_2]\text{-}[RhCl_2(CO)_2]$		781
987	$[PtRhC_{54}H_{47}ClO]^+$	$[ClPt(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Me)(\mu\text{-dppm})_2Rh(CO)][PF_6]$		782
988	$PtSiC_{47}H_{57}N_2P_3S$	$Pt(PPh_3)_2\{\eta^2PS\text{-}SP(NBu^t)NBu^tSiMe_3\}.0.5PhH$		783
989	$[PtSn_3C_8H_{12}Cl_9]^-$	$[AsPh_4][Pt(SnCl_3)_3(cod)]$		44
990	$[PtTe_2C_{48}H_{38}P_2]^{2+}$	$[Pt\{TePh(o\text{-}C_6H_4PPh_2)\}_2][Pt(SCN)_4].2DMF$		784
991	$[PtWC_{21}H_{31}O_2P_2]^+$	$[(Me_3P)_2PtW(CO)_2(Cp)\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(pTol)\}][BF_4]$		785
992	$PtWC_{21}H_{32}O_2P_2$	$(Me_3P)_2PtW(\mu\text{-}H)\{\mu\text{-}CH(pTol)\}(CO)_2(Cp)$	220	786
993	$[PtWC_{24}H_{37}OP_2]^+$	$[(Me_3P)_2PtW(CO)(\eta\text{-}C_2Me_2)(Cp)\{\mu\text{-}CH(pTol)\}][BF_4]$		229
994	$PtWC_{34}H_{26}O_8P_2$	$(OC)_4WPt(\eta^2\text{-DMAD})(\mu\text{-}PPh_2)_2$		787
995	$PtWC_{46}H_{35}O_4P_3$	$(OC)_4WPt(PPh_3)(\mu\text{-}PPh_2)_2$		787
996	$PtWC_{71}H_{58}O_3P_4$	$\{(pTol)C_2\}Pt(\mu\text{-}C_2(pTol))(\mu\text{-dppm})_2W(CO)_3$		788
997	$[Pt_2CH_{11}IO_{20}P_8]^{4-}$	$K_4[Pt_2IMe(\mu\text{-}P_2O_5H_2)_4].2H_2O$		789
998	$Pt_2C_{10}H_{26}Cl_2S_4$	$\{PtMe_3(\mu\text{-}Cl)\}_2(SCH_2SCH_2SCH_2SCH_2)$		790
999	$Pt_2C_{14}H_{40}P_4$	$Me_2Pt(\mu\text{-dmpm})_2PtMe_2$		791
1000	$Pt_2C_{24}H_{36}O_8$	$[Pt\{\eta^2\text{-}CH{=}CHCH_2CH_2CHCH(OCOMe)CH_2CH_2\}(\mu\text{-}O_2CMe)]_2$		792
1001	$Pt_2C_{30}H_{46}P_2S_4$	$Pt_2(PPhBu^t{}_2)_2(\mu\text{-}S{:}\eta^2\text{-}CS_2)_2$		793

No.	Formula	Structure	Details	Ref.
1002	$Pt_2C_{34}H_{66}N_4P_2$	$(PtCH_2CMe_2PBu^t{}_2)_2(\mu\text{-dmpz})_2$		794
1003	$[Pt_2C_{40}H_{71}P_4]^+$	$[Pt_2(C{\equiv}CPh)(\mu\text{-}C_2HPh)(PEt_3)_4][BF_4]$		795
1004	$Pt_2C_{54}H_{56}P_4$	$Me_2Pt(\mu\text{-dppm})_2PtMe_2$		791
1005	$Pt_2C_{55}H_{45}Cl_2OP_3$	$(Ph_3P)ClPt(\mu\text{-}CO)PtCl(PPh_3)_2.2PhCl$		796
1006	$[Pt_2C_{55}H_{53}P_4]^+$	$[Pt_2Me_2(\mu\text{-}\eta^1\text{-}C{\equiv}CMe)(\mu\text{-dppm})_2][BF_4]$		782
1007	$Pt_2C_{97}H_{94}O_3P_4$	$\{PtPh(PBz_3)_2\}_2(\mu\text{-O:O-}CO_3).PhMe$		797
1008	$[Pt_2Rh_9C_{22}O_{22}]^{3-}$	$[NEt_4]_3[Pt_2Rh_9(CO)_{11}(\mu\text{-CO})_{11}]$		798
1009	$Pt_2Se_2C_{11}H_{28}I_2$	$(PtMe_3)_2(\mu\text{-I})_2(\mu\text{-SeSeCH}_2CMe_2CH_2)$		799
1010	$Pt_2Sn_2C_{20}H_{30}Cl_8F_{12}P_2$	$[Pt\{C(CF_3){=}C(CF_3)SnCl_3\}(PEt_3)(\mu\text{-Cl})]_2$		800
1011	$Pt_2W_2C_{28}H_{40}O_6P_2$	$(Cp)_2W_2Pt_2(PEt_3)_2(\mu\text{-CO})_4(\mu_3\text{-CO})_2$		292
1012	$Pt_4C_{12}H_{36}I_4$	$[Me_3PtI]_4.CCl_4$		801
1013	$Pt_4C_{37}H_{44}O_5P_4$	$Pt_4(\mu\text{-CO})_5(PMe_2Ph)_4$		802
1014	$[ReC_5H_2O_6]^{\bullet}$	$[Re(CO)_5(OH_2)][AsF_6]$		803
1015	$[ReC_8H_6O_6]^-$	$[PhC(NH_2)_2][\underline{cis}\text{-}Re(COMe)_2(CO)_4]$		804
1016	$ReC_8H_7O_6$	$\underline{cis}\text{-}Re\{(CMeO)_2H\}(CO)_4$	N.	805
1017	$ReC_8H_{12}IO$	$ReOI(\eta\text{-}C_2Me_2)_2$	173	806
1018	$ReC_9H_{16}FN_2O_3$	$ReF(CO)_3(TMEDA)$		807
1019	$[ReC_9H_{18}N_2O_4]^+$	$[Re(CO)_3(OH_2)(TMEDA)][AsF_6]$ & $[BF_4]$		803
1020	$[ReC_{10}H_{10}]^+$	$[Re(Cp)_2][CuCl_2]$		808
1021	$[ReC_{12}H_{12}O_3]^+$	$[Re(CO)_3(\eta\text{-MesH})][AlBr_4]$		809
1022	$ReC_{12}H_{15}$	$ReH(\eta\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$		810
1023	$[ReC_{15}H_{16}N_2O_2]^+$	$[Re\{NHNMe(pTol)\}(CO)_2(Cp)][BF_4]$		811
1024	$ReC_{18}H_{27}Br_3O_2P_2$	$ReBr_3(CO)_2(PMe_2Ph)_2$		812
1025	$[ReC_{18}H_{33}F_2N_4O_6]^+$	$[\{ReF(CO)_3(TMEDA)\}_2H][BF_3OH]$		807
1026	$ReC_{24}H_{25}O_3$	$ReO(O_2C{=}CPh_2)(\eta\text{-}C_5Me_5)$		813
1027	$ReC_{28}H_{49}P_2$	$ReH_3(PPhPr^i{}_2)_2(\eta\text{-}C_2H_4)_2$	190	814
1028	$ReC_{30}H_{21}BrN_2O_4P$	$ReBr(CO)_4(PPhCHPhCPh{=}NNPh)$		815
1029	$ReC_{42}H_{41}P_2$	$ReH_3(PPh_3)_2(\eta^4\text{-}C_6H_8)$		816
1030	$[ReC_{50}H_{54}N_4P_2]^{2\bullet}$	$\underline{trans}\text{-}[Re(CNBu^t)_2(NCMe)_2(PPh_3)_2][BF_4]_2.0.5CH_2Cl_2$		817
1031	$ReC_{60}H_{54}ClP_4$	$\underline{trans}\text{-}ReCl(C{=}CHPh)(dppe)_2.THF$		818

No.	Formula	Structure	Details	Ref.
1032	$ReC_{61}H_{56}ClP_4$	$ReCl(\eta^2\text{-}H_2C{=}C{=}CHPh)(dppe)_2.1.5PhH$		819
1033	$[ReSeC_{24}H_{22}NOP]^+$	$[Re(NO)(PPh_3)(\eta^2\text{-}CH_2Se)(Cp)][PF_6]$		820
1034	$[ReWC_{17}H_8O_9]^-$	$[PPN][ReW(CO)_9\{\mu\text{-}CH(pTol)\}]$		821
1035	$ReWC_{21}H_{25}O_7P_2$	$ReW(CO)_7\{\mu\text{-}\eta^1{:}\eta^2CH\text{-}CH_2(pTol)\}(\mu\text{-}dmpm)$	200	821
1036	$ReWC_{43}H_{40}O_{10}P_3$	$ReW(CO)_6\{\mu\text{-}OCCH_2(pTol)\}(\mu\text{-}dmpm)\{P(OMe)_3\}.CH_2Cl_2$		821
1037	$ReW_2C_{29}H_{24}BrO_4$	$(OC)_3ReW_2(Cp)_2(\mu\text{-}Br)(\mu\text{-}O)\{\mu\text{-}C(pTol)\}\{\mu_3\text{-}C(pTol)\}$		822
1038	$ReW_2C_{30}H_{24}BrO_4$	$(OC)_3ReW_2(CO)(Cp)_2(\mu\text{-}Br)\{\mu\text{-}C(pTol)\}\{\mu_3\text{-}C(pTol)\}$		822
1039	$Re_2C_{10}H_4O_9$	$Re_2(CO)_8(\mu\text{-}H)\{\mu\text{-}O{:}C\text{-}OCMe)$		823
1040	$[Re_2C_{11}H_{13}O_9]^-$	$[C_7H_{15}N_4][Re_2(CO)_6(\mu\text{-}OMe)(\mu\text{-}OEt)_2]$		824
1041	$Re_2C_{12}H_{10}O_2S_5$	$Re_2(CO)_2(Cp)_2(\mu\text{-}S_2)(\mu\text{-}S_3)$		825
1042	$Re_2C_{14}H_9NO_9$	$Re_2(CO)_9(CNBu^t)$		826
1043	$Re_2C_{14}H_{10}S$	$Re_2(CO)_4(Cp)_2(\mu\text{-}S)$		825
1044	$Re_2C_{16}H_{24}Br_2N_2O_6P_2$	$Re_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}\underline{cis}\text{-}Me\overline{PNBu^tPMeNBu^t})$		827
1045	$Re_2C_{17}H_{24}$	$Re_2(\eta\text{-}C_6H_6)_2(\mu\text{-}H)_2(\mu\text{-}CHBu^t)$		828
1046	$Re_2C_{18}H_{24}$	$(\eta\text{-}C_6H_6)Re(\mu\text{-}H)_2Re(\eta^4\text{-}C_6H_8)_2$		810
1047	$Re_2C_{24}H_{30}O_5$	$Re_2(CO)_4(\eta\text{-}C_5Me_5)_2(\mu\text{-}O)$		813,829
1048	$Re_2C_{31}H_{24}O_7P_2$	$Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}dppm)$		830
1049	$Re_2C_{47}H_{30}O_5$	$Re_2(CO)_5(\eta\text{-}C_2Ph_2)(\mu\text{-}\eta^4{:}\eta^1,\eta^1\text{-}C_4Ph_4)$		831
1050	$Re_2C_{51}H_{41}Cl_3N_3P_3$	$Re_2Cl_3(\mu\text{-}P{:}N\text{-}Ph_2PC_5H_5N)_2(\mu\text{-}P{:}C,N\text{-}$ $PhP\{\underline{o}\text{-}C_6H_4)(C_5H_5N)\}$		832
1051	$Re_2C_{60}H_{40}O_4$	$Re_2(CO)_4(\eta\text{-}C_2Ph_2)(\mu\text{-}\eta^1,\eta^3{:}\eta^1,\eta^3\text{-}C_6Ph_6)$		831
1052	$[Re_2C_{82}H_{83}N_2P_4]^+$	$[Re_2H_2(\mu\text{-}H)_3(CNBu^t)_2(PPh_3)_4][PF_6]$		833
1053	$Re_2Sb_2C_{30}H_{20}Br_2O_6$	$(OC)_6Re_2(\mu\text{-}Br)_2(\mu\text{-}Sb_2Ph_4)$		834
1054	$[Re_3C_{17}H_9NO_{11}]^-$	$[NBu_4][Re_3(\mu\text{-}H)_3(CO)_{10}\{\mu\text{-}O{:}N\text{-}OC(Ph)NH\}]$		835
1055	$Re_3C_{17}H_{11}O_{10}$	$Re_3(\mu\text{-}H)(\mu_3\text{-}H)(CO)_{10}(\eta^5\text{-}C_7H_9)$		836
1056	$Re_4C_{20}H_{30}O_{11}$	$(\eta\text{-}C_5Me_5)ORe(\mu\text{-}O)_2Re(OReO_3)_2(\eta\text{-}C_5Me_5)$		813
1057	$Re_4Sn_2C_{52}H_{30}Cl_2O_{16}P_2$	$[(Ph_3P)(OC)_4ReSnCl\{\mu\text{-}Re(CO)_4\}]_2$		837
1058	$Re_4Sn_2C_{52}H_{30}I_2O_{16}P_2$	$[(Ph_3P)(OC)_4ReSnI\{\mu\text{-}Re(CO)_4\}]_2$		838
1059	$[Re_6C_{20}H_6NO_{21}]^-$	$[NEt_4][(Re_3(\mu\text{-}H)_3(CO)_{10})_2(\mu_4\text{-}\eta^2\text{-}NO)]$		839
1060	$[RhC_2Cl_2O_2]^-$	$[RhCl_2(CO)_2]^-$		357,781

