

21 Organometallic Chemistry of Monometallic Species

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1 Introduction

Important reviews have appeared on monometallic organo transition-metal complexes containing carbon monoxide as a σ donor,¹ tcne, tcnq, and related polynitrile π acceptors,² and water³ as a ligand. Reviews on TiCp_2 carboxylates and related complexes,⁴ $\text{Zr}^{\text{IV}}\text{Cp}_2$ and $\text{Hf}^{\text{IV}}\text{Cp}_2$ compounds with Si, Ge, Sn, N, P, As, Sb, O, S, Se, Te, or transition-metal centred anionic ligands,⁵ palladium(II) and platinum(II) five-coordinate alkene complexes,⁶ and metallocyclobutane complexes of the Group eight transition metals⁷ have appeared. Reviews concerning transition metals in the chemistry of vinylcyclopropanes⁸ and the activation of carbon-fluorine bonds⁹ have been published. Reviews have also been published on the patterns of stoichiometric and catalytic reactions of organozirconium and related complexes,¹⁰ recent advances in the chemistry and applications of high oxidation state alkylidene complexes,¹¹ the uses of irontricarbonyl lactone complexes in organic synthesis,¹² and sulfoxides and stereochemical control in organometallic chemistry.¹³ How orientations of alkene, alkyne, and alkylidene ligands reveal π -bonding features in tetrahedral transition-metal complexes has also been reviewed.¹⁴

2 Ti, Zr, and Hf

The synthesis and *X*-ray crystal structure of the first tris(naphthalene) complex $[\text{Zr}(\eta^4\text{-naphthalene})_3]^{2-}$, which is also the first structurally characterized homoleptic naphthalene metalate, have been described.¹⁵ The preparations of the first isolable

¹ F. Aubke and C. Wang, *Coord. Chem. Rev.*, 1994, **137**, 483.

² W. Kaim and M. Moscherosch, *Coord. Chem. Rev.*, 1994, **129**, 157.

³ U. Koelle, *Coord. Chem. Rev.*, 1994, **135/136**, 623.

⁴ Y. Dang, *Coord. Chem. Rev.*, 1994, **135/136**, 93.

⁵ E. Hey-Hawkins, *Chem. Rev.*, 1994, **94**, 1661.

⁶ V. G. Albano, G. Natile, and A. Panuzi, *Coord. Chem. Rev.*, 1994, **133**, 67.

⁷ P. W. Jennings and L. L. Johnson, *Chem. Rev.*, 1994, **94**, 2241.

⁸ R. I. Khusnutdinov and U. M. Dzhemilev, *J. Organomet. Chem.*, 1994, **471**, 1.

⁹ J. L. Kiplinger, T. G. Richmond, and C. E. Osterberg, *Chem. Rev.*, 1994, **94**, 373.

¹⁰ E. Negishi and T. Takahashi, *Acc. Chem. Res.*, 1994, **27**, 124.

¹¹ R. R. Schrock, *Pure Appl. Chem.*, 1994, **66**, 1447.

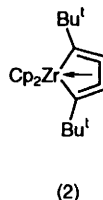
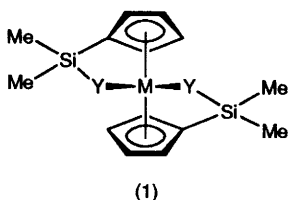
¹² S. V. Ley, *Pure Appl. Chem.*, 1994, **66**, 1415.

¹³ S. L. Griffiths, C. F. Marcos, S. Perrio, S. P. Saberi, S. E. Thomas, G. J. Tustin, and A. T. Wierchleyski, *Pure Appl. Chem.*, 1994, **66**, 1565.

¹⁴ V. C. Gibson, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1565.

¹⁵ M. Jang and J. E. Ellis, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1973.

terminal carbonyl complexes of zirconium(IV), $[\text{Zr}(\text{CO})(\eta^3\text{-C}_3\text{H}_5)\text{Cp}_2^*][\text{BPh}_4]$ (crystallographically characterized)¹⁶ and $[\text{Zr}(\text{CO})(\eta^2\text{-COMe})(\eta\text{-C}_5\text{R}_5)][\text{BMe}(\text{C}_6\text{F}_5)_3]$ ($\text{R} = \text{H}, \text{Me}$), which has been characterized by X-ray crystallography for the 'O-outside' and methyl isomer,¹⁷ have been reported. A series of catalytically active base-free zirconium methyl and benzyl complexes has been prepared, including the zwitterionic compound $[\text{ZrMe}\{1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ which has been crystallographically characterized.¹⁸ Reaction of cytotostatically active titanocene dichloride with α -amino acids gives the first titanium(IV) α -amino acid complexes, $[\text{Ti}(\alpha\text{-amino acid})_2\text{Cp}_2]\text{Cl}_2$, of which the α -2-methylalanine example was crystallographically characterized.¹⁹ The newly prepared *ansa*-bridged complexes $[\text{ZrClCp}\{(\text{CH}_2)_5\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}]$ and $[\text{ZrClCp}\{\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^3\text{-C}_{13}\text{H}_8)\}]$ show unusual modes of attachment of the indenyl or fluorenyl moieties.²⁰ The first quantitative and stereoselective synthesis of *rac*-metallocenes such as (1) [$\text{M} = \text{Zr}, \text{Y} = \text{NPh}, \text{C}_5\text{H}_4$ (both crystallographically characterized); $\text{M} = \text{Hf}, \text{Y} = \text{NPh}$] have been described.²¹



Treatment of $[\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_2]$ with $\text{Bu}'\text{C}_2\text{C}_2\text{Bu}'$ gives the smallest possible cyclic cumulene (2), which has been crystallographically characterized.²² The preparation and molecular structure of the unusual zirconocene complex (3) containing two alkynes have been reported.²³ Reaction of $[\text{ZrCl}_3\text{Cp}^*]$ with $[\text{Li}(\text{tmeda})]_2[\text{tmm}]$ ($\text{tmm} = \text{trimethylenemethane}$) gives the distorted η^4 -bonded trimethylenemethane complex (4),²⁴ whereas reaction of $[\text{ZrCl}_2\text{Cp}_2^*]$ with $[\text{Li}(\text{tmeda})]_2[\text{tmm}]$ affords the η^3 -bonded trimethylenemethane complex (5).²⁵

3 V, Nb, and Ta

The first stable mononuclear tantalum(0) carbonyl compound, $[\text{Ta}(\text{CO})_4(\text{dppe})]$, has been prepared.²⁶ The α -agostic n-ethyl and n-propyl compounds $[\text{NbCl}(\mu\text{-H-CHR})(\eta^2\text{-PhC}_2\text{R}')\text{Tp}^*]$ ($\text{R} = \text{Me}, \text{Et}; \text{R}' = \text{Me}, \text{Et}, \text{Pr}^n$) undergo thermolytic exchange

¹⁶ D. M. Antonelli, E. B. Tjaden, and J. M. Stryker, *Organometallics*, 1994, **13**, 763.

¹⁷ Z. Guo, D. C. Swenson, A. S. Guram, and R. F. Jordan, *Organometallics*, 1994, **13**, 766.

¹⁸ M. Bochmann, S. J. Lancaster, M. B. Hursthouse, and K. M. A. Malik, *Organometallics*, 1994, **13**, 2235.

¹⁹ T. M. Klapötke, H. Köpf, I. C. Tornieporth-Oetting, and P. S. White, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1518.

²⁰ G. M. Diamond, M. L. H. Green, P. Mountford, N. A. Popham, and A. N. Chernega, *J. Chem. Soc., Chem. Commun.*, 1994, 103.

²¹ W. A. Herrmann, M. J. A. Morawietz, and T. Priermeier, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1946.

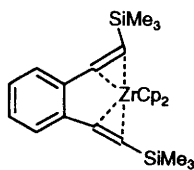
²² U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, and V. V. Burlakov, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1605.

²³ B. P. Warner, W. M. Davis, and S. L. Buchwald, *J. Am. Chem. Soc.*, 1994, **116**, 5471.

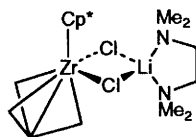
²⁴ G. C. Bazan, G. Rodriguez, and B. P. Cleary, *J. Am. Chem. Soc.*, 1994, **116**, 2177.

²⁵ G. E. Herberich, C. Kreuder, and U. Englert, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2465.

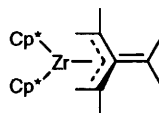
²⁶ M. D. Koeslag and M. C. Baird, *Organometallics*, 1994, **13**, 11.



