# 7  Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

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## 1 General

This Section contains reference to general topics and to reviews of the chemistry of the early transition elements.

Transition-metal–nitrogen multiple bonds form the topic of an interesting compilation[1] that stresses the variety of structural types possible in this area. Many vibrational spectroscopic data are included together with relevant structural data. The transition-metal co-ordination chemistry of the uncharged thio-, seleno-, and telluro-ethers is the subject of a 40-page review.[2] Complexes are systematically classified by group and available structural data of these complexes are used to discuss the likely bonding modes. Thio-species of a different type ($MS_4^{m-}$, thiometalate anions) are discussed in an extensive account[3] that stresses their wide range of interesting chemistry. Most of the species involve an early transition metal (e.g. V or Mo), and apart from a discussion of bonding schemes there is a useful didactic account of the application of spectroscopic methods.

The final section deals with the formation of heterometallic species (i.e. $MS_4^{m-}$ considered as a ligand) and includes data of relevance to the bioinorganic topics of nitrogenase and Cu–Mo antagonism in ruminants.

An extensive (500 references) review[4] of the co-ordination chemistry of sulphoxide transition-metal complexes includes a considerable amount of comment on the early metals. Structural, spectroscopic, and synthetic aspects of the area are covered.

It is not possible to write a sensible review of a 327-page volume dealing with a recent symposium on the reactivity of metal–metal bonds.[5] Suffice it to say that the work includes such diverse titles as 'Thermochemistry of metal–metal bonds' and 'Anything one can do, 2 can do too – and it's more interesting'. It is thus an essential addition to the literature of a current rapidly developing field.

[1] K. Dehnicke and J. Strähle, Angew. Chem., Int. Ed. Engl., 1981, 20, 413.
[2] S. G. Murray and F. R. Hartley, Chem. Rev., 1981, 81, 365.
[3] A. Müller, E. Diemann, R. Jostes, and H. Bögge, Angew. Chem., Int. Ed. Engl., 1981, 20, 934.
[4] J. A. Davies, Adv. Inorg. Chem. Radiochem., 1981, 24, 116.
[5] M. H. Chisholm (ed.), 'Reactivity of Metal–Metal Bonds', A.C.S. Symposium Series, American Chemical Society, Washington, 1981, Vol. 155.

## 2 Titanium, Zirconium, and Hafnium

Zirconium seems to attract more current attention than titanium. An interesting article[6] on extended metal–metal bonding in halides of the early transition metals includes much information on ZrX, which involves the condensation of $M_6X_8$ type clusters. Cyclic voltametric work[7] in a $2:1$ $AlCl_3:Bu(py)Cl$ melt (40 °C) shows that $Ti^{IV}$ exists in two reducible species (probably $TiCl_6^{2-}$ and $TiOCl_4^{2-}$). The equilibrium constant for the reaction (1) was found to be $K = 900$.

$$TiCl_6^{2-} + AlOCl_2^- \rightleftharpoons AlCl_4^- + TiOCl_4^{2-} \qquad (1)$$
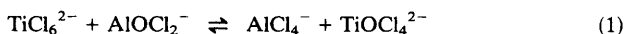
Melts at the somewhat higher temperature of around 2080 °C were used to prepare $LaTiO_3$ crystals.[8] $CeTiO_3$ was also prepared, although both products were found to contain a slight ($\sim 4\%$) excess of oxygen. The crystals were then examined for electrical resistance and magnetic behaviour over a wide temperature range. Several anomalies were observed and the results are discussed in terms of what the authors describe as highly speculative models for the electronic structure.

The ion-exchange capabilities of zirconium phosphate form the basis of several studies. Ion-exchange isotherms and distribution coefficients for the uptake of $Cd^{2+}$ and $Pb^{2+}$ (as acetates) have been obtained at temperatures up to 98 °C. The uptake was increased by the presence of sodium ions.[9] The ion-exchange mechanism involves use of the layered structure of zirconium phosphate, which exists in an $\alpha$-form $Zr(HPO_4)_2 \cdot H_2O$ and a $\gamma$-form $Zr(HPO_4)_2 \cdot 2H_2O$. The $\gamma$-form allows interlayer $HPO_4^{2-}$ ions to be replaced by $PhPO_3^{2-}$. $X$-Ray data indicate that this is accompanied by an increase in the basal spacing. One-quarter of the $HPO_4^{2-}$ were replaced, whereas similar experiments with n-alkyl phosphates showed that 50% exchange could be achieved.[10] Both the $\alpha$- and $\gamma$-forms were used in investigations on the uptake of $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ ions.[11]

Analysis of the electronic reflectance spectra suggests that the stereochemistry around the exchange ion is octahedral at room temperature, but that heating causes progressive collapse of the phosphate layer-structure leading to a five-co-ordinate environment.

Solution chemistry is a complicated area for the early transition metals. The oxidation of $Ti(h.e.d.t.a.)H_2O$ by $VO(h.e.d.t.a.)^-$, where $h.e.d.t.a.^{3-}$ is $N$-(hydroxyethyl)ethylenediaminetriacetate, is shown[12] to proceed by a series of steps that involve the participation of binuclear species $Ti^{IV}/V^{III}$ and $Ti^{III}/Ti^{IV}$. Similar kinetic investigations have also been applied[13] to the formation of $Ti(O_2)(e.d.t.a.)^{2-}$ over the pH range 2.0–5.2. Relationships between the various possible structural forms are established and activation parameters for the formation of the peroxo-complexes reported.

[6] J. D. Corbett, *Acc. Chem. Res.*, 1981, **14**, 239.
[7] H. Linga, Z. Stojec, and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1981, **103**, 3754.
[8] D. A. MacLean and J. E. Greedan, *Inorg. Chem.*, 1981, **20**, 1025.
[9] J. P. Gupta and D. V. Nowell, *J. Chem. Soc., Dalton Trans.*, 1981, 385.
[10] S. Yamanaka and M. Hattori, *Inorg. Chem.*, 1981, **20**, 1929.
[11] L. Alagna, A. A. G. Tomlinson, C. Ferragina, and A. La Ginestra, *J. Chem. Soc., Dalton Trans.*, 1981, 2376.
[12] F. J. Kristine and R. E. Shepherd, *Inorg. Chem.*, 1981, **20**, 215.
[13] F. J. Kristine, R. E. Shepherd, and S. Siddiqui, *Inorg. Chem.*, 1981, **20**, 2571.

Zirconium solution chemistry is often thought to be dominated by hydrolysis and various condensed compounds. Thus $Zr^{IV}$ solutions at relatively high molarities almost certainly contain the same cyclic tetrameric unit as found in the crystalline state. However, careful dilution of aqueous $HClO_4$ solutions of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in the presence of 2-thenoyltrifluoroacetone produces evidence[14] for the presence of the monomeric $Zr(H_2O)_8^{4+}$, *i.e.* $Zr_4 \rightarrow 4Zr$. The monomer is able to react with the dione, to form a coloured complex, but not the tetramer. A simple second-order rate law of $3.7 \times 10^{-3}$ $[H^+][Zr_4]$ was observed. Various acids (HX) also affect the rate and data are presented for a range of species to the more general equation (2). Turbimetric and electrophoretic measurements were used to delineate the pH dependence of zirconium(IV) in the presence of both maleic and phthalic acids.[15] Areas are observed where stable colloids, precipitates, or stable solutions exist. Two soluble maleic species were identified with quite distinct electrophoretic mobilities, but their identity could not be completely established.

$$\text{Rate} = k_H[H^+][Zr_4] + k_{HX}[HX][Zr_4] \qquad (2)$$

The rapid spread of n.m.r. techniques to metals has reached zirconium.[16] The nucleus $^{91}Zr$ with 11.23% abundance and $I = \frac{5}{2}$ has been used for spectra of the molecule $Zr(BH_4)_4$. Decoupling of the $^{11}B$ should give a 17-line multiplet (from the 16 equivalent hydrogens), but since the outer members of the series are of rather low intensity only about 12 peaks are clearly observed but the relative intensities of the remainder and the general broadness supports the authors interpretation.

Although Ti, Zr, and Hf alkoxides have been studied for many years, very little work seems to be currently in progress. However, during this relatively quiet period an interesting electrochemical preparative procedure has been published.[17] Synthesis of $M(OR)_4$ (M = Ti or Zr) has been achieved by simple electrolysis with a metal anode and a platinum cathode and an electrolyte of $(Bu_4N)Br$ or NaBr in ROH. No new compounds are reported, but the method should be capable of further development.

$[Ti_4(OPr^i)_{12}O]$, produced by the lithium borohydride reduction of $Ti(OPr^i)_4$, has been shown[18] to contain both $Ti^{III}$ and $Ti^{IV}$. E.s.r. measurements are used to support the assignments and to suggest that, although the tetramer exists in the solid state, a dimeric mixed-valence species such as $Ti_2(OR)_7$ and/or $Ti_2(OR)_5O$ is more likely in benzene solution. The structure of the bridged imido-complex $[(Me_2N)_2Ti]_2(\mu\text{-Bu}^tN)_2$ (1) has been reported.[19] The metal atoms are symmetrically bridged (Ti—N of 1.921 and 1.925 Å), whereas the related tungsten complex (2) is unsymmetrically bridged (W—N of 1.736 and 1.842 Å). Molecular orbital theory is employed to account for this distinction and a suggestion of 'aromatic' and 'anti-aromatic' behaviour invoked.

[14] D. H. Devia and A. G. Sykes, *Inorg. Chem.*, 1981, **20**, 910.
[15] H. Bilinski, N. Brničević, and Z. Conrad, *Inorg. Chem.*, 1981, **20**, 1882.
[16] (*a*) B. G. Sayer, J. I. A. Thompson, N. Hao, T. Birchall, D. R. Eaton, and M. J. McGlinchey, *Inorg. Chem.*, 1981, **20**, 3748. (*b*) B. G. Sayer, N. Hao, G. Dénès, D. G. Bickley, and M. J. McGlinchey, *Inorg. Chim. Acta*, 1981 **48**, 53.
[17] V. A. Shreider, E. P. Turevskaya, N. Koslova, and N. Ya. Turova, *Inorg. Chim. Acta*, 1981, **53**, L73.
[18] S. Sabo, R. Choukroun, and D. Gervais, *J. Chem. Soc., Dalton Trans.*, 1981, 2328.
[19] D. L. Thorn, W. A. Nugent, and R. L. Harlow, *J. Am. Chem. Soc.*, 1981, **103**, 357.

(1)



(2)
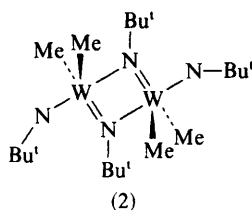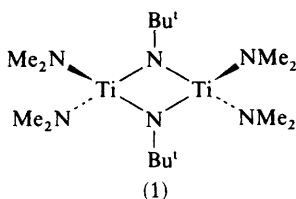
The structure of a nitrogen-bridged zirconium complex (3) of an unstable disposition has been reported.[20] $[ZrCl_4N_3]_2^{2-}$ was prepared from the reaction of $ZrCl_4$ with $Ph_4PN_3$, and contains symmetrically placed bridging azide groups and has approximate $D_{2h}$ symmetry. The paper also records the preparation of $[ZrCl_4(N_3)_2]^{2-}$ and $ZrCl_3N_3$.



(3)



(4)
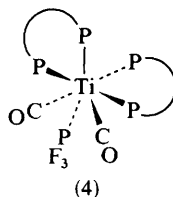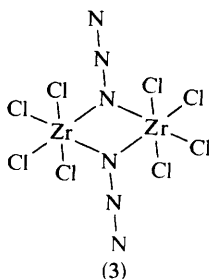
The less-sensitive $[ZrCl_3(PR_3)_2]_2$, where R = Et, Pr, or Bu has been prepared from $ZrCl_4(PR_3)_2$ by treatment with sodium amalgam.[21] The compound has bis-chloro-bridges and a $Zr-Zr$ bond of 3.182 Å. This is possibly the only authenticated example of metal–metal bonding for zirconium and is supported by the diamagnetic nature of the molecule and the $^1H$ and $^{32}P$ n.m.r. spectra.

The preparation of the compound $Cl_2Zrtpp$ (where tpp is *meso*-tetraphenylporphyrin) is reported.[22] Infrared spectra and various properties are discussed, together with measurements of the kinetics of dissociation in proton-donor solvents.

**Organometallic Compounds.**—There are relatively few titanium carbonyl compounds. The preparation and structure of what is called somewhat whimsically a derivative of the non-existent compound $Ti(CO)_7$ are reported.[23] $Ti(CO)_2(PF_3)$ $(dmpe)_2$, where dmpe = 1,2-bis(dimethylphosphino)ethane, is formed by the reaction of $PF_3$ on $[Ti(CO)_3(dmpe)_{3/2}]_n$. The immediate environment about the titanium could be called a capped trigonal prism (4).

A convenient electrochemical synthesis of $Ti(Cp)_2(CO)_2$ from a titanium anode, monomeric cyclopentadiene (with $Bu_4NBr$ as electrolyte) and carbon monoxide ($\sim110$ bar) is reported.[24] A current of 30 mA at 3 V was employed. $M(Cp)_2(CO)_2$

[20] W. M. Dijck, K. Dehnicke, G. Beyendorff-Gulba, and J. Strähle, *Z. Anorg. Allg. Chem.*, 1981, **482**, 113.
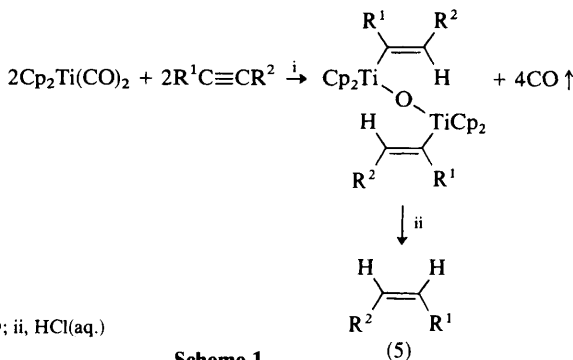
[21] J. H. Wengrovius, R. R. Schrock, and C. S. Day, *Inorg. Chem.*, 1981, **20**, 1844.

[22] B. D. Berezin and T. N. Lomova, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 1981, **26**, 203. (*Zh. Neorg. Khim*, 1981, **26**, 379).

[23] S. S. Wreford, M. B. Fischer, J.-S. Lee, E. J. James, and S. C. Nyburg, *J. Chem. Soc., Chem. Commun.*, 1981, 458.

[24] J. Grobe, B. H. Schneider, and H. Zimmermann, *Z. Anorg. Allg. Chem.*, 1981, **481**, 107.

and $M(\eta^5\text{-}C_5Me_5)_2(CO)_2$, where M = Ti, Zr, or Hf, have been prepared and the structures determined of the substituted species.[25] These are essentially similar but the titanium compound is less symmetric than its isostructural homologues. $Ti(Cp)_2(CO)_2$ reacts[26] with substituted alkynes to give bridged alkenyl complexes, which may then be hydrolysed to the corresponding *cis*-olefins (5) as shown in Scheme 1. It also reacts[27] with a stream of NO to produce an air-stable solid that has been analysed as $Ti_3(Cp)_3N_2O_2$. Reaction with excess NO in a static system however gave a complex mixture. E.s.r. work indicates the presence of two separate paramagnetic entities, which may be $Ti(Cp)_2(NO)(CO)$ and $Ti(Cp)_2NO$.

$$2Cp_2Ti(CO)_2 + 2R^1C{\equiv}CR^2 \xrightarrow{\text{i}}$$



Reagents: i, hexane–H$_2$O; ii, HCl(aq.)

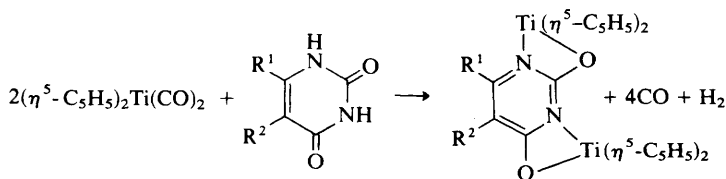**Scheme 1**

(5)

The carbonyl groups of $Ti(Cp)_2(CO)_2$ have been replaced by $PF_3$ by photolysis in hexane.[28] The reaction is readily reversible by bubbling carbon monoxide through the solution. The crystal structure of the phosphine complex (determined by $X$-ray methods) is reported. However no carbon monoxide was displaced on similar photolytic treatment of the per-methyl metallocene.

$Ti(Cp)_2(CO)_2$ is the starting material for a series of binuclear titanium(III) complexes.[29] The $Ti^{II}$ compound is reacted in t.h.f. with the dianion of various substituted uracils (or related heterocycles). The appropriate binuclear complex is then isolated by extraction (Scheme 2). Their binuclear status is supported by mass spectral data.

The compound formulated $Ti_2(Cp')_3O_2$ ($Cp' = C_5Me_5$), produced[30] by the reaction of $N_2O$ on $Ti(Cp')_2$ in toluene solution at 0 °C, has been shown by $X$-ray



**Scheme 2**

[25]  D. J. Sikora, M. D. Rausch, R. D. Rogers, and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 1265.
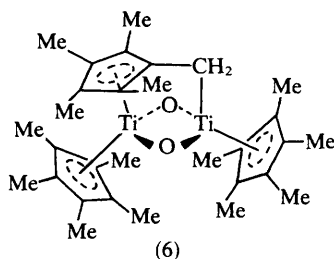
[26]  B. Demerseman and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1981, 665.

[27]  F. Bottomley and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 1981, 271.

[28]  D. J. Sikora, M. D. Rausch, R. D. Rogers, and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 982.

[29]  D. R. Corbin, L. C. Francesconi, D. N. Hendrickson, and G. D. Stucky, *Inorg. Chem.*, 1981, **20**, 2084.

[30]  F. Bottomley, I. J. B. Lin, and P. S. White, *J. Am. Chem. Soc.*, 1981, **103**, 703.

(6)

analysis to have the bridged structure (6). One of the Cp' rings is thus $\eta^1$-linked to one Ti and $\eta^5$-linked to the other Ti. A similar linkage is invoked, from spectroscopic data, in the structure of dimeric $Zr^{III}$ complexes,[31] formed by thermolysis of $(\eta^5\text{-Cp})_2Zr^{II}$bis(phosphine). In this case both strands of the bridge are formed of $(\eta^1:\eta^5\text{-Cp})$ units and it is suggested that the rather poorly characterized 'ziroconocene' $[Zr(Cp)_2]$ is therefore not isostructural with titanocene.

More orthodox $\eta^5$-bonding is shown[32] to be present in the $[(\eta^5\text{-C}_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ complex. The linkage between metals here is entirely by two three-centre, two-electron Zr–H–Zr bridges.

The latest note in the saga of $M(Cp)_4$ structures is reported.[33] The titanium entity has been established since 1971 as having[34] two $\sigma$- and two $\pi$-bonded ligands, and the zirconium[35] as having one $\sigma$- and three $\pi$-bonded ligands. It is now clear that the hafnium species resembles titanium rather than zirconium.

The Ti–O bond of $Ti(\eta^5\text{-Cp})_2(OOCR)_2$ has been shown[36] to have a bond enthalpy of 432 kJ mol$^{-1}$ for R = Ph and 417 kJ mol$^{-1}$ for R = CF$_3$. The corresponding standard enthalpies of formation, determined with a Calvet-type microcalorimeter for the process of dissolving the complex in 1 : 1 aqueous HCl: actone, are $\Delta H_f^\ominus(c) = -775.2$ and $-2219.0$ kJ mol$^{-1}$.

The thermal decomposition of a series of compounds $M(\eta^5\text{-Cp})_2R_2$ (M = Ti, Zr, or Hf) in pentane or toluene solutions has been shown[37] to give about 1% methane and ethene as well as the expected major alkane or alkene products. A possible mechanism involving a carbene intermediate receives some support with the isolation of norcarane (7) when the decompositions are carried out in the presence of cyclohexene.



(7)
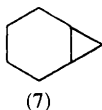
The tetrahedral ligand $Me_2Si(Cp)_2$, (L), forms an attractive site for co-ordination to titanium. Both cyclopentadienyl rings can be bonded in complexes such as $TiLCl_2$.

[31] K. I. Gell, T. V. Harris, and J. Schwartz, *Inorg. Chem.*, 1981, **20**, 481.
[32] S. B. Jones and J. L. Petersen, *Inorg. Chem.*, 1981, **20**, 2889.
[33] R. D. Rogers, R. V. Bynum, and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 692.
[34] J. L. Calderon, F. A. Cotton, B. G. De Boer, and J. Takats, *J. Am. Chem. Soc.*, 1971, **93**, 3592.
[35] R. D. Rogers, R. V. Bynum, and J. L. Atwood, *J. Am. Chem. Soc.*, 1978, **100**, 5238.
[36] J. C. G. Calado, A. R. Dias, M. S. Salema, and J. A. Martinho Simões, *J. Chem. Soc., Dalton Trans.*, 1981, 1174.
[37] B.-H. Chang, H.-S. Tung, and C. H. Brubaker, jun., *Inorg. Chim. Acta*, 1981, **51**, 143.

If one of the rings is methyl substituted then the resultant compound shows (38) a rather interesting n.m.r. spectrum. Orientation and fluxional character have been assessed for the resultant molecule.

In three major papers[39–41] the range of metallocenes characterized for zirconium and hafnium has been considerably expanded. The substituted $d^0$ species $M(\eta\text{-}C_5H_4R)Cl_2$, (M = Ti, Zr, or Hf[IV], R = Me, Et, Pr$^i$ Bu$^t$, or SiMe$_3$ are prepared[39] from the reaction of $MCl_4$ with $Li(C_5H_4R)$. Also reported are dialkyl and chloro-(alkyl) analogues. Zirconium can form $[Zr(\eta\text{-}C_5H_4R)_2\{CH(SiMe_3)_2\}Cl]$ for all R groups, but with hafnium[40] no product was obtained for R = SiMe$_3$. The crystal structure of the zirconium complex showed some strain in the substituted Cp ring but no major distortion elsewhere. Rotation barriers of around 60 kJ mol$^{-1}$ were found by $^1$H n.m.r. spectroscopy for the $ZrCH(SiMe_3)_2$ bond. An interesting range of compounds[41] containing this neopentyl-type moiety has also been reported. In particular complexes involving $-CH(SnMe_3)_2$ and $-CH_2SnMe_3$ have been synthesized.

Finally in this Section, some zirconium adducts with the ligand (8) have been reported.[42] $[Zr(\eta\text{-}Cp)_2(8)(X)]$ [X = Cl or (8)] has been characterized by e.s.r. and $^1$H n.m.r. spectroscopic methods. Some reactions of the compound are discussed



*meso-*(9)          *rac-*(9)
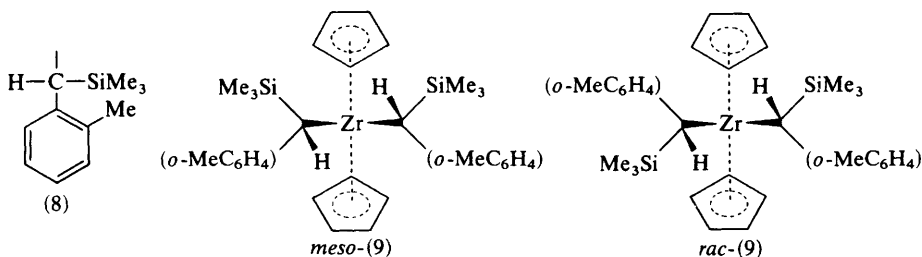
and the character of the ligand allows identification (9) of *meso-* and *rac-* diastereoisomers for X = (8). The ligand (8) possesses a chiral centre at the attachment point, the presence of the useful solubilizing $\alpha$-SiMe$_3$ group, and no $\beta$-hydrogen.