No.	Formula	Structure	Details	Ref.
1061	$[RhC_6H_6N_2O_2]^+$	$[Rh(CO)_2(MeCN)_2]_2[Rh_{14}C_2(CO)_{33}].0.3CH_2Cl_2$		840
1062	$[RhC_8H_{12}Cl_2]^-$	$[Rh\{PhP(OCH_2CH_2)_2NH\}_2][RhCl_2(cod)]$		841
1063	$RhC_{10}H_{18}P$	$Rh(PMe_3)(\eta\text{-}C_2H_4)(Cp)$	173	21
1064	$RhC_{10}H_{21}ClN_2O_4P$	$RhCl(CO)\{P(OMe)(OCH_2CH_2NMeCH_2\text{-})_2\}$	268	842
1065	$RhC_{12}H_{15}O_2$	$Rh(CO)_2(\eta\text{-}C_5Me_5)$		843
1066	$[RhC_{12}H_{20}ClOS_2]^+$	$[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)][ClO_4]$		844
1067	$[RhC_{15}H_{20}N_4]^+$	$[Rh(cod)(pz_2CH_2)][ClO_4].0.5C_2H_4Cl_2$		845
1068	$RhC_{15}H_{21}O_5$	$Rh(CO_2Me)_2(CO)(\eta\text{-}C_5Me_5)$		846
1069	$RhC_{15}H_{24}Cl$	$RhCl(\eta^3\text{-}MeHCCHCHMe)(\eta\text{-}C_5Me_5)$	153	847
1070	$RhC_{16}H_{29}BrP$	$RhBr(cyp)(PMe_3)(\eta\text{-}C_5Me_5)$		848
1071	$RhC_{16}H_{30}P$	$Rh(CH_2CH_2CH_2)(PMe_3)(Cp)$		849
1072	$RhC_{18}H_{38}O_9P_3$	$Rh(Mes)\{P(OMe)_3\}_3$		850
1073	$RhC_{19}H_{29}BrP$	$RhBrPh(PMe_3)(\eta\text{-}C_5Me_5)$		851
1074	$RhC_{20}H_{38}P$	$Rh(\eta^3\text{-}2\text{-}C_3H_4Me)(PHBu^t_2)(cod)$	140	500
1075	$[RhC_{22}H_{14}F_4]^+$	$[Rh(\eta^5\text{-}az)(\eta^4\text{-}tfb)][PF_6]$		852
1076	$RhC_{27}H_{23}ClN_3$	$Rh\{C(O)C_9H_6N\}(CH_2Ph)Cl(py)_2$		853
1077	$RhC_{28}H_{53}P_2$	$Rh(\eta^3\text{-}2\text{-}C_3H_4Me)(PHCy_2)_2$	140	500
1078	$RhC_{29}H_{25}O_5P_2$	$Rh(CO)(PPh_2CH_2COO)(PPh_2CH_2CO_2H)$		854
1079	$RhC_{30}H_{20}Cl_4O_3P$	$(Cp)Rh\{o\text{-}C(O)OC_6Cl_4O\}(PPh_3)_2.0.25CH_2Cl_2$		855
1080	$RhC_{30}H_{30}Cl_3P_2$	$RhCl_3\{\eta^2\text{-}C_2H_2(CH_2CH_2PPh_2)_2\}$		856
1081	$[RhC_{31}H_{46}N_2O_8]^+$	$[Rh(nbd)(NH_3)_2.dibenzo\text{-}24\text{-}crown\text{-}8][PF_6]$		857
1082	$[RhC_{32}H_{50}N_2O_8]^+$	$[Rh(cod)(NH_3)_2.dibenzo\text{-}24\text{-}crown\text{-}6][PF_6]$		857
1083	$RhC_{33}H_{44}O_6P_3$	<u>cis</u>-$Rh(Mes)\{P(OMe)_3\}_2PPh_3$		850
1084	$RhC_{36}H_{22}F_4N_2O_2P$	$Rh\{o\text{-}C_6F_4PPh_2\}(oxine)_2.CH_2Cl_2$		858
1085	$[RhC_{36}H_{36}N_4]^+$	$[Rh(2,6\text{-}Me_2C_6H_3NC)_4]^+$		124,859
1086	$[RhC_{36}H_{58}N_2O_{10}]^+$	$[Rh(cod)(NH_3)_2.dibenzo\text{-}30\text{-}crown\text{-}10][PF_6]$		857
1087	$RhC_{37}H_{30}NO_2P_2$	<u>trans</u>-$Rh(CO)(NSO)(PPh_3)_2$		860
1088	$RhC_{37}H_{33}I_2P_2$	$RhI_2Me(PPh_3)_2$		861
1089	$[RhC_{38}H_{38}P_2]^+$	$[Rh(norb)\{2,3\text{-}(PPh_3)_2\text{-}bicyclo[2.2.1]C_7H_9\}][ClO_4]$		862
1090	$[RhC_{38}H_{60}N_2O_{10}]^+$	$[Rh(cod)(NH_3)_2.(C_{30}H_{42}O_{10})][PF_6].CH_2Cl_2$		863

No.	Formula	Structure	Details	Ref.
1091	$[RhC_{42}H_{60}N_2O_{10}]^+$	$[Rh(cod)(NH_3)_2.(C_{34}H_{42}O_{10})][PF_6].CH_2Cl_2$		863
1092	$RhC_{44}H_{44}O_4P_3$	$Rh(pTol)\{OOC(O)O\}\{PhP(CH_2CH_2CH_2PPh_2)_2\}$		864
1093	$[RhC_{48}H_{56}N_4O_4]^+$	$[Rh\{(CNC_6H_3Bu^tOCH_2-3,6)_2\}_2][BPh_4]$		129
1094	$RhSb_2C_{63}H_{51}O_2$	$RhPh_2(OCPhCHCPhO)(SbPh_3)_2.2PhH$		865
1095	$RhSe_2C_{42}H_{39}ClP_3$	$RhCl(triphos)(\eta^2\text{-}CSe_2).PhH$		866
1096	$RhSi_2C_{22}H_{47}$	$RhH_2(SiEt_3)_2(\eta\text{-}C_5Me_5)$	X,N 20	867
1097	$RhSi_4C_{22}H_{50}Cl_2P$	$RhCl[PCl\{CH(SiMe_3)_2\}_2](cod)$	140	868
1098	$RhSi_8C_{29}H_{78}ClOP_2$	<u>trans</u>-$RhCl(CO)[PH\{CH(SiMe_3)_2\}_2]_2$	140	868
1099	$RhWC_{38}H_{29}O_2$	$(\eta^5\text{-ind})RhW(CO)_2(Cp)\{\mu\text{-}\eta^1:\eta^1:\eta^3\text{-}C(pTol)CPhCPh\}$		869
1100	$Rh_2C_{14}H_{14}N_4O_4$	$Rh_2(CO)_4(\mu\text{-dmpz})_2$		436
1101	$Rh_2C_{17}H_{21}Cl_2NO_5P$	$(OC)_2ClRh(\mu\text{-}Cl)Rh(CO)\{PPh(OCMe_2CH_2)_2N\}$		870
1102	$[Rh_2C_{18}H_{18}]^{2+}$	$[(Cp)_2Rh_2(\mu\text{-}\eta^5:\eta^5\text{-cot})][PF_6]_2$		871
1103	$Rh_2C_{20}H_{10}N_4O_6$	$Rh_2(CO)_4(\mu\text{-2-O-1,8-naphthyridine})_2.0.5H_2O$		872
1104	$Rh_2C_{21}H_{15}F_6NO$	$(Cp)_2Rh_2\{\mu\text{-}\mu N:\eta^1:\eta^2\text{-}C(CF_3)C(CF_3)C(O)NPh\}$		873
1105	$[Rh_2C_{21}H_{30}NO_2]^+$	$[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$		874
1106	$Rh_2C_{24}H_{32}O_3$	$Rh_2(CO)_2(\eta\text{-}C_5Me_5)_2(\mu\text{-CHCHO})$		875
1107	$[Rh_2C_{24}H_{34}O_2]^{2+}$	$[\{(\eta\text{-}C_5Me_5)Rh(CO)\}_2(\mu\text{-}CH_2)_2][BF_4]_2$		876
1108	$Rh_2C_{25}H_{39}O_5P$	$(\eta\text{-}C_5Me_5)Rh(\mu\text{-}CO)_2Rh\{P(OMe)_3\}(\eta\text{-}C_5Me_5)$		877
1109	$Rh_2C_{26}H_{36}O_2$	$Rh_2(CO)_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}\eta^1\text{-}CCH_2CH_2CH_2)$		878
1110	$[Rh_2C_{26}H_{37}N_4O]^+$	$[\{Rh(\eta\text{-}C_5Me_5)\}_2(\mu\text{-pz})_2(\mu\text{-OH})][ClO_4]$		879
1111	$Rh_2C_{26}H_{38}N_4$	$Rh_2(cod)_2(\mu\text{-dmpz})_2$		436
1112	$[Rh_2C_{26}H_{41}N_2O_6]^+$	$[\{Rh(\eta\text{-}C_5Me_5)\}_2(\mu\text{-mpz})(\mu\text{-OMe})_2][ClO_4]$		879
1113	$Rh_2C_{28}H_{24}F_{10}S_2$	$Rh_2(cod)_2(\mu\text{-}SC_6F_5)_2$		880
1114	$[Rh_2C_{30}H_{28}N_4]^{2+}$	$[Rh_2(\mu\text{-napy})_2(nbd)_2][ClO_4]_2.H_2O$		881
1115	$Rh_2C_{30}H_{40}O_4$	$(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}O,\eta^1:\eta^2\text{-}$ $OCCH_2CMe_2CH_2C(O)CCO\}$		882
1116	$Rh_2C_{30}H_{40}O_7$	$(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^1:\eta^2\text{-}$ $C(O)OC(CO_2Et)CCO_2Et\}$		882
1117	$[Rh_2C_{30}H_{48}N_4O_2]^{2+}$	$[\{Rh(\eta\text{-}C_5Me_5)(dmpzH)\}_2(\mu\text{-OH})_2][BF_4]_2$		879
1118	$Rh_2C_{30}H_{63}ClO_2P_2S$	$Rh_2(CO)_2(PBu^t_3)_2(\mu\text{-}Cl)(\mu\text{-}SBu^t)$		883