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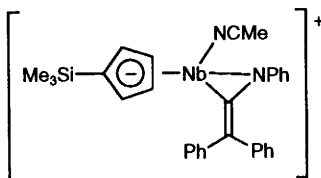
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(5)

of the Nb and the alkyne-bonded alkyl groups to afford $[\text{NbClR}'(\eta^2\text{-PhC}_2\text{CH}_2\text{R})\text{Tp}']$ via the unprecedented metathesis of metal–carbon and carbon–carbon bonds.²⁷

The sequential removal of chloride ions from $[\text{NbCl}_4\text{Cp}]$ using SbCl_5 in acetonitrile yields a series of novel cationic niobium(v) complexes including the ‘double’ $[\text{SbCl}_6]^-$ salt $[\text{NbCl}(\text{NCMe})_4\text{Cp}]^3+[\text{Nb}(\text{NCMe})_6\text{Cp}]^4+[\text{SbCl}_6]_7\cdot 7\text{NCMe}$, which has been crystallographically characterized.²⁸ Reaction of $[\text{V}(\text{NAr})(\text{PMe}_3)_2\text{Cp}]$ $[\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{CHMe}_2)_2]$ with $\text{Ph}_3\text{P}=\text{CHPh}$ gives the crystallographically characterized complex $[\text{V}(=\text{CHPh})(\text{NAr})(\text{PMe}_3)\text{Cp}]$, which is the first vanadium(v) alkylidene complex to be reported.²⁹ The synthesis, molecular structure, and reactions with water and methanol of the cationic ketimine complex (6) have been described.³⁰ Treatment of $[\text{MH}(\text{CO})\text{Cp}'_2]$ ($\text{M} = \text{Nb}, \text{Ta}$) with O_2 affords the metal formate complexes $[\text{M}(\text{O})(\eta^1\text{-O}_2\text{CH})\text{Cp}'_2]$ apparently via the CO_2 complexes $[\text{MH}(\eta^2\text{-CO}_2)\text{Cp}'_2]$.³¹ The first thermally stable Group 5 dihydrogen complex $[\text{Ta}(\eta^2\text{-H}_2)(\text{CO})\text{Cp}_2][\text{BF}_4]$ has been prepared.³²



(6)

4 Cr, Mo, and W

The preparation and isolation of the crystallographically characterized complex $[\text{Cr}(\eta^2\text{-H}_2)(\text{CO})_3(\text{PPr}^t)_2]$, which has the shortest ligated H–H bond length, have been

²⁷ M. Etienne, F. Biasotto, and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1994, 1661.

²⁸ G. R. Willey, M. L. Butcher, T. J. Woodman, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1994, 2721.

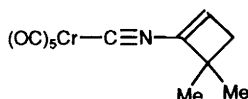
²⁹ J.-K. F. Buijink, J. H. Teuben, H. Kooijman, and A. L. Spek, *Organometallics*, 1994, 13, 2922.

³⁰ A. Antiñolo, M. Fajardo, R. Gil-Sanz, C. López-Mardomingo, A. Otero, A. Atmani, M. M. Kubicki, S. El Krami, Y. Mugnier, and Y. Mourad, *Organometallics*, 1994, 13, 1200.

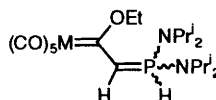
³¹ P.-F. Fu, A. K. Fazlur-Rahman, and K. M. Nicholas, *Organometallics*, 1994, 13, 413.

³² S. Sabo-Etienne, B. Chaudret, H. Abou el Makarim, J.-C. Barthelat, J.-P. Daudey, C. Moïse, and J.-C. Leblanc, *J. Am. Chem. Soc.*, 1994, 116, 9335.

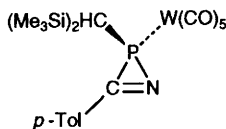
described.³³ Reaction of $[\text{Mo}(\text{CO})\{\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2\}_2]$ ($\text{R} = \text{Et}, \text{CH}_2\text{Ph}, \text{Ph}$) with $\text{SiH}_2\text{R}'\text{R}''$ gives a series of η^2 -silane complexes, *cis*- $[\text{Mo}(\text{CO})\{\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2\}_2(\eta^2\text{-HSiHR}'\text{R}'')]$, which has been crystallographically characterized for $\text{R} = \text{Et}, \text{R}' = \text{H}, \text{R}'' = \text{Ph}$.³⁴ The synthesis and crystallographic characterization of the complex-stabilized alkynyl $[\text{Cr}(\text{CO})_5(\text{C}\equiv\text{NC}\equiv\text{CPh})]$ and cyclobutenyl (7) complexes have been reported.³⁵ Treatment of $[\text{M}\{\text{C}(\text{OEt})\text{CH}_2\text{Li}\}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{W}$) with $\text{PCl}(\text{NPr}_2)_2$ affords the P-H functionalized ylide-carbene complexes (8) (crystallographically characterized for the chromium case) *via* transient $\{\alpha\text{-(phosphino)alkyl}\}$ carbene complexes.³⁶ The electrochemical reduction of *trans*- $[\text{WCl}(\text{CN})(\text{dppe})_2]$ in the presence of phenol yields the crystallographically characterized complex *trans*- $[\text{WCl}(\text{CNH}_2)(\text{dppe})_2]$, which when oxidized chemically or electrochemically gives the crystallographically characterized paramagnetic cation *trans*- $[\text{WCl}(\text{CNH}_2)(\text{dppe})_2][\text{BF}_4]$. The X-ray results indicate that the CNH_2 group at both the 18 and 17-electron tungsten centres is best described as an iminomethylenium ($=\text{C}=\text{NH}_2^+$) ion.³⁷ Reaction of $[\text{WCl}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$ with $\text{Li}[\text{CH}_2\text{R}]$ ($\text{R} = \text{Me}, \text{Pr}, \text{SiMe}_3, \text{Bu}^t$) or $\text{K}[\text{CH}_2\text{Ph}]$ at room temperature affords the alkylidyne complexes $[\text{W}\equiv\text{CR}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$ *via* spontaneous loss of H_2 from the tungsten(IV) alkyl complexes $[\text{W}(\text{CH}_2\text{R})\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$.³⁸



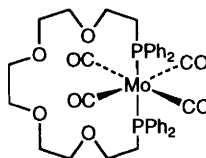
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(8)



(9)



(10)

The preparation and molecular structure of the first 2*H*-1-aza-2-phosphirene complex (9) have been described.³⁹ Photolysis of the *cis* isomer of (10) yields *trans*-(10), which is the first example of a metallo-crown ether in which the α,ω -bis(phosphine) polyether ligand is *trans* coordinated.⁴⁰ Treatment of $[\text{Se}(\sigma\text{-C}_5\text{Me}_5)_2]$ with $[\text{M}(\text{CO})_5(\text{thf})]$ ($\text{M} = \text{Cr}, \text{W}$) yields the crystallographically characterized complexes $[\text{M}(\text{CO})_5\{\text{Se}_2(\sigma\text{-C}_5\text{Me}_5)_2\}]$, providing the first examples of selenide to diselenide

³³ G. J. Kubas, J. E. Nelson, J. C. Bryan, J. Eckert, L. Wisniewski, and K. Zilm, *Inorg. Chem.*, 1994, **33**, 2954.

³⁴ X.-L. Luo, G. J. Kubas, J. C. Bryan, C. J. Burns, and C. J. Unkefer, *J. Am. Chem. Soc.*, 1994, **116**, 10 312.

³⁵ R. Kunz and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 330.

³⁶ R. Streubel, M. Hobbold, J. Jeske, and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1994, 2457.

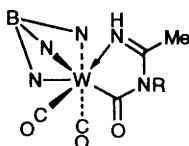
³⁷ D. L. Hughes, S. K. Ibrahim, H. Moh'd Ali, and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1994, 425.

³⁸ K.-Y. Shih, K. Totland, S. W. Seidel, and R. R. Schrock, *J. Am. Chem. Soc.*, 1994, **116**, 12 103.

³⁹ R. Streubel, J. Jeske, P. G. Jones, and R. Herbst-Irmer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 80.