### 3 Vanadium, Niobium, and Tantalum

Further magnetic data have been obtained[43] for the tungsten-bronze analogues $M_xVF_3$ (M = K, Rb, or Tl, 0.2 < $x$ < 0.3). For these compounds a transition between two unique orthorhombic unit cells occurs at around $x$ = 0.25, whereas for M = Cs only one lattice type is found. The crystal structure[44] of the complex fluoride $Na_2[NbF_5(O_2)]2H_2O$ is a similar slightly distorted pentabipyramidal shape to that of the monohydrate reported last year. Two other complex halo-ions have

[38] N. Klouras and H. Köpf, *Monatsh Chem.*, 1981, **112**, 887.
[39] M. F. Lappert, C. J. Pickett, P. I. Riley, and P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1981, 805.
[40] M. F. Lappert, P. I. Riley, P. I. W. Yarrow, J. L. Atwood, W. E. Hunter, and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 1981, 814.
[41] J. Jeffrey, M. F. Lappert, N. T. Luong-Thi, M. Webb, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1981, 1593.
[42] M. F. Lappert and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1981, 173.
[43] Y. S. Hong, R. F. Williamson, and W. O. J. Boo, *Inorg. Chem.*, 1981, **20**, 403.
[44] R. Stromberg, *Acta Chem. Scand., Ser. A*, 1981, **35**, 489.

been studied by $X$-ray analysis. $[V_2O_2F_6(H_2O)_2]^{2-}$ has been shown[45] to contain vanadium in an approximate octahedral environment with two fluoro-bridges *i.e.* $[(\mu\text{-}F)_2\{VOF_2(H_2O)\}_2]^{2-}$. Details are also given of the infrared and Raman spectra and correlation made with the extensive hydrogen bonding that links the dimers into chains. $[Ta_2Cl_{10}O]^{2-}$ has been ascribed a serendipitous origin.[46] It is found to have a virtually linear M–O–M bridge and is the first example of this type of linkage where the metal has no $d$ electrons. $[TaCl_5O\cdot TaCl_5]^{2-}$ has the approximate $d_{4h}$ symmetry that has been previously associated with a desire to maximize $\pi$-bonding.

Reduction and oxidation processes involving a vanadium centre have led to a number of interesting observations. Vanadium(V) peroxo-species are possible inter-mediates in the $V^V$-catalysed $H_2O_2$ olefin-epoxidation reaction. Circular dichroism data indicates[47] that when $H_2O_2$ reacts with the chiral menthyl vanadate, $VO(OMent)_3$, the monoperoxo-compound is optically active and the diperoxo is inactive. This information is used to support the suggested side-on co-ordination of the $O_2$ moiety to vanadium.

$V^{II}$ is able to reduce $NH_2NO_2$ in a 2-electron process directly to dinitrogen,[48] and by use of $^{15}N$ labelled substrate (in the $NO_2$ group), the product was shown to be entirely $^{14}N$–$^{15}N$ with no $^{15}N$–$^{15}N$ production. Other reductions are also possible, for example $V^{II}$–catechol complexes can produce methanol from CO in water or methanol solutions.[49] Analysis of the results of $^{14}C$-labelling studies suggest that the methanol is produced mainly directly in the $V^{II}$–catechol complex without the release of 'free' formaldehyde.

Vanadium(II) hydroxide incorporated in a support matrix such as $Mg(OH)_2$ is known to reduce dinitrogen to hydrazine and ammonia in aqueous solution. Further studies are reported to support the observation[50,51] that the reduction occurs step-wise *via* the di-imide $N_2H_2$. This involves $V^{II} \rightarrow V^{IV}$, and the authors now conclude that the $V^{IV}$ then reacts with $V^{II}$ to produce $V^{III}$ rather than postulating a cluster-mechanism where the reduction process requires four $V^{2+}$ ions each to be oxidized to $V^{3+}$ in a concerted four-electron scenario.

The range of known vanadate(V) species has been increased to about 15 by the use of $^{51}V$ high-field FT n.m.r. Ammonium vanadate was studied in solution over the pH range 7—14. Most of the possible linear and cyclic catenations of $VO_4$ tetrahedra were found, with the assumption of tetrahedral co-ordination based on $^{17}O$ n.m.r. data. $pK_a$ values are tabulated for several of the vanadates.[52] Further $^{51}V$ n.m.r. studies are reported[53] for a series of thirteen mononuclear (involving a wide range of ligand types) and three binuclear complexes (*e.g.* $[\{VO(ONR_2)_2\}_2\mu\text{-}O]$). A correlation between ligand type and observed shielding effects is explained by recourse to various stereochemical and electronic dispositions.

Vanadium(IV) complexes are mainly of the vanadyl, $VO^{2+}$, type. However it is known that complexes of this ion can be readily deoxygenated to give the dichloro-

[45] P. Bukovec, S. Milicév, A. Demšar, and L. Golič, *J. Chem. Soc., Dalton Trans.*, 1981, 1802.
[46] F. A. Cotton and R. C. Najjar, *Inorg. Chem.*, 1981, **20**, 1886.
[47] O. Bortolini, F. D. Furia, G. Modena, and E. Scattolin, *Nouv. J. Chim.*, 1981, **5**, 537.
[48] M. N. Hughes, M. Okolow-Zubkowska, and H. L. Wallis, *J. Chem. Soc., Dalton Trans.*, 1981, 2009.
[49] S. A. Isaeva, L. A. Nikonova, and A. E. Shilov, *Nouv. J. Chim.*, 1981, **5**, 21.
[50] G. N. Schrauzer, N. Strampach, M. R. Palmer, and S. I. Zones, *Nouv. J. Chim.*, 1981, **5**, 5.
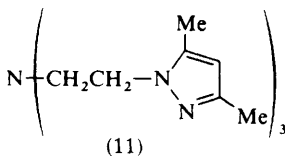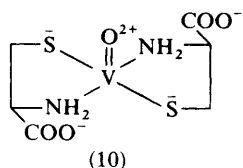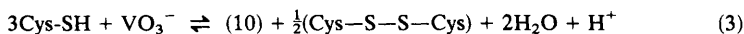[51] G. N. Schrauzer and M. R. Palmer, *J. Am. Chem. Soc.*, 1981, **103**, 2659.
[52] E. Heath and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1981, 1105.
[53] D. Rehder and K. Wieghardt, *Z. Naturforsch., Teil B*, 1981, **36**, 1251.

product, *e.g.* $VX_2L_4$, where $X = Cl$ or Br and $L_4$ is either a quadridentate or two bidentate ligands. It was previously thought that such substitution, by thionyl chloride for example, produced the complex in the all-*trans* configuration. However e.s.r. spectra of a series of such complexes have now[54] shown that both *cis*- and *trans*- isomers are possible. Unambiguous identification is feasible since the entities show considerable differences in their e.s.r. characteristics.

Vanadyl complexes can be produced directly from vanadate(V) by reaction with a reducing ligand. 3 moles of cysteine produces the complex (10) by reaction (3).[55]

$$3\text{Cys-SH} + VO_3^- \rightleftharpoons (10) + \tfrac{1}{2}(\text{Cys}-S-S-\text{Cys}) + 2H_2O + H^+ \qquad (3)$$



(10)                                    (11)

The preparation of some niobium and tantalum terpyridyl complexes, $NbCl_5$terpy, $Ta_2Cl_{10}$terpy, and $M_2Br_8$terpy ($M = Nb$ or Ta), formed by admixture under a dry nitrogen atmosphere, has been described.[56] An unusual amine complex of vanadium, formulated as $[V(NCS)_2(11)]$, has been reported.[57] Various dimethylamido-compounds of tantalum(V) have been synthesized.[58] Single-crystal $X$-ray diffraction studies have been done for several of the compounds and in both mononuclear and binuclear cases the tantalum is found in a distorted octahedral environment. $TaCl_3(NMe_2)_2(HNMe_2)$, $Ta(NMe_2)_3Cl_2(HNMe_2)$, $[Ta(NMe_2)_3Cl_2]_2$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ are found to have short $Ta-N$ bonds (average 1.96 Å), which, taken with the planarity of $Ta-NR_2$, may indicate $p_\pi-d_\pi$ bonding. No $Ta-Ta$ bonding was observed however and the binuclear species have, respectively, a planar $Ta_2(\mu-Cl)_2$ and a planar $Ta-O-Ta$ centre.

Relatively few reports have concerned ligands involving nitrogen and oxygen donors. Magnetic susceptibility and e.s.r. measurements are discussed[59] for the vanadium(IV) complex, $VO(cmap)_2$, where cmap is the ligand (12). An interesting series of Schiff-base complexes of oxo-vanadium(IV) have been prepared.[60] These have variation in the methylene chain linking the two halves of the quadridentate



(12)                                    (13)
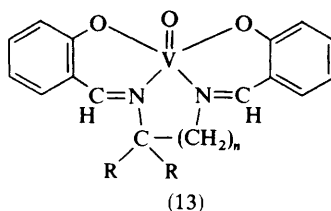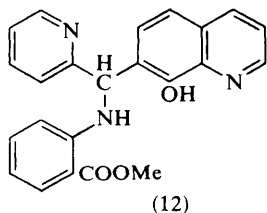
[54] A. Jezierski and J. B. Raynor, *J. Chem. Soc., Dalton Trans.*, 1981, 1.
[55] H. Sakurai, S. Shimomura, and K. Ishizu, *Inorg. Chim. Acta*, 1981, **55**(B2), L67.
[56] B. Begolli, V. Valjak, V. Allegretti, and V. Katovic, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2785.
[57] F. Mani, *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 45.
[58] M. L. Chisholm, J. C. Huffman, and L.-S. Tan, *Inorg. Chem.*, 1981, **20**, 1859.
[59] R. Stösser, A. Rericha, and G. Röbisch, *Z. Chem.*, 1981, **21**, 332.
[60] G. A. Kolawole and K. S. Patel, *J. Chem. Soc., Dalton Trans.*, 1981, 1241.

ligand (13; $2 < n < 10$, R = H or Me). Various stereochemical environments are suggested from a study of their vibrational and electronic specta.

Direct electrochemical syntheses are becoming quite popular. $Nb(OR)_5$ and $Ta(OR)_5$ can be readily synthesized[17] by electrolysis using the appropriate metal anode and ROH with $(Bu_4N)Br$ or NaBr as the supporting electrolyte. No new compounds were reported, but the method is more convenient than the previous indirect procedures. It is also possible to produce cationic complexes by this method.[61] $[V(d.m.s.o.)_6](BF_4)_2$ was formed using 2 V at 100 mA in a 1 : 1 mixture of d.m.s.o. and an aqueous solution of $HBF_4$. It is recommended as a method for other similar species by merely substituting the d.m.s.o. with the desired ligand.

Electrochemical studies of a different type have been conducted[62] with $V(acac)_3$ and $VO(acac)_2$, where acac is the acetylacetonate anion. These complexes can be reduced to the same vanadium(V) species. Cyclic voltammograms displaying the various reversible and irreversible processes are presented.

The structure has been determined[63] of the thiovanadyl species reported last year (14). As expected, it shows an approximate rectangular pyramidal shape with a V—S bond length of 2.061 Å, consistent with multiple-bond character. No significant intermolecular association was evident. A more complex thiovanadium compound is formed[64] from the reaction of $VOCl_2$ and $CH_3CSOH$. The brown solid formed, which appears to be completely insoluble in all solvents, analyses to the empirical formula $V(CH_3CS_3)_2$ and has been shown by single-crystal $X$-ray analysis to be a layered polymer (15). It is able to intercalate alkali metals, for example lithium is taken up on reaction with n-BuLi–hexane.



(14)                                                                                   (15)
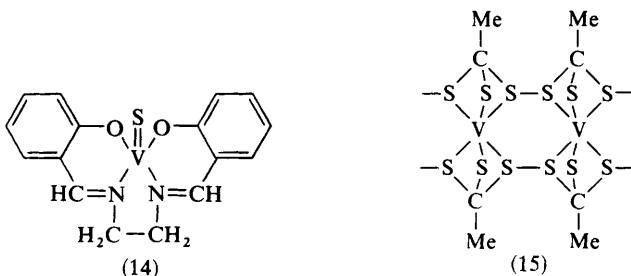
Metal–metal bonds are not so prolific in group V as is currently the case for their neighbours of group VI. The conjunction of halogen and sulphur ligands does seem to produce suitable conditions and several new examples are reported. $[NbCl_4(NCMe)_2]NCMe$ has a *cis*-octahedral structure[65] and on treatment with $Sb_2S_3$ in NCMe forms adducts of formula $NbX_2S \cdot (solvent)_n$, where $n = 1$ or 2. These both contain niobium in a pseudo-octahedral situation with *cis*-sulphur bridging, *cis*-nitrogen, and *trans*-chlorine. The Nb—Nb distance is around 2.86—2.87 Å and is taken to imply a single metal–metal bond. This interaction accounts for the distortions introduced into the octahedral symmetry. Double bonding is
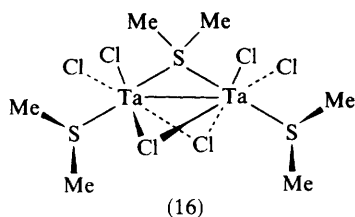
[61] J. J. Habeeb, F. F. Said, and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1981, 118.
[62] M. A. Nawi and T. L. Riechel, *Inorg. Chem.*, 1981, **20**, 1974.
[63] M. Sato, K. M. Miller, J. H. Enemark, C. E. Strouse, and K. P. Callahan, *Inorg. Chem.*, 1981, **20**, 3571.
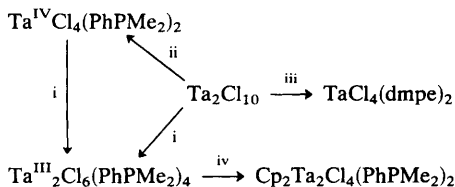[64] S. Son, R. Kanno, and M. Koizumi, *Inorg. Chem.*, 1981, **20**, 1927.
[65] A. J. Benton, M. G. B. Drew, R. J. Hobson, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1981, 1304.

(16)

observed[66] for $Ta_2Cl_2(Me_2S)_3$ (16) with a Ta—Ta bond of 2.691 Å. The analogous thiophene complex has a bond of 2.681 Å. The compounds were prepared by direct action of the sulphide on $TaCl_5$ in the presence of sodium amalgam.

Various tantalum phosphine complexes with $PhPMe_2$ and $Me_2PCH_2CH_2PMe_2$ are reported.[67] The paper deals with the essential conditions for preparation and various interconnections are noted between the species (Scheme 3). Using the

$$Ta^{IV}Cl_4(PhPMe_2)_2$$

$$Ta_2Cl_{10} \xrightarrow{iii} TaCl_4(dmpe)_2$$

$$Ta^{III}_2Cl_6(PhPMe_2)_4 \xrightarrow{iv} Cp_2Ta_2Cl_4(PhPMe_2)_2$$

Reagents: i, $PhPMe_2$–Mg; ii, $PhPMe_2$; iii, dmpe–Mg–$CH_2Cl_2$; iv, $Me_3SnCp$

**Scheme 3**

sub-halides of niobium and tantalum $M_6Cl_{14}\cdot8H_2O$ and $M_6Cl_{15}\cdot7H_2O$, phosphine complexes $(M_6Cl_{12})Cl_2(PR_3)_4$ are produced.[68] The $(M_6Cl_{12})^+$ cluster core is assigned on the basis of electrochemical investigations. Oxidations such as $(Ta_6Cl_{12})Cl_2(PR_3)_4 \rightarrow [(Ta_6Cl_{12})Cl_2(PR_3)_4](PF_6)_n$, where $n = 1$ or 2, have also been accomplished.

Finally in this Section on co-ordination chemistry there are a few papers dealing with macrocyclic ligands. A complex series (Scheme 4) of interconversions is reported.[69] The assignments of structure are based on assorted spectroscopic data (infrared and e.s.r. mainly). The interesting aim of the project was to extend knowledge of the vanadium(IV) state by preparing various de-oxygenated species. Compound (17) is prepared from $VO(MeCO_2)_2$ and the macrocyclic ligand (Scheme 4). Of particular interest is (18) where the dimeric nature, with the most unusual $\mu$-nitrido-bridge, is supported by mass spectral data ($m/e = 818$).

The niobium(V) porphyrin, Nb(O)(tpp)(OAc), where tpp is the anion of tetraphenylporphyrin, has been studied[70] by cyclic voltammetry in dichloromethane. The separation of the half-wave potentials for the reductions $Nb^V \rightarrow Nb^{IV} \rightarrow Nb^{III}$ was found to be only 0.16 V compared to the corresponding molybdenum species which have a 1.24 V separation. This is attributed to increased $\pi$-electron density from delocalization of $d$-electrons in the Nb complex. The compound $NbCl_3$(tpp)

[66] F. A. Cotton and R. C. Najjar, *Inorg. Chem.*, 1981, **20**, 2716.
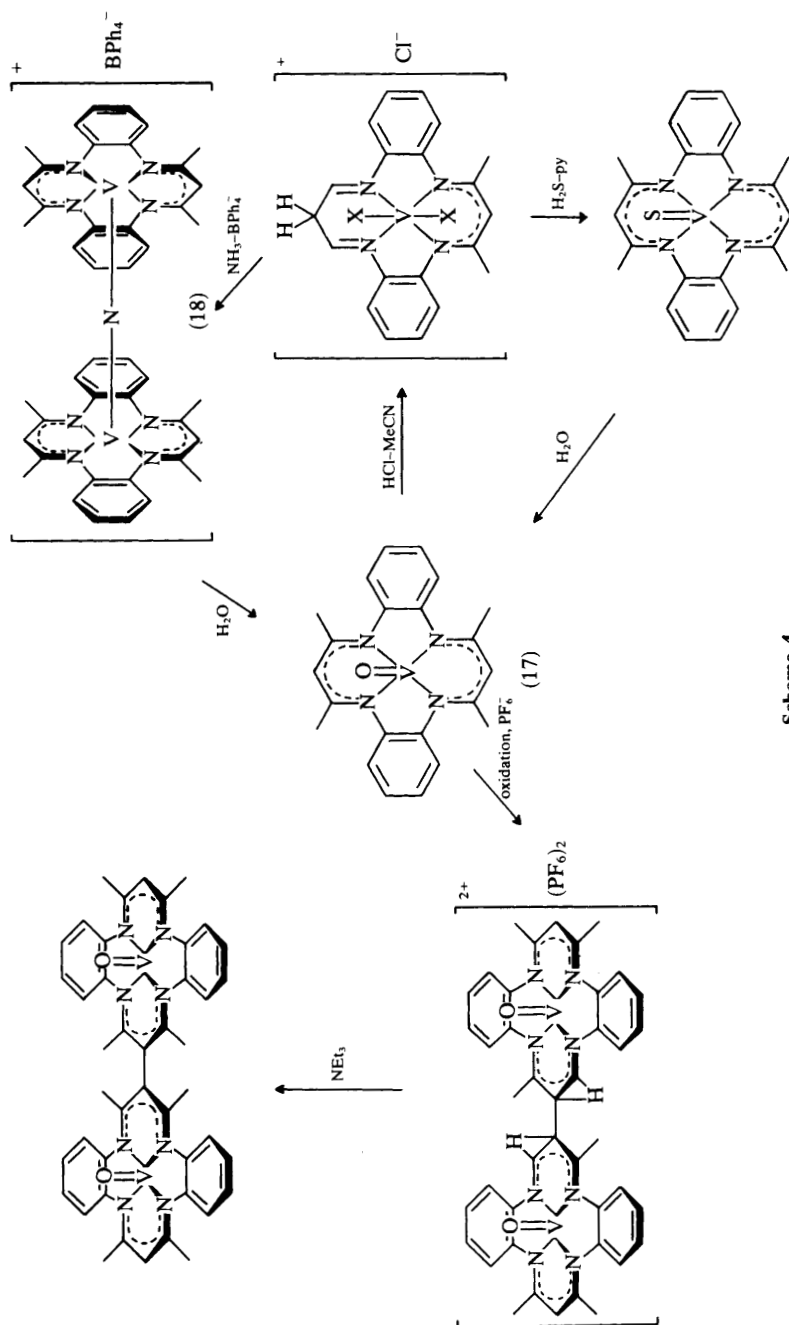[67] L. G. Hubert-Pfalzgraf, M. Tsunoda, and J. G. Reiss, *Inorg. Chim. Acta*, 1981, **52**, 231.
[68] D. D. Klendworth and R. A. Walton, *Inorg. Chem.*, 1981, **20**, 1151.
[69] V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 1981, 910.
[70] Y. Matsuda, S. Yamada, T. Goto, and Y. Murakami, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 452.

**Scheme 4**

has been shown[22] to have enhanced kinetic stability to dissociation in proton-donor solvents over $ZrCl_2(tpp)$.

**Organometallic Compounds.**—Acetylenes are known to act as bridging ligands and side-on bidentate ligands to niobium and tantalum. Reaction[71] of $Ta_2Cl_6(SC_4H_8)$ with $MeC{\equiv}CCMe_3$ gave a binuclear species where the bridging groups are chlorines and each tantalum has a side-on acetylene. The C—C distance of the acetylene is found to be 1.32 Å and the attached groups (Me and $CMe_3$) make angles of around 138°.

A rather unusual bridging dinitrogen compound has been described.[72] $[\{Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2\}_2(\mu\text{-}N_2)]$ shows each tantalum(V) in trigonal-bipyramidal co-ordination with axial phosphines and equatorial neopentylidenes. The N—N bond length however is lengthened to 1.298 Å, whereas the majority of other M-N-N-M compounds show bond lengths not too dissimilar from the free dinitrogen (1.0976 Å). Mononuclear neopentylidene tantalum complexes have some potentiality as catalysts.[73] $Ta(CHCMe_3)(PR_3)_2Cl_3$ is not able to promote metathesis products from terminal olefins, but the related $Ta(CHCMe_3)$ $(OCMe_3)Cl(PR_3)$ produces only metathesis products. The detailed arguments concerning the design of the compound are based on assessments of hard and soft character in the ligands. Other neopentylidene complexes are able[74] to promote the dimerization of ethene to but-1-ene. Detailed analysis is given to a scheme that is mechanistically indistinguishable from the assumed insertion mechanism for such dimerizations, namely that the process occurs *via* a 'tantalacyclopentane' mechanism. Detailed n.m.r. results are given[75] for related complexes such as $[Cl(\eta^5\text{-}Cp)(\eta^3\text{-}C_9H_7)Ta(CHCMe_3)]$. This also reacts with ethene.

Synthetic methods for the preparation of $[(\eta\text{-}Cp)_2V(halogen)_2]$ are discussed[76] and high yields are obtained with the suggested improved procedures. The reactions proposed involve refluxing $Cp_2V$ with $PX_3$ (X = Cl, Br, or I) to give the bis(halogen) complex or IBr or ICl, giving mixed-halogen species. The bis-iodide and mixed-iodo-complexes are reported for the first time. The synthesis of assorted niobium(V) Cp phenoxides is reported.[77] A limited amount of spectroscopic data are given for these species that were produced by reflux in dry benzene. They are reportedly stable in dry conditions.