No.	Formula	Structure	Details	Ref.
1119	$Rh_2C_{30}H_{69}P_4$	$\{(dippe)Rh\}_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}CH{=}CH_2)$		884
1120	$Rh_2C_{31}H_{53}ClP_2$	$(Cp)Rh_2Cl(PPr^i_3)(\mu\text{-}H)(\mu\text{-}P,\eta^1:\eta^2\text{-}$ $PPr^i_2CHMeCHCCH_2Ph)$		885
1121	$Rh_2C_{32}H_{58}Cl_2O_2P_2S$	$Rh_2(CO)_2(PBu^t_3)_2(\mu\text{-}Cl)(\mu\text{-}SC_6H_4Cl\text{-}\underline{p})$		883
1122	$Rh_2C_{32}H_{70}P_4$	$Rh_2(Pr^i_2PCH_2CH_2PPr^i_2)_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^4\text{-}C_4H_5)$		886
1123	$Rh_2C_{36}H_{32}OP_2$	$Rh_2(Cp)_2(\mu\text{-}CO)(\mu\text{-}dppm)$		887
1124	$Rh_2C_{36}H_{40}O_3$	$Rh_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^1:\eta^2\text{-}C(O)OCPhCPh\}$		882
1125	$Rh_2C_{44}H_{42}O_8$	$Rh_2(AcOH)_2(\mu\text{-}AcO)_2(\mu\text{-}Ph_2PC_6H_4\text{-}\underline{o})_2$		705
1126	$Rh_2C_{48}H_{38}I_2N_2O_2P_2$	$Rh_2I_2(CO)_2(PPh_3)_2(\mu\text{-}1,8\text{-}(NH_2)_2C_{10}H_6).0.5CH_2Cl_2$		888
1127	$Rh_2C_{51}H_{42}Cl_2N_2O_3P_4$	$Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}Ph_2PNHPPh_2).MeOH$		889
1128	$Rh_2C_{51}H_{45}Cl_3OP_4$	$Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)_2$		890
1129	$[Rh_2C_{54}H_{40}NO_3P_4]^+$	$[Rh_2(\mu\text{-}CN)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)][ClO_4].CH_2Cl_2$		891
1130	$[Rh_2C_{54}H_{50}Cl_2NOP_4S]^+$	$[Rh_2Cl(\mu\text{-}Cl)(CO)(\eta^2\text{-}SCNMe_2)(\mu\text{-}dppm)_2][BF_4]$		892
1131	$Rh_2C_{57}H_{44}Cl_4O_3P_4$	$Rh_2(\underline{o}\text{-}O_2C_6Cl_4)(CO)(\mu\text{-}dppm)_2$	140	893
1132	$[Rh_2C_{58}H_{50}ClF_6N_2P_4]^+$	$[Rh_2Cl(CNMe)_2(\mu\text{-}\eta^1:\eta^1\text{-}C_4F_6)(\mu\text{-}dppm)_2][BF_4]$		894
1133	$Rh_2C_{62}H_{54}Cl_2N_2O_3P_4S_2$	$Rh_2Cl_2(CO)\{\mu\text{-}S,C:S\text{-}SCNC(S)NPhCO_2Et\}(\mu\text{-}dppm)_2$		895
1134	$Rh_2C_{66}H_{58}N_6O_2P_2$	$[Rh(CO)(PPh_3)\{\mu\text{-}(pTol)NNN(pTol)\}]_2.PhMe$	220	896
1135	$[Rh_2C_{66}H_{58}N_6O_2P_2]^+$	$[Rh_2(CO)_2(PPh_3)_2\{\mu\text{-}(pTol)NNN(pTol)\}_2][PF_6].CH_2Cl_2$		896
1136	$Rh_2Ru_2C_{12}H_2O_{12}$	$Rh_2Ru_2(CO)_9(\mu\text{-}H)_2(\mu\text{-}CO)_3$		897
1137	$Rh_2Ru_3C_{25}H_{20}O_{13}P_2$	$(OC)_9Ru_3Rh_2(CO)_3(\mu\text{-}CO)(PEt_3)(\mu_4\text{-}PPh)$		95
1138	$Rh_2Si_8C_{44}H_{106}Cl_2P_2$	$\underline{trans}\text{-}[Rh(\mu\text{-}Cl)(PH\{CH(SiMe_3)_2\}_2)(\eta^2\text{-}C_8H_{14})]_2$	140	868
1139	$[Rh_3C_6O_6S_2]^-$	$[PPh_4][Rh_3(CO)_6(\mu_3\text{-}S)_2]$		898
1140	$Rh_3C_{12}H_{12}Cl_2N_3O_4$	$Rh_3Cl(\mu\text{-}Cl)(CO)_4(\mu_3\text{-}tz)(\eta^3\text{-}C_3H_5)_2.0.5CH_4Cl_2$		899
1141	$Rh_3C_{18}H_8Cl_2F_4N_3O_4$	$Rh_3Cl(\mu\text{-}Cl)(CO)_4(\mu_3\text{-}tz)(\eta^4\text{-}tfb).0.5CH_2Cl_2$		899
1142	$Rh_3C_{41}H_{30}O_5P_3$	$Rh_3(\mu\text{-}PPh_2)_3(CO)_5$		900
1143	$Rh_3C_{43}H_{30}O_7P_3$	$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$		900
1144	$Rh_3C_{54}H_{41}O_6P_4$	$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H).CH_2Cl_2$		900
1145	$[Rh_3C_{65}H_{58}I_4OP_6]^+$	$[Rh_3I(CO)(\mu\text{-}I)_2(\mu_3\text{-}I)(\mu_3\text{-}dppmpp)_2][BPh_4]$	140	132
1146	$[Rh_3C_{69}H_{60}O_5P_6S_4]^+$	$[Rh_3(S_2COEt)(\mu\text{-}S_2COEt)(CO)(\mu\text{-}CO)_2(\mu_3\text{-}dppmpp)_2]\text{-}$ $[BPh_4].0.5CH_2Cl_2$		136

No.	Formula	Structure	Details	Ref.
1147	$[Rh_3Se_2C_6O_6]^-$	$[NMe_4][Rh_3(CO)_6(\mu_3\text{-}Se)_2]$		898
1148	$Rh_4C_{12}H_6O_9S_3$	$Rh_4(CO)_5(\mu\text{-}CO)_4(\mu_3\text{-}\overline{SCH_2SCH_2SCH_2})$		901
1149	$Rh_4C_{32}H_{26}Cl_2N_4O_4$	$\{Rh_2(CO)(nbd)(\mu\text{-}CO)(\mu\text{-azaind})\}_2(\mu\text{-}Cl)_2$		902
1150	$[Rh_4C_{40}H_{64}]^{2+}$	$[Rh_4(\mu_3\text{-}H)_4(\eta\text{-}C_5Me_5)_4][BF_4]_2$	N 12	903
1151	$[Rh_4RuC_{15}O_{15}]^{2-}$	$[PPN]_2[RuRh_4(CO)_9(\mu\text{-}CO)_6]$		904
1152	$[Rh_7C_{15}NO_{15}]^{2-}$	$[PPh_4]_2[Rh_7N(CO)_{10}(\mu\text{-}CO)_4(\mu_3\text{-}CO)].THF$		225
1153	$[Rh_{14}C_{35}O_{33}]^{2-}$	$[RhC_6H_6N_2O_2]_2[\{Rh_7C(CO)_6(\mu\text{-}CO)_9\}_2(\mu\text{-}CO)_3]$		840
1154	$RuC_{10}H_8F_4N_3P_3$	$Ru(\eta\text{-}C_5H_4)_2(1,3\text{-}\overline{PFNPFNPF_2N})$		317
1155	$RuC_{10}H_8F_6N_4P_4$	$Ru(\eta\text{-}C_5H_4)_2(1,5\text{-}\overline{PFNPF_2NPFNPF_2N})$		317
1156	$RuC_{10}H_9BrO$	$RuBr(\eta^4\text{-}C_5H_4O)(Cp)$		905
1157	$RuC_{13}H_{14}$	$Ru\{(\eta\text{-}C_5H_4CH_2)_2CH_2\}$		906
1158	$RuC_{14}H_{16}$	$Ru\{(\eta\text{-}C_5H_4CH_2CH_2\text{-})_2\}$		906
1159	$RuC_{14}H_{40}P_4$	$Ru(PMe_3)_4(\eta\text{-}C_2H_4)$		907
1160	$RuC_{14}H_{42}P_4$	$RuHEt(PMe_3)_4$		907
1161	$RuC_{15}H_{23}IN_2$	$RuI(CNBu^t)_2(Cp)$		908
1162	$RuC_{16}H_{10}Cl_2N_2O_2$	$RuCl_2(CO)_2(NCPh)_2$		909
1163	$RuC_{16}H_{11}Cl_2N_3O$	$RuCl_2(CO)(terpy)$ <u>cis</u> & <u>trans</u>		910
1164	$RuC_{17}H_{11}Br_2N_3O_2$	$RuBr_2(CO)_2(\eta^2\text{-terpy})$		910
1165	$RuC_{26}H_{23}PS_2$	$Ru(\overline{S_2CCHMeC_6H_4PPh_2\text{-}\underline{o}})(Cp)$		695
1166	$[RuC_{28}H_{35}]^+$	$[Ru(\eta^5\text{-}C_6H_5(1,4\text{-}CH_2CH_2C_6H_4CH_2CH_2\text{-}\underline{p}))(\eta\text{-}C_6Me_6)]\text{-}[HCl_2]$		911
1167	$[RuC_{30}H_{33}P]^{2+}$	$[Ru(\eta\text{-}C_6Me_6)(\eta^6\text{-}C_6H_5PPh_2)][PF_6]_2$		912
1168	$RuC_{30}H_{42}$	$Ru(\eta^4\text{-}C_{10}Me_8)(\eta^6\text{-}C_6Me_6)$		913
1169	$RuC_{31}H_{30}Cl_2OP_2$	$\overline{RuCl_2(CO)\{\eta^2\text{-}C_2H_2(CH_2CH_2PPh_2)_2\}}$		856
1170	$[RuC_{32}H_{42}P_3]^+$	$[Ru(PMe_2Ph)_3\{\eta^5\text{-}\overline{CH(CH)_5CHCH_2}\}][PF_6]$		914
1171	$RuC_{33}H_{26}$	$(Cp)Ru(\eta^4\text{-}CPhCPhCPhCHPh)$		915
1172	$[RuC_{34}H_{34}NP_2]^+$	$[(\underline{S})\text{-}Ru(NCMe)\{(\underline{R})\text{-}MeCH(PPh_2)CH_2PPh_2\}(Cp)][PF_6]$		916
1173	$RuC_{34}H_{38}IOP$	$RuI(CO)(PPh_3)(\eta\text{-}C_5H_4(neomenthyl))$		917
1174	$[RuC_{35}H_{28}N]^+$	$[Ru(MeCN)(\eta^4\text{-}C_4Ph_4)(Cp)][BF_4]$	230	918
1175	$[RuC_{38}H_{30}ClN_2O_2P_2S_2]^+$	$[RuCl(CO)_2(\overline{NSNS})(PPh_3)_2][AlCl_4]$		919

No.	Formula	Structure	Details	Ref.
1176	$RuC_{39}H_{30}O_3P_2$	$Ru(CO)_3(PPh_3)_2.0.5THF$		920
1177	$RuC_{43}H_{41}Cl_2FO_2P_2$	$RuCl_2(FCOCH_2Bu^t)(CO)(PPh_3)_2.C_2H_2Cl_4$		921
1178	$[RuC_{47}H_{52}O_3P_3]^+$	$[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$		922
1179	$RuC_{52}H_{41}N_2O_6P_2$	$Ru(OC_6H_4NO\text{-}\underline{o})(OC_6H_4NO_2\text{-}\underline{o})(CO)(PPh_3)_2$		923
1180	$RuC_{58}H_{36}Cl_2N_4O_2$	$Ru(CO)_2(\eta^1\text{-}C_{54}H_{36}Cl_2N_4).CH_2Cl_2$		924
1181	$RuC_{70}H_{60}O_{14}P_2$	$Ru(CO)_2(PPh_3)_2\{O_2CCH_2OC_6H_4\text{-}\underline{o}\text{-}O(C_8H_8O_2)\}$		925
1182	$RuC_{72}H_{58}O_{12}P_4$	$\underline{cis}\text{-}Ru\{\underline{o}\text{-}C_6H_4OP(OPh)_2\}_2(P(OPh)_3)_2$		926
1183	$Ru_2C_{12}H_{10}O_8$	$Ru_2(CO)_6(\mu\text{-}O{:}C\text{-}OCEt)_2$	118	927
1184	$Ru_2C_{13}H_{16}N_2O_5$	$Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}N,N{:}\eta^4\text{-}Pr^iNCHCHNPr^i)$		928
1185	$Ru_2C_{14}H_{12}O_3$	$Ru_2(CO)_2(Cp)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$		929
1186	$Ru_2C_{15}H_{10}O_3$	$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2H_2)(\mu\text{-}\eta^5{:}\eta^5\text{-}fulv)$		630
1187	$[Ru_2C_{15}H_{21}O_3]^+$	$[Ru_2(\eta\text{-}C_6H_6)_2(\mu\text{-}OMe)_3][BPh_4]$		121
1188	$Ru_2C_{17}H_{34}N_2O_{13}P_4$	$Ru_2(CO)_4(\mu\text{-}CO)[\mu\text{-}EtN(P(OMe)_2)_2]$		930
1189	$[Ru_2C_{18}H_{27}O_3]^+$	$[Ru_2(\eta\text{-}Mes)_2(\mu\text{-}OH)_3][Cl].3H_2O$		123
1190	$Ru_2C_{24}H_{26}F_{12}O_9$	$(cod)_2Ru_2(TFAcO)_2(\mu\text{-}TFAcO)_2(\mu\text{-}OH_2)$		931
1191	$Ru_2C_{25}H_{36}N_6$	$(cod)(pzH)Ru(\mu\text{-}H)(\mu\text{-}pz)_2RuH(cod)$		932
1192	$Ru_2C_{30}H_{66}$	$Ru_2(CH_2CMe_3)_6$		933
1193	$Ru_2C_{32}H_{22}O_{12}$	$\{Ru(CO)_2(PhCO_2H)\}_2(\mu\text{-}O_2CPh)_2$		934
1194	$[Ru_2C_{37}H_{33}OP_2]^+$	$[(Cp)_2Ru_2(\mu\text{-}CH)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$	200	935
1195	$Ru_2C_{50}H_{36}O_3$	$Ru_2(CO)_2(\mu\text{-}CO)(\eta^4\text{-}C_4Ph_4)(Cp)(\mu\text{-}\eta^1{:}\eta^2\text{-}CPh{=}CHPh)$		915
1196	$Ru_2C_{64}H_{54}N_4O_4P_2$	$Ru_2Ph_2(\mu\text{-}O{:}N\text{-}PhCONH)_2(\mu\text{-}P{:}\mu N\text{-}NCPhOPPh_2)_2$		936
1197	$Ru_2ZrC_{24}H_{20}O_4$	$\{(Cp)(OC)_2Ru\}_2Zr(Cp)_2$		937
1198	$Ru_3C_9HIO_9$	$Ru_3(\mu\text{-}H)(\mu_3\text{-}I)(CO)_9$	115	938
1199	$Ru_3C_{10}I_2O_{10}$	$Ru_3(CO)_{10}(\mu\text{-}I)_2$	115	938
1200	$Ru_3C_{10}HBrO_{10}$	$Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Br)$	115	938
1201	$Ru_3C_{14}H_9NO_9$	$Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^3\text{-}H_2CCCNMe_2)$		939
1202	$Ru_3C_{15}H_7NO_9$	$Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)$		940
1203	$Ru_3C_{17}H_7NO_{10}$	$Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NCHPh)$		941,942
1204	$Ru_3C_{21}H_{10}N_2O_9$	$Ru_3(\mu_3\text{-}NPh)_2(CO)_9$		943
1205	$Ru_3C_{26}H_{19}O_8P$	$Ru_3(CO)_8(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CPr^i{=}C{=}CH_2)$		944