⁴⁰ G. M. Gray and C. H. Duffey, *Organometallics*, 1994, **13**, 1542.

reduction within the coordination sphere of a transition metal and the first crystallographically characterized complexes to contain a terminal diselenide ligand.⁴¹ The synthesis and molecular structures of the anionic complexes $[\text{Na}(2,2,2\text{-crypt})]_3[\text{MoSb}_7(\text{CO})_3]$,⁴² $[\text{K}(2,2,2\text{-crypt})]_3[\text{CrP}_7(\text{CO})_3]\text{en}^{43}$ and $[\text{K}(2,2,2\text{-crypt})]_3[\text{CrSb}_7(\text{CO})_3]^{43}$ have been reported. Reaction of $[\text{W}(\text{CO})_3(\text{PPr}^i_3)_2]$ with half a mole of RSSR (R = Me, Ph, *p*-tolyl, CH_2Ph) or I_2 gives the stable radicals $[\text{W}(\text{SR})(\text{CO})_3(\text{PPr}^i_3)_2]$ or $[\text{WI}(\text{CO})_3(\text{PPr}^i_3)_2]$ respectively; the latter has been crystallographically characterized.⁴⁴ Treatment of $[\text{WI}_2(=\text{CHPh})(\text{CO})(\text{PMe}_3)_2]$ with CS_2 and PPh_3 gives the crystallographically characterized η^2 -phenylalkynyl complex $[\text{WI}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-PhC}_2\text{SH})]$, which reacts with LiBu^n and isocyanides to give the stable η^2 -thioketenyl complexes $[\text{WI}(\text{CO})(\text{CNR})(\text{PMe}_3)_2(\eta^2\text{-PhC}_2\text{S})]$ (R = Bu^t, 2,6- $\text{C}_6\text{H}_3\text{Me}_2$) (crystallographically characterized for R = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$).⁴⁵ Reaction of $[\text{W}(\text{CO})_3(\text{NCMe})\text{Tp}][\text{BF}_4]$ (generated *in situ*) with NH_3 or NH_2Bu^n gives the neutral complexes (11) (R = H, Buⁿ) by the amine-induced coupling of



(11)

carbonyl and nitrile ligands; protonation of (11) at the acyl oxygen atom yields the cationic metallocycle hydroxycarbene complexes $[\text{W}=\text{C}(\text{OH})-\text{N}(\text{R})-\text{C}(\text{Me})=\text{N}(\text{H})(\text{CO})_2\text{Tp}][\text{BF}_4]$ (R = H, Buⁿ), of which the *n*-butyl example was crystallographically characterized.⁴⁶ Protonation of $[\text{WMe}(\text{CO})(\eta^2\text{-MeC}_2\text{Ph})\text{Tp}]$ in the presence of ketones (acetone, 2-butanone, acetophenone, 3,3-dimethyl-2-butanone) or aldehydes (benzaldehyde, trimethylacetaldehyde) gives the η^1 -ketone or η^1 -aldehyde products $[\text{W}(\text{CO})(\eta^1\text{-OCRR}')(\eta^2\text{-MeC}_2\text{Ph})\text{Tp}]^+$; further reaction with $\text{K}[\text{HBBu}_3^s]$ yields the neutral alkoxide complexes $[\text{W}(\text{OCHRR}')(\text{CO})(\eta^2\text{-MeC}_2\text{Ph})\text{Tp}]$ which was crystallographically characterized for R = H, R' = Bu^t.⁴⁷

Variable temperature ¹H, ¹³C, and ³¹P NMR spectroscopy demonstrates that the 16-electron η^3 -2-methallyl complex $[\text{MoH}(\eta^3\text{-C}_4\text{H}_7)(\text{dppe-}\kappa^2\text{P})(\text{dppe-}\kappa\text{P})]$ rapidly interconverts intramolecularly into the 18-electron η^4 -trimethylenemethane complex $[\text{MoH}_2\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{dppe-}\kappa^2\text{P})(\text{dppe-}\kappa\text{P})]$.⁴⁸ Treatment of the cyclopropylcarbyne complexes $[\text{MoC}\equiv\text{CCRCH}_2\text{CH}_2]\{\text{P}(\text{OMe})_3\}_2\text{Cp}$ (R = H, D, Me) with HCl affords the diene complexes $[\text{MoCl}\{\text{P}(\text{OMe})_3\}(\eta^4\text{-CH}_2=\text{CRCH}=\text{CH}_2)\text{Cp}]$, of which one of the methyl isomers has been crystallographically characterized.⁴⁹ Condensation of

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⁴² U. Bolle and W. Tremel, *J. Chem. Soc., Chem. Commun.*, 1994, 217.

⁴³ S. Charles, B. W. Eichhorn, A. L. Rheingold, and S. G. Bott, *J. Am. Chem. Soc.*, 1994, **116**, 8077.

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⁴⁵ T.-Y. Lee and A. Mayr, *J. Am. Chem. Soc.*, 1994, **116**, 10 300.

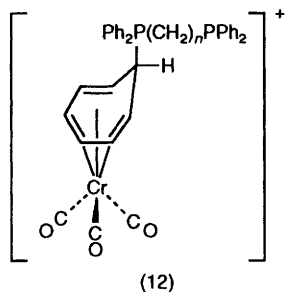
⁴⁶ S. G. Feng, P. S. White, and J. L. Templeton, *Organometallics*, 1994, **13**, 1214.

⁴⁷ J. L. Caldarelli, L. E. Wagner, P. S. White, and J. L. Templeton, *J. Am. Chem. Soc.*, 1994, **116**, 2878.

⁴⁸ R. A. Henderson and K. E. Oglieve, *J. Chem. Soc., Dalton Trans.*, 1994, 767.

⁴⁹ K. B. Kingsbury, J. D. Carter, L. McElwee-White, R. L. Ostrander, and A. L. Rheingold, *Organometallics*, 1994, **13**, 1635.

molybdenum vapour with the phosphalkyne $P\equiv C\text{Bu}^t$ gives the crystallographically characterized complex $\text{tris}(\eta^4\text{-}2,4\text{-di-}t\text{-butyl-}1,3\text{-diphosphacyclobutadiene})\text{Mo}(0)$.⁵⁰ Reaction of $[\text{Mo}(\text{CO})_2(\text{NCMe})_2(\eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]$ with an excess of $P\equiv C\text{Bu}^t$ yields the unusual η^3 -ligated 1,3-diphosphacyclobutadiene molybdenum complex $[\text{Mo}(\text{CO})_2\{\text{P-}\eta^3\text{-(Bu}^t\text{)CPC(Bu}^t\text{)PFBF}_3\}(\eta^5\text{-C}_9\text{H}_7)]$, which has been characterized by X-ray crystallography.⁵¹ The first spin triplet ground state 16-electron complexes, $[\text{MoClL}_2\text{Cp}^*]$ (L = tertiary phosphine), have been prepared and preliminary studies of their reactivity have also been made.⁵² The stepwise hydrolysis of a terminal nitrosyl ligand has been achieved by reaction of $[\text{W}(\text{CH}_2\text{SiMe}_3)(\text{NCMe})_2(\text{NO})\text{Cp}^*][\text{BF}_4]$ with one equivalent of H_2O to give the crystallographically characterized complex $[\text{W}(\text{CH}_2\text{SiMe}_3)(\text{O})(\eta^2\text{-NH}_2\text{O})\text{Cp}^*][\text{BF}_4]$; the latter reacts with one more equivalent of H_2O to yield $[\text{W}(\text{CH}_2\text{SiMe}_3)(\text{O})_2\text{Cp}^*]$ and $[\text{NH}_3\text{OH}][\text{BF}_4]$.⁵³ The synthesis of the first *ansa*-molybdenocene and tungstenocene complexes have been described including the X-ray crystallographically characterized complex $[\text{MoMe}_2\{\text{O}(\text{SiMe}_2\text{C}_5\text{H}_4)_2\}]$.⁵⁴ Treatment of $[\text{MoBr}(\text{CO})(\text{PR}_3)(\eta^7\text{-C}_7\text{H}_7)]$ (R = Me, Ph) with a but-3-yn-1-ol/ $[\text{NH}_4][\text{PF}_6]$ mixture in methanol gives the first examples of stable cycloheptatrienylmolybdenum carbene complexes $[\text{Mo}(\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}})(\text{CO})(\text{PR}_3)(\eta^7\text{-C}_7\text{H}_7)][\text{PF}_6]$.⁵⁵ The reaction of $[\text{Cr}(\text{CO})_3(\eta^7\text{-C}_7\text{H}_7)][\text{BF}_4]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2$, and 4) at low temperature yields two new series of complexes, the 7-*exo* ring adducts (12) (for $n = 1, 2$) and the phosphine-linked binuclear species $[\{\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7)\}_2\{7,7'\text{-exo-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}][\text{BF}_4]_2$, which has been crystallographically characterized.⁵⁶



5 Mn, Tc, and Re

Reaction of the cyclometalated complex $[\text{ReBr}(\text{CO})_4\{\overline{=\text{C}(\text{NHPr}^i)(\text{NHC}_6\text{H}_4)}\}]$ with I_2 affords $[\text{ReI}(\text{CO})_4\{\overline{=\text{C}(\text{NHPr}^i)(\text{NHC}_6\text{H}_4\text{I-}2)}\}]$ which, when reacted with NHET_2 , induces the intramolecular activation of a C–H bond to yield $[\text{Re}(\text{CO})_4\{\eta^2\text{-}$

⁵⁰ F. G. N. Cloke, K. R. Flower, P. B. Hitchcock, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1994, 489.