A series of papers have appeared with details of Cp–phosphine adducts. Thus, $Nb(\eta\text{-}Cp)_2(CH_2Ph)_2$ has been shown[78] by single crystal $X$-ray analysis to be roughly tetrahedral. This compound was one of a series $Nb(\eta\text{-}C_5H_4X)RR^1$, where X = $SiMe_3$, H, or Me and R = $R^1$ = Cl, $CH_2SiMe_3$, $CH_2CMe_3$, or $CH_2Ph$. These are red/brown solids and those analysed show a 10-line e.s.r. spectrum due to hyperfine coupling to $^{93}Nb$. No $\alpha$-hydrogen (of the alkyl ligands) coupling was observed even on cooling to −80 °C.

[71] F. A. Cotton and W. T. Hall, *Inorg. Chem.*, 1981, **20**, 1285.
[72] M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 2899.
[73] S. M. Rocklage, J. D. Fellmann, G. A. Rupprecht, L. W. Messerle, and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 1440.
[74] J. D. Fellmann, R. R. Schrock, and G. A. Rupprecht, *J. Am. Chem. Soc.*, 1981, **103**, 5752.
[75] A. W. Gal and H. van der Heijden, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 978.
[76] M. Moran, *Transition Met. Chem.*, 1981, **6**, 42.
[77] M. K. Rastogi and S. N. Nigam, *J. Chin. Chem. Soc.*, 1981, **28**, 111.
[78] P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180.

*J. E. Newbery*

The diphosphine ligand dmpe ($= Me_2PCH_2CH_2PMe_2$) is thoroughly occupied in an intricate network of fourteen inter-related niobium complexes, part of which is shown in Scheme 5. A wealth of analytical and spectroscopic data are included in the report.[79] Some similar species were synthesized in an unsuccessful search for dinitrogen complexes of niobium and tantalum. Much interesting work is reviewed and summarized in this report.[80]
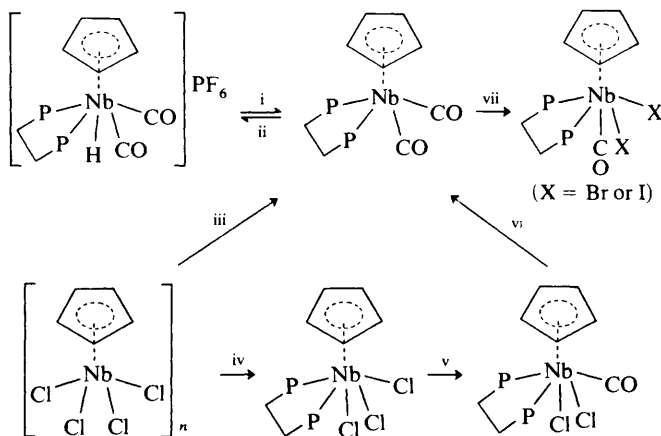


Reagents: i, NaOH; ii, HCl–PF$_6^-$; iii, Na–Hg–dmpe–CO; iv, $(AlEtCl_2)_2$–dmpe; v, CO–Mg–Hg; vi, Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$]–CO; vii, MeI–toluene or benzyl bromide

**Scheme 5**

Alkyne complexes of tantalum have already been mentioned in this Report. The alkyne linkage is normally found to be sideways on and the pendant groups of the alkyne are folded back. This arrangement has also been confirmed[81] for Ta($\eta^5$-C$_5$Me$_5$)(PhC≡CPh)Cl$_2$. The compound is quite stable thermally and apart from sensitivity to oxygen is fairly unreactive. This could be due to the very strong attachment between the alkyne and the metal.

There are only a few reports of bridged Cp species. One of the more interesting topics concerns the formyl grouping. [{TaCl$_2$($\eta^5$-C$_5$Me$_4$Et)}$_2$(H)(CHO)] has been shown[82] by single crystal $X$-ray study to contain (19) a bridging formyl group in the 'side-on' configuration. Neither the proton of the CHO nor the bridging H were located in the analysis, but both were assigned positions on the basis of $^1$H and $^{13}$C n.m.r. spectra.



(19)
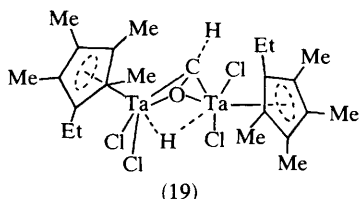
[79] M. J. Bunker and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 85.
[80] R. J. Burt, G. J. Leigh, and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1981, 793.
[81] G. Smith, R. R. Schrock, M. R. Churchill, and W. J. Youngs, *Inorg. Chem.*, 1981, **20**, 387.
[82] M. R. Churchill and H. J. Wasserman, *J. Chem. Soc., Chem. Commun.*, 1981, 274.

The compound will react[83] with $PMe_3$ to produce $[\{(\eta^5\text{-}C_5Me_4Et)TaCl_2\}(H)$ $(CHO)(PMe_3)]$ which on $X$-ray analysis is shown to be $[\{(\eta^5\text{-}C_5Me_4Et)TaCl_2\}_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)]$ (20). The hydride again was not located.



(20)
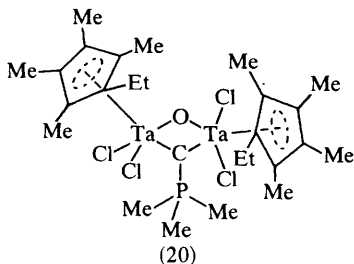
A more novel type of linkage has been constructed between vanadocene units.[84] By reacting the vanadocene halide with $\alpha, \omega$-dimetallated hydrocarbons it becomes possible to form linked species (21). Various types of linking group are involved and substituted Cp rings are also used. N.m.r. and $X$-ray results are included to confirm that the bridging does involve giving a tilt to the Cp$\cdots$Cp axis about the central metal.



(21)
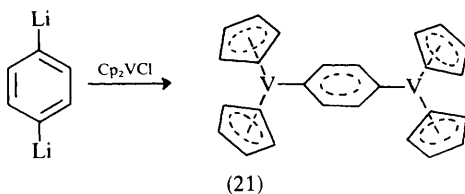
A rather larger vanadium–Cp entity is encountered with $Cp_5V_5O_6$. This shows[85] a trigonal bipyramid of vanadium atoms each capped by a Cp ring. The oxygen atoms complete the cluster by being symmetrically located above each of the six faces. The species has a 74 electron count and the authors note that application of the usual carbonyl rules leads to the observed two unpaired electrons.

The inter-sandwich compound (22) is obtained[86] from the mono-nuclear compound by metallation with $Bu^nLi$ then reacting with the mono-brominated



(22)
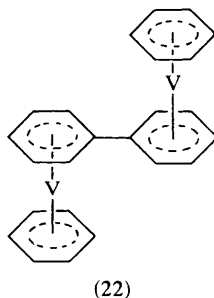
[83] M. R. Churchill and W. J. Youngs, *Inorg. Chem.*, 1981, **20**, 382.
[84] F. H. Köhler, W. Prössdorf, and U. Schubert, *Inorg. Chem.*, 1981, **20**, 4096.
[85] F. Bottomley and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1981, 28.
[86] C. Elschenbroich and J. Heck, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 267.

(Ph)(PhBr)V. The air-sensitive species displays a sharp e.s.r. spectrum at room temperature, which becomes much more complex than that of the mononuclear when cooled to the rigid glassy state. This is taken as evidence for the presence of a triplet radical.

### 4 Chromium, Molybdenum, and Tungsten

**Simple Compounds.**—This sub-section includes work on binary compounds and co-ordination chemistry involving simple monodentate ligands such as $F^-$. It is obvious, from only a cursory glance at the current literature, that the published work on the Cr, Mo, and W far exceeds the cumulative total of that on the other early transition metals. This is not a result of excessive attention to one class of compounds, since the preponderance of papers covers the entire range of inorganic topics.

$MoCl_4$ has been observed to have two modifications. $\alpha$-$MoCl_4$, which probably has linear chains of edge-sharing octahedra, and a $\beta$-form. The structure of this has been re-examined and is now suggested[87] to contain hexameric units (23). These are believed to be unique. The molecular units are stacked in layers but in such a fashion that no interaction between metal atoms of adjacent molecules is feasible (Mo $\cdots$ Mo = 367 pm). Excellent infrared spectra have been recorded for $MOX_4$ (M = Mo or W, X = Cl or Br) by use of the matrix-isolation technique.[88] With nitrogen as a lattice one trapping site was observed and thus spectral complications from the presence of dimers could be ignored.



(23)
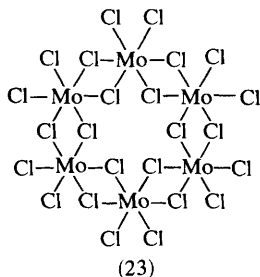
The synthesis of $NF_4 \cdot WOF_5$ by the reaction of $WOF_4$ with a strong solution of $NF_4 \cdot HF_2$ in anhydrous HF has been reported.[89] It seems thermally stable up to around 60 °C.

The $Mo_6Cl_{14}^{2-}$ ion is recommended as a candidate for intensive photochemical studies.[90] It shows a fairly long phosphorescence lifetime (*e.g.* 180 $\mu$s at 300 K in MeCN solution) and also has useful redox relationships with related metal cluster ions.

A review has appeared where the aquo ions of molybdenum[91] are classified under oxidation states (II)—(VI) and degree of oligomerization. Perhaps the most useful

[87] U. Müller, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 692.
[88] W. Levason, R. Narayanaswamy, J. S. Ogden, A. J. Rest, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1981, 2501.
[89] W. W. Wilson and K. O. Christe, *Inorg. Chem.*, 1981, **20**, 4139.
[90] A. W. Maverick and H. B. Gray, *J. Am. Chem. Soc.*, 1981, **103**, 1298.
[91] D. T. Richens and A. G. Sykes, *Comments Inorg. Chem.*, 1981, **1**, 141.

part of the report are the printed spectra (u.v. and visible range). These should prove a handy reference for students of these species. One such aquo-ion has now been isolated from solution for the first time.[92] $[Mo_3O_4F_9]^{5-}$ (24) has been isolated as a red ammonium salt. The basic structure conforms to the $B_1$-type of trinuclear electron-poor transition-metal cluster where the metals are in a distorted octahedral environment. The compound is isostructural with the corresponding tungsten species.



(24)
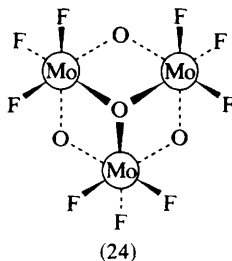
Electrochemical work on the $Mo^{VI}$ oxidation state is simplified[93] if carried out with dilute ($<10^{-4}$ mol dm$^{-3}$) solutions. Reversible voltammograms obtained suggest straight reduction to $Mo^V$ is accompanied by the consumption of two protons per molybdenum atom. The monomeric $Mo^V$ produced then spontaneously dimerizes.

The preparation and structure of an interesting sulphide ion has been described.[94] $[MoS_9]^{2-}$ has an approximate square-pyramidal sulphur configuration about the metal, with a single sulphur at the apex and the molybdenum displaced upwards from the basal plane by about 0.73 Å. The remaining sulphurs form two $S_4$ chains. The S—S distances in these linkages are 2.166, 2.01, and 2.107 Å thus showing considerable variation. The ion was produced from $(Et_4N)_2MoS_4$ and sulphur in MeCN solution.

The final papers in this sub-section concern the extensive range of heteropolyanions, the majority of which involve the nitrogen group elements. However, exceptions are the fluorotungstates $HW_{12}F_nO_{40-n}^{(7-n)-}$ ($n = 1$, 2, or 3). These have been studied[95] by various methods, such as n.m.r., and the kinetic stability of the species related to the implied structural type. The single central proton gives rise to some novel phenomena for the equilibrium between $HW_{12}F_2O_{38}^{5-}$ and $H_2W_{12}F_2O_{38}^{4-}$. These Keggin-type structures contain tungstens in various environments and these may be observed by the use of $^{183}W$ n.m.r. spectra: typical coupling constants and chemical shifts are reported.[96] This is exceptionally useful for this class of compounds which present great difficulties when studied by $X$-ray methods. $^{183}W$ n.m.r. spectra are also reported[97] for other heteropolyanions. $[As_2W_{21}O_{69}(H_2O)]^{6-}$ has been studied by both $X$-ray and n.m.r.

[92] A. Müller, A. Ruck, M. Dartmann, and U. Reinsch-Vogell, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 483.
[93] M. T. Paffett and F. C. Anson, *Inorg. Chem.*, 1981, **20**, 3967.
[94] E. D. Simhon, N. C. Baenziger, M. Kanatzidis, M. Draganjac, and D. Coucouvanis, *J. Am. Chem. Soc.*, 1981, **103**, 1218.
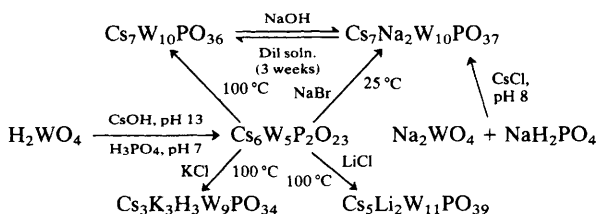[95] P. Doppelt and J. Lefebvre, *Nouv. J. Chim.*, 1981 **5**, 463.
[96] J. Lefebvre, F. Chauveau, P. Doppelt, and C. Brevard, *J. Am. Chem. Soc.*, 1981, **103**, 4589.
[97] (a) Y. Jeannin and J. Martin-Frère, *J. Am. Chem. Soc.*, 1981, **103**, 1664; (b) R. G. Finke, M. Droege, J. R. Hutchinson, and O. Gansow, *ibid.*, p. 1587.

methods.[97a] It shows two $AsW_9O_{33}$ units joined asymmetrically together by three tungsten atoms. Two of these bridging atoms are in the rather unusual square-pyramidal configuration. Thus in one species there are many different types of tungsten that can be assigned unambiguously to particular W n.m.r. chemical shifts. A similar position exists for the ion, $P_2W_{18}M_4(H_2O)_2O_{68}{}^{10-}$ (M = Co, Cu, or Zn), which has been shown to have the same structure in solution as in the solid state.[97b]

$Cs_6W_5P_2O_{23}$, $Cs_7W_{10}PO_{36}$, and $Cs_7Na_2W_{10}PO_{37}$ have been synthesized by addition of caesium hydroxide to tungstic acid.[98] This deposits the $Cs_6$ compound on cooling, whereas at temperatures near to 100 °C the $Cs_7W_{10}PO_{36}$ salt is produced (Scheme 6). The structures of the first two compounds were determined by $X$-ray methods. The $Cs_7W_{10}PO_{36}$ is particularly interesting since the $W_{10}PO_{36}{}^{7-}$ ion is shown to be capped at two opposite sides by caesium ions. This, together with the various replacement reactions shown in (Scheme 6), raises the question of the role

$$Cs_7W_{10}PO_{36} \underset{\substack{\text{Dil soln.} \\ \text{(3 weeks)} \\ 100\,°C \quad NaBr}}{\overset{NaOH}{\rightleftharpoons}} Cs_7Na_2W_{10}PO_{37}$$

$$H_2WO_4 \xrightarrow[\text{H}_3\text{PO}_4,\ \text{pH}\ 7]{\text{CsOH, pH 13}} Cs_6W_5P_2O_{23} \qquad Na_2WO_4 + NaH_2PO_4$$

25 °C ↗  CsCl, pH 8 ↑

KCl ↙ 100 °C    LiCl ↘ 100 °C

$$Cs_3K_3H_3W_9PO_{34} \qquad\qquad Cs_5Li_2W_{11}PO_{39}$$

**Scheme 6**

of the counter-ion in solutions of these species. Their $^{183}W$ n.m.r. should prove to be of great value in this respect. Indeed, $^{17}O$ and $^{183}W$ n.m.r. were used[99] to demonstrate fluxionality in heteropolyanions for the first time. $[(RPO_3)_2W_5O_{15}]^{4-}$ gives a single ($^{183}W$) peak split $1:2:1$ by two equivalent $^{31}P$ nuclei ($J = 1.95$ Hz). This is consistent with an intramolecular exchange process with a concerted rotation of the $RPO_3$ group about the R—P axes.

Oxygen-replacement reactions in heteropolyanions are usually expected to involve the loss of terminal oxygens.[100] Reaction of $Me_3O \cdot BF_4$ with $M_{12}PO_{40}{}^{3-}$ (M = Mo or W) produces $MeOM_{12}PO_{39}{}^{2-}$, which is shown by $X$-ray analysis to retain the basic structure but with the —OMe group acting as a bridge between two edge-sharing octahedra.

**Co-ordination Compounds.**—These are arranged in order of increasing complexity, starting with mononuclear species and progressing through macrocyclic ligands, bridged, and finally cluster species of various types. Of general interest in this Section however is the extensive review (346 references) that has recently appeared on the co-ordination chemistry of tungsten.[101] This presents an accurate account of the many recent advances in chemistry of this metal and gives a very clear classification of structural types. Rather more restricted areas reviewed include

[98] W. H. Knoth and R. L. Harlow, *J. Am. Chem. Soc.*, 1981, **103**, 1865.
[99] P. R. Sethuraman, M. A. Leparulo, M. T. Pope, F. Zonnevijlle, C. Brévard, and J. Lemerle, *J. Am. Chem. Soc.*, 1981, **103**, 7665.
[100] W. H. Knoth and R. L. Harlow, *J. Am. Chem. Soc.*, 1981, **103**, 4265.
[101] Z. Dori, *Prog. Inorg. Chem.*, 1981, **28**, 239.

$Cr^{III}$ photochemistry and photophysics[102] and the fluoro-diamine complexes of chromium(III).[103]

**Mononuclear Complexes.**—Treatment of $WCl_4S$ with $[PPh_3(CH_2Ph)]Cl$ yields[104] the salt $[PPh_3(CH_2Ph)][WCl_5S]$. This has been studied by single-crystal $X$-ray methods and shown to contain considerable variation in the $W-Cl$ bond lengths. The longest bond is found, as expected, *trans* to the $W=S$ linkage. The tungsten is located 0.21 Å above the equatorial plane (towards the sulphur) in contrast to 0.45 Å found for $WCl_4S$. Admixture of a solution of $NEt_4SnCl_3$ in dichloromethane to a suspension of $MoCl_4$, produced, after a few days,[105] a mauve-pink solid analysing to $(NEt_4)_2[MoCl_4(SnCl_3)_2]$. A series of similar species was also prepared. They appear to be typical six-co-ordinate complexes. Reactions with nitrate, chlorate, and perchlorate ions were studied.

The preparation of $KrF_2MOF_4$ (25), $XeF_2MOF_4$, $KrF_2\cdot2MOF_4$(26), and $XeF_2\cdot2MOF_4$ (M = Mo or W) is achieved by the reaction of $KrF_2$ or $XeF_2$, with $MOF_4$ in $SO_2ClF$ solution.[106a] Detailed $^{19}F$ n.m.r., Raman, and infrared spectroscopy studies have indicated that structures such as (25) and (26) can be invoked to



(25)                  (26)
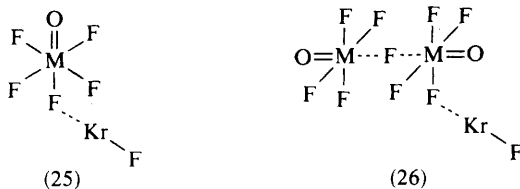
explain the major observations. Similar 1 : 1 adducts with antimony,[106b] $MF_4O\cdot SbF_5$, are shown by single-crystal $X$-ray analysis to contain polymeric zig-zag chains of alternate antimony and molybdenum atoms linked by fluorine bridges. Raman spectra and some mass spectral data are also listed.

Very few papers in this Section deal solely with oxygen donor ligands, though a preliminary report[107] on $^{95}Mo$ n.m.r. shows that for dioxo $Mo^{VI}$ complexes, negative shifts are given by all oxygen donor ligands tested whereas $N,N$- and $S,S$-donors gave uniformly (larger) positive shifts. A substitution-labile $Cr^{III}$ complex has been described.[108] $Cr(H_2O)$(h.e.d.t.a.) was analysed (27) by single-crystal $X$-ray diffraction to ascertain the reason for this lability. The bond angles of the octahedron around the central atom have about a 5.1° deviation from 90°, and if transferred into the solution state may be the answer. The water-soluble $Cr^V$ complex (28) has been shown[109] to oxidize hydrazinium ion, one mol requiring 2 mol of $Cr^V$. Dinitrogen is evolved and an uncharacterized $Cr^{III}$ complex formed. A kinetic law

[102] A. D. Kirk, *Coord. Chem. Rev.*, 1981, **39**, 225.

[103] J. W. Vaughn, *Coord. Chem. Rev.*, 1981, **39**, 265.

[104] M. G. B. Drew, G. W. A. Fowles, E. M. Page, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1981, 2409.

[105] I. W. Boyd, G. P. Haight, jun., and N. C. Howlader, *Inorg. Chem.*, 1981, **20**, 3115.

[106] (a) J. H. Holloway and G. J. Schrobilgen, *Inorg. Chem.*, 1981, **20**, 3363; (b) J. Fawcett, J. H. Holloway, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1981, 1212.

[107] K. A. Christensen, P. E. Miller, M. Minelli, T. W. Rockway, and J. H. Enemark, *Inorg. Chim. Acta*, 1981, **56**, L27.

[108] L. E. Gerdom, N. A. Baenziger, and H. M. Goff, *Inorg. Chem.*, 1981, **20**, 1606.

[109] V. S. Srinivasan and E. S. Gould, *Inorg. Chem.*, 1981, **20**, 3176.

(27)                                    (28)
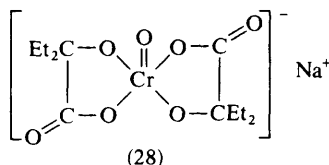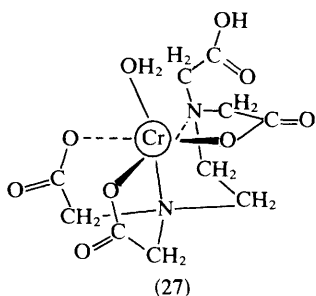
is obtained and is shown to be consistent with a two-path mechanism. The preparation of $cis$-$WF_4(OTeF_5)_2$ and $WF_5(OTeF_5)$ is reported.[110] [19]F n.m.r. spectra were used in the characterization of these complexes.

The complex $Mo(NO)(Me_2CNO)(NCS)_4$ has been prepared and its structure determined[111] by single-crystal $X$-ray studies. It is a slightly distorted octahedron with the NO group $trans$ to an NCS. The unusual feature, and probably accounting for the distortion, is that the oximato-group is bidentate, $i.e.$ co-ordinated sideways through both the nitrogen and the oxygen atoms.

Bis-histidine complexes, taking histidine as terdentate, could potentially exist in three co-ordination isomers (29)—(31).[112] Type (29) has the imidazole nitrogen $trans$, (30) has $trans$-carboxylates, and (31) has $trans$-amines. The reaction mixture from an alkaline solution of L-histidine and chromium(III) nitrate yielded two types of bis-histidine complex, which were shown to be the types (29) and (30) species



(29)                         (30)                         (31)
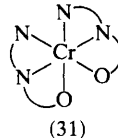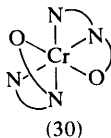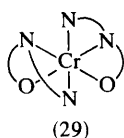
on the basis of electronic spectra and the corresponding ligand field (10 Dq) parameter. More complicated compounds have also been studied. Isomers of the complexes $[Cr(D-$ or L-aspartate)(L-histidine)]$ and $[Cr(L-aspartate)_2]^-$ have been separated[113] by high-performance liquid chromatography using a strong cation-exchange resin and water as an eluant. A similar conclusion is reached to the previous paper, namely that isomers with $trans$-amino-groups do not appear to be stable. Circular dichroism is used to assist the assignment of configuration to the various complexes.