No.	Formula	Structure	Details	Ref.
1206	$Ru_3C_{26}H_{21}O_7P$	$Ru_3(CO)_7(\mu\text{-}CH_2)(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}CPr^i{=}C{=}CH_2)$		944
1207	$Ru_3C_{26}H_{21}O_7P$	$Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}PPh_2)\{\mu_3\text{-}\eta^2:\eta^3:\eta^1\text{-}CH_2{=}CCPr^i{=}CH\}$		944
1208	$Ru_3C_{30}H_{22}NO_{13}P$	$Ru_3(\mu\text{-}H)(CO)_9\{P(OPh)_3\}(\mu\text{-}O{:}C\text{-}OCNMe_2)$	115	945
1209	$Ru_3C_{35}H_{21}O_9P$	$Ru_3(\mu\text{-}H)(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Ph_2).0.5C_2Ph_2$		946
1210	$Ru_3C_{35}H_{22}O_{10}P_2$	$Ru_3(CO)_{10}(\mu\text{-dppm})$		947
1211	$Ru_3C_{43}H_{31}O_7P_3$	$Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}PPh_2)_3$		948
1212	$[Ru_4C_{24}H_{28}O_5]^{2+}$	$[\{(\eta\text{-}C_6H_6)_2Ru_2(\mu\text{-}OH)_2\}_2(\mu_4\text{-}O)][BPh_4]_2.2Me_2CO$		123
1213	$Ru_4C_{28}H_{27}O_8P$	$Ru_4(CO)_3\{P(OMe)_3\}(\mu\text{-}CO)_2(Cp)_2(\mu_3\text{-}\eta^1:\eta^1:\eta^5\text{-}C_5H_4)$		949
1214	$Ru_4C_{29}H_{16}O_{11}$	$Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^1:\mu\eta^2:\eta^1\text{-}PhCCMe)_2$		950
1215	$Ru_4C_{38}H_{52}N_4O_{10}$	$[Ru_2(CO)_4\{\mu_3\text{-}\eta^5:N{:}\mu O\text{-}C_5(O)Me_2(NEt_2)_2\}]_2$		395
1216	$Ru_4C_{46}H_{35}O_9P_3$	$Ru_4(\mu\text{-}H)_4(CO)_9\{(Ph_2P)_3CH\}$		951
1217	$Ru_4C_{46}H_{56}O_{20}$	$\{Ru(CO)_2(RCO_2H)(\mu\text{-}RCO_2)(\mu_3\text{-}RCO_2)\}_2$	R=CHMeEt	934
1218	$Ru_5C_{35}H_{24}O_{12}P_2$	$Ru_5(CO)_{12}(\mu_3\text{-}CCH_2Pr^i)(\mu\text{-}PPh_2)(\mu_4\text{-}PPh)$		952
1219	$Ru_5C_{40}H_{26}O_{10}P_4$	$Ru_5(\mu_3\text{-}H)(CO)_{10}(\mu\text{-}PPh_2)(\mu_3\text{-}PPh)(\mu_4\text{-}PPh)_2.0.5PhH$		952
1220	$Ru_5C_{48}H_{25}O_{12}P$	$Ru_5(CO)_{12}(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}PhCCC_2Ph)(\mu_5\text{-}\eta^2\text{-}CCPh)$		946
1221	$[Ru_{12}TlC_{33}O_{32}]^-$	$[AsPh_4][\{Ru_6C(CO)_{16}\}_2Tl]$		39
1222	$SbC_7H_{13}O_4S_2$	$SbMe(S_2COEt)_2$		953
1223	$Sb_2C_4H_{12}$	Sb_2Me_4	113,134,252K	954,955
1224	$Sb_2C_5H_{14}Br_4$	$CH_2(SbBr_2Me_2)_2$	173	956
1225	$Sb_2C_5H_{14}Cl_4$	$(Me_2Cl_2Sb)_2CH_2.CH_2Cl_2$	173	957
1226	$Sb_2C_{22}H_{26}O_{10}$	$[SbMe(EtOH)\{\mu\text{-}o\text{-}C_6H_4(CO_2)_2\}]_2$		958
1227	$Sb_2C_{32}H_{32}O_9$	$\{Ph_2Sb(OAc)\}_2O$		959
1228	$Sb_2C_{43}H_{35}P$	$Ph_3P{=}C(SbPh_2)_2$		960
1229	$Sb_2Si_2C_8H_{18}Cl_8N_4$	$Sb_2Cl_8(\mu\text{-}NCNSiMe_3)_2$		961
1230	$Sb_4C_{54}H_{52}O_{12}$	$Ph_8Sb_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2.HOAc.CH_2Cl_2$		959
1231	$SeC_5H_{11}NO_2$	$MeSeCH_2CH_2CH(NH_3)CO_2$		962
1232	$SeC_8H_6N_2O_2$	$p\text{-}O_2NC_6H_4CH_2SeCN$		963
1233	SeC_6H_7N	$PhCH_2SeCN$		963
1234	$[SeC_{10}H_{13}]^+$	$[PhCH_2C(SeMe)_2][SbCl_6]$	173	964
1235	$SeC_{12}H_{10}Cl_2O_2$	$SeC_6H_4\text{-}o\text{-}C(OCOMe)CHClCHClCH$		965

No.	Formula	Structure	Details	Ref.
1236	$SeWC_{12}H_6O_5$	$W(CO)_5(\eta^2\text{-}SeCHPh)$		966
1237	$Se_2C_{14}H_{14}$	$Se_2(pTol)_2$		967
1238	$Se_2ZrC_{24}H_{30}$	$Zr(\underline{o}\text{-}Se_2C_6H_4)(\eta\text{-}C_5H_4Bu^t)_2$		968
1239	Se_4CBr_2	$Br_2SeCSeSeSe$		969
1240	$Se_4C_6H_4$	$[TSeF)_3][ClO_4]_2$		970
1241	$Se_4C_{10}H_4$	1,8:4,5-bis(Se_2)naphthalene		971
1242	$Se_4C_{10}H_{12}$	$[(TMSF)_2][SiF_5]$	125	972
1243	$Se_4C_{10}H_{12}$	$[(TMSF)_2][ReO_4]$	120	973
1244	$Se_4C_{18}H_8$	$(TSeT)_2[Hg_2I_6]$		974
1245	$Se_6C_{36}H_{16}O_4$	5,5′,12,12′-(Se_3naphthacene-6,11-quinone)$_2$.PhCN		975
1246	$Se_6C_{42}H_{30}$	$C_6(SePh)_6.2CBr_4$		976
1247	$SiC_3H_3F_3$	$H_3SiC{\equiv}CCF_3$	E	977
1248	$SiC_3H_{11}N$	$MeSiH_2NMe_2$	E	978
1249	$SiC_4H_{13}N$	$Me_2SiHNMe_2$	E	978
1250	$SiC_6H_{12}S_4$	$Me_2SiCH_2CHS_4CHCH_2$		979
1251	$SiC_7H_{12}ClNO_4$	$ClCH_2SiOC(O)CH_2N(CH_2CH_2O)_2$		980
1252	$SiC_8H_{19}FO$	$SiF(OH)Bu^t.C_5H_5NO$	153	981
1253	$SiC_8H_{20}O_2$	$Bu^t_2Si(OH)_2$		982
1254	$[SiC_9H_{20}NO_3S]^+$	$[N(CH_2CH_2O)_3Si(CH_2SMe_2)]I$	153	983
1255	$[SiC_{10}H_{13}O_4]^-$	$[NH_3(CH_2)_6NH_3][SiPh(OCH_2CH_2O)_2]_2$		984
1256	$SiC_{10}H_{18}N_2O_3$	$N(CH_2CH_2O)_3Si(CH_2)_3CN$		985
1257	$SiC_{10}H_{18}N_2O_3S$	$N((CH_2)_2O)_3Si(CH_2)_3SCN$		986
1258	$[SiC_{12}H_{10}F_3]^-$	$[NMe_4][SiF_3Ph_2]$		987
1259	$SiC_{14}H_{28}N_4$	$Si(CH_2CMeNNBu^t)_2$		988
1260	$SiC_{15}H_{14}Br_2FN$	$MeFSiCH_2(5\text{-}BrC_6H_3\text{-}2)_2NMe$		989
1261	$SiC_{15}H_{33}NP_2S_2$	$Bu^tPC(NMe_2)=C(SSiMe_3)P(S)Bu^t$		990
1262	$SiC_{16}H_{14}S_2$	$Me_2Si(\underline{o}\text{-}C_6H_4CH_2SSCH_2C_6H_4\text{-}\underline{o})$		991
1263	$SiC_{17}H_{23}NOS$	$Si(OH)Ph(CH_2SCH_2CH_2NMe_2)$		992
1264	$[SiC_{18}H_5Cl_8O_4]^-$	$[NEt_4][SiPh(\underline{o}\text{-}O_2C_6Cl_4)_2]$		984
1265	$[SiC_{18}H_{11}ClO_4]^-$	$[pyH][Si(C_6H_4Cl)(\underline{o}\text{-}O_2C_6H_4)_2]$		993