⁵¹ P. B. Hitchcock, M. J. Maah, J. F. Nixon, and M. Green, *J. Organomet. Chem.*, 1994, **466**, 153.

⁵² F. Abugideiri, D. W. Keogh, and R. Poli, *J. Chem. Soc., Chem. Commun.*, 1994, 2317.

⁵³ P. Legzdins, S. J. Rettig, and S. F. Sayers, *J. Am. Chem. Soc.*, 1994, **116**, 12 105.

⁵⁴ T. Mise, M. Maeda, T. Nakajima, K. Kobayashi, I. Shimizu, Y. Yamamoto, and Y. Wakatsuki, *J. Organomet. Chem.*, 1994, **473**, 155.

⁵⁵ R. W. Grime and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1994, 1671.

⁵⁶ D. A. Brown, J. Burns, W. K. Glass, D. Cunningham, T. Higgins, P. McArdle, and M. M. Salama, *Organometallics*, 1994, **13**, 2662.

C(NHPrⁱ)(NHC₆H₃I-2)}]. This complex and I₂ give [ReI(CO)₄{C(NHPrⁱ)(NHC₆H₃I₂-2,6)}] via reopening of the Re–C σ bond.⁵⁷ The preparation, molecular structure, and reactivity of the rhenium oxovinylalkylidene complex *syn,mer*-[ReO{=C(H)CH=CHPh₂}{OC(CF₃)₂Me}₃(thf)] have been reported.⁵⁸ The coordinated acetone of [Mn(CO)₃(BuⁱN=CHCH=NBuⁱ)(OCMe₂)](ClO₄) undergoes intramolecular addition to the coordinated diazabutadiene to give *fac*-[Mn(CO)₃{BuⁱCN=CHCH(CH₂COMe)N(H)Buⁱ}] (ClO₄). Deprotonation of *fac*-[Mn(CO)₃{BuⁱCN=CHCH(CH₂COMe)N(H)Buⁱ}] (ClO₄) with KOH yields the enolate complex *fac*-[Mn(CO)₃{BuⁱN=CHCH(CH=C{O}Me)N(H)Buⁱ}] which reacts further, with CNBuⁱ, to give the crystallographically characterized [2.2.1] bicyclic complex *fac*-[Mn(CO)₃{BuⁱN=CHCH(C{=CN(H)Buⁱ}COMe)N(H)Buⁱ}]⁵⁹. A general method for obtaining new types of diphosphines involves a series of deprotonation/halogenation reactions with [Mn(CO)₄(dppm)](ClO₄) to give [Mn(CO)₄{(PPh₂)₂CH}], [Mn(CO)₄{(PPh₂)₂CHX}][X₃] (X = Br, I), [Mn(CO)₄{(PPh₂)₂CX}], and [Mn(CO)₄{(PPh₂)₂CBr₂}] (Br₃). The molecular structure of [Mn(CO)₄{(PPh₂)Cl}]-CH₂Cl₂ has also been determined.⁶⁰ The preparation and molecular structures of [Tc(=C=CHPh)Cl(dppe)₂] and [Tc(≡CCH₂Buⁱ)Cl(dppe)₂][BPh₄], the first examples of technetium carbene or carbyne complexes, have been reported.⁶¹ The synthesis and molecular and electronic structures of the unusual anionic oxo bis(but-2-yne) complex [Na(crypt)][ReO(η²-MeC₂Me)₂] and related compounds have been described.⁶²

Reaction of [Mn(CO)L₂Cp] [L₂ = dmpe, dmpp, dmpm, (PMe₃)₂] with SiPh_nH_{4-n} gives the oxidative-addition products [MnH(SiPh_nH_{3-n})L₂Cp], which has been crystallographically characterized for *n* = 2, L₂ = dmpe.⁶³ The addition, cycloaddition, and metathesis reactions of the vinylidene complexes [M{=C=C(H)R}(CO)₂Cp] (M = Mn, Re) and the cationic carbyne complexes [Mn(≡CCH₂R)(CO)₂Cp]⁺ have been described. A wide range of products was observed from these reactions, including (13), which has been crystallographically characterized.⁶⁴ Reaction of [Mn(≡CPh)(CO)₂Cp]⁺ with R₂NC₂NR₂ (R = Me, Et) yields the cyclopropenyl cations [C₃(NR₂)₂Ph]⁺, whereas the reaction with MeC₂NR₂ (R = Me, Et) affords the novel η⁴-carbene complexes (14) (R = Me) and (15) (R = Et).⁶⁵ The enantioselective preparation of organosulfur complexes by the [2,3] sigmatropic rearrangements of ylides of diallyl and dipropargyl sulfonium salts of rhenium, including the crystallographically characterized complex (*S,S*)-[Re(NO)(PPh₃)(SCHRR')Cp] (R = CH=CH₂, R' = CH₂CH=CH₂), have been reported.⁶⁶ Reaction of [Re(NO)(PPh₃)(ClCH₂Cl)Cp]⁺ with thiophenes gives

⁵⁷ K.-L. Lu, H.-H. Lee, C.-M. Wang, and Y.-S. Wen, *Organometallics*, 1994, **13**, 593.

⁵⁸ B. T. Flatt, R. H. Grubbs, R. L. Blanski, J. C. Calabrese, and J. Feldman, *Organometallics*, 1994, **13**, 2728.

⁵⁹ F. J. García Alonso, V. Riera, M. Vivanco, S. García-Granda, and A. Gutiérrez Rodríguez, *Organometallics*, 1994, **13**, 3209.

⁶⁰ J. Ruiz, R. Arazu, V. Riera, M. Vivanco, S. García-Granda, and A. Menéndez-Velázquez, *Organometallics*, 1994, **13**, 4162.

⁶¹ A. K. Burrell, J. C. Bryan, and G. J. Kubas, *Organometallics*, 1994, **13**, 1067.

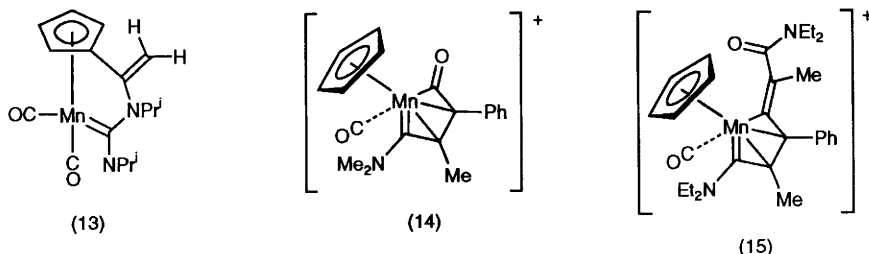
⁶² T. R. Cundari, R. R. Conry, E. Spaltenstein, S. C. Critchlow, K. A. Hall, S. K. Tahmassebi, and J. M. Mayer, *Organometallics*, 1994, **13**, 322.

⁶³ J. Sun, R. S. Lu, R. Bau, and G. K. Yang, *Organometallics*, 1994, **13**, 1317.

⁶⁴ M. R. Terry, L. A. Mercado, C. Kelley, G. L. Geoffroy, P. Nombel, N. Lukan, R. Mathieu, R. L. Ostrander, B. E. Owens-Waltermire, and A. L. Rheingold, *Organometallics*, 1994, **13**, 843.

⁶⁵ H. Fisher and C. Troll, *J. Chem. Soc., Chem. Commun.*, 1994, 457.