A potentiometric study of $Mo^{VI}$:histidine complex formation is reported[114] in the range 4—7 pH. A polymeric 1:1 complex is observed and the stability constants of this and several other species are reported. Reacting[115] hexa-ammine-chromium(III) nitrate and L-proline produces a purple complex formulated $[Cr(L-$

[110] O. Leitzke and F. Sladky, Z. Anorg. Allg. Chem., 1981, **480**, 7.
[111] A. Müller, N. Mohan, S. Sarka, and W. Eltzner, Inorg. Chim. Acta, 1981, **55**, L33.
[112] P. E. Hoggard, Inorg. Chem., 1981, **20**, 415.
[113] M. Watabe, H. Yano, Y. Odaka, and H. Kobayashi, Inorg. Chem., 1981, **20**, 3623.
[114] E. S. Johansen and O. Jons, Acta Chem. Scand., Ser. A, 1981, **35**, 233.
[115] H. Oki and H. Yoneda, Inorg. Chem., 1981, **20**, 3875.

Pro)$_2$OH]$_2$4H$_2$O. This has again demonstrated the lack of *mer*-tris(amino acidato)chromium(III) species. The structure of the species confirms the di-$\mu$-hydroxo-bridges and also that the prolinato-ligands are co-ordinated through nitrogen and oxygen. Although both metals are octahedral, the two sections have different configurations with the nitrogens *trans* to one metal and *cis* to the other.

Further examples of (hydroxylamido-*O,N*) complexes have been reported.[116,117] In both [Mo$_2$O$_4$(Et$_2$NO)$_2$(C$_2$O$_4$)$_2$]$^{2-}$ and [MoO(Me$_2$NO)(BzH)Bz], where Bz is the ligand species (Ph·CO·NHO)$^-$, the metal atom is found at the centre of a pentagonal bipyramid. The R$_2$NO groups are bidentate and in the former species the two sections are bridged by oxo-ligands. The benzohydroxamato (Bz) ligand is however *O,O*-co-ordinated. This mode of attachment is also found in the *X*-ray structure of dioxomolybdenum(VI) hydroxamates derived from various acetalides.[118] The hydroxamic acids are of significance since they may well be toxic metabolites of various drugs. Complexes of acetanilide, *p*-chloroacetanilide, *p*-benzoyloxyacetanilide, benzanilide, and phenacetin were synthesized and the structural analyses carried out on the phenacetin (32) and acetanilide compounds.



(32)
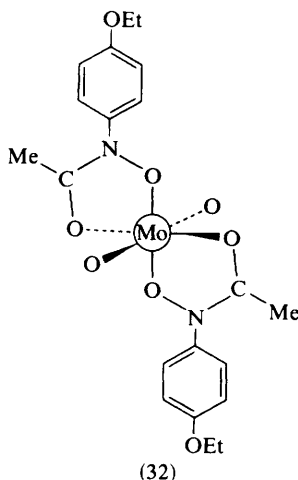
The compounds are formulated MoO$_2$L$_2$ with *cis*-oxo-groups and a markedly distorted octahedral environment. The complexes are isolated by an interesting route. The first stage is silylation of the relevant amide by reaction with bis(trimethylsilyl)acetamide, then a solution of oxodiperoxo(hexamethylphosphoramide) molybdenum(VI) [MoO$_5$(hmpt)] is added. Oxidation to the hydroxamates then proceeds with the advantage that the product is stabilized by co-ordination to the molybdenum.

Many of the potential, or actual, *N,O*-donor ligands are of the Schiff-base class. A few of the more interesting reports of this type of compound have been selected to illustrate current work. A wide range of complexes formulated Mo(VI)O$_2$(L)(D)

[116] K. Wieghardt, W. Holzbach, and J. Weiss, *Inorg. Chem.*, 1981, **20**, 3436.
[117] K. Wieghardt, W. Holzbach, E. Hofer, and J. Weiss, *Inorg. Chem.*, 1981, **20**, 343.
[118] G. A. Brewer and E. Sinn, *Inorg. Chem.*, 1981, **20**, 1823.

*J. E. Newbery*

have been reported.[119] [L is a terdentate ligand (33) and D is a donor molecule, such as MeCHO, PhCHO, EtOH, d.m.f., $Me_2SO$, *etc*]. These are formed from the relevant $MoO_2L$ or $MoO_2L(EtOH)$ species by crystallizing from the donor solvent (D). The binding of D is fairly weak and it can be readily removed by gentle heating. Infrared data supports the oxo-ligands as being in the *cis*-orientation.



(33) (Z = O or S)                          (34)
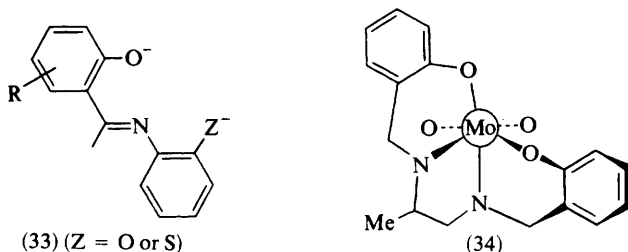
Quadridentate ligands on to the same molybdenum species ensure that all likely co-ordination sites are filled. The *cis*-oxo arrangement is maintained[120] in these species as shown by the $X$-ray crystal structure of (34). Thus the potential square-planar Schiff-base template is bent considerably to conform to this preference. The ligand contains a chiral centre and this helps in solution studies to deduce likely conformations with the aid of $^1H$ and $^{13}C$ n.m.r. and circular-dichroism spectra. If $Mo^V$ is taken then a similar ligand [no Me substitution in the $-CH_2-CH_2-$ section of (34)] is able to make an approximate square planar configuration.[121] $[MoOL(MeOH)]Br$ shows, by a single-crystal $X$-ray study, that the oxo-group is *trans* to the MeOH. The methanol is 2.338 Å away from the metal compared with 1.962 Å (average) for the ligand oxygens and 1.666 Å for the oxo-group. The molybdenum is thus raised above the basal plane towards the oxo-species and away from the methanol.

Sulphur linkages are very important for molybdenum, but most of the interest lies in very large molecular systems such as clusters and only a few authentic mononuclear species are of current interest. Complexes between molybdenum and cysteine have been studied in solution[122] and solid state.[123] Resonance Raman spectra were found to be of great assistance in the assignment of $Mo=O$, Mo–S–Mo, or $Mo-S-CH_2$ vibrations. A correct understanding of the bonding in these amino-acidato-complexes should be of assistance when considering potential molybdenum sites in enzymes. The preparation is reported[124] of $Mo(Hdmt)_2Cl_3 \cdot H_2O$, where $H_2dmt$ is the ligand (35). A better characterized species is the eight co-ordinate $W(mpd)_4$, where mpd is the ligand (36). This molecule is shown[125] by single-crystal $X$-ray analysis to be of the dodecahedral type ($D_{2d}$ symmetry) with the ligands in the *mmmm* arrangement. The shape follows exactly from the precepts suggested

[119] O. A. Rajan and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 660.
[120] M. Gulloti, A. Pasini, G. M. Zanderighi, G. Ciani, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1981, **20**, 902.
[121] S. F. Gheller, J. R. Bradbury, M. F. Mackay, and A. G. Wedd, *Inorg. Chem.*, 1981, **20**, 3899.
[122] M. Lamache-Duhameaux, *J. Inorg. Nucl. Chem.*, 1981, **43**, 208.
[123] N. Ueyama, N. Nakata, T. Araki, A. Nakamura, S. Yamashita, and T. Yamashita, *Inorg. Chem.*, 1981, **20**, 1934.
[124] M. B. Ferrari, G. G. Fava, and C. Pelizzi, *Inorg. Chim. Acta*, 1981, **55B2**, 167.
[125] F. A. Cotton and W. H. Ilsley, *Inorg. Chem.*, 1981, **20**, 614.

(35)



(36)
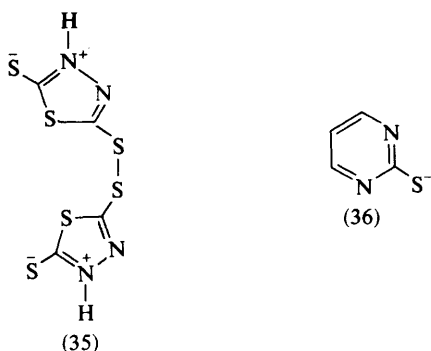
by Fay,[126] which in particular allow for the number of $d$ electrons (2 in the present case) and the character of the ligand atoms. Here the nitrogen should be a good $\pi$-acceptor and the sulphur a good $\pi$-donor.

Homoleptic complexes are usually of some interest but the reported[127] synthesis of $Mo(Bu^tS)_4$ is especially welcome since it should show versatility as a starting material for a range of thiolate complexes. The diamagnetic red-coloured complex was prepared by treating anhydrous $MoCl_4$ with $(Bu^tS)Li$ in 1,2-dimethoxyethane. $X$-ray diffraction studies confirm the monomer status and show an approximate tetrahedral ligand arrangement. It undergoes several interesting[128] reactions such as addition of $Bu^tNC$ to give *cis*-$[Mo(Bu^tS)_2(Bu^tNC)_4]$ which has been shown to have a distorted octahedral configuration with SMoS of 115.3° and the (equatorial) CMoC of 73.7°. Molecular orbital analysis suggests that the $d^4$ state may be responsible for this distortion. This is not a Jahn–Teller-type effect located in filled 'metal' MOs but results from the MO two below the HOMO which is formed from two sulphur $p$-orbitals. Distortion allows substantial relief from repulsive interactions.[129]

Venturing towards the even more exotic sulphur ligand types, the synthesis of $MoO_2L_2$, where L is $-CS_2$ monosubstituted ferrocene, has been reported.[130] Spectroscopic evidence is used to support *cis*-orientation for the oxo groups and a bidentate nature for the $-CS_2$ group.

Several molybdenum–sulphur bond enthalpies have been estimated for SR type ligands.[131] Mean values of 237, 202, 211, and 193 kJ mol$^{-1}$ were found for Mo$-$SR where R = Pr$^n$, Pr$^i$, Bu$^n$, and Bu$^t$, respectively.

The nitrogen donor ligands cover a very wide range of types, from cyanides and azides through amines and finally to dinitrogen complexes. Some novel mixed-ligand complexes, *cis*- and *trans*-$[Cr(NH_3)_4(H_2O)(CN)]^{2+}$ and *cis*-$[Cr(NH_3)_4(Me_2SO)(CN)]^{2+}$ are reported.[132] Standard methods of conductance, chromatography, and vibrational spectra were used to characterize the complexes. The route of their aquation reaction was followed by isolating all the intermediate

[126] J. K. Burdett, R. Hoffmann, and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 2553.
[127] S. Otsuka, M. Kamata, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 3011.
[128] M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 3572.
[129] M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida, and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 5772.
[130] M. Nakamoto, K. Shimizu, and K. Tanaka, *Inorg. Chim. Acta*, 1981, **53**, L51.
[131] A. R. Dias, J. A. Martinho Simões, and C. Teixeira, *J. Chem. Soc., Dalton Trans.*, 1981, 1178.

stages. A more unusual cyanide species is the compound $K_4[WH(CN)_7]2H_2O$ which was shown[133] to have the hydride ligand by careful $^{13}C$ and $^1H$ n.m.r. spectroscopy. This is the first eight co-ordinate cyanide hydride reported.

Reaction of $MoCl_4(py)_2$ with $Me_3SiN_3$ in 1,2-dichloroethane produces two complexes, $MoN(N_3)Cl_2(py)$ and $MoN(N_3)_3(py)$. Both are found[134] to be explosive. Despite this drawback a structural determination has been possible of the tris-azide by single-crystal $X$-ray diffraction and has shown a square-pyramidal configuration about the metal. The single nitrogen occupies the apex and is 163.4 pm from the metal, compared to 204 pm for the azide nitrogens and 225.8 for that of the pyridine (37).



(37)
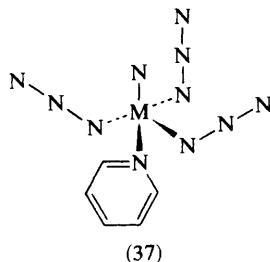
Chromium(III) species hold a special place in inorganic co-ordination chemistry in general and reaction mechanisms in particular. Even such a well known species as $[Cr(en)_3]^{3+}$ can still repay careful study. As the introduction to one recent paper[135] would have it: 'In this, the third decade of investigation of chromium(III)–amine photochemistry, there lurks a question that was asked before: Does reactivity occur from the lowest excited state, a doublet state, and/or from the lowest excited quartet state?' The answer would appear to be most likely as the latter, but perhaps the most interesting section of the work is concerned with a careful appraisal, with full annotation, of the various stereochemical paths available to the photoaquation process.

Ammination of *trans*-$[Cr(en)_2FBr]^+$ by liquid ammonia produces a mixture of the *cis*- and *trans*-$[Cr(en)_2FNH_3]^+$ complex ion, but if propane-1,3-diamine is substituted for the (en) ligand, only the *trans*-isomer is produced.[136] This has been shown by single-crystal $X$-ray studies to have non-equivalent chelate rings. One is in a chair conformation and the other is twisted.

A convenient route to diamine (*e.g.* $Me_2NCH_2CH_2NMe_2$) or diazadiene (*e.g.* $RN=CHCH=NR$) complexes of molybdenum is claimed[137] by refluxing the appropriate ligand with $MoCl_3(t.h.f.)_3$ in $CH_3CN$ as solvent.

Chromium has no significant $\pi$-back bonding (Cr–py) in the compound $Cr(CO)_5L$. This was one of the main conclusions[138] from a CNDO-type of molecular orbital

[132] P. Riccieri and E. Zinato, *Inorg. Chem.*, 1981, **20**, 3722.
[133] (a) A.-M. Soares and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1981, 1886.
(b) A.-M. Soares, P. M. Kiernan, D. J. Cole-Hamilton, and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 1981, 84.
[134] E. Schweda and J. Strähle, *Z. Naturforsch., Teil B* 1981, **36**, 662.
[135] M. C. Cimolino and R. G. Linck, *Inorg. Chem.*, 1981, **20**, 3499.
[136] J. W. Vaughn, *Inorg. Chem.*, 1981, **20**, 2397.
[137] A. J. L. Pombeiro and R. L. Richards, *Transition Met. Chem.*, 1981, **6**, 255.
[138] (a) H. van Dam, G. Boxhoorn, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1981, **53**, L235; (b) G. Boxhoorn, D. J. Stufkens, P. J. F. M. van der Coolwijk, and A. M. F. Hezemans, *Inorg. Chem.*, 1981, **20**, 2778.

study for L = pyridine or piperidine. The charge distributions found were virtually identical for the two species indicating that imine and amines co-ordinate in the same fashion. Further studies in this area[138b] have used MCD spectra to elucidate the MO diagram for such complexes. $Cr(CO)_5PCl_3$, for example, has a very similar spectrum to $Cr(CO)_6$ indicating near octahedral symmetry of electron distribution for both.

$Mo_2X_4(py)_4$ (X = Br, I, or NCS) have been prepared[139] and it was found from $X$-ray powder photography that their unit cells are very similar.

A rather surprising claim[140] of four co-ordinate status is made for the compound $[(Mepy)_2 \cdot Cr^{II} \cdot (OOCCF_3)_2]$. This was prepared in two stages from $Cr(t.h.f.)(BH_4)_2$ by firstly reacting with $CF_3COOH$ then followed by the substituted pyridine. Single-crystal $X$-ray studies are used to support a square-planar configuration for the metal with *trans*-monodentate perfluoroacetates.

Molybdenum(III) evidently is able to form bis-chelates with phenanthroline and bipyridyl but attempts to produce the tris-analogues were unsuccessful.[141] *Cis*-$[MoCl_2(phen)_2]Cl$ and *cis*-$[MoCl_2(bipy)_2]Cl$ were prepared by direct action, and their major properties and spectral features are reported. The structure of another molybdenum–bipyridyl complex has been reported.[142] $Mo(OPr^i)_2(bipy)_2$ is produced by cleavage of the metal–metal triple bond of $Mo_2(OPr^i)_6$ by bipyridyl in hydrocarbon solvents. A notable point, apart from the *cis*-alkoxy-ligands (38), is that the Mo—N distances are *ca.* 2.12 Å compared to 2.35 Å in $Mo(py)_2(OBu^t)_2$. This observation is taken as evidence for metal $d$-to-bipyridyl $\pi^*$ bonding. Support for this view as given by resonance Raman observations which show a shift to lower frequencies of the (bipy) bands.



(38)
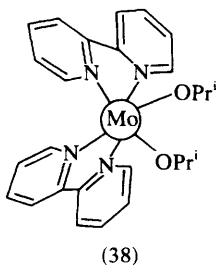
Several significant papers have appeared in recent years on the various molybdenum complexes that are able to be co-ordinated by dinitrogen. Some of these have been shown to be capable of irreversible hydrolysis to ammonia or organonitrogen species. An advance of some significance has been reported this year with the description of a complete cycle of steps (Scheme 7) for the fixation of dinitrogen into organohydrazine.[143] Starting with the species $[MoBr(diphos)_2\{NNCH_2(CH_2)_3CH_2\}]^+$, controlled potential electrolysis under a nitrogen atmosphere gives a rapid 2e change to the neutral $[Mo(NNR_2) \cdot (diphos)_2]$ complex and a further 2e reduction at a slower rate. From the final mixture up to

[139] D. Dobčnik and B. Volavšek, *Monatsh. Chem.*, 1981, **112**, 437.
[140] I. L. Eremenko, A. A. Pasynskii, and V. T. Kalinnikov, *Inorg. Chim. Acta*, 1981, **54**, L85.
[141] T. S. Morita, Y. Sasaki, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2678.
[142] M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress, and W. H. Woodruff, *J. Am. Chem. Soc.*, 1981, **103**, 4945.
[143] C. J. Pickett and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1981, 1033.

45% of the presumed starting complex *trans*-[Mo(N₂)₂(diphos)₂] has been obtained, and also around 60—70% of the calculated yield of free hydrazine (based on the charge passed), thus completing the cycle.

Schemes such as Scheme 7 rely greatly on structural studies of intermediates and potential intermediates. Hydrazido-complexes then are of great interest and a recent study of one such species has shown the presence of a linear M–N–N linkage. [M(NNH₂)(quin)(PhMe₂P)₃]X (M = Mo or W, X = Cl, Br, or I, and quin = quinolin-8-olate) forms crystals suitable for $X$-ray studies.[144] The main structural features about the metal are similar in each compound with an approximate octahedral configuration. Minor differences occur in the position of the counter-ions.
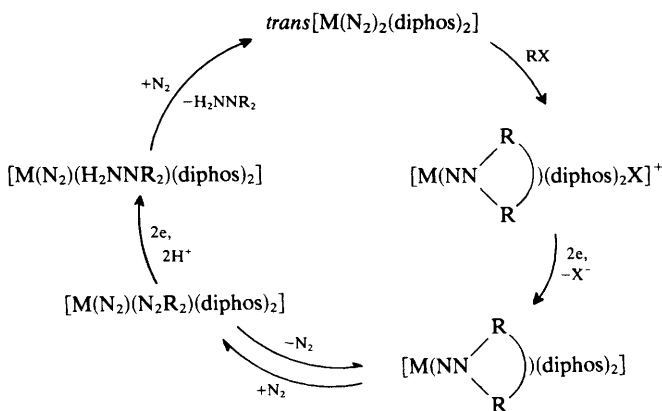


**Scheme 7**

Reaction kinetic data have appeared on the release of ammonia from *trans*-[Mo(NH)X(diphos)₂]⁺ (X = halogen), which occurs in basic solution although the complexes are inert in acid.[145] Details are presented of a two-stage mechanism, whereby an initially rapid substitution of OMe⁻ for X⁻ that occurs *via* a solvent-separated ion pair [Mo(N)(diphos)₂]⁺[X]⁻, is followed by a slower stage as the diphos ligands un-chelate. This eventually allows ammonia release. The synthesis of further species of this type has been reported.[146] *trans*-[Mo(N₂)₂(Ph₂MeP)₄], *cis*-[Mo(N₂)₂(PhMe₂P)₄], *trans*-[Mo(N₂)₂(diphos)(Ph₂MeP)₂], and [Mo(N₂)₂(triphos)(Ph₂MeP)] were prepared by standard procedures involving either the displacement from a complex of monophosphines by a chelate phosphine or the co-ordination of the phosphine during the step at which the nitrogen is attached.

Several new molybdenum and tungsten complexes are included in a report on the acylation of ligated dinitrogen complexes.[147] For example, *trans*-[M(N₂)₂(diphos)₂] can be acylated by trifluoroacetic anhydride to form the trifluoroacetyldiazenido complex (containing N–COF₃). Some spectroscopic details of the products are included.

[144] I. R. Hanson and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1981, 390.
[145] R. A. Henderson, G. Davies, J. R. Dilworth, and R. N. F. Thorneley, *J. Chem. Soc., Dalton Trans.*, 1981, 40.
[146] T. A. George and R. A. Kovar, *Inorg. Chem.*, 1981, **20**, 285.
[147] H. M. Colquhoun, *Transition Met. Chem.*, 1981, **6**, 57.

A preliminary report of what should be an essential investigative procedure for these dinitrogen species has appeared.[148] [15]N n.m.r. spectra have been obtained for several species and various ^{15}N chemical shifts correlated with the known properties of the complex.

For example for $[WH(N_2)_2(diphos)_2]HCl_2$, contributions from the various forms such as $M-N_2$, $M-N{\equiv}N$, $M{=}N-NH_2$, $M{=}N-NH_3^+$, $M{\equiv}N$, and $M{=}NH$ are assessed. The method clearly shows great promise for the elucidation of synthetic pathways within the general framework of the search for reversible nitrogen-fixing cycles.

This Section on mononuclear complexes concludes with reports dealing with macrocyclic ligands, or to be precise, with potentially macrocyclic ligands, since the first paper[149] records a failure to produce a macrocyclic complex. The ligand (39) could potentially form bimetallic macrocyclic species, and does indeed form



(39)
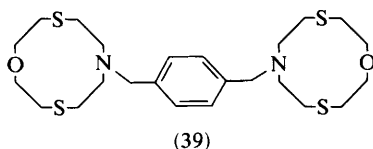
a 1:2 complex with $MoOCl_4$. However structural analysis shows this to be formulated as $[H_2{\cdot}39]^{2+}[MoOCl_4(t.h.f.)]_2^-$, where the molybdenum is in an octahedral environment with *trans*-oxygen donors. The metal presumably is unable to take up the potential complexing position once the nitrogens are protonated. Turning to actual macrocyclics, virtually all the species of interest are porphyrins. A major paper has appeared that is to be the start of a series on the electronic structure of atypical metalloporphyrins.[150] It contains an exceptionally full bibliography of reviews and articles on structural and theoretical aspects of the area. The need for optimal metal–oxygen $\pi$-interactions is used to explain the difference in structure observed between $(Mtpp)_2O_3$ for M=Mo and Nb (tpp = tetraphenylporphyrin). In the former case a linear system is observed (O–M–O–M–O), whereas the latter has three $\mu$-oxo-ligands.