No.	Formula	Structure	Details	Ref.
1266	$SiC_{18}H_{13}ClS$	$S(\underline{o}\text{-}C_6H_4)_2SiH(\underline{p}\text{-}C_6H_4Cl)$		994
1267	$SiC_{18}H_{23}NO_2$	$Si(OH)Ph_2(CH_2CH_2NCH_2CH_2OCH_2CH_2)$		995
1268	$SiC_{19}H_{15}ClN_2O_2$	$SiClMe(quin)_2$		996
1269	$SiC_{19}H_{16}OS$	$S(\underline{o}\text{-}C_6H_4)_2SiH(\underline{p}\text{-}C_6H_4OMe)$		994
1270	$SiC_{19}H_{16}S$	$S(\underline{o}\text{-}C_6H_4)_2SiH(pTol)$		994
1271	$SiC_{19}H_{18}S$	Ph_3SiSMe		448
1272	$SiC_{19}H_{25}NO_2$	$Si(OH)Ph_2(CH_2CH_2CH_2NCH_2CH_2OCH_2CH_2)$		997
1273	$SiC_{20}H_{28}N_4$	$SiMe_2\{N(Ph)NCMe_2\}_2$		998
1274	$SiC_{21}H_{20}O_2S$	$S(\underline{o}\text{-}C_6H_4)_2Si(OEt)(\underline{p}\text{-}C_6H_4OMe)$		999
1275	$[SiC_{22}H_{15}O_4]^-$	$[pyH][Si(naphth)(\underline{o}\text{-}O_2C_6H_4)_2]$		993
1276	$SiC_{22}H_{27}N_4OPS$	$Ph_2SiNMeNMeP(S)(OPh)NMeNMe$		1000
1277	$SiC_{24}H_{18}O$	$O(\underline{o}\text{-}C_6H_4)_2SiPh_2$		1001
1278	$SiC_{24}H_{18}S$	$S(\underline{o}\text{-}C_6H_4)_2SiPh_2$		1001
1279	$SiC_{24}H_{38}P_2$	$Bu^t_2PPh_2{=}CHSiMe_3$		1002
1280	$[SiC_{26}H_{17}O_4]^-$	$[pyH][SiPh(\underline{o}\text{-}O_2C_{10}H_6)_2]$		993
1281	$SiC_{30}H_{16}F_{12}N_2O_2$	$Si(\underline{o}\text{-}C_6H_4C(CF_3)_2O)_2(phen)$		1003
1282	$SiC_{30}H_{26}NP$	$Ph_3SiNHPPh_2$	233	1004
1283	$SiC_{31}H_{38}S$	$(Mes)_2SiSCCMe_2C_6H_4CMe_2\text{-}\underline{o}$		1005
1284	$SiSnC_{16}H_{20}$	$Me_2Sn(\mu\text{-}\underline{o}\text{-}C_6H_4)_2SiMe_2$		456
1285	$SiTiC_{14}H_{20}$	$Ti(CH_2SiMe_2CH_2)_2(Cp)_2$		1006
1286	$SiWC_{27}H_{43}I_2N_2P_3$	$\underline{mer}\text{-}WI_2(NNSiMe_3)_2(PMe_2Ph)_3$		1007
1287	$SiWC_{35}H_{53}IN_2P_4$	$\underline{trans}\text{-}WI(NNSiMe_3)_2(PMe_2Ph)_4$		1007
1288	$SiZrC_{14}H_{20}$	$Zr(CH_2SiMe_2CH_2)_2(Cp)_2$		631
1289	$SiZrC_{15}H_{22}O$	$Zr(CH_2SiMe_2CH_2CH_2O)_2(Cp)_2$		1008
1290	$Si_2C_4H_{15}N$	$HN(SiMe_2H)_2$	E	1009
1291	$Si_2C_7H_{19}NO_2$	$Me_3SiOC(O)NHSiMe_3$		1010
1292	$Si_2C_9H_{21}NO_3$	$Me_2SiOCH_2CH_2N(CH_2CH_2O)_2SiMe$	143	1011
1293	$Si_2C_{16}H_{29}PS$	$(Me_3Si)_2C{=}P(S)(Mes)$		1012
1294	$Si_2C_{16}H_{29}PS_2$	$(Me_3Si)_2CSP(S)(Mes)$		1012
1295	$Si_2C_{20}H_{45}FO_3$	$(Bu^t_2SiOSiFBu^tOSiBu^t_2)(\mu\text{-}O)$		982

No.	Formula	Structure	Details	Ref.
1296	$Si_2C_{20}H_{46}N_2$	$Pr^i_2SiNBu^tSiPr^i_2NBu^t$		1013
1297	$Si_2C_{24}H_{24}O$	$Ph_3SiOSi(CH{=}CH_2)_3$		1014
1298	$Si_2C_{25}H_{47}P$	$(Me_3Si)_2C{=}P(2,4,6\text{-}Bu^t_3C_6H_2)$		686
1299	$Si_2C_{26}H_{26}$	$\{(naphth)SiCH_2CH_2CH_2\}_2\text{-}(\underline{Si}\text{-}\underline{Si})$		1015
1300	$Si_2C_{26}H_{40}$	<u>trans</u>-$Si_2Bu^t_2Mes_2$	248	1016
1301	$Si_2C_{29}H_{39}OP$	$(Me_3Si)_2C{=}PPh_2C(O)Mes$		1002
1302	$Si_2C_{32}H_{62}N_6$	$\{H_2C(CH_2CMe_2)_2NSiCHCMeNNBu^t\}_2$		988
1303	$Si_2C_{36}H_{30}$	$Si_2Ph_6.Pb_2Ph_6$		455
1304	$Si_2C_{36}H_{30}O$	$(Ph_3Si)_2O.2PhH$		1017
1305	$Si_2C_{36}H_{44}$	$Si_2Mes_4.PhMe$	188	1016
1306	$Si_2C_{36}H_{44}O_2$	$\{Si(Mes)_2(\mu\text{-}O)\}_2.PhMe$		1018
1307	$Si_2C_{40}H_{52}$	$Si_2(2,6\text{-}Et_2C_6H_3)_4$		1019
1308	$Si_2SnC_{32}H_{38}$	$Ph_2Sn\{CH(SiMe_3)C_6H_4\text{-}\underline{o}\}_2$		1020
1309	$Si_2TeC_{20}H_{30}Cl_2$	$TeCl_2(\underline{p}\text{-}C_4H_4CH_2SiMe_3)_2$		1021
1310	$Si_2TiC_{16}H_{26}S_5$	$Ti(S_5)(\eta\text{-}C_5H_4SiMe_3)_2$		1022
1311	$Si_2Zn_2C_{21}H_{33}N$	$\{Zn(\eta^1\text{-}C_5H_5)\}_2\{\mu\text{-}N(SiMe_3)_2\}(\mu\text{-}\eta^1{:}\eta^1\text{-}C_5H_5)$		1023
1312	$Si_2ZrC_{24}H_{34}$	$Zr\{\underline{o}\text{-}CH(SiMe_3)C_6H_4CHSiMe_3\}(Cp)_2.1.3PhH$		1024
1313	$Si_3C_5H_{10}Cl_7P$	$Me_2ClPC(SiCl_2CH_2)_2SiCl_2$		1025
1314	$Si_3C_6H_{18}O_3$	$\{SiMe_2(\mu\text{-}O)\}_3$	108	1026
1315	$Si_3C_{10}H_{29}P$	$(Me_3Si)_3CPH_2$	E	1027
1316	$Si_3C_{11}H_{28}BrP$	$Me_2BrPC(SiMe_2CH_2)_2SiMe_2$		1025
1317	$Si_3C_{12}H_{30}F_3N_3$	<u>cis</u> & <u>trans</u> $Bu^tSiFNHSiBu^tFNHSiBu^tFNH$		1028
1318	$Si_3C_{18}H_{44}O_4$	$Bu^t_2Si(OH)OSiMe_2OSi(OH)Bu^t_2$		982
1319	$Si_3C_{19}H_{44}O$	$(Bu^t_2MeSi)(Me_3Si)C{=}SiMe_2(THF)$	228	1029
1320	$Si_3C_{24}H_{30}$	$\{Me_2Si(\underline{o}\text{-}C_6H_4)\}_3$		1030
1321	$Si_3C_{24}H_{54}$	$(Bu^t_2Si)_3$		1031
1322	$Si_3C_{24}H_{57}N_3$	$Bu^t_2SiNHSiBu^t_2NHSiBu^t_2NH$		1032
1323	$Si_3C_{25}H_{34}$	$(PhMe_2Si)_3CH$		1033
1324	$Si_3C_{30}H_{66}$	$Si_3(CH_2Bu^t)_6$		1034
1325	$Si_3C_{39}H_{36}$	$\{Ph_2Si(\mu\text{-}CH_2)_3\}$		1035

No.	Formula	Structure	Details	Ref.
1326	$Si_3ThC_{28}H_{52}$	$Th(CH_2SiMe_3)_2\{(\eta\text{-}C_5Me_4)_2SiMe_2\}$		1036
1327	$Si_4C_9H_{26}O_3$	$Me_2SiOSiMe_2OSiMe_2CHSiMe_2(OH)$		1037
1328	$Si_4C_{12}H_{30}Cl_2$	$\{Me_2SiCCl(SiMe_3)\}_2$		1038
1329	$Si_4C_{16}H_{36}$	$(Me_3Si)MeSi\{C(Me)C(Me)\}_2SiMe(SiMe_3)$		
		<u>cis</u> & <u>trans</u> isomers	208,218	1039
1330	$Si_4C_{22}H_{37}NO_3$	$Ph_2MeSiC(SiMe_3)_2SiMe_2ONO_2$		1040
1331	$Si_4C_{39}H_{58}P_2$	$(Me_3Si)_2C{=}PPh_2C{=}PPh_2CH(SiMe_3)_2$		1002
1332	$Si_4C_{76}H_{62}N_{16}O_3$	$\{Bu^tMe_2SiOSi(Pc)\}_2(\mu\text{-}O)$		1041
1333	$Si_4TaC_{16}H_{45}ClN_3$	$TaCl(NBu^t)\{N(SiMe_3)_2\}_2$		1042
1334	$Si_4WC_2H_{16}Cl_{18}$	$WCl_3(\mu\text{-}Cl)\{\eta^2\text{-}C_2(SiMe_3)_2\}$		1043
1335	$Si_4ZnC_{12}H_{36}N_2$	$\{(Me_3Si)_2N\}_2Zn$	E	1044
1336	$Si_5C_{20}H_{40}$	$\{(CH_2)_4Si\}_5\text{-}(\underline{Si}\text{-}\underline{Si})$	188	1045
1337	$Si_5C_{25}H_{50}$	$\{(CH_2)_5Si\}_5\text{-}(\underline{Si}\text{-}\underline{Si})$	183	1045
1338	$Si_5C_{28}H_{46}$	$(Me_3Si)_2SiC(=CPhSiMe_3)CPh{=}CSiMe_3$		1046
1339	$Si_6C_{20}H_{54}P_2$	$(Me_3Si)_3CP{=}PC(SiMe_3)_3$		60,1047
1340	$Si_6SnC_{28}H_{58}$	$Sn\{\eta^5\text{-}1,2,4\text{-}C_5H_2(SiMe_3)_3\}_2$		1048
1341	$Si_6TaC_2H_{18}Br_4N_4$	$[TaBr(\mu\text{-}Br)(NSiMe_3)\{N(SiMe_3)_2\}]_2$		1042
1342	$Si_6WC_2H_{38}$	$W_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)(\mu\text{-}\eta^3\text{-}CPhCPhCSiMe_3)$	113	1049
1343	$Si_8C_{18}H_{40}$	Me_8-octasilaheptacyclooctadecane		1050
1344	$Si_8C_{22}H_{56}$	$\{Me_2Si(CH_2SiMe_2)_2C(\mu\text{-}SiMe_2)\}_2$		1051
1345	$Si_8C_{28}H_{78}N_6$	$(Me_3SiNMe)_2SiN(SiMe_2Bu^t)SiMe(NMeSiMe_3)N\text{-}SiBu^tNMeSiMe_3$		1052
1346	$Si_8TiC_{96}H_{80}O_{10}$	$Ti\{O(SiPh_2O)_3SiPh_2O\}_2$		1053
1347	$SmC_{20}H_{30}$	$Sm(\eta\text{-}C_5Me_5)_2$		1054
1348	$[SnC_2H_6Cl_4]^{2-}$	$[\underline{o}\text{-}C_6H_4(NH_3)(CONH_2)]_2[SnCl_4Me_2].2H_2O$	138	1055
1349	$SnC_5H_{15}OPS$	$[Me_3Sn(\mu\text{-}O{:}S\text{-}(O)P(S)Me_2)]_n$		1056
1350	$SnC_6H_{14}NS_2$	$SnMe_2\{(SCH_2CH_2)_2NMe\}$		1057
1351	$SnC_6H_{16}O_2S_4$	$SnMe_2(S_2COEt)_2$		1058
1352	$[SnC_8H_{10}FOS]^-$	$[NEt_4][SnFMe_2(\underline{o}\text{-}OC_6H_4S)]$		1059
1353	$[SnC_8H_{10}IOS]^-$	$[PPh_4][SnIMe_2(\underline{o}\text{-}OC_6H_4S)]$		1059