⁶⁶ P. C. Cagle, A. M. Arif, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1994, **116**, 3655.



the stable S-coordinated thiophene complexes $[\text{Re}(\text{NO})(\text{PPh}_3)\{\eta^1\text{-(S)-Th}\}]^+$ (Th = thiophene, 2,5-dimethylthiophene, benzo[*b*]thiophene, and 2-methylbenzo[*b*]thiophene). Bases abstract a proton from C-2 of the $\eta^1\text{-S}$ -coordinated thiophenes to yield neutral 2-thienyl and 2-benzothienyl complexes; the reaction of the 2,5-dimethylthiophene complex with base gives the 3-(2,5-dimethylthienyl) complex *via* proton abstraction at the C-3 atom.⁶⁷

6 Fe, Ru, and Os

The preparation, molecular structure, and reactions of the carbon dioxide complex $[\text{Fe}(\eta^2\text{-CO}_2)(\text{depe})_2]$ have been described.⁶⁸ Complexes of monodentate hydroxylamine, hydrazine, and diazine ligands, namely $[\text{MX}(\text{CO})_2(\eta^1\text{-NH}_2\text{OH})(\text{PPh}_3)_2][\text{SO}_3\text{CF}_3]$ (M = Ru, Os; X = Cl, Br), $[\text{MX}(\text{CO})_2(\eta^1\text{-NH}_2\text{NH}_2)(\text{PPh}_3)_2][\text{SO}_3\text{CF}_3]$ (M = Ru, Os; X = Cl, Br), and $[\text{MX}(\text{CO})_2(\eta^1\text{-NH=NH})(\text{PPh}_3)_2][\text{SO}_3\text{CF}_3]$ (M = Ru, Os; X = Cl, Br) respectively have been synthesized; $[\text{OsBr}(\text{CO})_2(\eta^1\text{-L})(\text{PPh}_3)_2][\text{SO}_3\text{CF}_3]$ (L = NH_2NH_2 , NH=NH) represent the first structurally characterized complexes containing η^1 -bonded NH_2NH_2 and HN=NH ligands.⁶⁹ The reaction of $[\text{OsHCl}(\text{CO})(\text{PPr}^i_3)_2]$ with 1-phenyl-2-propyn-1-ol gives a mixture of products from which $[\text{OsCl}_2(\text{=CHCH=CHPh})(\text{CO})(\text{PPr}^i_3)_2]$ and the heterocycle (16) were isolated and crystallographically characterized.⁷⁰ Treatment of $[\text{RuH}_2(\text{PMe}_3)_4]$ with PhCHO at -20°C gives the crystallographically characterized oxaruthenocycle complex (17), which is hydrogen-bonded to benzyl alcohol.⁷¹ Photolysis of *cis*- $[\text{FeH}_2(\text{dmpe})_2]$ in the presence of simple thiophenes affords insertion products of the Fe into both C–H and C–S bonds; the molecular structure of $[\text{Fe}(\text{SCMeCHCHCH})(\text{dmpe})_2]$ suggests that the ring is best described as a localized diene rather than a delocalized ‘ferrathiabenzene’.⁷² Reaction of $[\text{Ru}(\text{CO})_3(\text{dppe})]$ with $\text{NO}_2\text{C}_6\text{H}_3\text{-2-CF}_3\text{-4-Cl}$ gives the crystallographically characterized complex $[\text{Ru}(\text{CO})_2(\text{dppe})(\eta^2\text{-ONC}_6\text{H}_3\text{-2-CF}_3\text{-4-Cl})]$, which contains a π -bonded nitrosoarene.⁷³ The activation of terminal alkynes using *cis*- $[\text{RuCl}_2(\text{dppe})_2]$ results either in monoalkynyl complexes, *via* a vinylidene, or bis(alkynyl) ruthenium complexes, which are the essential precursors of *trans*-

⁶⁷ M. J. Robertson, C. J. White, and R. J. Angelici, *J. Am. Chem. Soc.*, 1994, **116**, 5190.

⁶⁸ S. Komiya, M. Akita, N. Kasuga, M. Hirano, and A. Fukuoka, *J. Chem. Soc., Chem. Commun.*, 1994, 1115.

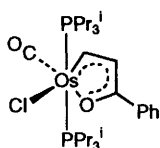
⁶⁹ T.-Y. Cheng, A. Ponce, A. L. Rheingold, and G. L. Hillhouse, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 657.

⁷⁰ M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, and B. Zeier, *Organometallics*, 1994, **13**, 1662.

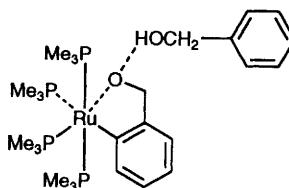
⁷¹ F. Ozawa, I. Yamagami, and A. Yamamoto, *J. Organomet. Chem.*, 1994, **473**, 265.

⁷² I. E. Buys, L. D. Field, T. W. Hambley, and A. E. D. McQueen, *J. Chem. Soc., Chem. Commun.*, 1994, 557.

⁷³ S. J. Skoog, J. P. Campbell, and W. L. Gladfelter, *Organometallics*, 1994, **13**, 4137.

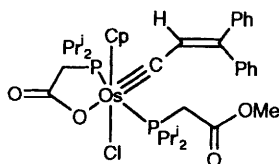


(16)



(17)

$[\text{Ru}(\text{C}\equiv\text{CR})(\text{NH}_3)(\text{dppe})_2][\text{PF}_6]$ and $[\text{Ru}(\text{C}\equiv\text{CPh})(=\text{C}=\text{C}=\text{CPh}_2)(\text{dppe})_2][\text{PF}_6]$ derivatives.⁷⁴ Hydrolysis of the chloro(2-pyrrolyl) carbene complex $[\text{RuCl}_2\{\text{=CCl}(2\text{-pyrrolyl})\}(\text{CO})(\text{PPh}_3)_2]$ is followed by rearrangement to give $[\text{RuCl}(\sigma\text{-2-pyrrolyl})(\text{CO})_2(\text{PPh}_3)_2]$.⁷⁵ Several carbyne(dichloro) and carbyne(dichloro)hydrido osmium complexes have been prepared from alkyne precursors including the crystallographically characterized complex (18).⁷⁶



(18)

The preparation and molecular structure of the novel dinitrosyl complex $[\text{Fe}(\text{PPh}_3)(\eta^2\text{-tcne})(\text{NO})_2]$ have been described.⁷⁷ A series of $[\text{Fe}(\text{CO})_3(\text{acac})]$ compounds with electron donor C-5substituents (OMe, OCOR, NR_2) have been resolved *via* oxazolidine or imine derivatives or through incorporation of a homochiral dialkylamino auxiliary. The absolute configurations of the complexes have been confirmed by X-ray crystallography.⁷⁸ The novel coupling of $[\text{Fe}(\text{CO})_3(7\text{-azabenzonorbornadiene})]$ with cyclohexene occurs both thermally and photochemically to give the crystallographically characterized complex (19); C–C bond formation from the *exo* face of 7-azabenzonorbornadiene is accompanied by the generation of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cyclohexadiene})]$ *syn* to the new C–C bond.⁷⁹ The first example of the selective reaction of a diastereoisomeric mixture of $[\text{Fe}(\text{CO})_3(2\text{-isobornoxy-5-methylcyclohexadienylium})][\text{PF}_6]$ with achiral K[dimethylmalonate] gives the highly enantiomerically enriched diene complex (20) (84% ee).⁸⁰

⁷⁴ D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1994, 859.

⁷⁵ M. M. P. Ng, W. R. Roper, and L. J. Wright, *Organometallics*, 1994, **13**, 2563.

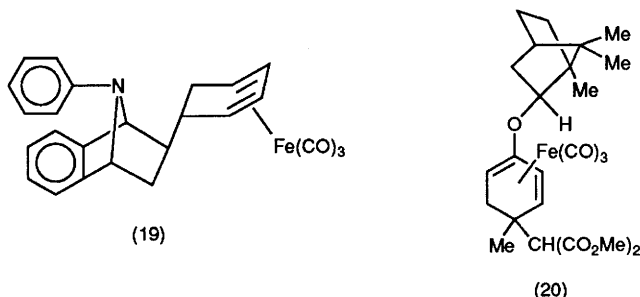
⁷⁶ B. Weber, P. Steinert, B. Windmüller, J. Wolf, and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1994, 2595.

⁷⁷ L. Li, G. D. Enright, and K. F. Preston, *Organometallics*, 1994, **13**, 4686.

⁷⁸ J. A. S. Howell, A. G. Bell, P. J. O'Leary, P. McArdle, D. Cunningham, G. R. Stephenson, and M. Hastings, *Organometallics*, 1994, **13**, 1806.

⁷⁹ C.-H. Sun, N.-C. Shang, L.-S. Liou, and J.-C. Wang, *J. Organomet. Chem.*, 1994, **481**, 179.

⁸⁰ C. W. Ong and R. H. Hsu, *Organometallics*, 1994, **13**, 3952.