A possible $Cr^V$ porphyrin species has been detected by e.s.r. evidence.[151] The oxidation of $[Cr^{III}(tpp)Cl]$ by iodosylbenzene could involve electrons from the ring or the metal. The shape of the e.s.r. spectrum of the product seems to be characteristic of a $d^1$ ion. Furthermore, use of $^{17}OIPh$ showed that the oxygen is transferred to the chromium. The same $Cr^{III}$ porphyrin has also been studied by electrochemical procedures in dichloroethane.[152] Several different species were detected by a combination of cyclic voltammetry and thin-layer spectrochemical procedures. Potentials were then measured for the system in the presence of donor pyridine-type molecules. A correlation between the half-wave potential and the ligand $pK_a$ was observed. It is claimed that the evidence supports the existence of the complex ion $[Cr(tpp)(py)_2]^+$.

[148] J. R. Dilworth, S. Donovan-Mtunzi, C. T. Kan, R. L. Richards, and J. Mason, *Inorg. Chim. Acta*, 1981, **53**, L161.

[149] P. H. Bird and W. A. Wickramasinghe, *Can. J. Chem.*, 1981, **59**, 2879.

[150] K. Tatsumi and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 3328.

[151] J. T. Groves and R. C. Haushalter, *J. Chem. Soc., Chem. Commun.*, 1981, 1165.

[152] L. A. Bottomley and K. M. Kadish, *J. Chem. Soc., Chem. Commun.*, 1981, 1212.

Alternatively, if [Cr$^{III}$(tpp)Cl] is treated with a reducing agent (Zn/Hg in THF) then Cr$^{II}$(tpp) may be generated.[153] This adds oxygen immediately on exposure to air to produce [Cr(tpp)O], which has been shown by single-crystal $X$-ray analysis to have a very characteristic five-co-ordinate porphyrin structure. The Cr atom is located 0.489 Å above the plane. It is suggested that the oxidation reaction proceeds in two stages *via* a $\mu$-oxo–Cr$^{II}$ intermediate.

The range of molybdenum porphyrin species has been increased by the synthesis of a molybdenum(II) complex that also has a $\pi$-bonded alkyne (40). It was pro-



(40)
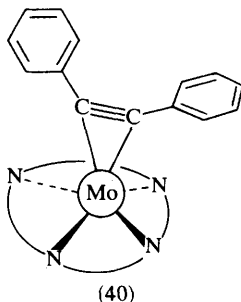
duced[154] from [Mo$^{IV}$(tpp)Cl$_2$] by lithium aluminium hydride reduction, followed by addition of diphenylethyne. The metal atom is displaced by 0.63 Å from the nitrogen basal plane, and slight puckering of the pyrroles is also observed. Viewed from above, the alkyne linkage eclipses the opposite Mo—N bonds, which are thus about 2.148 Å compared with 2.104 Å for the other pair of Mo—N bonds. The alkyne bond length at 1.324 Å is taken as evidence for the ligand acting as a four-electron donor.

The well established species MoO(tpp)OEt has been used[155] to produce a series of complexes with a monodentate ligand (X) substituted for the OEt group. The red-shift of the absorption maximum was found to increase in the order X = OEt$^-$ < BF$_4^-$ ~ F$^-$ < NCO$^-$ < N$_3^-$ < NCS$^-$ < Cl$^-$ < Br$^-$. Similar complexes (X = OMe, OAc, or Cl) have been studied by cyclic voltammetry in dichloromethane solution.[156] The electrochemical behaviour was found to be markedly dependent upon X with very similar behaviour for the OAc and Cl species ($E_{\frac{1}{2}}$ for oxidation ~1.25 V and reduction at −0.05 V, *versus* SCE) but quite distinct (>1.7 V and −0.74 V, respectively) for the species X = OMe. It is suggested that these, and other differences, are a reflection of varying degrees of covalency in the Mo—X bond.

It is possible that the differing electrochemical behaviour is a factor in another report[157] that is concerned with the use of these complexes as catalysts for the selective epoxidation of cyclohexene by Bu$^t$OOH. MoO(tpp)OMe was found to be most effective. No metal–olefin co-ordination is involved in the process, which proceeds *via* peroxy-bond heterolysis. This model system is proposed as the first

[153] J. R. Budge, B. M. K. Gatehouse, M. C. Nesbit, and B. O. West, *J. Chem. Soc., Chem. Commun.*, 1981, 370.
[154] A. de Cian, J. Colin, M. Schappacher, L. Ricard, and R. Weiss, *J. Am. Chem. Soc.*, 1981, **103**, 1850.
[155] T. Imamura, T. Numatatsu, M. Terui, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 170.
[156] Y. Matsuda, S. Yamada, and Y. Murakami, *Inorg. Chem.*, 1981, **20**, 2239.
[157] H. J. Ledon, P. Durbut, and F. Varescon, *J. Am. Chem. Soc.*, 1981, **103**, 3601.

example of a simple chemical analogue to the olefin–hydrocarbon oxidation steps carried out by cytochrome P-450-dependent mono-oxygenases.

**Bridged Complexes.**—Bridging groups for these elements mostly involve oxygen or sulphur donor atoms. Reaction of $[WBr(diphos)_2N_2H_2]^+Br^-$ with $CHFBr_2$ in the presence of $Ph_2I^+Br^-$ and aqueous base yields[158] the dinuclear cationic complex $[(WBr(diphos)_2\}\{\mu\text{-}CH(N_2)_2\}]^+$, which was isolated as the $[Cr(NH_3)_2(NCS)_4]^-$ salt. A single-crystal $X$-ray study of this complex showed that each tungsten has an approximate octahedral configuration with *trans*-equatorial phosphines. In the axial positions are a bromine and the bridging $(N_2CHN_2)$ group. The seven-atom chain W–N–N–C–N–N–W appears roughly $sp^2$ hybridized about the central (NCN) fragment (*ca.* 122° bond angles for all three atoms), and is essentially planar.

*Trans*-$[(NH_3)_4(H_2O)Cr(\mu\text{-}OH)Cr(NH_3)_5]Cl_5\cdot3H_2O$ has been shown[159] by single-crystal $X$-ray analysis to be symmetrically bridged by the hydroxo-group with a Cr–O–Cr angle of 155.1°. Each metal has four equatorial ammine groups and the *trans*-ligand in each case is disordered.

$W_2(NMe_2)_6$ reacts[160] with ROH to give dark coloured crystals of empirical formula $W(OR)_4$ (R = Me or Et). These have now been shown by $X$-ray structural analysis to be tetrameric, with a striking resemblance to $[Ti(OR)_4]_4$ (41). These



(41)
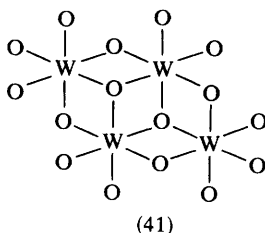
seem to conform to the structural theory for alkoxides, namely that the degree of oligomerization is that required to reach octahedral co-ordination. The structure can be viewed as a bridged species, but there is a strong possibility of delocalized M—M bonding.

$[MoO(S_2CNEt_2)_3]BF_4$ reacts[161] with $Ph_3P$ in methanol to form the green-black coloured $\mu$-oxygen occupies an axial position in the pentagonal-bipyramidal configuration around each metal, with the M–O–M angle of 175.7°. This is believed to be the first such species with a near linear oxy-bridge between sulphur-co-ordinated molybdenum centres. The magnetic properties ($\mu = 2.17$ BM) are consistent with one unpaired electron *per* molecule. Thus, although the molybdenums are crystallographically identical, the compound is a mixed-valence type with a formal (average) oxidation state of 4.5.

The disproportionation of the $\mu$-oxo compound $Mo^V_2O_3L_4$ to give $MO^{IV}OL_2$ and *cis*-$[Mo^{VI}O_2L_2]$ (L = $S_2CSPr^i$) has been followed by concentration-jump

[158] (a) H. M. Colquhoun and K. Hendrick, *J. Chem. Soc., Chem. Commun.*, 1981, 85; (b) *Inorg. Chem.*, 1981, **20**, 4074.
[159] S. J. Cline, J. Glerup, D. J. Hodgson, G. S. Jensen, and E. Pedersen, *Inorg. Chem.*, 1981, **20**, 2229.
[160] M. H. Chisholm, J. C. Huffman, and J. Leonelli, *J. Chem. Soc., Chem. Commun.*, 1981, 270.
[161] J. A. Broomhead, M. Sterns, and C. G. Young, *J. Chem. Soc., Chem. Commun.*, 1981, 1262.

relaxation procedures[162] and shown to proceed *via* molybdenum(VI) species that involves a unidentate thioxanthato-ligand.

Malonate ligands are shown[163] to be involved in extensive co-ordination to molybdenum in the tetrameric $Mo^V$ complex $[\{Mo_2O_4(mal)_2\}_2mal]^{6-}K_6$. This consists of 2 binuclear species bridged together into a tetramer by a malonate moiety (42). Each metal is therefore co-ordinated by two $\mu$-oxygens, one single oxygen, one oxygen from the bridging malonate (bidentate), and two (unidentate) oxygens from a single bidentate malonate. These latter ligands form an approximate boat configuration with the molybdenum.



(42)    (43)
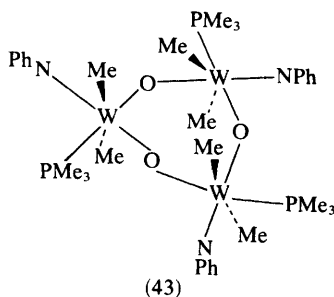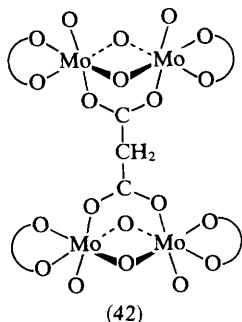
$W_3(\mu\text{-}O)_3Me_6(PhN)_3(Me_3P)_3$ is the somewhat unlikely product of the reaction of phenylimidotungsten tetrachloride with dimethylmagnesium in the presence of trimethylphosphine.[164] It has been shown by $X$-ray structural analysis to be a trimeric species with the structure shown (43). The $(WO)_3$ core is virtually coplanar and has $W\hat{O}W$ of *ca.* 153°. The metal–oxygen bond *trans* to the phosphine is significantly shorter (*ca.* 1.80 Å) than that *trans* to the N—Ph group (*ca.* 2.18 Å). The two methyl groups are also in a *trans* configuration, to give a distorted octahedral environment to each tungsten.

The preparation and crystal structures of several bridged molybdenum species have been reported.[165] $[Mo_2O_nS_{4-n}(R\text{-pdta})]^{2-}$, where (pdta) is the propylenediaminetetra-aceto ligand, has been synthesized for $n = 4$, 3, and 2. Both the tetradentate ligand and the O/S atoms act as bridging groups in these complex ions. For the ($n = 3$) species two isomeric forms exist that differ in the orientation of the ligand methyl group (44).

The range of bridged species remaining are now those involving sulphur ligands. The structural types range from simple binuclear complexes through thiometallates to the cubane-type of heterometallic species. Those species that involve a metal–metal bond are however dealt with in the next Section.

Many of the species following are used as structural analogues for bioinorganic molecules. Much current evidence is thus based on solid-state analysis, and the

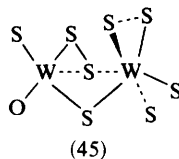[162] S. Miyake, K. Tanaka, and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1981, 292.

[163] T. Shibahara, H. Kuroya, K. Matsumoto, and S. Ooi, *Inorg. Chim. Acta*, 1981, **54**, L75.

[164] D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, and A. J. Nielson, *J. Chem. Soc., Chem. Commun.*, 1981, 103.

[165] A. Kojima, S. Ooi, Y. Sasaki, K. Z. Suzuki, K. Saito, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2457.
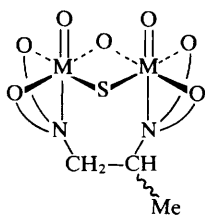
(44)



(45)

rapid development of high-field FT n.m.r., which is increasing the range of nuclei that can be studied by this important solution structural method, should be of great significance in this area. A preliminary report[166] has shown how this might be used for molybdenum. $^{95}$Mo n.m.r. chemical shifts are reported for a wide range of anions $[MoX_nY_{-n}]^{2-}$ (X = Y = O, S, or Se). Relative to $[MoO_4]^{2-}$ solvent-sensitive shifts of over 3000 p.p.m. can be observed $[MoSe_4]^{2-}$ and a scale is reported: $[MoSe_4]^{2-}$ > $[MoS_4]^{2-}$ > $[MoOSe_3]^{2-}$ > $[CNCuMoS_4]^{2-}$ > $[MoOS_3]^{2-}$ > $[MoO_2Se_2]^{2-}$ > $[Et_4NCuMoS_4]$ > $[MoO_2S_2]^{2-}$ > $[MoO_3Se]^{2-}$ > $[MoO_3S]^{2-}$ > $[MoO_4]^{2-}$.

$[W_2S_8OH_3]^-$ has been shown[167] to contain several distinct types of sulphur linkages. It contains an $S_2{}^{2-}$ group bidentate to one tungsten, and another that as well as being bidentate to one metal, bridges between the two centres (45). One tungsten is in approximate square-pyramidal configuration (raised *ca.* 0.7 Å above the basal plane of four sulphurs), whereas the other has an exceptionally distorted octahedral environment. The W—W distance is 3.512 Å and thus excludes the possibility of metal–metal bonds. Similar diversity is shown[168] in the structure of $[Mo_2S_{10}]^{2-}$: again the two metals are in different environments with one having a persulphido-group and a sulphido-ligand and the other a terminal sulphido- and a tetrasulphido-group. The metals are joined by two bridging sulphido-groups.

A general review on thiometallate anions has already been mentioned,[3] and a specific account of the $(MS_4)^{2-}$ anions (Mo or W) dealing with the relevance of Fe–M–S complexes as structural analogues for nitrogenase enzymes has also appeared.[169] This gives a clear structural classification of the various compounds that have been synthesized and also advances the concept of a model compound by showing how their spectral features may be matched against those of authentic species (*e.q.* Fe–Mo–S proteins from *Desulfovibrio gigas*).

Regarding $[MS_4]^{2-}$ as the ligand (L) complexes can be classified by increasing co-ordination number. The structure of $Ag_2(Ph_3P)_4(MoS_4)$ has been determined by what is described as a 'textbook example' of the application of the resonance Raman effect.[170] It shows the expected symmetric pattern (46). The resonance Raman measurements are enhanced by the totally symmetric vibrations of the $(MS_4)^{2-}$ ligand.

[166] S. T. Gheller, P. A. Gazzana, A. F. Masters, R. T. C. Brownlee, M. J. O'Connor, A. G. Wedd, J. R. Rodgers, and M. R. Snow, *Inorg. Chim. Acta*, 1981, **54**, L131.
[167] F. Sécheresse, J. Lefebvre, J. C. Daran, and Y. Jeannin, *Inorg. Chim. Acta*, 1981, **54**, L175.
[168] W. Clegg, G. Christou, C. D. Garner, and G. M. Sheldrick, *Inorg. Chem.*, 1981, **20**, 1562.
[169] D. Coucouvanis, *Acc. Chem. Rev.*, 1981, **14**, 201.
[170] A. Müller, A.-M. Dommröse, W. Jaegermann, E. Krickemeyer, and S. Sarkar, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1061.

Ph₃P, S, S, PPh₃ ... Ag—Mo—Ag ... Ph₃P S S PPh₃

(46)

(47)
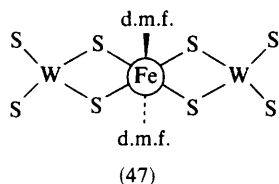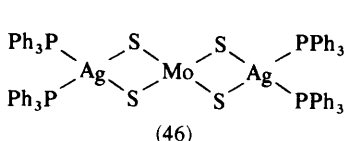
The majority of $(MS_4)^{2-}$ species seem to confer tetrahedral status on the acceptor metal, but this can no longer be regarded as inevitable with the synthesis of an $FeL_2$ complex, where the iron is in an approximate octahedral environment,[171] with planar sulphur co-ordination (47). $[Fe(WS_4)_2(d.m.f.)_2]^{2-}$ may be prepared from a one-electron reduction of the $[Fe(WS_4)_2]^{3-}$ complex ion in dichloromethane with $Et_4NBH_4$. A colour change from green to reddish brown is followed by precipitation of the impure salt on addition of diethyl ether. Recrystallization from a donor solvent (dimethylformamide or pyridine) then gave the appropriate complex ion.

The more common tetrahedral situation is inferred[172] by multinuclear n.m.r. and iron Mössbauer spectroscopy for the complex ion $[(PhO)_2FeMoS_4]^{2-}$. This is said to be the first Fe–Mo–S species that contains oxygen donors co-ordinated to the iron. Though if the previous report can also be applied to molybdenum, this will clearly not be the last such substance.

The structure of a similar species is also reported.[173] $[(NO)_2FeMoS_4]^{2-}$ shows $N$-bonded NO groups and has tetrahedral co-ordination about each metal with an Fe—Mo distance of 2.835 Å.

Several interesting nickel(II), platinum(II), and palladium(II) complexes in two series are reported,[174] $[M^1(MOS_3)_2]^{2-}$ and $[M^1(MS_4)(S_2CNEt_2)]^-$, ($M^1$ = Ni, Pt, or Pd, M = Mo or W). Conductivity, infrared, and u.v.–visible spectroscopic data are reported. The $(MOS_3)^{2-}$ complexes are almost certainly co-ordinated through sulphurs, though it was not possible to decide whether the non-co-ordinated oxygens were *cis* or *trans* to each other. U.v. evidence that the spectra of the mixed-ligand complexes could not be obtained by simple addition of the spectra of the appropriate bis(ligand)complex ions, was the principal reason for their assigned formulae.

One reason for the interest in these thiometallates is the well known Cu–Mo antagonism that is very important in veterinary medicine. Structures, determined by single-crystal $X$-ray analysis, have now[175] appeared for two new Mo–Cu–S complexes. The first (48) shows the arrangement of atoms in $[CuCN(MoS_4)]$-$(Ph_4P)_2$. This has a linear Mo···Cu···CN with virtual trigonal-planar co-ordination to the copper and the expected tetrahedral environment for the molybdenum. The second (49) is of $[(CuCH)_2(MoS_4)](Me_4N)_2$ which has infinite chains of complex anions aligned parallel to the $x$-axis. The zig-zag spine of the *catena*-anion has a fold angle of 107.2° between the linear arms (CuCNCu). It is perhaps easiest visualized as a CuCN chain with the anion (48) co-ordinated to each copper.

[171] P. Stremple, N. C. Baenziger, and D. Coucouvanis, *J. Am. Chem. Soc.*, 1981, **103**, 4601.
[172] H. C. Silvis and B. A. Averill, *Inorg. Chim. Acta*, 1981, **54**, L57.
[173] D. Coucouvanis, E. D. Simhon, P. Stemple, and N. C. Baenziger, *Inorg. Chim. Acta*, 1981, **53**, L135.
[174] K. P. Callahan and E. J. Cichon, *Inorg. Chem.*, 1981, **20**, 1941.
[175] A. Müller, M. Dartmann, C. Römer, W. Clegg, and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1060.

(48)    (49)
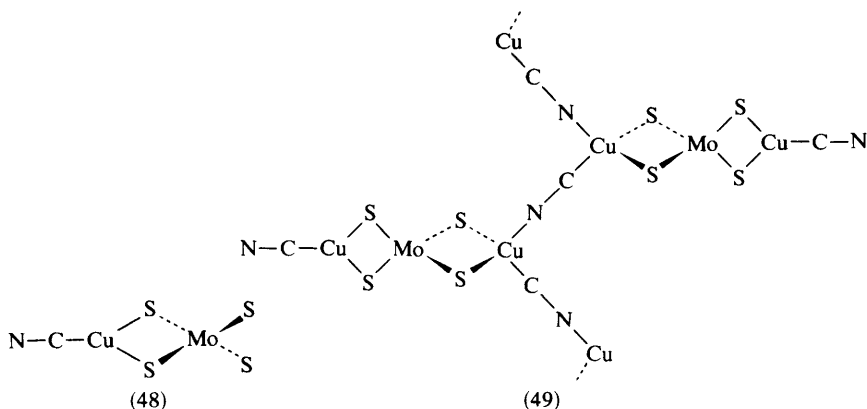
As a final example of the range of 1 : 1 complexes, admixture of $(MoS_4)(NH_4)_2$ and $RuCl_2(bipy)_2$ in aqueous ethanol solution has been shown[176] to produce $Ru(bipy)_2(MoS_4)$. The electrochemistry of this species has been studied, and it is also said to display catalytic activity towards alkynes.

$[WX(WS_4)_2](Ph_4P)$ (X = O or S) has been synthesized.[177] It is a mixed-valence compound and its crystal structure, determined by $X$-ray analysis, has been refined to show the expected tetrahedral configuration around the ligand tungstens, and a square pyramidal environment for the central metal.

These thiometallate species based on the tetrahedral $(MS_4)^{2-}$ represent one main group of Mo–Fe–S compounds and the cubane (and related) systems represent the other main class. An important new type of compound has now been synthesized,[178] where the molybdenum occupies a square-pyramidal site (50). Reaction of

(50)
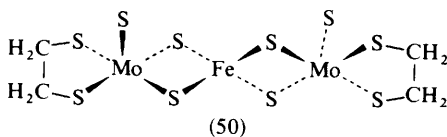
$(NH_4)_2MoS_4$ with disodium ethane-1,2-dithiolate in d.m.f.–MeCN and ferric chloride gave the anion $[\{SCH_2CH_2S)MoS_3\}_2Fe]^{3-}$, which was separated as the air-stable $[Me_4N]^+$ salt by precipitation after addition of isopropanol. Three distinct Mo–S linkages are evident and the ion has a distinctly bent orientation with Mo–Fe–Mo at 155.7°. The exact electronic structure is not reported, but preliminary evidence supports a structure in which two $Mo^V$ ($d^1$) atoms antiferromagnetically coupled to high-spin $d^5$ iron(III).

Complex ions containing a cubane Mo–Fe–S core (where alternate corners of a trigonally-distorted cube are occupied by sulphur atoms) have previously been shown to be of the 'double-cubane' type. That is, two cubane fragments linked by various different bridging groups (*e.g.* sulphides, thiols, or $Fe(SR)_6$ moieties). If the

[176] K. Tanaka, M. Morimoto, and T. Tanaka, *Inorg. Chim. Acta*, 1981, **56(B3)**, L61.
[177] F. Sécheresse, G. Lavigne, Y. Jeannin, and J. Lefebvre, *J. Coord. Chem.*, 1981, **11**, 11.
[178] P. L. Dahlstrom, S. Kumar, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1981, 411.

$Fe^{III}$-bridged complex $[Mo_2Fe_7S_8(SEt)_{12}]^{12-}$ is reacted with catechol in MeCN, then the bridge can be cleaved and a new mono-cubane structure (51) isolated.[179] The single-crystal $X$-ray structural analysis of compound (51) confirms the cleavage and shows an iron atom co-ordinated by three bidentate catecholato-ligands $[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]^{3-}$. The arrangement about the iron is virtually trigonal-prismatic however, rather than octahedral. The cubane core has very similar geometry to those previously identified in bridged double-cubane structures. The position of the phenyl rings in this compound would be expected to produce strong steric interactions if a substituted catechol were employed in the reaction. Thus if 3,6-di-n-propyl catechol ($Pr_2$cat) is used instead of catechol, a complex ion $[M_2Fe_6S_8(SEt)_6(Pr_2cat)_2]^{4-}$ (M = Mo or W) can be isolated.[180] The crystal structure of this compound shows that the 'double-cubane' nature has been retained, but that the mode of bridging has been altered (52).