No.	Formula	Structure	Details	Ref.
1354	$SnC_8H_{22}Cl_2N_4S_2$	trans-$SnCl_2Me_2(SC(NHMe)_2)_2$		1060
1355	$[SnC_9H_{10}ClO_2S]^-$	$[NEt_4][SnClMe_2(o\text{-}OCOC_6H_4S)]$		1059
1356	$SnC_{10}H_{18}ClNO$	$SnClMe_3(ONC_5H_3Me_2\text{-}2,6)$		1061
1357	$SnC_{10}H_{18}Cl_2N_4$	$SnCl_2Me_2(Meimid)_2$		1062
1358	$SnC_{10}H_{22}O_2$	$(SnBu_2(\mu\text{-}OCH_2CH_2O))_n$		1063
1359	$SnC_{12}H_{10}Cl_2$	$Ph_2SnCl_2.0.75pyz$		1064
1360	$[SnC_{12}H_{10}N_2O_7Br]^-$	$[Ag(PPh_3)_4][SnPh_2(NO_3)_2X]$ X=0.5Cl,0.5NO_3		1065
1361	$SnC_{13}H_{29}NO_2$	$SnBu^t_2((OCH_2CH_2)_2NMe)$		1057
1362	$SnC_{14}H_{42}Cl_2N_6O_2P_2$	trans-$SnCl_2Me_2(OP(NMe_2)_3)_2$		1066
1363	$[SnC_{15}H_{20}N]^+$	$[Sn(\eta\text{-}C_5Me_5)(py)][CF_3SO_3]$		1067
1364	$SnC_{18}H_{17}ClO$	$SnClPh_3(OH_2)$.diphenyltriazinephen		1068
1365	$SnC_{18}H_{17}ClO$	$SnClPh_3(OH_2)$.phen		1069
1366	$SnC_{18}H_{26}Cl_2N_4S_2$	trans-$SnCl_2Ph_2(SC(NHMe)_2)_2$		1060
1367	$SnC_{19}H_{18}S$	Ph_3SnSMe		448
1368	$SnC_{19}H_{19}Cl_2NO$	$SnCl_2Ph_2(ONC_5H_3Me_2\text{-}2,6)$		1061
1369	$SnC_{20}H_{18}$	$SnPh_3(CH{=}CH_2)$		1070
1370	$SnC_{20}H_{18}O_2$	$SnPh_3(OAc)$		1071
1371	$[SnC_{20}H_{23}N_2]^+$	$[Sn(\eta\text{-}C_5Me_5)(bipy)][CF_3SO_3]$		1067
1372	$SnC_{22}H_{24}Cl_3P$	$SnCl_3Bu(PPh_3)$		1072
1373	$[SnC_{22}H_{39}N_2]^+$	$[Sn(Cy)_3(NCMe)_2][SbF_6]$	173	1073
1374	$SnC_{23}H_{27}ClN_2O$	$SnClPh_3(OC(NMe_2)_2)$		1060
1375	$SnC_{25}H_{20}O_3$	$SnPh_3(o\text{-}O_2CC_6H_4OH)$		1074
1376	$SnC_{25}H_{21}NO_2$	$SnPh_3(o\text{-}O_2CC_6H_4NH_2)$		1075
1377	$SnC_{25}H_{21}NO_2$	$SnPh_3(p\text{-}O_2CC_6H_4NMe_2).0.5PhH$		1075
1378	$SnC_{25}H_{28}N_2O_2$	$SnEtPr(2\text{-}Mequin)_2$		1076
1379	$SnC_{26}H_{22}$	$Ph_2Sn((CH_2C_6H_4\text{-}o)_2)$		1020
1380	$SnC_{26}H_{22}O_2S$	$Ph_3Sn(p\text{-}O_2CC_6H_4SMe)$		1074
1381	$SnC_{26}H_{22}O_3$	$Ph_3Sn(o\text{-}O_2CC_6H_4OMe)$		1074
1382	$SnC_{27}H_{25}NO_2$	$SnPh_3(o\text{-}O_2CC_6H_4NMe_2)$		1075
1383	$SnC_{27}H_{30}ClN_7O_2$	SnBuCl(dapa)		1077

No.	Formula	Structure	Details	Ref.
1384	$SnC_{29}H_{32}F_6O_3$	$Sn(\underline{o}\text{-}C_6H_4CF_3)_2(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}4,6)_2.MeOH$	173	1078
1385	$SnC_{30}H_{24}BrOPS_3$	$Sn(CCHSCHCH)_3Br(OPPh_3)$		1079
1386	$SnC_{35}H_{31}N_7O_2$	$SnPh_2(dapa)$		1077
1387	$SnC_{36}H_{28}$	$Sn(\eta^1\text{-ind})_4$		450
1388	$SnC_{44}H_{43}N_3O_2$	$Bu^t_2SnCPhCPhCPhCPhCNC(O)NPhCO.H_2O$		1080
1389	$SnC_{70}H_{50}$	$Sn(\eta^5\text{-}C_5Ph_5)_2$	138	1081
1390	$[SnWC_{60}H_{45}]^-$	$[NEt_4][W(\eta\text{-}C_2Ph_2)_3(SnPh_3)]$		1082
1391	$Sn_2C_7H_{16}Br_4OS$	$Me_2Br_2Sn_2(\mu\text{-}Br)_2(\mu\text{-}CHCH_2CH_2SEtO)$		1083
1392	$Sn_2C_7H_{16}Cl_4OS$	$Me_2Cl_2Sn_2(\mu\text{-}Cl)_2(\mu\text{-}CHCH_2CH_2SEtO)$		1083
1393	$Sn_2C_9H_{22}Br_2OS$	$Me_2BrSn(\mu\text{-}Br)(\mu\text{-}CHCH_2CH_2SEtO)SnMe_2$		1083
1394	$Sn_2C_9H_{22}Cl_2OS$	$Me_2ClSn(\mu\text{-}Cl)(\mu\text{-}CHCH_2CH_2SEtO)SnMe_2$		1083
1395	$Sn_2C_{16}H_{40}Cl_4O_8$	$[\{SnClMe_2(OH_2)(\mu\text{-}Cl)\}_2(18\text{-crown-}6)]_n$	120	1084
1396	$Sn_2C_{23}H_{34}N_2S_4$	$H_2C(SnPh(SCH_2CH_2)_2NMe)_2$		1085
1397	$Sn_2C_{31}H_{40}Br_2N_3OP$	$Ph_2Br_2Sn_2(\mu\text{-}CH_2)SnPh_2(HMPT)$		1086
1398	$Sn_2C_{31}H_{40}Cl_2N_3OP$	$Ph_2Cl_2Sn_2(\mu\text{-}CH_2)SnPh_2(HMPT)$		1086
1399	$Sn_2C_{36}H_{26}Cl_2S_4$	$\{Ph_2Sn_2(\mu\text{-}1,3,4\text{-}S_2ClC_6H_3)\}_2$		1087
1400	$Sn_2C_{36}H_{58}$	$PhSn\{\mu\text{-}(CH_2)_8\}_3SnPh$		1088
1401	$Sn_3C_{24}H_{54}O_3$	$(Bu^t_2SnO)_3$		1089
1402	$Sn_3C_{30}H_{66}O_3$	$\{(EtMe_2C)_2SnO\}_3$		1089
1403	$Sn_4C_8H_{24}Cl_4O_2$	$\{Sn_2Me_4(\mu\text{-}Cl)(\mu_3\text{-}O)\}_2$		1090
1404	$Sn_4C_{12}H_{32}$	$CHMe(SnMe_2SnMe_2)_2CHMe$		1091
1405	$Sn_4C_{16}H_{32}Cl_4O_{10}$	$[\{Me_2Sn(\mu\text{-}O_2CCH_2Cl)\}_2(\mu_3\text{-}O)]_2$		1092
1406	$Sn_4C_{48}H_{40}Cl_4O_2$	$\{Sn_2Ph_4Cl(\mu\text{-}Cl)(\mu_3\text{-}O)\}_2$		1093
1407	$Sn_4C_{48}H_{42}Cl_2O_4$	$\{Sn_2Ph_4Cl(\mu\text{-}OH)(\mu_3\text{-}O)\}_2.2Me_2CO$		1093
1408	$Sn_6C_{72}H_{60}$	$(Ph_2Sn)_6\text{-}(\underline{Sn}\text{-}\underline{Sn})$	185	1094
1409	$Sn_6C_{72}H_{60}$	$(Ph_2Sn)_6.2PhMe$		1095
1410	$Sn_6C_{84}H_{84}$	$\{(CH_2Ph)_2Sn\}_6.DMF$		1094
1411	$TaZnC_2H_{22}25$	$TaH\{Zn(Cp)\}_2(\eta\text{-}C_5H_4Me)_2$		1096
1412	$Ta_2C_{24}H_{42}Cl_6N_6$	$(Pr^iNC)_4Cl_2Ta\{\mu\text{-}\eta^2\text{:N,N-}C_2(NPr^i)_2\}TaCl_4$		666
1413	$TeC_8H_6N_2O_2$	$\underline{p}\text{-}O_2NC_6H_4CH_2TeCN$		963

No.	Formula	Structure	Details	Ref.
1414	$[TeC_{9}H_{11}]^{+}$	$[MeTe(o\text{-}CH_2C_6H_4CH_2)][BPh_4]$		118
1415	$TeC_{10}H_8I_2N_2$	2-TeI_2-H quinoxaline.2,3-$(ICH_2)_2$quinoxaline		1097
1416	$TeC_{10}H_8N_2$	o-$C_6H_4NCHCH_2TeCH_2CHN$		1098
1417	$[TeC_{10}H_{13}]^{+}$	$[PhTeCH_2CH_2CH_2CH_2][BPh_4]$		118
1418	$TeC_{12}H_8$	$Te(2,2'\text{-}(C_6H_4)_2).TCNQ$		1099
1419	$[TeC_{12}H_9Cl_4O]^{-}$	$[NH_2Et_2][TeCl_4(p\text{-}C_6H_4OPh)]$		1100
1420	$TeC_{12}H_{10}I_2$	Ph_2TeI_2		1101
1421	$TeC_{14}H_{14}Cl_2O_2$	$TeCl_2(C_6H_3Me(OH)\text{-}3,4)_2$	1102,1103	
1422	$TeC_{16}H_{10}F_6O_4$	$Ph_2Te(OTFAc)_2$		1104
1423	$TeC_{17}H_{11}Br_3O_2$	$TeBr_2(C(CBrCPhO)(CHCPhO))$		1105
1424	$TeC_{17}H_{12}O_2$	$Te(CCHCPhO)_2$		1105
1425	$TeC_{18}H_8F_{12}O_2$	$Te(o\text{-}C_6H_4C(CF_3)_2O)_2$		1106
1426	$[TeC_{18}H_{15}]^{+}$	$[TePh_3]_2[Hg_2Cl_6]$		1107
1427	$TeC_{18}H_{20}F_2O_2$	$TeF_2(o\text{-}C_6H_4CMe_2O)_2$		1106
1428	$TeC_{18}H_{20}O_6$	$Te(p\text{-}C_6H_4OMe)_2(OAc)_2$		1108
1429	$Te_2C_{12}H_8Cl_2$	$Te_2(p\text{-}ClC_6H_4)_2$		1109
1430	$Te_2C_{12}H_{10}I_6$	cis & trans-$(TeI_2Ph)_2(\mu\text{-}I)_2$	173	1101
1431	$Te_2C_{20}H_{20}F_6O_5$	$\{Ph_2Te(O_2CCF_3)\}_2.0.5H_2O$		1108
1432	$Te_4C_{14}H_{12}S_2$	$(Me_2thieno)_2Te_4$fulvalene		1110
1433	$Te_4C_{24}H_{60}Br_4$	$\{Et_3Te(\mu\text{-}Br)\}_4$		1111
1434	$ThC_{34}H_{44}P_2$	$Th(CH_2Ph)_4(dmpe)$		1112
1435	$TiC_5H_5Cl_3$	$TiCl_3(Cp)$		1113
1436	$TiC_{10}H_{10}S_5$	$(Cp)Ti(\eta^4C_2S_2\text{-}C(S)CH(SS_2)CH_2CH_2CS)$		1114
1437	$TiC_{11}H_{17}Cl_3$	$TiCl_3(\eta\text{-}C_5Me_4Et)$		1115
1438	$TiC_{12}H_{12}$	$Ti(\eta\text{-}C_6H_6)_2$		1116
1439	$TiC_{14}H_{16}$	$Ti(\eta\text{-}C_6H_5Me)_2$		1116
1440	$TiC_{14}H_{16}O_2$	$Ti(OCH{=}CH_2)_2(Cp)_2$		1117
1441	$TiC_{14}H_{20}Cl_2N_2$	$TiCl_2(\eta\text{-}C_5H_4NMe_2)_2$		1118
1442	$TiC_{15}H_{13}ClN_4$	TiCl(purinato)$(Cp)_2$		1119
1443	$TiC_{17}H_{24}S_4$	$Ti(SSCH_2SS)(\eta\text{-}C_5H_4Pr^i)_2$		1120