Reaction of $[\text{FeH}(\text{CO})_2(\eta\text{-C}_5\text{Ph}_4\text{Ar})]$ ($\text{Ar} = \text{Ph}, p\text{-tol}$) with the trityl radical, CPh_3 , gives the 17-electron complexes $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Ph}_4\text{Ar})]$ *via* hydrogen atom abstraction.⁸¹ The preparation and molecular structures of $[\text{Ru}\{(\text{R})\text{-(binap)}\}\text{Cp}]$ [binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] and $[\text{Ru}\{(\text{R})\text{-(binap)}\}\text{Cp}][\text{CF}_3\text{SO}_3]$ have been described. The latter is of particular interest since it contains the unprecedented tridentate mode of attachment of a binap ligand by η^2 -bonding of one of the naphthyl rings as well as both phosphorus atoms.⁸² The stoichiometric activation of eth-1-ynyl-1-cyclohexanol by $[\text{RuCl}(\text{PPh}_3)_2(\eta^5\text{-ind})]$ in the presence of $\text{Na}[\text{PF}_6]$ gives the crystallographically characterized complex (21), which contains a new spirobicyclic system, obtained by an unprecedented coupling process.⁸³ Deprotonation of $[\text{Ru}\{\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}\}(\text{PPh}_3)_2\text{Cp}]\text{I}$ with $[\text{NBu}_4]^+\text{F}^-$ affords the neutral, crystallographically characterized cyclopropenyl complex (22), which reacts with H^+ or $[\text{CPh}_3]^+$ to regenerate the vinylidene complex.⁸⁴ The first silylene complexes not stabilized by heteroatom π donation to silicon, $[\text{Ru}(\text{SiR}_2)(\text{PMe}_3)_2\text{Cp}^*][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{Me}, \text{Ph}$), have been prepared and the methyl example has been characterized by X-ray crystallography.⁸⁵ Treatment of $[\text{RuMe}(\text{PPh}_3)_2\text{Cp}]$ with $\text{Me}_2\text{SiHSiMe}_2\text{OME}$ yields the first donor-stabilized bis(silylene) ruthenium complex (23), which has been crystallographically characterized.⁸⁶ The preparation and molecular structure of the six-coordinate intermediate-spin iron(II) complex $[\text{Fe}(\sigma\text{-O}=\text{CMe}_2)(\text{dppe})\text{Cp}^*][\text{CF}_3\text{SO}_3]$, which shows unexpected paramagnetic behaviour, have been described.⁸⁷ Reaction of $[\text{RuBr}(\eta^4\text{-C}_5\text{H}_4\text{O})\text{Cp}]$ with Br_2 gives the novel crystallographically characterized η^3 -allyl complex $[\text{RuBr}_2(\eta^3\text{-C}_5\text{H}_4\text{OBr})\text{Cp}]$. Reaction of $[\text{RuBr}(\eta^4\text{-C}_8\text{H}_{12})\text{Cp}]$ with 3-bromocyclopent-4-ene-1-one affords the crystallographically characterized cyclopentenoyl complex $[\text{RuBr}_2(\eta^3\text{-C}_5\text{H}_5\text{O})\text{Cp}]$, which reacts further in the presence of NET_3 to give the cyclopentadienone complex $[\text{RuBr}(\eta^4\text{-C}_5\text{H}_4\text{O})\text{Cp}]$.⁸⁸ Treatment of $[\text{RuCl}(\eta^4\text{-nbd})\text{Cp}^*]$ with $\text{Ag}[\text{BF}_4]$ in ethanol gives $[\text{Ru}(\eta^4\text{-nbd})\text{Cp}^*][\text{BF}_4]$, which undergoes a skeletal rearrangement of the attached norbornadiene *via* C-1–C-2 bond cleavage to yield a 6-methylfulvene complex, $[\text{RuCp}^*(\eta^6\text{-$

⁸¹ I. Kuksis and M. C. Baird, *Organometallics*, 1994, **13**, 1551.

⁸² D. D. Pathak, H. Adams, N. A. Bailey, P. J. King, and C. White, *J. Organomet. Chem.*, 1994, **479**, 237.

⁸³ V. Cadierno, M. P. Gamasa, J. Gimeno, E. Lastra, J. Borge, and S. Garcia-Granda, *Organometallics*, 1994, **13**, 745.

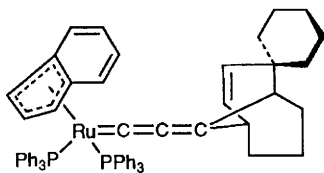
⁸⁴ P.-C. Ting, Y.-C. Lin, M.-C. Cheng, and Y. Wang, *Organometallics*, 1994, **13**, 2150.

⁸⁵ S. K. Grumbine, T. D. Tilley, F. P. Arnold, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1994, **116**, 5495.

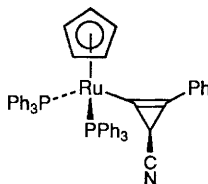
⁸⁶ H. Tobita, H. Wada, K. Ueno, and H. Ogino, *Organometallics*, 1994, **13**, 2545.

⁸⁷ P. Hamon, L. Toupet, J.-R. Hamon, and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1994, 931.

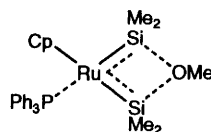
⁸⁸ K. Kirchner, K. Mereiter, and R. Schmid, *J. Chem. Soc., Chem. Commun.*, 1994, 161.



(21)



(22)



(23)

$C_5H_4CHCH_3$)[BF_4]; the last can be prepared directly from $[RuCl(\eta^4\text{-nbd})Cp^*]$ and $Ag[BF_4]$ in CH_2Cl_2 .⁸⁹ The first stable silacyclopentadienyl complex $[RuHCp^*\{\eta^5\text{-Me}_4C_4SiSi(SiMe_3)_3\}][BPh_4]$, which has been crystallographically characterized and can be described as a protonated metallocene, has been synthesized. The complex $[RuHCp^*\{\eta^5\text{-Me}_4C_4SiSi(SiMe_3)_3\}][BPh_4]$ can be deprotonated with $(thf)_3Li[Si(SiMe_3)_3]$ to yield the silacyclopentadienyl ruthenocene $[RuCp^*\{\eta^5\text{-Me}_4C_4SiSi(SiMe_3)_3\}]$.⁹⁰ The first ring-tilted, highly strained [2]ruthenocenophane containing only an ethylene bridge across the $RuCp_2$ unit has been prepared and crystallographically characterized; it undergoes thermal ring-opening polymerization to give poly(ruthenocenylethylene).⁹¹ The synthesis and molecular structure of the unusual η^5 -monophospholyl complex $[RuCp^*(\eta^5\text{-2,5-Bu}^i_2C_4H_2P)]$ have been described.⁹²

The preparation, molecular structure (for arene = C_6Me_6), and C–H activation of $[RuH_2(SiMe_3)_2(\eta^6\text{-arene})]$ (arene = C_6H_6 , *p*-cumene, C_6Me_6) have been reported.⁹³ The metal atom synthesis and X-ray crystal structure of the unusual iron(IV) complex $[FeH_2(SiCl_3)_2(\eta^6\text{-C}_6\text{H}_5\text{Me})]$ have been described.⁹⁴ Treatment of $[RuCl_2L(\eta^6\text{-C}_6\text{Me}_4R_2)]$ ($R = H, Me$; $L = PMe_3, PPh_3$) with $HC\equiv CC(H)(OH)\{C_6H_4(NMe_2)\text{-}p\}$ in the presence of $Na[PF_6]$ gives the oxametalocyclic complexes $[Ru\{CH=C(C_6H_4(NMe_2)\text{-}p)CHO\}L(\eta^6\text{-C}_6\text{Me}_4R_2)][PF_6]$ (crystallographically characterized for $R = H$, $L = PPh_3$) via an unprecedented 1,2-migration of the dimethylaminophenyl substituent.⁹⁵ Condensation of Ru or Os atoms with mixtures of C_6F_6 and a second arene at $-196^\circ C$ affords the novel complexes $[M(\eta^4\text{-C}_6F_6)(\eta^6\text{-arene})]$ ($M = Ru$ or Os ; arene = C_6H_6 , $C_6H_4Me_{2-1,3}$, or $C_6H_3Me_{3-1,3,5}$), crystallographically characterized for $M = Ru$, arene = $C_6H_3Me_{3-1,3,5}$.⁹⁶

7 Co, Rh, and Ir

Reaction of $CoCl_2$ and $NiCl_2$ with two equivalents of LiR_F [$R_F = 2,4,6\text{-tris(trifluoromethyl)phenyl}$] gives $[Co(R_F)_2]$ and $[Ni(R_F)_2]$ respectively, the first homoleptic

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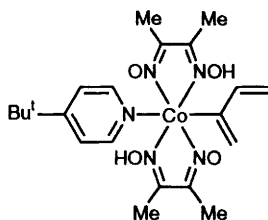
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⁹⁶ A. Martin, A. G. Orpen, A. J. Seeley, and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1994, 2251.

transition-metal complexes containing σ -bonded R_F ligands.⁹⁷ Several substituted-pyridine cobalt bis(dimethylglyoxime) buta-1,3-diene complexes with unusual structures such as (24) and their Diels–Alder reactions with a variety of dienophiles have