(51)

(52)
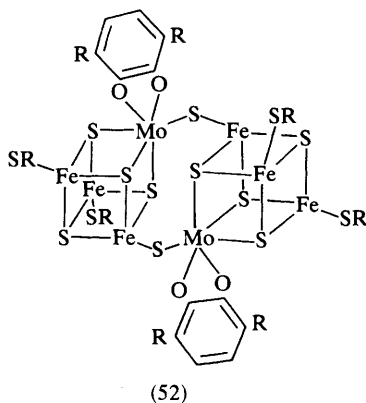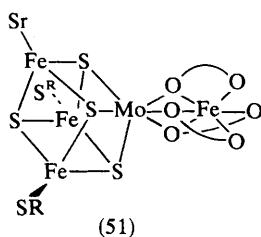
**Metal–Metal Bonded Compounds.**—These species will be dealt with in order of increasing numbers of metal atoms. Commencing with binuclear unbridged species, the first report deals with the use of such compounds as starting materials in the synthesis of novel seven co-ordinate mononuclear complexes,[181] $[W_2L_4]$ (L = 2-hydroxy-6-methylpyridine) reacts with cyclohexyl and t-butyl isocyanides to form homoleptic isocyanide complexes $[W(CNR)_7](PF_6)_2$.

The simplest type of M–M species have the empirical formula $M_2L_6$ and their configurations are similar to those found for ethane. $Mo_2(NMe_2)_4(CH_2pyMe)_2$ has a *gauche*-type solid-state structure[182] and a Mo–Mo triple bond of 2.204 Å. The pyridine fragment is bonded through the $CH_2$ group, which is in the 6-position (methyl at position 2) of the pyridine. $Mo_2(NMe_2)_4Et_2$ shows virtually the same Mo—Mo distance and also adopts the *gauche* configuration.[183] Using various alkyl substituents it was established, by n.m.r. observations, that in solution the equilibrium between *anti*- and *gauche*-rotamers moves towards the *gauche* option as the bulkiness of the alkyl group increases.

[179] T. E. Wolff, J. M. Berg, and R. H. Holm, *Inorg. Chem.*, 1981, **20**, 174.
[180] W. H. Armstrong and R. H. Holm, *J. Am. Chem. Soc.*, 1981, **103**, 6246.
[181] W. S. Mialki, R. E. Wild, and R. A. Walton, *Inorg. Chem.*, 1981, **20**, 1380.
[182] M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *Inorg. Chem.*, 1981, **20**, 1496.
[183] M. H. Chisholm, D. A. Haitko, K. Folting, and J. C. Huffman, *J. Am. Chem. Soc.*, 1981, **103**, 4046.

The molybdenum compound $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ has been prepared by direct action of the triazine on $Mo_2(NMe_2)_6$. It forms red crystals[184] that have been shown by single-crystal $X$-ray structural analysis to be of the same type as the previously-studied tungsten compound. There is an unbridged $Mo-Mo$ triple bond of 2.212 Å and each metal is co-ordinated to four nitrogens in a plane (53). The structure appears to exist in solution, or at least the n.m.r. time scale does not allow any other forms to be detected. Steric reasons are invoked to account for the observed non-bridged structure.



(53)
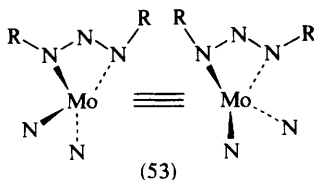
Compounds of formula $M_2Cl_4(Me_3P)_4$ (M = Mo or W) have been shown to be isomorphous,[185] with the ligands attached to form a dimer, *i.e.* $[MCl_2(Me_3P)_2]_2$, with an overall eclipsed conformation but with staggered ligands (*viz* a chlorine opposite a phosphine). The metal–metal bonds are 2.130 and 2.262 Å for the Mo and W, respectively, thus qualifying as quadruple bonds. A similar orientation is shown (54) as a projection along the $M-M$ bond, for the complex molecule $[Mo\{Et_2B(pz)_2\}_2\{Et_2B(OH)(pz)\}_2]$. This has been found by single-crystal $X$-ray diffraction to contain four chelating ligands, but no monodentate or bridging ligands.[186] One interesting point about the structure is that the oxygens on adjacent molybdenums are eclipsed. The molecule is formed by reaction of $[Et_2B(pz)_2]Na$, where pz is 2-pyrazoyl, with $Mo_2(CH_3COO)_4$. If the four chelating groups are identical,[187] *e.g.* $Mo_2(C_6H_4\cdot CH_2NMe_2)_4$, where the co-ordination is through a



(54)



(55)
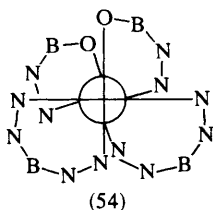
carbon of the phenyl ring and the nitrogen of the adjacent $CH_2NMe_2$ group, then a different eclipsed form is taken up (55). Here the chelate rings are also eclipsed, but with reversed orientations. Actually the whole structure has a slight twist (11°) away from the fully eclipsed conformation but this is said not to weaken appreciably the assumed contribution from the $\delta$-bond.

Not all molybdenum $M-M$ compounds are air-sensitive and further studies have been reported[188] on their aqueous chemistry. The ion $[Mo_2(HPO_4)_4]^2$ shows virtually

[184] M. H. Chisholm, D. A. Haitko, J. C. Huffman, and K. Folting, *Inorg. Chem.*, 1981, **20**, 171.

[185] F. A. Cotton, M. W. Extine, T. R. Felthouse, B. W. S. Kolthammer, and D. G. Lay, *J. Am. Chem. Soc.*, 1981, **103**, 4040.

[186] F. A. Cotton, B. W. S. Kolthammer, and G. M. Nott, *Inorg. Chem.*, 1981, **20**, 3890.

[187] F. A. Cotton and G. M. Nott, *Inorg. Chem.*, 1981 **20**, 3896.

[188] A. Bino *Inorg. Chem.*, 1981, **20**, 623.

the same visible spectrum in aqueous solution as in the solid state where the presence of a triple Mo—Mo bond has been shown by crystallographic methods. Electrochemical studies on quadruply-bound molybdenum dimers have been carried out in dichloromethane. Half-wave oxidation potentials for several complexes formulated $Mo_2X_2(phos)_4$, where $X = Cl$, Br, or NCS and phos represents various phosphine ligands, are reported.[189] The thiocyanate species have values about 0.5 V more positive than the corresponding chloride, and some of their processes were irreversible. However the majority of the complexes showed that the bond-order change from $4 \to 3.5$ is readily accessible for most of these dimers (corresponding to $\sigma^2\pi^4\delta^2 \to \sigma^2\pi^4\delta^1$).

Before commencing an account of bridged M—M species, one report[190] offers a rather unique account, in a characteristic style, of the stereochemistry of $W_2Cl_4(diphos)_2$, a sample of which was found to consist of green crystals and brown crystals. The brown form has bridging 1,2-bis(diphenylphosphine)ethane ligands and has a virtual staggered configuration (twist of $31.3°$) about the W—W axis, whereas the green form has chelating phosphines and is almost exactly eclipsed.

The majority of the binuclear bridged class of M—M compounds are those involving carboxylate ligands. Mostly these show tendencies to bind further ligands in either an axial position or a non-axial position. Chromium species virtually all contain axial ligands, for example $Cr_2L_4(t.h.f.)_2$, where L is the anion of 2-phenylbenzoic acid has the expected four bridging carboxylates with axial t.h.f. groups. If the synthesis is attempted in a non-donor solvent then the moiety produced is shown to be the tetranuclear $(Cr_2L_4)_2$, where the dimers are linked *via* axial co-ordination to each other.[191] Similar linking is not found for the corresponding molybdenum species, which consists of isolated dimers with no axial co-ordination. Axial co-ordination is not the only possibility when interactions between the dinuclear carboxylates and donors occur. t-Butylisocyanide is able to cleave molybdenum quadruple bonds producing seven co-ordinate mononuclear complexes.[192]

Phosphines, however, do co-ordinate to dimolybdenum carboxylates but not in the axial position.[193] $Mo(Ph_3P)_2(CF_3 \cdot COO)_4$ has two *trans* bridging and two monodentate carboxylates and two phosphines. The whole configuration being eclipsed when viewed along the intermetallic bond.

Rather surprisingly there is very little known about any ditungsten carboxylates. $W_2(CF_3COO)_4$ has now been synthesized[194] starting from $W_2Cl_6(t.h.f.)_4$ by reduction with sodium amalgam followed by addition of sodium trifluoroacetate. Infrared evidence is used to support the formulation of a tetra-bridged carboxylate and some confirmation obtained from an $X$-ray crystal structure on the related $W_2(CF_3COO)_4 \cdot (\frac{2}{3})$diglyme. This has the standard eclipsed conformation with three dimers linked together *via* axial co-ordination of one solvent molecule.

[189] T. C. Zietlow, D. D. Klendworth, T. Nimry, D. J. Salmon, and R. A. Walton, *Inorg. Chem.*, 1981, **20**, 947.

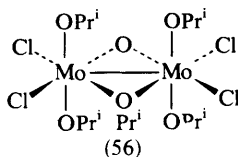[190] F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1981, **20**, 3880.

[191] F. A. Cotton and J. L. Thompson, *Inorg. Chem.*, 1981, **20**, 1292, *ibid.*, p. 3887.

[192] G. S. Girolami and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 2040.

[193] F. A. Cotton and D. G. Lay, *Inorg. Chem.*, 1981, **20**, 935.

[194] A. P. Sattelberger, K. W. McLaughlin, and J. C. Huffman, *J. Am. Chem. Soc.*, 1981, **103**, 2880.

Alkoxides are the other main group of bridged M—M-bonded moieties. $Mo_2(OR)_6$ can undergo several types of reaction, for example[195] $Mo_2(OPr^i)_6$ reacts with 2-hydroxy-6-methylpyridine (LH) to give $Mo_2(OPr^i)_4L_2$ where the M—M triple bond is now bridged by bidentate *cis*-bridging $L^-$ anions. Each metal has three oxygen and one nitrogen donor atoms making an approximate square planar configuration. Similar reactions are also recorded for $Mo_2(NMe_2)_6$. Oxidative addition is used to describe reactions where both the oxidation number and the co-ordination number increase by two. Triply-bonded $Mo_2(OPr^i)_6$ reacts[196] with diisopropylperoxide to give the M—M doubly-bound molecule $Mo_2(OPr^i)_8$, or with dihalogens to give singly-bound $Mo_2(OPr^i)_6X_4$. Similar structures are found for both the chloride and bromide molecules, with approximate octahedral ligation to each metal (56). Another example of this triple-to-single bond change is shown by

$$\text{Cl} \underset{\text{Cl}}{\overset{\text{OPr}^i}{\underset{|}{\text{Mo}}}} \xrightarrow[\text{O}]{\text{O}} \underset{\text{OPr}^i \quad Pr^i \quad OPr^i}{\overset{\text{OPr}^i}{\underset{|}{\text{Mo}}}} \overset{\text{Cl}}{\underset{\text{Cl}}{}}$$

(56)

the reaction product of $Mo_2(OPr^i)_6$ with diphenyldiazomethane in pyridine, $Mo_2(OPr^i)_6(N_2CPh_2)_2(py)$. This has been shown[197] to have Mo—Mo of 2.622 Å and each molybdenum has a terminal $Ph_2CN_2$ group rather than bridging. The single Mo—Mo bond is indeed bridged by three alkoxides, which ensures an unsymmetric partition of two alkoxides to one metal and one alkoxide and the pyridine to the other. In agreement with the crystal structure, $^1H$ n.m.r. spectra confirm the presence of six different $OPr^i$ groups in $[^2H_8]$toluene solution. Although subtle changes in bond-order are possible, cleavage is also relatively easy and the alkoxide $Mo_2(OBu^t)_6$ can be ruptured by both aryl azides or dioxygen under mild conditions. $[Mo(OBu^t)_2(NAr)_2]_2$ is shown[198] to have two bridging (NAr) groups but no M···M interaction (Mo···Mo = 3.247 Å).

The dioxygen reaction with $Mo_2(OPr^i)_6$ yields $MoO_2(OPr^i)_2(py)_2$ as a major product and $Mo_4O_8(OPr^i)_4(py)_4$ as the minor (15%) product. This latter species has now been shown[199] to have a four-metal cluster closely related to the $M_4O_{16}$ skeleton found in such classic compounds as $[Ti(OEt_4)]_4$. The framework $M_4X_aY_bZ_c$, where $(a + b + c) = 16$, and where the cluster has 0–12 electrons is thus proposed as a model for a whole new class of compounds, where the metal atoms all achieve octahedral co-ordination.

It will indeed be fairly obvious that the vast majority of these M—M compounds are molybdenum derivatives. Tungsten does have M—M compounds, as for example

[195] M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *Inorg. Chem.*, 1981, **20**, 1854; *ibid.*, p. 2215.
[196] M. H. Chisholm, C. C. Kirkpatrick, and J. C. Huffman, *Inorg. Chem.*, 1981, **20**, 871.
[197] M. H. Chisholm, K. Folting, J. C. Huffman, and A. L. Ratermann, *J. Chem. Soc., Chem. Commun.*, 1981, 1229.
[198] M. H. Chisholm, K. Folting, J. C. Huffman, C. C. Kirkpatrick, and A. L. Ratermann, *J. Am. Chem. Soc.*, 1981, **103**, 1305.
[199] M. H. Chisholm, J. C. Huffman, C. C. Kirkpatrick, J. Leonelli, and K. Folting, *J. Am. Chem. Soc.*, 1981, **103**, 6093.

*J. E. Newbery*

the first carboxylate reported previously, and also other interesting types such as $[W_2H_4(\mu\text{-}H)(\mu\text{-}PMe_2)(PMe_3)_5]^{200}$ or $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$, which has been shown[201] to have a confacial bioctahedral structure with a double W—W bond of 2.524 Å (57).



(57)                                      (58)
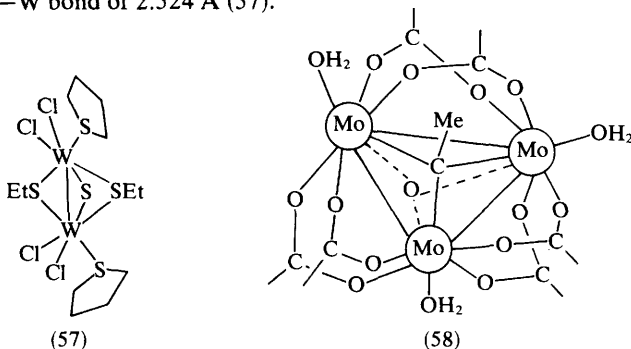
A considerable number of papers this year deal with a range of trinuclear metal clusters. For example, many complexes of the type $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)\text{-}(OAc)_6(H_2O)_3]^+$ (X, Y = O or CMe)[202] are reported. They are synthesized by refluxing $M(CO)_6$ with AcOH and $(AcO)_2O$. The structure (58) gives a typical example of the species studied. It is of $[Mo_3(O)(CMe)(OAc)_6(H_2O)_3]^+$. The –CMe has been shown by $^{13}C$ tracer study to arise from reduction of an acetate group. Up to eight electrons are involved in the various clusters reported.

$[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6]$ (R = Pr$^i$ or neopentyl) has also been synthesized,[203] and *triangulo*-clusters are involved in $[Mo_3S_7(R_2PS_2)_3]^+$,[204] and $[Mo_3S(S_2)_6]^{2-}$.[205]

Tungsten also forms these trinuclear clusters and the crystal structure analysis[206] of $[W_3O_3Cl_5(OAc)(Bu_3P)_3]$ shows that the triangle is capped by one chlorine and the edges are bridged (on the opposite side) by each of three oxygens (59). A



(59)
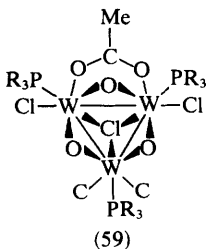
[200] K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 1892.
[201] P. M. Boorman, K. A. Kerr, and V. D. Patel, *J. Chem. Soc., Dalton Trans.*, 1981, 506.
[202] (a) A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1981, **103**, 243; (b) M. Ardon, A. Bino, F. A. Cotton, Z. Dori, M. Kaftory, B. W. S. Kolthammer, M. Kapon, and G. Reisner, *Inorg. Chem.*, 1981, **20**, 4083; (b) A. Bino, F. A. Cotton, Z. Dori, and B. W. S. Kolthammer, *J. Am. Chem. Soc.*, 1981, **103**, 5779.
[203] M. H. Chisholm, K. Folting, J. C. Huffman, and C. C. Kirkpatrick, *J. Am. Chem. Soc.*, 1981, **103**, 5967.
[204] H. Keck, W. Kuchen, J. Mathow, B. Meyer, D. Mootz, and H. Wunderlich, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 975.
[205] F. Diemann, A. Müller, and P. J. Aymonio, *Z. Anorg. Allg. Chem.*, 1981, **479**, 191.
[206] F. A. Cotton, T. R. Felthouse, and D. G. Lay, *Inorg. Chem.*, 1981, **20**, 2219.

potential tetranuclear tungsten cluster $[W_4(\mu\text{-H})_2(OPr^i)_{14}]$ has been shown[207] to have two metal–metal bonds only. It is centrosymmetric with a chain of four tungstens separated by 2.446, 3.407, and 2.446 Å. The centre gap is bridged by two alkoxy-groups and the shorter gaps by two alkoxy- and one hydrido-ligand.

**Organometallic Compounds.**—This Section commences with carbonyls then deals with $\sigma$-bound alkyls, $\eta$-bound complexes, and finally with bimetallic species. Obviously there is much overlap between these areas and the classification could have been chosen to reflect other ideas.

Many of the complexes involving carbonyls are synthesized through photochemically-induced substitution reactions. Production of $Cr(CO)_4(Ph_3P)_2$, as an example, has been shown to be very efficiently undertaken by an electrochemical route (Scheme 8)[208] and examples involving tungsten and molybdenum are also quoted.
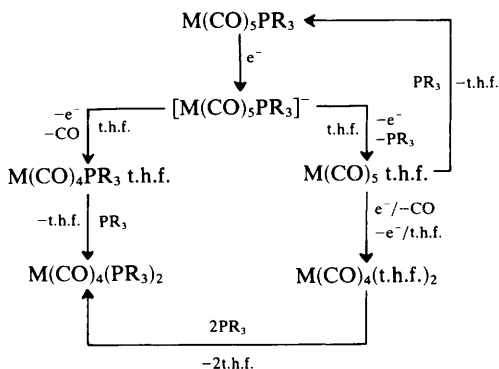


**Scheme 8**

The ions $[HM(CO)_5]^-$ (M = Cr, Mo, or W) can be readily prepared[209] from $M(CO)_5NMe_3$ in t.h.f. solution by the addition of excess sodium naphthalenide followed by methanolic $(Ph_3PNPPh_3)Cl$. Addition of hexane then precipitates the appropriate species. Infrared data are reported and show rather low intensities for the high-frequency carbonyl stretches. Proton chemical shifts range from $\delta = -7.0$ for the chromium ion to $-4.0$ for the molybdenum. These compare with *ca.* $-19$ and $-12$, respectively, for bridging protons (*e.g.* in $[(\mu\text{-H})(Mo(CO)_5)_2]^-$).

Many papers have been published dealing with compounds formulated $M(CO)_5L$. For example, when L = py, subs-py, or piperidine, there seems to be no significant effect on the $Cr(CO)_5$ group. Thus the ability, or otherwise, of the ligand to act as a $\pi$-acceptor appears irrelevant to structural parameters and CO is thus a far better $\sigma$-donor than the various amines.[210] Several interesting vibrational spectra have been measured[211] for this series, where L = CX (X = O, S, or Se), in the solid-,

[207] M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, J. Leonelli, and D. Little, *J. Am. Chem. Soc.*, 1981, **103**, 779.

[208] J. Grobe and H. Zimmermann, *Z. Naturforsch., Teil B* 1981, **36**, 301; *ibid.*, p. 483.

[209] (*a*) M. Y. Darensbourg and J. C. Deaton, *Inorg. Chem.*, 1981, **20**, 1644; (*b*) M. Y. Darensbourg and S. Slater, *J. Am. Chem. Soc.*, 1981, **103**, 5914.

[210] F. A. Cotton, D. J. Darensbourg, A. Fang, B. W. S. Kolthammer, D. Reed, and J. L. Thompson, *Inorg. Chem.*, 1981, **20**, 4090.

[211] A. M. English, K. R. Plowman, and I. S. Butler, *Inorg. Chem.*, 1981, **20**, 2553.

solution-, and gas-phase. Normal co-ordinate analysis is attempted and force constants (corrected for anharmonicity) reported.

The anions $[M(CO)_5L]^-$ (L = SH) have been isolated[212] as salts of sodium 18-crown-6-ether for Cr, Mo, and W, after photolysis of $M(CO)_6$ with sodium sulphide in ethanol. It is possible that the crown ether enhances the stability of anionic carbonyls to a greater extent than other large cations. The compound is chain-polymeric in nature (60) with Na—OC *ca.* 2.44 Å and Na—S of 3.01 Å.



(60)
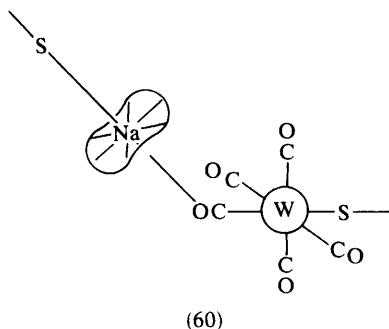
$[W(CO)_5\{C(SMe)_2\}]$ reacts in two different fashions with phosphines[213] depending on the number of their alkyl groups (Scheme 9). Reactions with amines are also discussed.
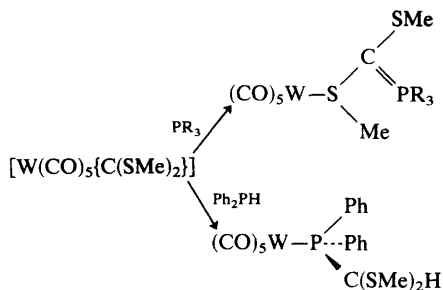


**Scheme 9**

Bicyclic aminophosphane ligands can have configurations where both the nitrogen and phosphorus atoms are in pyramidal symmetry and seemingly equally accessible for co-ordination. For a series[214] of molybdenum and tungsten complexes $M(CO)_{6-n}L_n$, however, no evidence was apparent from multinuclear n.m.r. (*e.g.* $^{31}P-^{95}Mo$ coupling constants) to support nitrogen donation.

Further subtle stereochemical influences are shown[215] with various diazophosphole complexes, $M(CO)_5L$ and $M(CO)_4L_2$, where L is (61) and/or (62). Binding is through the phosphorus atom. It was observed that the *cis*- and *trans*-forms of

[212] M. K. Cooper, P. A. Duckworth, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1981, 2357.
[213] (a) R. A. Pickering, R. A. Jacobson, and R. J. Angelici, *J. Am. Chem. Soc.*, 1981, **103**, 817; (b) R. A. Pickering and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 2977.
[214] J. Febvay, D. Grec, and J. G. Riess, *Inorg. Chem.*, 1981, **20**, 4285.
[215] G. Baccolini, K. Busetto, and E. Foresti, *J. Chem. Soc., Dalton Trans.*, 1981, 1544.