No.	Formula	Structure	Details	Ref.
1444	$TiC_{18}H_{18}$	$Ti\{o\text{-}(CH_2)_2C_6H_4\}(Cp)_2$		472
1445	$TiC_{18}H_{26}Cl_2$	$TiCl_2(\eta\text{-}C_5H_4Bu^t)_2$		1121
1446	$TiC_{18}H_{30}P_2$	$Ti(dmpe)(\eta\text{-}C_5H_4Me)_2$		1122
1447	$TiC_{19}H_{21}OPS_3$	$Ti\{SP(S)(p\text{-}C_6H_5OMe)S\}(\eta\text{-}C_5H_4Me)_2$		1123
1448	$[TiC_{28}H_{20}Cl_3]^-$	$[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_3(\eta^4\text{-}C_4Ph_4)]$		1124
1449	$Ti_4C_{36}H_{44}Cl_4O_4$	$\{TiCl(\eta^5\text{-ind})(\mu\text{-}O)\}_4$		1125
1450	$TlC_{19}H_{32}N_2O_3$	$(PrCO_2)Tl\{CCHCMe_2N(O)CMe_2CHCH_2NC_5H_{10}$		479
1451	$UC_{17}H_{41}Cl_3N_6O_2P_2$	$UCl_3\{OP(NMe_2)_3\}_2(Cp)$		1126
1452	$UC_{28}H_{40}P_2$	$UMe(CH_2Ph)_3(dmpe)$		1112
1453	$UC_{31}H_{32}NP$	$U\{NCMeCHPPh_2Me\}(Cp)_3.PhMe$		1127
1454	$UC_{36}H_{39}Cl$	$UCl(\eta^5\text{-1,4,7-Me}_3\text{indenyl})_3$		1128
1455	$UC_{36}H_{40}NP$	$U(\eta^2NC\text{-}CyNCCHPPh_2Me)(Cp)_3$		1129
1456	$UC_{41}H_{35}Cl_3O_2P_2$	$UCl_3(OPPh_3)_2(Cp).THF$		1126
1457	$UC_{47}H_{47}P_3$	$U(CH_2PPh_2CH_2)_3(Cp)$		1130
1458	$U_2C_{42}H_{67}O_2P$	$\{U(OMe)(\eta\text{-}C_5Me_5)_2\}_2(\mu\text{-}PH)$		1131
1459	$VC_{14}H_{22}$	$V(\eta^5\text{-}CH_2CMeCHCMeCH_2)_2$		268
1460	$VC_{16}H_{19}$	$(Cp)_2VC{\equiv}CBu^t$		1132
1461	$VC_{20}H_{28}S$	$(Cp)_2V(\eta^2CS\text{-}S{=}C{=}CBu^t_2)$		1133
1462	$VC_{20}H_{30}$	$V(\eta\text{-}C_5Me_5)_2$		1134
1463	$VC_{21}H_{28}S$	$(Cp)_2V(\eta^2CS\text{-}S{=}C{=}CCMe_2CH_2CH_2CH_2CMe_2)$		1133
1464	$VC_{21}H_{30}N$	$V(CN)(\eta\text{-}C_5Me_5)_2$		1134
1465	$VC_{21}H_{30}O$	$V(CO)(\eta\text{-}C_5Me_5)_2$		1134
1466	$VC_{26}H_{35}N$	$V(NPh)(\eta\text{-}C_5Me_5)_2$		1135
1467	$VC_{27}H_{35}NS$	$V(\eta^2\text{-SCNPh})(\eta\text{-}C_5Me_5)_2$		1136
1468	$VC_{28}H_{41}N_2$	$V(CN)(CNPh)(\eta\text{-}C_5Me_5)_2$		1134
1469	$VC_{31}H_{41}O$	$V(Mes)_3(THF)$		1137
1470	$VC_{44}H_{55}N_2S_2$	$V\{NPhC(C_5Me_5)S\}_2(\eta\text{-}C_5Me_5)$		1136
1471	$VWC_{25}H_{22}O_2$	$(Cp)_2VW(CO)_2(Cp)\{\mu\text{-}C(pTol)\}$		1138
1472	$V_2C_{14}H_{18}S_4$	$[\{V(Cp)\}\{(\mu\text{-}S)CH_2CH_2(\mu\text{-}S)\}]_2$		1139
1473	$[WC_5N_3O_5]^-$	$[PPN][W(CO)_5N_3]$	200	1140

No.	Formula	Structure	Details	Ref.
1474	$[WC_8H_{12}O_4P]^-$	cis-[PPN][WMe(CO)$_4$(PMe$_3$)]	174	1141
1475	$WC_9H_8Br_2O_2$	WBr$_2$(CO)$_2$(norb)		1142
1476	$WC_9H_{10}Cl_2O_2$	WCl$_2$(CO)(η^2-OCEt)(Cp).CH$_2$Cl$_2$	233	1143
1477	$WC_9H_{15}Cl_3$	W{η^3-CMeCMeCBu^t}Cl$_3$		1144
1478	$WC_{10}H_{10}ClNO_3$	W(CO)(NO)(η^2-ClHC=CHCOMe)		1145
1479	$WC_{11}H_{10}O_5$	(OC)$_4$W{η^2-CH=CHCH$_2$CH(COMe)CH$_2$}		1146
1480	$WC_{11}H_{11}NO_3S_2$	W(η^1-detc)(CO)$_3$(Cp)	138	1147
1481	$WC_{11}H_{12}O_5$	(OC)$_4$W{η^2-CH$_2$=CH(CH$_2$)$_3$COMe}		1148
1482	$WC_{12}H_{10}O_6$	W(CO)$_5$(C(OMe)CHCH$_2$CH=CHCH$_2$}		1146
1483	$WC_{12}H_{12}O_3$	W(CO)$_3$(η-MesH)		809
1484	$WC_{12}H_{14}O_5$	(OC)$_4$W{η^2-CH(Me)=CH(CH$_2$)$_2$COEt}		1148
1485	$WC_{13}H_8F_6O_3S$	W{η^2-F$_3$CC(CF$_3$)C(O)SMe)(CO)$_2$(Cp)		1149
1486	$WC_{13}H_9NO_5$	W(CPhNHMe)(CO)$_5$		1150
1487	$WC_{13}H_{17}O_4P$	W(POCMe$_2$CMe$_2$O)(CO)$_2$(Cp)		1151
1488	$[WC_{13}H_{38}IP]^+$	[WI(CH$_2$)(PMe$_3$)$_4$][CF$_3$SO$_3$]		1152
1489	$WC_{14}H_{19}O_3P$	W(CO)$_2$(Cp)(η^2-CHAc=CHPMe$_3$)		1153
1490	$WC_{14}H_{21}O_5P_3$	W(CO)$_5$(P$_3$Pr$^i_3$)		1154
1491	$WC_{14}H_{23}ClO_2P_2$	W(PMe$_2$CMeCO)(CO)(PMe$_3$)(Cp)	233	1155
1492	$WC_{15}H_{12}O_2S_2$	W{S$_2$C(pTol)}(CO)$_2$(Cp)		609
1493	$WC_{15}H_{31}Cl_3N_2$	WCl$_3$(TMEDA)(η^3-MeCCMeCBu^t)		1156
1494	$[WC_{16}H_{10}Br_2Cl_5]^-$	[PPh$_4$][WCl$_5$(η^2-PhCCCBr=CBrPh)].CCl$_4$		1157
1495	$[WC_{16}H_{10}Cl_5]^-$	[PPh$_4$][WCl$_5$(η^2-PhCCCCPh)].CCl$_4$		1157
1496	$WC_{16}H_{12}F_{12}S$	W{C(CF$_3$)C(CF$_3$)SPr^i}(η^2-C$_4$F$_6$)(Cp)		1158
1497	$[WC_{17}H_{10}O_6P]^-$	[NHEt$_3$][W(OPPh$_2$)(CO)$_5$]		1159
1498	$WC_{18}H_{18}F_{18}O_3$	W(η^3-C$_3$Et$_3$){OCH(CF$_3$)$_2$}$_3$		1160
1499	$WC_{19}H_{21}NO_4$	(OC)$_4$W(η^2-H$_2$C=CHCMe$_2$CH$_2$NMeC(pTol))	183	1161
1500	$WC_{19}H_{32}O_3$	W(CPh)(OBu^t)$_3$	166	1162
1501	$WC_{20}H_{10}O_5S_3$	W(CO)$_5$S=CCPh=CPhSS		1163
1502	$WC_{20}H_{15}NO_5$	(OC)$_5$W{C(SEt)N=CPh$_2$}		1164
1503	$WC_{20}H_{25}O_4$	W{CH(pTol)CO$_2$Me}(CO)$_2$(PMe$_3$)(Cp)		1165

No.	Formula	Structure	Details	Ref.
1504	$WC_{20}H_{35}Cl_2P$	$WCl_2(\eta^3\text{-}CMeCBu^tCBu^t)(PMe_3)(Cp)$		1166
1505	$WC_{21}H_{44}O_3P_2$	$W(\eta^2\text{-}H_2)(CO)_3(PPr^i{}_3)_2$	X 173,N	1167
1506	$WC_{22}H_{14}N_2O_4$	$W(CO)_4\{bipy\text{-}6\text{-}(\underline{p}\text{-}C_6H_4CHCH_2)\}$		1168
1507	$WC_{22}H_{38}N_2O_6$	$W\{C(OEt)NPr^i{}_2\}_2(CO)_4$		1169
1508	$WC_{24}H_{24}$	$W(\underline{o}\text{-}CH_2C_6H_4CH_2)_3.0.5PhH$		562
1509	$WC_{25}H_{24}O_4$	$W(CPh_2)(CO)_4(\eta^2\text{-}C_8H_{14})$		1170
1510	$WC_{28}H_{23}O_4P$	$W(\eta^5\text{-}C_5H_4CH_2CH_2OCO)(CO)_2(PPh_3)$		1171
1511	$WC_{31}H_{35}NO_6$	$(OC)_4W\{C(OEt)CHPhCHPhC{=}CMeC(OEt)NEt_2\}$		1172
1512	$WC_{36}H_{26}O_5P_2$	$W(CO)_4\{Ph_2POCPh{=}CHPPh_2\}$		1173
1513	$WC_{36}H_{28}O_6P_2$	$W(CO)_4(PPh_2OH)\{PPh_2CH_2CPhO\}$		1173
1514	$WC_{38}H_{30}Br_2O_2P_2$	$WBr_2(CO)_2(PPh_3)_2$		1142
1515	$WC_{45}H_{66}O_3$	$W(\eta^3\text{-}C_3Et_3)(OC_6H_3Pr^i{}_2\text{-}2,6)_3$		1174
1516	$W_2C_{14}H_{14}S_6$	$\{W(SCH{=}CHS)(Cp)(\mu\text{-}S)\}_2$		1139
1517	$W_2C_{16}H_4Br_2O_8$	$\underline{p}\text{-}C_6H_4\{CW(CO)_4Br\}_2$		1175
1518	$W_2C_{16}H_8O_6$	$W_2(CO)_6(\mu\text{-}\eta^5{:}\eta^5\text{-fulv})$		1176
1519	$W_2C_{17}H_6O_{10}$	$W_2(CO)_{10}(\mu\text{-}CPh)$		1177
1520	$W_2C_{18}H_{34}N_6$	$W_2Me_6(NPh)_2(\mu\text{-}NH_2NH_2)(\mu\text{-}\eta^2\text{-}N_2H_2)$	250	1178
1521	$[W_2C_{20}H_{54}Cl_4P_6]^{2+}$	$[\{WCl(CPMe_3)(PMe_3)_2\}_2(\mu\text{-}Cl)_2][AlCl_4]_2$		1179
1522	$W_2C_{22}H_{42}O_8$	$W_2(CH_2Bu^t)_2(\mu\text{-}O_2CEt)_4$	115	1180
1523	$W_2C_{24}H_{48}O_6$	$W_2(OPr^i)_5(\mu\text{-}OPr^i)(\eta\text{-}C_2H_2)(\mu\text{-}\eta^4{:}\eta^1{:}\eta^1\text{-}C_4H_4)$	113	1181
1524	$W_2C_{26}H_{34}O_8$	$W_2(CH_2Ph)_2(\mu\text{-}O_2CEt)_4$	116	1180
1525	$W_2C_{30}H_{54}N_2O_6$	$W_2(OPr^i)_4(py)_2(\mu\text{-}OPr^i)_2(\mu\text{-}\eta^2\text{-}C_2H_2)$	108	1182
1526	$W_2C_{30}H_{57}NO_7$	$W_2(OPr^i)_5(\mu\text{-}OPr^i)_2(\mu\text{-}C{:}\mu N\text{-}CH_2CHCPhN)$		1183
1527	$W_2C_{30}H_{60}O_6$	$W_2(OPr^i)_5(\mu\text{-}OPr^i)(\eta\text{-}C_2Me_2)(\mu\text{-}\eta^4{:}\eta^1{:}\eta^1\text{-}C_4Me_4)$	104	1181
1528	$W_2C_{30}H_{66}O_3$	$\{WO(CH_2Bu^t)_3\}_2(\mu\text{-}O)$		1184
1529	$W_2C_{31}H_{61}NO_6$	$W_2(OBu^t)_5(py)(\mu\text{-}OBu^t)(\mu\text{-}\eta^2\text{-}C_2H_2)$	113	1182
1530	$W_2C_{33}H_{61}NO_6$	$W_2(OBu^t)_5(\mu\text{-}OBu^t)(\mu\text{-}C{:}\mu N\text{-}CHCHCPhN)$		1183
1531	$W_2C_{36}H_{32}Cl_4N_2O_4$	$\{WCl_2(DME)(\eta^2\text{-}C_2Ph_2)\}_2(\mu\text{-}N_2).0.5DME$		1185
1532	$W_2C_{36}H_{62}I_2N_2$	$\{WI(CBu^t)(\eta\text{-}C_5Me_4Bu^t)\}_2(\mu\text{-}N_2H_2)$		1186
1533	$W_2C_{39}H_{84}N_6O_6$	$W_2(OCH_2Bu^t)_6(\eta^2\text{-}NCNMe_2)(\mu\text{-}C{:}N\text{-}NCNMe_2)$-		