(24)

been reported.⁹⁸ Irradiation of *trans*-[RhCl(CO)(PMe₃)₂] in benzene/thf (1 : 3 v/v) at 230 K gives three main products, [RhHCl(Ph)(CO)(PMe₃)₂] (two stereoisomers) and *trans*-[RhPh(CO)(PMe₃)₂], all of which revert into *trans*-[RhCl(CO)(PMe₃)₂] when the reaction mixture is allowed to warm to room temperature.⁹⁹ The unusual activation of two equivalents of C₆H₆ at 333 K by [IrH(CH=CH₂)(η^2 -C₂H₄)Tp] gives [IrPh₂Tp], which reacts with N₂ to afford the dinitrogen complexes [IrPh₂(N₂)Tp] and [{IrPh₂Tp}(μ -N₂)], which has been crystallographically characterized.¹⁰⁰ Two key intermediates in the rhodium-catalysed carbonylation of ethene, [RhH₃(CO)₂][−] and [Rh(COEt)I₃(CO)₂][−], have been characterized at low temperature.¹⁰¹ The preparation and *X*-ray crystal structure of the first isonitrile transition-metal complex [K(dme)][Co{CN(2,6-C₆H₃Me₂)₄}] have been reported.¹⁰² Treatment of [IrCl(CO)(PPh₃)₂] with NSF₃ gives the first thiazyldifluoride complex, [IrFCl(NSF₂)(CO)(PPh₃)₂], which has been crystallographically characterized.¹⁰³ Reaction of [{IrCl(η^2 -C₂H₄)₂}] with PrⁱPCH₂CO₂Me gives *trans*-[IrCl(η^2 -C₂H₄)(PrⁱPCH₂CO₂Me- κ P)₂], which reacts with CO to afford *trans*-[IrCl(CO)(PrⁱPCH₂CO₂Me- κ P)₂], and with HC₂R (R = Ph, CO₂Me) to yield [IrH(C \equiv CR)Cl(PrⁱPCH₂CO₂Me- κ P)(PrⁱPCH₂CO₂Me- κ^3 P,O)]. When heated, these σ -alkynyls give the vinylidene complexes *trans*-[IrCl(=C=CHR)(PrⁱPCH₂CO₂Me- κ P)₂], which react with Al₂O₃/H₂O to afford [Ir(=C=CHR)(PrⁱPCH₂CO₂Me- κ P)(PrⁱPCH₂CO₂- κ^2 P,O)] *via* cleavage of the Me–O bond of one of the phosphino ester ligands.¹⁰⁴ The first structurally characterized example of a transition-metal complex with an O-bonded methyl sulfito ligand, [Ir(CO){OS(O)OMe}{SO₂}(PPh₃)₂].0.5toluene, has been described.¹⁰⁵

Reaction of [Ir(triphos)(η^4 -C₆H₆)]X (X = BPh₄, PF₆) with benzo[*b*]thiophene (BT) gives the unprecedented complex [Ir(triphos)(η^3 -C,C,S-C₈H₆S)]X in which the

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⁹⁸ M. W. Wright, T. L. Smalley, Jr., M. E. Welker, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1994, **116**, 6777.

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¹⁰⁰ E. Gutiérrez, A. Monge, M. C. Nicasio, M. L. Poveda, and E. Carmona, *J. Am. Chem. Soc.*, 1994, **116**, 791.

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¹⁰² P. A. Leach, S. J. Geib, J. A. Corella, II, G. F. Warnock, and N. J. Cooper, *J. Am. Chem. Soc.*, 1994, **116**, 8566.

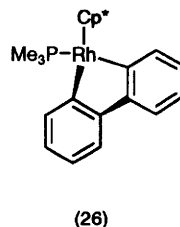
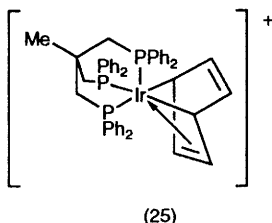
¹⁰³ P. G. Watson, E. Lork, and R. Mews, *J. Chem. Soc., Chem. Commun.*, 1994, 1069.

¹⁰⁴ P. Steinert and H. Werner, *Organometallics*, 1994, **13**, 2677.

¹⁰⁵ S. L. Randall, C. A. Miller, T. S. Janik, M. R. Churchill, and J. D. Atwood, *Organometallics*, 1994, **13**, 141.

BT ligand is attached to the iridium through the S atom and a C=C of the thiophene ring. Mild thermolysis of this complex yields the iridabenzothiabenzenes complexes $[\text{Ir}(\text{triphos})(\eta^2\text{-C}_8\text{H}_6\text{S})]\text{Y}$, which has been crystallographically characterized ($\text{Y} = \text{BPh}_4$).¹⁰⁶ Treatment of crystalline $[\text{IrH}_2(\text{triphos})(\eta^2\text{-C}_2\text{H}_4)][\text{BPh}_4]$ with ethyne (4 atm) at 343 K for 3 h gives ethene, but-2-ene, and five different mononuclear organometallic products including (25), which is the catalytic precursor when a similar reaction is carried out at 373 K.¹⁰⁷ The preparation and reactivity of the unsupported (η^3 -oxaallyl) complexes $[\text{Rh}(\text{PR}_3)_2\{\eta^3\text{-CH}_2\text{C}(\text{O})\text{R}'\}]$ ($\text{R} = \text{Et}$, Ph ; $\text{R}' = \text{Bu}^t$, Ph), crystallographically characterized for $\text{R} = \text{Ph}$, $\text{R}' = \text{Bu}^t$, have been reported.¹⁰⁸ The synthesis and molecular structure of the chiral bidentate *P,N*-ligand complex $[\text{Rh}\{\text{2}-(1\text{S},2\text{S},5\text{R})-(\text{---})\text{menthoxydiphenylphosphino}\}\text{pyridine}](\eta^4\text{-cod})[\text{ClO}_4]$ have been described.¹⁰⁹ The preparation and X-ray crystal structure of $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2](\eta^4\text{-nbd})$, which initiates the living polymerization of phenylalkynes, have been reported.¹¹⁰

Reaction of $[\text{RhHPh}(\text{PMe}_3)\text{Cp}^*]$ with 1.5 equivalents of biphenylene rapidly affords $[\text{RhH}(\sigma\text{-biphenylenyl})(\text{PMe}_3)\text{Cp}^*]$ where C–H activation occurs at the α -position. Heating this complex gives the C–C inserted product (26) which has been crystallographically characterized.¹¹¹ The synthesis, molecular structure, and reactions of the nitrosyl complex $[\text{Ir}(\text{NO})(\eta^2\text{-C}_2\text{H}_4)\text{Cp}^*][\text{BF}_4]$ have been described.¹¹²



Heating (27) gives the cyclobutadiene complex $[\text{Rh}(\eta^4\text{-C}_4\text{MeBu}^t_3)\text{Cp}^*]$ via a hydrogen shift and ring-closure pathway.¹¹³ Treatment of $[\text{Co}(\eta^4\text{-4-vinylcyclopentene})\text{Cp}^*]$ with $\text{HBF}_4\cdot\text{OME}_2$ yields the ethylcyclopentenyl complex (28) in which the electron-deficient metal centre is stabilized by a three-centre, two-electron (agostic) interaction. Complex (28) easily undergoes disrotatory 'inwards' ring opening to give $[\text{Co}\{\eta\text{-C}_5\text{H}_6(\text{syn-Et-5})\}\text{Cp}^*][\text{BF}_4]$, which contains an acyclic 5-ethylpentadienyl ligand.¹¹⁴ Reaction of $[\text{RhCp}^*][\text{PF}_6]$ with excess KOH and MeI in dme for two days at 60 °C affords the first decaisopropylmetallocene, $[\text{Rh}(\eta\text{-C}_5\text{Pr}^i_5)_2][\text{PF}_6]$, by forming twenty C–C bonds.¹¹⁵ The chemical and electrochemical formation of the hydride-forming

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¹⁰⁸ G. A. Slough, R. Hayashi, J. R. Ashbaugh, S. L. Shamblyn, and A. M. Aukamp, *Organometallics*, 1994, **13**, 890.

¹⁰⁹ C. G. Arena, F. Nicolò, D. Drommi, G. Bruno, and F. Faraone, *J. Chem. Soc., Chem. Commun.*, 1994, 2251.