(61)                    (62)
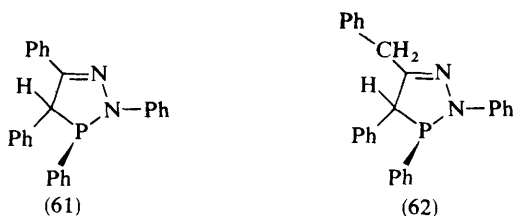
$[M(CO)_4$ $(61)_2]$, with (61) in the *cis*-configuration, interconvert to produce a $2:3$ ratio of products, but that this does not occur with L = (62) (*trans*-conformer). Conversion of $M(CO)_5L$ to $M(CO)_4L_2$ however always gave the *trans*-product (six different reactions) except for the ligand (61) (*cis*-form), which again gave a $2:3$ ratio of products.

Mass spectral data were used[216] to formulate the product obtained from the photolysis, in t.h.f. solution, of molybdenum hexacarbonyl and antimony alkyls as $[(CO)_5Mo(R_2)Sb-Sb(R_2)Mo(CO)_5]$. The action of Bu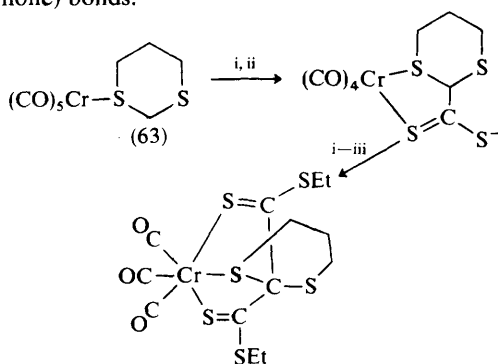Li on (63) followed by $CS_2$ and finally $(OEt_3)(BF_4)$ is assumed[217] to follow Scheme 10 as shown. The structure of the product has shown the carbonyls to be in the *fac*-orientation, with short (2.33 Å) Cr—S (thione) bonds.



Reagents: i, BuLi; ii, $CS_2$; iii, $[OEt_3]^+[BF_4]^-$

**Scheme 10**

New ligands always have an appeal and the terdentate $P[N(Ph)PF_2]_3$ has a double claim to fame in that it is produced[218] *in situ*. Reaction of *fac*-$[(MeCN)_3Mo(CO)_3]$ with $PhN(PF_2)_2$ is thought to proceed as a normal substitution of monodentate ligands. The product however has the structure shown (64), where the bridgehead phosphorus is not bonded to the metal.

Hexamethyltungsten(VI) gives[219] a $1:1$ complex with $PMe_3$, which can be photolysed, in excess $PMe_3$, in high yield to a carbyne complex *trans*-$[WMe(\equiv CMe)-(PMe_3)_4]$. Variable-temperature n.m.r. spectra are used to support a trigonal

[216] H. J. Breunig and W. Fichtner, *Z. anorg. allg. chem.*, 1981, **477**, 119.
[217] H. G. Raubenheimer, J. C. Viljoen, S. Lotz, A. Lombard, and G. Kruger, *J. Chem. Soc., Chem. Commun.*, 1981, 749.
[218] G. M. Brown, J. E. Finholt, R. B. King, and T. W. Lee, *J. Am. Chem. Soc.*, 1981, **103**, 5249.
[219] K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1981, 1204.

prismatic arrangement of methyl groups in $W(Me)_6(PMe_3)$ with the phosphine co-ordinated *via* one face. In this arrangement P—H coupling should occur with four methyl groups. $^{13}C$ n.m.r. results confirm this assignment with the detection of two environments for the W—Me moieties. The carbyne complex is shown by single-crystal *X*-ray diffraction to be roughly *trans*-octahedral. The synthesis and structure of a thermally robust metallatricycle is reported.[220] $WCl_4O$ reacts with excess of the di-Grignard $o$-$C_6H_4(CH_2MgCl)_2$ in t.h.f. to produce $\overline{W(CH_2C_6H_4CH_2\text{-}o})_3$ having the structure shown (65). It can be sublimed at 160 °C, $10^{-2}$ Torr and undergoes reversible electrochemical reduction (10 mV s$^{-1}$, $E_{\frac{1}{2}}^{red}$ = 1.68 V *vs*. SCE).



(64)                                              (65)
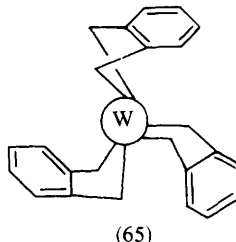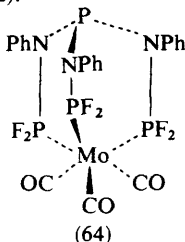
Reaction of TlLL (where LL$^-$ = pyridine-2-thiolato, pyrimidine-2-thiolato, or thiazoline-2-thiolato) with the bis(alkyne)-tungsten or -molybdenum species produces[221] the novel $\eta^2$-vinyl complex shown (66). This type of structure could well prove to be the type of linkage involved in alkyne insertion reactions that eventually produce $\eta^1$-vinyl species such as those reported[222] involving binuclear tungstens.



(66)
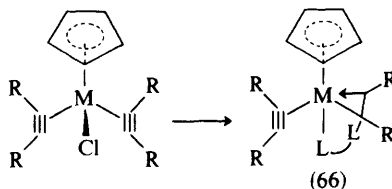
*X*-Ray studies on $[W(\equiv CH)(Cl)(PMe_3)_4]$ proved to be rather imprecise owing to an inherent disorder, but the adduct species $[W(\equiv CH)(Cl)(PMe_3)_3\text{-}(AlMe_{2-x}Cl_{1+x})]$, where $x \simeq 0.18$, gave a clear structure with an $R$ factor of 3.1%. These compounds, let alone the structures, are claimed as the only known examples for any metal of terminal methylidenes.[223] Tungsten has approximate octahedral configuration with *mer*-phosphines, the aluminium species being linked *trans* to the chlorine *via* the methylidene. The last octahedral site is occupied by a weak interaction with a disordered $CH_3/Cl$ on the $(AlMe_{2-x}Cl_{1+x})$ group.

[220] M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1981, 485.
[221] J. L. Davidson, I. E. P. Murray, P. N. Preston, M. V. Russo, L. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1981, 1059.
[222] (a) J. Levisalles, F. Rose-Munch, H. Rudler, J.-C. Daran, Y. Dromzée, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1981, 152; (b) J. Levisalles, F. Rose-Munch, H. Rudler, J.-C. Daran, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1981, 1057.
[223] (a) P. R. Sharp, S. J. Holmes, R. R. Schrock, M. R. Churchill, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1981, **103**, 965; (b) M. R. Churchill, A. L. Rheingold, and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 3392; (c) S. J. Holmes and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 4599.

$[W(CO)(R^1C\equiv CR^2)(S_2CNR_2)_2]$ can be oxidized[224] by $[Mo_2O_3\{S_2P(OEt)_2\}_4]$ to give $[OW(R^1C\equiv CR^2)(S_2CNR_2)_2]$, where the Mo(V) complex acts as an oxygen-atom transfer agent, *i.e.* it can be regarded as a source of kinetically activated oxygen atoms. The tungsten complex is quite stable towards alkyne dissociation. Variable-temperature n.m.r. studies are used to support a possible fluxional five-co-ordinate intermediate for an exachange of alkyl sites rather than alkyne rotation or rotation about the C—N bond.

As a final example of the range of species possible with alkynes, the cation $[Mo(NCMe)(MeC_2Me)_2(\eta^5\text{-Cp})]^+$ reacts rapidly with $[(\eta^5\text{-Cp})Fe(CO)_2]Na$ to give $[Fe_2(CO)_4(\eta^5\text{-Cp})_2]$ and a complex that analyses to $[Mo_2(MeC_2Me)_4(\eta^5\text{-Cp})_2]$. N.m.r. spectra concurred with this formulation, but when the single-crystal X-ray structure was evaluated[225] it was found to be a complex of octamethylmolybdena-cyclononotetraene bonded to a second molybdenum atom. Each molybdenum is then bound to a Cp ring. The metallacyclo-compound takes up a folded configuration with its metal $\sigma$-bonded to two carbons and double-bonded to the other molybdenum. A similar, though less dramatic process has also been reported[226] to give a hexyne-derived metallacycle.

$(\eta^5\text{-MeCp})Mo(CO)_2I_3$ has, for an organometallic complex, the rather high oxidation number of $Mo^{IV}$. It has been shown[227] to have a rather distorted 'octahedral' type of configuration, where the MeCp is regarded as occupying one site. The 'equatorial' plane, above which (in the sense of towards the MeCp group) the molybdenum is raised, is occupied by *cis*-iodines and *cis*-carbonyls. The final position, *trans* to the MeCp, is taken by the third iodine. In slight contrast $(\eta^5\text{-Cp})M(CO)_3Cl$ (M = Mo or W) have been found[228] to be isostructural with a type of square-pyramidal arrangement with the Cp at the apex and the other ligands at the base. $(\eta^5\text{-Cp})Mo(CO)_2(XYCNMe_2)$ (X, Y = O, S, or Se) have been prepared and studied by electrochemical procedures. A complex scheme of species, some of which are solvent stabilized, was outlined.[229]

When utilized in the bridging mode, the cyclopentadienyl ligand tends to act in $\mu(\eta^1:\eta^5)$ fashion rather than by $\eta^1$-carbene/$\eta^4$-diolefin co-ordination. This is confirmed by the reported preparation[230] and structure of $Mo_2(CO)_3(Cp)_3$, but the related iron complex does show the alternative arrangement. Both were prepared by carbene addition to complexes containing metal–metal bonds, of diazocyclopentadiene. The observed difference in product stereochemistry is a reflection of the $(\eta^1:\eta^5)$ aromaticity rather than synthetic method or the nature of the other ligands. Some stability may be achieved for the $\eta^1:\eta^4$ arrangement when bridging M—M single bonds.

Cp groups are rarely found with water as a co-ligand. Addition of chromocene ($Cp_2Cr$) to a cold, deoxygenated perchloric acid solution gives a colour change

[224] J. L. Templeton, B. C. Ward, G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, 1981, **20**, 1248.
[225] M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, 1981, **103**, 1269
[226] S. Slater and E. L. Muetterties, *Inorg. Chem.*, 1981, **20**, 946.
[227] B. S. Erler, J. C. Dewan, S. J. Lippard, and D. R. Tyler, *Inorg. Chem.*, 1981, **20**, 2719.
[228] C. Bueno and M. R. Churchill, *Inorg. Chem.*, 1981, **20**, 2197.
[229] K. Tanaka, K. U. Eda, and T. Tanaka, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2029.
[230] W. A. Herrmann, G. Kriechbaum, C. Bauer, E. Guggolz, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 815.

from orange-red to deep violet, and hydrogen gas is evolved[231] and a polymeric material, that analysed to give a formula $(\eta^5\text{-Cp})\text{Cr}(\text{OH}_2)_n{}^{2+}$, was deposited. Some preliminary kinetic data on the eventual aquation of this ion to $[\text{Cr}(\text{OH}_2)_6]^{3+}$ ($k_1 = ca.\ 1 \times 10^{-2}\,\text{s}^{-1}$) is included.

A number of diphosphine (LL) complexes of molybdenum with bis(dimethylphosphino)ethane have been reported, and $\text{Mo}(\eta\text{-Cp})(\text{LL})\text{H}_3$ has been shown[232] to be an effective transfer agent for exchanges such as per-deuteriotoluene by photolysis in $\text{C}_6\text{D}_6$. With 1,4-dimethylbenzene it took four days for the aliphatic protons to exchange and two days for the aromatic, whereas for 1-methyl-4-methoxybenzene aromatic and methoxy exchange is complete in 6 hours but methyl exchange takes 10 days.

Sandwich compounds, $\text{L}_2\text{Cr}$, where L is $p\text{-C}_6\text{H}_4(\text{CF}_3)_2$, $m\text{-C}_6\text{H}_4(\text{CF}_3)_2$, or $m\text{-C}_6\text{H}_4(\text{CF}_3)\text{Cl}$, have been studied by single-crystal $X$-ray methods.[233] The arene ligands are planar and mutually parallel in each case. The disposition of the substituents, however, is used to support an argument that $-\text{CF}_3$ does not act as a strongly $\sigma$-withdrawing group, but exerts polarity effects by 'through-space' rather. than 'through-bond' methods. Monoarene complexes of the type $\text{LMo}(\text{CO})_3$ exist in the 'piano-stool' type of structure. When L = hexaethylbenzene the molecule is found in the solid-state to take up an eclipsed configuration of carbonyls with respect to three of the ring substituents.[234] Although the $-\text{CH}_2$ and aromatic carbons all lie ($\pm 0.1$ Å) in a plane, the methyls of the eclipsed groups are displaced away from, and those of the uneclipsed towards, the metal atom. $^{95}\text{Mo}$ n.m.r. spectra have been recorded[235] for several such species and the nuclear shielding, as measured by the chemical shift, found to decrease in the order L = Cp > toluene > $o$-xylene > $p$-xylene > $m$-xylene > mesitylene > cycloheptatriene. As a class of compounds they share large negative shifts (from $-2120$ to $-1684$ p.p.m.), generally associated with low formal oxidation states, and within the class, shielding decreases with increasing methyl content (hence greater ring electron density). $(\text{C}_9\text{H}_7)\text{Cr}(\text{CO})_2\text{NO}$ shows[236] a broadly similar shape with the monodentate ligands opposite to the $\eta^5$-ring of the indyl group as shown (67). The arrangement is unsymmetrical with the carbons at the fused junction further (2.29 Å) away from the metal than the other three atoms (2.19 Å).

The first thiabenzene complex has been reported.[237] It was synthesized by the displacement of MeCN groups from $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ through the action of $[\text{BF}_4]$ [1-methyl-3,5-diphenyl-thiabenzene]$^+$ in the presence of potassium t-butanolate–DMSO. Crystal-structure $X$-ray analysis shows that the compound (68) is better formulated as an $\eta^5$-ylide rather than an arene complex. The sulphur atom is 0.76 Å above the $\eta^5$-carbon plane. An E–molybdenum bond (E = S, Se, or Te) has been produced in an $\eta^7$-complex by a direct insertion[238] reaction of $\text{EO}_2$ into $\text{Mo}-\sigma$-Me. $(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{Me}$ was added as a t.h.f. solution ($-78\,^\circ\text{C}$) to $\text{SeO}_2$ or $\text{TeO}_2$

[231] L. O. Spreer and I. Shah, *Inorg. Chem.*, 1981, **20**, 4025.

[232] (*a*) G. S. B. Adams and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 353; (*b*) P. D. Grebenik, M. L. H. Green, and A. Izquierdo, *J. Chem. Soc., Chem. Commun.*, 1981, 186.

[233] M. W. Eyring, E. C. Zuerner, and L. J. Radonovich, *Inorg. Chem.*, 1981, **20**, 3405.

[234] D. J. Iverson, G. Hunter, J. F. Blount, J. R. Damewood, and K. Mislow, *J. Am. Chem. Soc.*, 1981, **103**, 6073.

[235] A. F. Masters, R. T. C. Brownlees, M. J. O'Connor, and A. G. Wedd, *Inorg. Chem.*, 1981, **20**, 4183.

[236] R. Shakir and J. L. Atwood, *Acta Crystallogr., Sect. B*, 1981, **37**, 1656.

[237] L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 279.

[238] W. Dell and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 471.

(67)



(68)
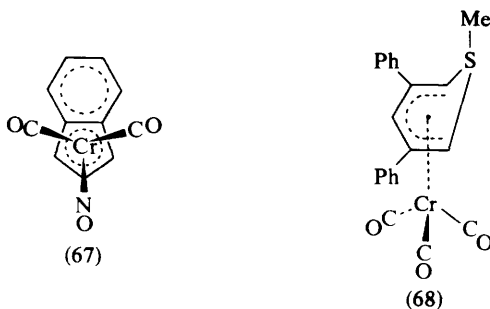
evaporated in a metal evaporator on to an ether matrix. The product $[(\eta^{7}-C_{7}H_{7})Mo(CO)_{2}\{E(O_{2})Me\}]$ was assigned a configuration mainly on the basis of $^{1}H$ n.m.r. spectra.

The final group of papers to be considered deal with bimetallic entities: first binuclear and then cluster types. $Ph_{2}PCH_{2}CH_{2}PPh_{2}$ (diphos) is well known as a chelating ligand, but can also act in a bridging mode. For example, two $(OC)_{5}MY$ moieties could be bridged by a displacement of ligand Y to form $[(OC)_{5}M(L-L)M(CO)_{5}]$. This would not be a useful method to form a mixed-metal complex since a mixture of $M^{1}M^{2}$, $M^{1}M^{1}$, and $M^{2}M^{2}$ species would be produced. However, the product can be obtained by a simple reaction between $(OC)_{5}M^{1}PPh_{2}CH=CH_{2}$ and $(OC)_{5}M^{2}PPh_{2}H$ in the presence of potassium t-butoxide, and either combination of $M^{1}$ and $M^{2}(=Cr, Mo, or W)$ will produce the desired result.[239]

The molecule $[(C_{5}Me_{5})Rh(\mu\text{-}PMe_{2})_{2}Mo(CO)_{4}]$ has been prepared[240] by reacting lithiated $Mo(CO)_{4}(HPMe_{2})_{2}$ with $[(C_{5}Me_{5})RhCl_{2}]_{2}$ in t.h.f. It is moderately air-stable (~1 h) and shows a single carbonyl $^{13}C$ n.m.r. peak. The crystal structure determined by single-crystal $X$-ray diffraction shows the bridging phosphine groups on the same side of the Rh—Mo axis. The ring (RhPMoP) has a folded shape with an angle of 109.37° between the triangular $RhP_{2}$ and $MoP_{2}$ planes. The Rh—Mo distance is 2.921 Å, probably indicative of a single M—M bond.

Phosphole ligands have been used[241] to make novel bimetallic sandwich complexes involving iron and molybdenum (Scheme 11). The interesting observation that molybdenum is co-ordinated *via* the diene system and one phosphorus, rather than solely with the phosphorus donors is confirmed by multinuclear n.m.r. studies that show non-equivalence for both the phosphorus atoms and the dienes.

The proposed structure (69) of $[WCp_{2}H_{3}Ir(PEt_{3})_{2}]PF_{6}$, prepared from $WH_{2}(\eta^{5}\text{-}Cp_{2})$ and $[IrH_{2}(PEt_{3})_{2}(EtOH)_{2}]PF_{6}$, is made[242] on the basis of n.m.r. evidence. Thus



(69)
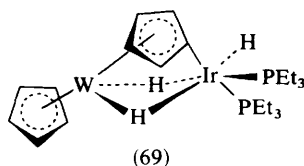
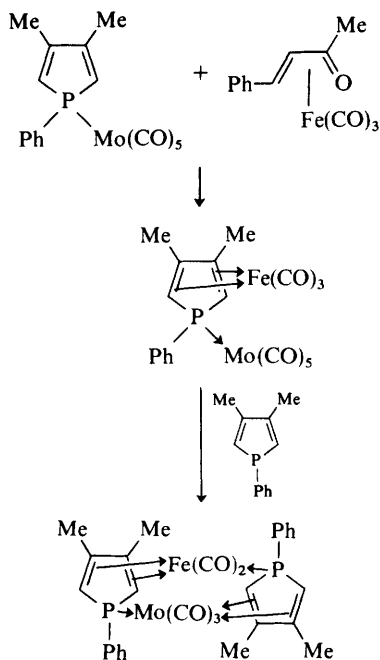[239] R. L. Keiter, S. L. Kaiser, N. P. Hansen, J. W. Brodack, and L. W. Cary, *Inorg. Chem.*, 1981, **20**, 283.
[240] R. G. Finke, G. Gaughan, C. Pierpoint, and M. E. Cass, *J. Am. Chem. Soc.*, 1981, **103**, 1394.
[241] C. C. Santini, J. Fischer, F. Mathey, and A. Mitschler, *Inorg. Chem.*, 1981, **20**, 2848.
[242] P. S. Pregosin, A. Togni, and L. M. Venanzi, *Angew. Chem.*, Int. Ed. Engl., 1981, **20**, 668.

**Scheme 11**

two proton resonances (at $-17.57$ and $-18.86$ p.p.m.) show $^{183}$W satellites, whereas the other (at $-23.78$ p.p.m.) does not. $^{13}$C spectra show one resonance for the $\eta^5$-Cp ring and multiple peaks for the bridging. The carbon bound to the iridium shows the highest resonance at 110.3 p.p.m., compared to 89.9 to 95.1 p.p.m. for the others.

Reactions between metal carbynes and polynuclear metal carbonyls have been shown[243] to yield a plethora of mixed-metal cluster compounds. For example $Os_3(CO)_{10}(cyclo\text{-}C_8H_{14})_2$ reacted with $W\equiv CR(CO)_2(\eta^5\text{-Cp})$ (R = $o$-MePh) over 5 days in toluene solution to give $[\{Os(CO)_3\}_3W(CO)_2(\eta^5\text{-Cp})CR]$. This was shown to have a tetrahedron of metals, one face of which is capped by the CR ligand. Similar reactions, and X-ray structures are also reported by another group.[244] The same alkyne has also been shown[245] to react with $Pt(C_2H_4)_3$ to produce $[(\eta^5\text{-Cp})(CO)_2WCR]_2Pt$ with a bent W–Pt–W backbone (165.5°), each strand bridged $\{W=C(R)—Pt\}$ by the alkylidyne ligand $—C—C_6H_4Me$. The angle WCPt is *ca.* 87.6°. Similar compounds involving Ni and Pd instead of Pt were also produced.

A similar bridging system in $[(\eta^5\text{-Cp})(CO)_2W(=CR)Co(CO)(\eta^5\text{-}C_5Me)]$ has been converted[246] into a carbene bridge by treatment with $HBF_4\cdot Et_2O$. This changed

[243] L. Busetto, M. Green, J. A. K. Howard, B. Hessner, J. C. Jeffrey, R. M. Mills, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 1101.
[244] J. R. Shapley, J. T. Park, M. R. Churchill, C. Bueno, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1981, **103**, 7385.
[245] T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 763.
[246] J. C. Jeffrey, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1981, 1255.

the W—C interaction to a single bond and co-ordinated the phenyl ring to the tungsten. Addition of PMe$_2$Ph gives a further change as it co-ordinates to the tungsten and transfers a carbonyl to bridging mode, with the carbene bridge now becoming $\succ$CH(R). Both of the last bimetallic species were isolated as BF$_4^-$ salts.

Cp$_2$M(Hg dtc)$_2$ can be prepared[247] from the reaction of Cp$_2$M(HgX)$_2 \cdot x$HgX$_2$ with $(2 + x)$ moles of sodium (dtc) (M = Mo or W, X = Cl, Br, I, SCN, or OAC, $0 \leq x \leq 1$, and dtc = diethyldithiocarbamate). A single-crystal $X$-ray structural study of the molybdenum compound showed the Cp rings inclined at 132.7° to each other, almost as if each occupied two positions of a roughly octahedral molybdenum atom. The Mo—Hg distance is short at 2.643 Å.