No.	Formula	Structure	Details	Ref.
		$(\mu\text{-}\eta^2\text{:N-NCNMe}_2)$	113	1187
1534	$W_2C_{44}H_{82}N_2O_6$	$W_2(OCH_2Bu^t)_5(py)_2(\mu\text{-}OCH_2Bu^t)(\mu\text{-}\eta^2\text{-}C_2Me_2)$	113	1182
1535	$W_3C_{29}H_{66}O_9$	$W_3(\mu_3\text{-}CMe)(OPr^i)_6(\mu\text{-}OPr^i)_3$	115	1188
1536	$YC_{19}H_{22}N$	$(Cp)_2Y\{\underline{o}\text{-}C_6H_4CH_2NMe_2\}$		1189
1537	$Y_2C_{20}H_{20}Cl_2$	$\{Y(Cp)_2(\mu\text{-}Cl)\}_2$		1190
1538	$Y_2C_{30}H_{40}N_2$	$\{Y(Cp)_2(\mu\text{-}N{=}CHBu^t)\}_2$		1191
1539	$YbC_{24}H_{41}NO$	$Yb(NH_3)(THF)(\eta\text{-}C_5Me_5)_2$		1192
1540	$Yb_2C_{34}H_{20}F_{10}O_4$	$\{Yb(Cp)_2(\mu\text{-}O_2CC_6F_5)\}_2$		1193
1541	$Yb_3C_{78}H_{86}$	$Yb\{(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2Yb(\eta\text{-}C_5Me_5)_2\}_2.PhH$		314
1542	ZnC_8H_{14}	$Zn\{(CH_2)_2CH{=}CH_2\}_2$	E	1194
1543	$ZnC_8H_{18}O_2$	$Zn\{(CH_2)_3OMe\}_2$	E	1195
1544	$ZnC_{10}H_{18}$	$Zn\{(CH_2)_3CH{=}CH_2\}_2$	E	1194
1545	$ZnC_{10}H_{22}O_2$	$Zn\{(CH_2)_4OMe\}_2$	E	1195
1546	$Zn_2C_{20}H_{38}Br_2O_6$	$[ZnBr(THF)\{\mu\text{-}C\text{:}O\text{-}CH_2C(O)OBu^t\}]_2$		1196
1547	$Zn_4C_{16}H_{36}N_4O_4$	$[MeZn\{\mu_3\text{-}N(O)CMe_2\}_4]$		1197
1548	$ZrC_5H_5Cl_3$	$\{ZrCl(Cp)(\mu\text{-}Cl)_2\}_n$		1113
1549	$[ZrC_{10}H_{16}O_3]^{2+}$	$[Zr(OH_2)_3(Cp)_2][CF_3SO_3]_2.THF$	173	1198
1550	$ZrC_{12}H_{16}$	$Zr(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_6)(Cp)$		1199
1551	$[ZrC_{13}H_{15}O]^-$	$Na[ZrMe(OC{=}CH_2)(Cp)_2].2THF$		1200
1552	$ZrC_{16}H_{44}P_4$	$ZrMe_4(dmpe)_2$		1201
1553	$ZrC_{17}H_{16}ClN$	$ZrCl(NCHPh)(Cp)_2$		1202
1554	$ZrC_{18}H_{18}$	$Zr\{\underline{o}\text{-}(CH_2)_2C_6H_4\}(Cp)_2$		472
1555	$ZrC_{19}H_{22}$	$(Cp)_2Zr\{\eta^4\text{-}2,3\text{-}(CH_2)_2bicyclo[2.2.1]heptane\}$		1203
1556	$ZrC_{22}H_{26}$	$(Cp)_2Zr\{\eta^4\text{-}3,4\text{-}(CH_2)_2\text{-}1,2,5,6\text{-}$ $Me_4tricyclo[3.1.0.0]hexane\}$		1203
1557	$ZrC_{31}H_{50}O$	$Zr(CH_2CH{=}CHCH_2CPr^i_2O)(\eta\text{-}C_5Me_5)_2$		1204
1558	$ZrC_{32}H_{52}O$	$Zr(CH_2CH{=}CMeCH_2CPr^i_2O)(\eta\text{-}C_5Me_5)_2$		1204
1559	$ZrC_{34}H_{40}P_2$	$Zr(CH_2Ph)_4(dmpe)$		1201
1560	$Zr_2C_{10}H_{12}N_4O_{14}$	$\{Zr(NO_3)_2(Cp)\}_2(\mu\text{-}OH)_2.2THF$		1205
1561	$Zr_2C_{24}H_{27}Cl_2OP$	$\{ZrCl(Cp)\}_2\{\mu\text{-}P,O\text{:}\eta^2CO\text{-}PMe_2CH{=}CO\}$		541

No.	Formula	Structure	Details	Ref.
1562	$[Zr_2C_{28}H_{38}Cl_3N_2O]^-$	$[Li(DME)_3][\{ZrCl(NC_4H_4)(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}O)(\mu\text{-}Cl)]$		1206
1563	$Zr_2C_{32}H_{41}IO_2$	$(\eta\text{-}C_5Me_5)_2\overline{ZrOCH{=}C(O)}ZrI(Cp)_2.0.5PhH$		1207
1564	$Zr_2C_{34}H_{31}Cl_2OP$	$\{(Cp)_2ZrCl\}_2(\mu\text{-}P,O{:}\eta^2CO\text{-}PPh_2CH{=}CO)$	140	1208,1209
1565	$Zr_2C_{34}H_{50}IOP$	$(\eta\text{-}C_5Me_5)_2IZrOCHZr(PMe_3)(Cp)_2$		1207

Additional abbreviations used in Main Table

az	azulene	azaind	7-azaindolate
cyp	cyclopropyl	detc	diethydithiocarbamate
dippe	$(Me_2CH)_2PCH_2CH_2P(CHMe_2)_2$	DMAD	$MeO_2CC{\equiv}CCO_2Me$
dmpm	$Me_2PCH_2PMe_2$	dmpz	3,5-dimethylpyrazol-1-yl
dmtc	dimethyldithiocarbamate	dppmpp	$PhP(CH_2PPh_2)_2$
fulv	fulvalene		
H_2dapa	2,6-diacetylpyridinebis(2-aminobenzoylhydrazone)		
H_2Tcbiim	tetracyano-2,2′-biimidazole	H_3xanth	xanthine ($C_5H_4N_4O_2$)
imid	imidazole	ind	indenyl
Meimid	N-methylimidazole	menth	menthyl
Mes	$2,4,6\text{-}Me_3C_6H_2$	mpz	3-methylpyrazolyl
8-mq	8-methylquinolyl	napy	1,8-naphthyridine
np_3	$N(CH_2CH_2PPh_2)_3$	oTol	o-tolyl
oxine	8-oxoquinolate	pTol	p-tolyl
pyz	1,4-pyrazine	SacSac	dithioacetylacetonate
TCTTN	tetrachlorotetrathionaphthalene	tedip	tetraethyldiphosphite
TFAc	CF_3CO	tfb	5,6,7,8-tetrafluorobarrelene
TMSF	tetramethyltetraselenofulvalene	TSeF	tetraselenofulvalene
TSeT	tetraselenatetracene	ttas	$MeAs(C_6H_4AsMe_2\text{-}o)_2$
tz	1,2,4-triazolate	Xy	$2,6\text{-}Me_2C_6H_3$

3 Metals Cross Reference Table

A list of mixed metal compound numbers which are listed alphabetically in the Main Table under another metal.

Metal	*Compound Numbers*
Au	2, 3
B	86
Co	9, 43, 44, 73, 87, 88, 89, 111, 132, 168, 178, 209
Cr	45, 58, 59, 60, 61, 62, 78, 90, 91, 169, 239, 240, 241, 242
Cu	133, 281
Fe	10, 44, 87, 88, 134, 135, 136, 164, 175, 179, 186, 210, 243, 244, 245, 276, 320, 339
Ge	321
Hg	277, 282, 419, 478, 479, 553
Ir	170, 180, 181, 187, 540
Li	13, 112, 137, 199, 211, 360, 585
Lu	668
Mg	14, 554, 643, 659
Mn	46, 63, 64, 92, 246, 268, 333, 340, 341, 420, 421, 422, 423, 424, 425, 480, 481, 541, 644, 645
Mo	44, 74, 138, 139, 140, 426, 542, 639, 640
Na	47, 361, 427
Nb	588, 696
Ni	48, 65, 93, 160, 182, 201, 278, 287, 322, 482, 510, 525, 543, 555
Os	4, 93, 113, 165, 351, 428, 582, 615, 697, 802
Pb	544, 803
Pd	49, 60, 61, 114, 247, 334, 429, 698, 762, 763
Pt	7, 50, 66, 94, 95, 115, 248, 323, 335, 352, 430, 431, 483, 526, 553, 574, 616, 617, 629, 633, 660, 724, 764, 765, 804, 898, 899, 900, 901, 902, 903, 930, 931
Re	15, 16, 141, 358, 520, 584, 805, 809, 904, 985
Rh	23, 66, 75, 183, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 249, 324, 325, 353, 432, 433, 434, 484, 485, 517, 521, 527, 575, 576, 577, 618, 765, 766, 767, 768, 824, 877, 986, 987, 1008
Ru	5, 67, 68, 87, 88, 89, 96, 97, 98, 99, 100, 101, 111, 116, 117, 118, 120, 121, 161, 250, 251, 269, 270, 271, 282, 359, 435, 436, 437, 438, 439, 486, 487, 488, 489, 490, 578, 579, 769, 855, 1136, 1137, 1151
Sb	354, 440, 491, 725, 729, 1053, 1094
Se	76, 846, 922, 938, 1009, 1033, 1095, 1147
Si	6, 8, 17, 24, 25, 51, 59, 65, 69, 137, 142, 143, 144, 162, 171, 176, 211, 213, 252, 272, 279, 288, 326, 327, 336, 355, 361, 425, 440, 441, 442, 443, 444, 491, 492, 545, 546, 556, 557, 558, 560, 644, 645, 646, 647, 648, 649, 650, 661, 662, 663, 664, 665, 666, 671, 699, 700, 726, 770, 771, 772, 773, 806, 811, 813, 814, 847, 848, 849, 850, 851, 857, 869, 905, 960, 988, 1096, 1097, 1098, 1138, 1229
Sn	70, 145, 171, 198, 283, 328, 445, 774, 775, 807, 815, 816, 817, 905, 939, 989, 1010, 1057, 1058, 1284, 1308, 1340
Ta	146, 1333, 1341
Te	337, 481, 701, 727, 990, 1309
Th	669, 1326
Ti	18, 26, 52, 71, 172, 808, 1285, 1310, 1346
Tl	1221
U	162, 166, 173, 702
V	147, 174, 446, 818
W	19, 20, 86, 94, 102, 103, 117, 135, 148, 149, 150, 151, 195, 196, 253, 352, 356, 447, 448, 492, 493, 619, 620, 630, 676, 776, 777, 824, 870, 871, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 949, 991, 992, 993, 994, 995, 996, 1011, 1034, 1035, 1036, 1037, 1038, 1099, 1236, 1286, 1287, 1334, 1342, 1390, 1471

Metals Cross Reference Table (continued)

Metal	*Compound Numbers*
Y	27, 28, 29
Yb	279, 703, 811
Zn	819, 1311, 1335, 1411
Zr	21, 329, 810, 852, 872, 1197, 1238, 1288, 1289, 1312

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