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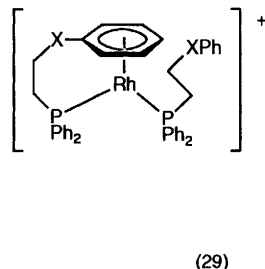
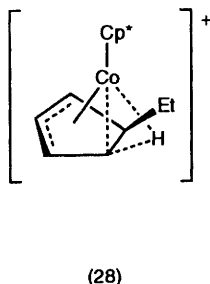
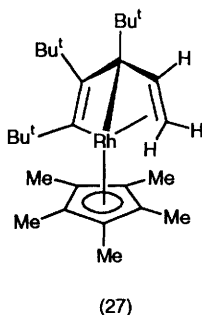
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catalytic intermediates $[M(\text{bipy})\text{Cp}^*]$ ($M = \text{Rh}, \text{Ir}$) and $[M(\text{bipy})(\eta^6\text{-arene})]$ ($M = \text{Ru}, \text{Os}$; arene = C_6H_6 , C_6Me_6 , $p\text{-MeC}_6\text{H}_4\text{Pr}^1$) have been reported.¹¹⁶ The preparation and reactions of the novel rhodium(I) piano-stool complexes (29) ($X = \text{CH}_2, \text{O}$), crystallographically characterized for $X = \text{O}$, have been described.¹¹⁷

8 Ni, Pd, and Pt

The first carbon dioxide palladium(0) complex, $[\text{Pd}(\text{PMePh}_2)_2(\eta^2\text{-CO}_2)]$, has been prepared.¹¹⁸ Several novel σ -acetylide complexes of platinum(II) have been synthesized, of which (30) has been crystallographically characterized.¹¹⁹ The thermolytic rearrangement of *cis*- $[\text{Pt}(\text{CH}_2\text{SiMe}_3)_2\text{L}_2]$ ($\text{L} = \text{PMe}_3, \text{PEt}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3$) results in an unusual migratory isomerization, to give the asymmetric organoplatinum(II) complexes *cis*- $[\text{PtMe}(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3)\text{L}_2]$; a detailed mechanistic study of this rearrangement has been made.¹²⁰ The first examples of the successive insertion of CO and strained alkenes have been observed for $[\text{PdRX}(\text{Ar-bian})]$ ($X = \text{Cl}, \text{Br}, \text{I}$) and $[\text{PdR}(\text{NCMe})(\text{Ar-bian})][\text{SO}_3\text{CF}_3]$ {Ar-bian = bis(arylimino)acenaphthene; $\text{Ar} = p\text{-MeOC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, o,o'\text{-Pr}_2\text{C}_6\text{H}_3$ }, giving new products of the type $[\text{Pd}\{\text{CH}(\text{R}')\text{CH}(\text{R}')\text{C}(\text{O})\text{CH}(\text{R}')\text{CH}(\text{R}')\text{C}(\text{O})\text{R}\}\text{X}(\text{Ar-bian})]$.¹²¹ The reaction of $[\text{Pd}(\text{CNBu}^t)_2]$ with bis(disilanyl)methane derivatives activates two Si-Si bonds and gives cyclic bis(silyl)Pd(CNBu^t)₂ complexes, one of which, (31), has been crystallographically characterized.¹²² A series of Δ^2 -oxazolines has been prepared from cationic platinum(II) nitrile complexes; the molecular structure of (32) is also reported.¹²³ Treatment of equimolar amounts of $\text{PR}_2(\text{C}_6\text{Cl}_5)$ ($\text{R} = \text{Et}, \text{Ph}$), $[\text{Ni}(\eta^4\text{-cod})_2]$, and L [$\text{L} = \text{PMe}_2\text{Ph}, \text{PEt}_3, \text{P}(\text{CH}_2\text{Ph})_3$] gives three types of organometallic product, namely the phosphonickelocycles $[\text{Ni}\{\text{C}_6\text{Cl}_4(\text{P}\text{R}_2)_2\}_2]$

¹¹⁶ W. Kaim, R. Reinhardt, and M. Sieger, *Inorg. Chem.*, 1994, 33, 4453.

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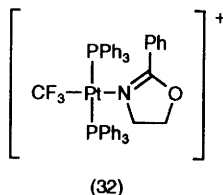
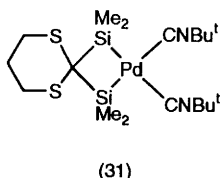
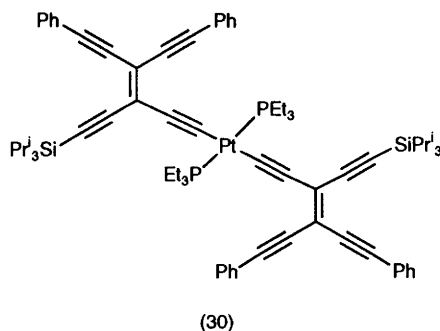
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¹²⁰ B. C. Ankanian, V. Christou, D. T. Hardy, S. K. Thomson, and G. B. Young, *J. Am. Chem. Soc.*, 1994, 116, 9963.

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(crystallographically characterized for $R = Et$), $[NiCl\{C_6Cl_4(PR_2)_2\}L]$, and $[NiCl\{C_6Cl_4(PR_2)_2\}L_2]$ (crystallographically characterized for $R = Ph$, $L = PEt_3$). However, when one equivalent of a bidentate phosphine, $L-L$ [$L-L = Ph_2P(CH_2)_nPPH_2$], is used in place of L the unusual five-coordinate complexes $[NiCl\{C_6Cl_4(PR_2)_2\}\{Ph_2P(CH_2)_nPPH_2\}]$ ($n = 2, 3$) and the bis(monodentate) dppm complex $[NiCl\{C_6Cl_4(PPh_2)_2\}(\eta^1-dppm)_2]$ were obtained.¹²⁴ The preparation, molecular structure ($R = Me$) and properties of the first octahedral diorganonickel(IV) complexes (33) ($R = Me, Bu^t$) have been described.¹²⁵

The synthesis and X -ray crystal structures of the 14-electron bis(carbene) complexes (34) ($M = Ni, Pt$) have been reported.¹²⁶ The preparation and molecular structure of the first donor-free bis(silylene) complex of nickel, $[Ni\{Si(Bu^tNCH=CHNBu^t)\}_2(CO)_2]$, have been described.¹²⁷ The preparation, X -ray crystal structure, and chemistry of the first pure mono(alkyne) complex of nickel, $[Ni\{\eta^2-HO(CH_3)_2CC\equiv CC(CH_3)_2OH\}_2]$ have been reported; hydrogen bonding dictates the structure of this complex.¹²⁸ The first examples of quantitative allene, 1,1-dimethylallene, and tetramethylallene migratory insertion reactions into alkyl and acyl palladium compounds of bidentate and tridentate nitrogen donors have been described; the structure of $[Pd(bipy)(\eta^3-2-acetyl-1,1,3,3-tetramethylallyl)][CF_3SO_3]$ and the preparation of an unusual η^1 -allyl palladium complex with a terpy ligand have also been reported.¹²⁹ The reactions of η^3 -oxatrimethylenemethane platinum complexes with

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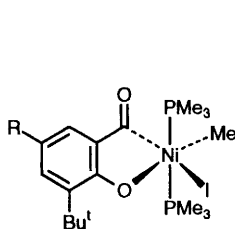
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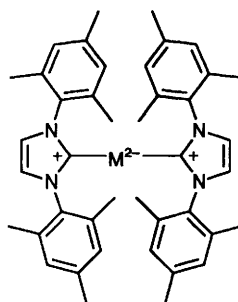
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(33)



(34)

selected nucleophiles provide the first examples of nucleophilic substitution of the central carbon of an allyl group *via* a platinocyclobutane intermediate.¹³⁰ Treatment of $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{CCPh})][\text{CF}_3\text{SO}_3]$ with $\text{Na}[\text{CH}(\text{CO}_2\text{Me})_2]$ yields the first platinum trimethylenemethane complex, $[\text{Pt}(\text{PPh}_3)_2\{\eta^3\text{-CH}_2\text{C}(\text{C}\{\text{CO}_2\text{Me}\}_2)\text{CHPh}\}]$, which has the trimethylenemethane ligand η^3 -bonded to the platinum.¹³¹ The reaction of $[\text{Ni}\{\eta^1\text{-Bu}_2\text{P}(\text{CH}_2)\text{P}(\text{CH}_2)\text{PBu}_2\}(\eta^2\text{-C}_2\text{H}_4)_2]$ with ethyne at low temperature gives $[\text{Ni}\{\eta^1\text{-Bu}_2\text{P}(\text{CH}_2)\text{P}(\text{CH}_2)\text{PBu}_2\}(\eta^6\text{-C}_6\text{H}_6)]$, the first example of a nickel(0) complex with an arene coordinated as a six-electron donor.¹³²

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