IrCl(CO)$_2$NH$_2$C$_6$H$_4$Me and excess CpW(CO)$_3$H were reacted (CH$_2$Cl$_2$, 60 °C, 6 h, 40 p.s.i. of CO) over zinc[248] and produced the known [CpW(CO)$_3$]$_2$, CpWIr$_3$(CO)$_{11}$, and Cp$_2$W$_2$Ir$_2$(CO)$_{10}$. The single-crystal $X$-ray structures of these clusters are simlar to Ir$_4$(CO)$_{12}$ where one and two (respectively) Ir(CO)$_3$ units are replaced by the isoelectronic moieties CpW(CO)$_2$.

## 5 Manganese, Technetium, and Rhenium

One feature of this group is the increasing attention that technetium chemistry is receiving. This is not simply a filling-in of the gaps approach either, since several reports this year deal with effects first observed with that element.

A useful synthetic route to MnF$_5^{2-}$ ions that does not involve the use of either HF or MnF$_3$ has been reported.[249] Potassium permanganate is reduced by acetylacetone in the presence of excess alkali-metal difluoride (AHF$_2$), and the salt A$_2$MnF$_5$ (A = NH$_4$ or Na) or A$_2$MnF$_5 \cdot$H$_2$O (A = K or Cs) forms as a precipitate in quantitative yield.

Differences in the edge structure of the K $X$-ray absorption (EXAFS) spectra are observed[250] for KMnO$_4$ (solid) and KMnO$_4$ and K$_2$MnO$_4$ in aqueous solution. A slight peak shifting is attributable to instrumental factors, but the interest comes in a significant peak broadening that may be associated with some interaction between the solvent and the $4p$ orbitals of the MnO$_4^-$ ion. The study also shows that the MnO$_4^-$ group has substantially the same structure (*e.g.* bond lengths) in solution as found by $X$-ray diffraction for the solid.

Technetium has been studied by n.m.r. for the first time. Resonances are reported[251] for $^{99}$Tc and $^{17}$O for the ion TcO$_4^-$. The same ion has also been shown[252] to produce a catalytically active species. HTcO$_4$ was heated with hydrogen in an autoclave and then found to promote the hydrogenation of anhydrides of cyclic dicarboxylic acids.

A study of mixed-metal sulphides (Mn, Fe)S$_2$ has shown[253] a 6% solubility of FeS$_2$ in MnS$_2$ and 3.9% solubility (molar basis) of MnS$_2$ in FeS$_2$. Mössbauer effect

[247] M. M. Kubicki, R. Kergoat, J. E. Guerchais, R. Mercier, and J. Douglade, *J. Cryst. Mol. Struct.*, 1981, **11**, 43.
[248] J. R. Shapley, S. J. Hardwick, D. S. Foose, G. D. Stucky, M. R. Churchill, C. Bueno, and J. P. Hutchinson, *J. Am. Chem. Soc.*, 1981, **103**, 7383.
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[251] M. J. Buckingham, G. E. Hawkes, and J. Thornback, *Inorg. Chim. Acta*, 1981, **56**, L41.
[252] B. Bayerl and M. Wahren, *Z. Chem.*, 1981, **21**, 149.
[253] A. K. Cheetham, A. J. Cole, and G. J. Long, *Inorg. Chem.*, 1981, **20**, 2747.

spectroscopy was used to show that iron changes its spin state from high spin when doped into $MnS_2$, to low spin when it is the major component.

Electronic spectra of $Mn^{2+}$ ($d^5$) in the trigonally-distorted octahedral sites of $MnPS_3$ (a layered structure of parallel planes of metal ions separated by two planes of sulphurs) have been recorded.[254] They are interpreted by using values of 10 Dq = 8750 $cm^{-1}$ and Racah parameters $B$ = 494 $cm^{-1}$ and $C$ = 3349 $cm^{-1}$.

**Complex Compounds.**—Much interest in manganese chemistry concerns its role as a trace element in biological molecules. For technetium, the biological interest is similar except that the motivation comes from its extensive use as a radiotracer, for example in heart-imaging procedures. Manganese has been shown[255] to be directly involved in photosynthesis operations by being found to be bound to the membrane wall of spinach chloroplasts. EXAFS data was obtained from several chloroplasts and by comparison with model compounds the oxidation state is thought to be somewhere between 2+ and 3+. This was achieved by a correlation (regression line) between the $K$-edge energy and the co-ordinate charge for the model compounds (calculated from Allred–Rochow electronegativities).

Manganese is in a centrosymmetric octahedral environment in the compound $Mn(2,4,5-T)_2(H_2O)_4·2(2,4,5,-TH)$, where 2,4,5-TH is trichlorophenoxyacetic acid. This is one of the few reports[256] that deal solely with oxygen-donor complexes for these elements. The acid molecules are not co-ordinated to the metal, but are hydrogen-bonded to the unco-ordinated carbonyl oxygens of the ligand 2,4,5-T species.

$O,N$-donor ligands however seem slightly more popular. For example $Mn^{II}$ complexes of (70) have been reported[55] and their e.p.r. spectra observed. Schiff-base complexes for $Mn^{II}$ and $Mn^{III}$ with the ligand (70), where $n,m$ = 2, 3, or 4 and



(70)
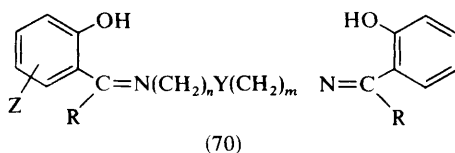
$Y$ = NH or O, have prepared.[257] The $Mn^{III}$ complexes show an interesting electrochemistry and are arranged in an order based on their reduction potentials ($Mn^{III}/Mn^{II}$). In particular the effect of substitution in one of the aromatic rings is studied and the reduction potential found to vary from +0.1 V through 0.07 V to −0.29 V for 5-$NO_2$-, 3-$NO_2$-, and 5-OMe-substitution in the complexes [Mn(70; $n$ = 3, $m$ = 4; $Y$ = NH].

Various thiocyanate complexes have been synthesized[258] for technetium and rhenium, $Re(NCS)_6^{3-}$, $ReO(NCS)_5^{2-}$, $Re(NCS)_6^{2-}$, and $TcO(NCS)_5^{2-}$, which has previously been postulated from cyclic voltammetry studies. Although reaction of

[254] J. Boerio-Goates, E. Lifshitz, and A. H. Francis, *Inorg. Chem.*, 1981, **20**, 3019.

[255] J. A. Kirby, D. B. Goodin, T. Wydrzynski, A. S. Robertson, and M. P. Klein, *J. Am. Chem. Soc.*, 1981, **103**, 5537.

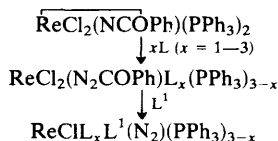[256] C. H. L. Kennard, G. Smith, E. J. O'Reilly, and K. E. Brown, *Inorg. Chim. Acta*, 1981, **52**, 55.

[257] W. M. Coleman, R. K. Boggess, J. W. Hughes, and L. T. Taylor, *Inorg. Chem.*, 1981, **20**, 700; *ibid.*, p. 1253.

[258] (*a*) H. S. Trop, A. Davison, and A. G. Jones, *Inorg. Chim. Acta*, 1981, **54**, L61; (*b*) A. Davidson, A. G. Jones, L. Müller, R. Tatz, and H. S. Trop, *Inorg. Chem.*, 1981, **20**, 1160.

$ReCl_5$ with $Cl_3CNO_2$ produces $ReCl_3(NO)_2$, which is associated *via* chlorine bridges, use of acetonitrile as solvent gives a mononuclear complex $ReCl_3(NO)_2(MeCN)$. This has been shown by single-crystal $X$-ray diffraction studies to have an octahedral configuration with *fac*-chloro-groups.[259] $[Mn(NSF_3)_4(AsF_6)_2]$ has been prepared by reacting $Mn(SO_2)_2(AsF_6)_2$ with $NSF_3$ in liquid $SO_2$ solvent.[260] The $X$-ray-determined structure shows a number of interesting features. The compound has a reasonably symmetric octahedral structure with *trans*-$AsF_6$ groups, and is perhaps the only recorded example of this group acting as a ligand. The structure of the $AsF_6$ moiety is much the same as that of a free $AsF_6^-$ ion, except that the As—F bond is lengthened (from 1.67 Å to 1.74 Å) for the co-ordinated fluorine.

Many papers deal with co-ordinated nitrogen. $(ReNCl_4)[AsPh_4]$ has been prepared by admixture of $ReNCl_4$ and $AsPh_4Cl$ in $POCl_3$. This reaction exploits the $Re^{VII}$ compound as a starting material for the production of species containing a Re—N triple bond.[261] $ReNCl_4^-$ is shown by $X$-ray structural analysis and infrared spectroscopy to have $C_{4v}$ symmetry, with a Re—N bond of 1.619 Å and Re—Cl of 2.322 Å. A series of dinitrogen–rhenium(I) compounds has been systematically prepared[262] according to Scheme 12, where $L,L^1 = CO, PR_3, P(OR)_3$, diphos, *etc.*

$$\overline{ReCl_2(NCOPh)}(PPh_3)_2$$
$$\downarrow xL\ (x = 1\text{---}3)$$
$$ReCl_2(N_2COPh)L_x(PPh_3)_{3-x}$$
$$\downarrow L^1$$
$$ReClL_xL^1(N_2)(PPh_3)_{3-x}$$

**Scheme 12**

These show clear correlations between redox potential and the $N_2$ stretching frequency. Furthermore, LiMe reacts only with those complexes where $E_{1/2}$ (*versus* SCE) is greater than 0.8 V. In one of these compounds, *trans*-$[ReCl(N_2)(diphos)_2]$, the dinitrogen can be displaced by an isocyanide (RNC). The reaction is accelerated by irradiation from a tungsten bulb.[263] The compound produced can undergo electrophilic attack by acid ($HBF_4$) at the (RNC) nitrogen atom to give a carbyne complex *trans*-$[ReCl(CNHR)(diphos)_2]^+$. $X$-Ray diffraction studies for R = Me, show that the bond Re—C is 1.80 Å and that the nitrogen is $sp^2$ hybridized (C–N–Me = 123°). Technetium has now also been shown to give compounds with a metal–nitrogen triple bond.[264] Reduction of $NH_4.TcO_4$ with hydrazine, followed by addition of sodium diethyldithiocarbamate gives $[Tc(S_2CNEt_2)_2N]$. The single-crystal $X$-ray structure shows that $Tc\equiv N$ is 1.604 Å, with the metal in a distorted square-pyramidal configuration raised 0.745 Å above the basal sulphur plane. Some $Tc^{VII}$ nitrogen-donor complexes have also been synthesized.[265] $TcO_3XL$ (X = Cl

[259] N. Mronga, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1981, **482**, 95.
[260] B. Buss, W. Clegg, G. Hartmann, P. G. Jones, R. Mews, M. Noltemeyer, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 61.
[261] W. Liese, K. Dehnicke, R. D. Rogers, R. Shakir, and J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, 1981, 1061.
[262] G. J. Leigh, R. H. Morris, C. J. Pickett, D. R. Stanley, and J. Chatt, *J. Chem. Soc., Dalton Trans.*, 1981, 800.
[263] A. J. L. Pombeiro, M. F. N. N. Carvalho, P. B. Hitchcock, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1981, 1629.
[264] J. Baldas, J. Bonnyman, P. M. Pojer, G. A. Williams, and M. F. Mackay, *J. Chem. Soc., Dalton Trans.*, 1981, 1798.
[265] A. Davison, A. G. Jones, and M. J. Abrams, *Inorg. Chem.*, 1981, **20**, 4300.

or Br, L = bipy or phen) was precipitated by adding (for example) 12 M-HCl to an alcoholic solution of $NH_4TcO_4$ containing a slight molar excess of bipyridine. Reduction to the $Tc^V$ compound $TcOX_3L$ occurs when the complex is warmed in ethanolic HX.

Other $Tc^V$ species reported include amide thiolate (71)[266] and dithiolate[267] complexes. The ligands (71) were designed (Scheme 13) to form a square-planar
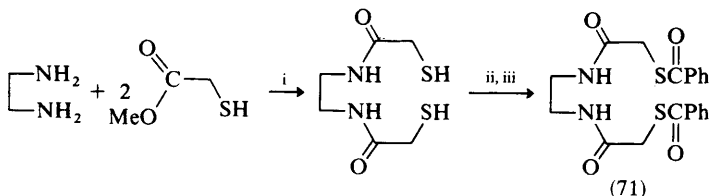


Reagents: i, EtOH, 50°C; ii, NaOH; iii, PhCOCl

**Scheme 13**

basal plane for the $Tc=O$ group, so as to give kinetic stability to the low-spin $d^2$ metal. 1:1 complex ions are formed with $Tc^V$, and isolated as $AsPh_4^+$ salts. Similar square-pyrimidal shape is probably taken up by the reported range of ten $[Tc^VObis(dithiolate)]$ complexes.[267] These were formed with saturated, olefinic, and aromatic dithioles. The chelating ligands diphos and diars can co-ordinate to $Tc^{III}$. $[Tc(diars)_2Cl_2]^+$ and $[Tc(diphos)_2Br_2]^+$ have been prepared and shown by single-crystal $X$-ray diffraction to have *trans* configurations.[268] The $Tc^{III}/Tc^{II}$ reduction potential of several such compounds is shown to increase in the order Cl < Br < I and diars < diphos. $[Tc(diphos)_2H_2Cl]$ has also been prepared.[269]

Turning now to the macrocyclic ligands, the tetra-amine 'cyclam' (1,4,8,11-tetra-azacyclotetradecane) has been shown[270] to form a 1:1 complex with $Tc^V$, *trans*-$[Tc(cyclam)(O)_2]\cdot ClO_4\cdot H_2O$, the structure of which has been confirmed by single-crystal $X$-ray analysis. This appears to be the only *trans*-dioxo-species so far characterized for technetium.

The amine, t.r.p., $N(CH_2CH_2N=CH-2-azoyl)_3$ has the ability to make approximately octahedral co-ordination to a metal using the six nitrogens of its three arms, the central (amine) nitrogen not being co-ordinated.[271] The complex $Mn^{III}$ (t.r.p.), where the ligand is formed by loss of the pyrrole-N–H protons, is twisted about the three-fold axis by 50.8°, compared to 60° and 0° required for octahedral and trigonal-prismatic geometry, respectively. The interesting feature of the complex is the change in spin state from four to two unpaired electrons that occurs at temperatures around 40–50 K. This could be described as $^5E_g \rightleftharpoons {}^3T_{1g}$ cross-over, and is the first recorded example for a $d^4$ ion.

Manganese(III) tetraphenylporphyrin, Mn(tpp)Cl, has been shown[272] to catalyse the specific oxidation of olefins to ketones by $O_2$–$BH_4^-$. It was found that the

[266] A. Davison, A. G. Jones, C. Orvig, and M. Sohn, *Inorg. Chem.*, 1981, **20**, 1629.
[267] H. Spies and B. Johannsen, *Inorg. Chim. Acta*, 1981, **48**, 255.
[268] R. W. Hurst, W. R. Heineman, and E. Deutsch, *Inorg. Chem.*, 1981, **20**, 3298.
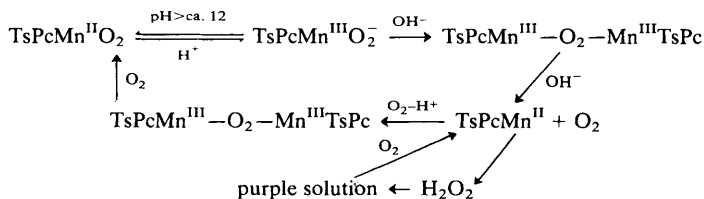[269] L. Kaden, B. Lorenz, K. Schmidt, and H. Sprinz, *Z. Chem.*, 1981, **21**, 232.
[270] S. A. Zuckman, G. M. Freeman, D. E. Troutner, W. A. Volkert, R. A. Holmes, D. G. Van Derveer, and E. K. Barefield, *Inorg. Chem.*, 1981, **20**, 2386.
[271] P. G. Sim and E. Sinn, *J. Am. Chem. Soc.*, 1981, **103**, 241.
[272] M. Perrée-Fauvet and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, 1981, 874.

reactions proceed quite happily with air as an oxidant, but that pure oxygen has to be alternated with nitrogen gas for effective oxidation to proceed. High yields of ketones were achieved and around 80% of the porphyrin could be recovered. Oxidation of a metalloporphyrin could take place at the ligand or the metal site. An infrared band at 1270—1295 cm$^{-1}$ is claimed[273] to be a diagnostic of processes centred on the ligand (*e.g.* in [Mn(tpp)Cl]ClO$_4$). The highly reactive dimeric Mn$^{IV}$ porphyrin, $(\mu\text{-}O)$–{N$_3$Mn$^{IV}$(tpp)]}$_2$]·3PhCl, has been prepared[274] by reacting the Mn$^{III}$(tpp) (azide) with iodosylbenzene in chlorobenzene, followed by precipitation with hexane. The complex is very reactive (being able to oxidize water), and solvents need to be rigorously purified from dissolved oxygen or olefin content. The single-crystal *X*-ray structure shows that the solvent is packed between the dimers. The azides, metals and the bridging oxygen lie along a two-fold axis running through the dimer. Each metal is displaced towards the oxygen, away from the ring of ligating nitrogens.

The electrochemical behaviour of manganese(II) phthalocyanine has been studied[275] in a variety of donor solvents such as py, d.m.s.o., d.m.a. and d.m.f. The values obtained showed very little dependence upon either the solvent or the supporting electrolyte, and appear to be reversible (except at fairly high scan rates in cyclic voltammetry). The same Mn$^{II}$ compound, in pyridine solution, had previously been observed to bind dioxygen in a reversible fashion. This has now been re-investigated[276] and shown not to occur in highly pure dry pyridine, but to work quite well with d.m.a. It is suggested that the species present is probably a bound superoxide, O$_2$Mn$^{III}$Pc. This is supported by ready, reversible, conversion into the known species PcMn$^{III}$–O–Mn$^{III}$Pc (similar to the porphyrin dimer above) and by infrared magnetic and e.s.r. measurements on the solid oxygen-adduct. A similar superoxide compound, Mn$^{III}$(TsPc)O$_2^-$, where TsPc is tetrasulphonated phthalocyanine, has also been prepared.[277] The structure is assigned on the basis of solid-state spectra (such as Raman effect and e.s.r., which shows a characteristic O$_2^-$ spectrum and a *g* value of 1.99), and in solution studies by e.s.r., infrared, and u.v. spectroscopy. A series of equilibria to relate the pH-dependent species is shown (Scheme 14). Polarized neutron diffraction measurements[278] were used to produce spin populations for the molecule Mn$^{II}$Pc. The manganese orbital populations were: $3d_{xy} = 0.74$; $3d_{xy,yz} = 1.17$; $3d_{z^2} = 0.84$; $3d_{x^2-y^2} = -0.15$; and $4s = -0.44$, and a

$$\text{TsPcMn}^{II}\text{O}_2 \underset{\text{H}^+}{\overset{\text{pH}>\text{ca. 12}}{\rightleftharpoons}} \text{TsPcMn}^{III}\text{O}_2^- \xrightarrow{\text{OH}^-} \text{TsPcMn}^{III}-\text{O}_2-\text{Mn}^{III}\text{TsPc}$$

$$\uparrow \text{O}_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \diagup \text{OH}^-$$

$$\text{TsPcMn}^{III}-\text{O}_2-\text{Mn}^{III}\text{TsPc} \underset{\text{O}_2}{\overset{\text{O}_2-\text{H}^+}{\longleftarrow}} \text{TsPcMn}^{II} + \text{O}_2$$

$$\text{purple solution} \leftarrow \text{H}_2\text{O}_2 \diagup$$

**Scheme 14**

[273] E. T. Shimomura, M. A. Phillippi, and H. M. Goff, *J. Am. Chem. Soc.*, 1981, **103**, 6778.

[274] B. C. Schardt, F. J. Hollander, and C. L. Hill, *J. Chem. Soc., Chem. Commun.*, 1981, 765.

[275] A. B. P. Lever, P. C. Minor, and J. P. Wilshire, *Inorg. Chem.*, 1981, **20**, 2550.

[276] A. B. P. Lever, J. P. Wilshire, and S. K. Quan, *Inorg. Chem.*, 1981, **20**, 761.

[277] N. T. Moxon, P. E. Fielding, and A. K. Gregson, *J. Chem. Soc., Chem. Commun.*, 1981, 98.

[278] B. N. Figgis, G. A. Williams, J. B. Forsyth, and R. Mason, *J. Chem. Soc., Dalton Trans.*, 1981, 1837.

total −0.31 on the macrocyclic nitrogen and carbon atoms. The negative ligand spin-densities are similar to those previously found for the corresponding cobalt compound.

Among the few papers dealing with bridged complexes is a short note on the possible synthesis of a species having four octahedral $Mn(CO)_4Br$ moieties linked (*cis* to the bromine) by the co-ordination of the linear, stereochemically rigid, molecule dicyanobiphenyl to a central atom of either rhodium or iridium. A possible square-planar configuration for the Rh or Ir is suggested.[279] $[\{(H_2 \text{ e.d.t.a.})Tc^{IV}\}_2(\mu\text{-}O)_2]\cdot 5H_2O$ has been prepared[280] and studied by single-crystal $X$-ray diffraction. The $Tc(\mu\text{-}O)_2Tc$ section was found to be almost planar. Interest in the compound comes from the fairly short $Tc—Tc$ (2.33 Å) distance and the diamagnetic character of the complex. It is possible that this is evidence for a $\sigma^2\pi^2\delta^{*2}(d^6)$ configuration, rather than $\sigma^2\pi^2\delta^2$.

EXAFS data have been collected for three di-$\mu$-oxo manganese dimers $[(MnX_2)\text{-}\mu\text{-}O_2]^{n+}$ perchlorates, where Mn is III/IV or IV/IV and X = phen or bipy; and compared to that obtained from spinach chloroplasts.[281] This is the first direct observation of manganese in such an environment. The chloroplasts were very dilute in manganese and the spectra were thus rather noisy, with rather better results coming from the 'active' chloroplasts rather than the 'inactive'.

**Organometallic Compounds.**—A useful compilation of co-ordination chemistry of the moiety $CpM(CO)_2$ (M = Mn or Re) considered as a ligand has been made.[282] Complexes are classified according to stability, structure and properties. The $X$-ray structure of $Mn_2(CO)_{10}$ has been redetermined[283] and refined to an $R$ factor of 2.3%. The basic framework remains, as generally known, with a crystallographic $C_2$ axis and roughly $D_{4d}$ overall. Each metal has one axial and four equatorial ligands, the latter being staggered around the $Mn—Mn$ bond. The main objective was to refine the metal–metal bond length to 2.904 Å (Mn) and to 3.041 Å for the isomorphous $Re_2(CO)_{10}$. The three heteronuclear carbonyls $M_2(CO)_{10}$ (M = Mn, Tc, or Re) have also been prepared,[284] by reacting $[M(CO)_5]^-$ with $M^1(CO)_5Br$ in carbon disulphide. Around 1 g of $Tc_2(CO)_{10}$ was available for these syntheses. Pure samples of the heterocarbonyls were collected by preparative c.c. procedures. The homonuclear carbonyls show three infrared active CO stretching peaks, as expected for $D_{4d}$ ($2B_2 + E_1$). However, very similar spectra are given by the heteronuclear carbonyls as well, which with $C_{4v}$ symmetry should give six i.r. active bands ($4A_1 + 2E$).

The radical $Mn(CO)_5$ has been prepared[285] by u.v. photolysis of $HMn(CO)_5$ in a CO matrix at 10—20 K. The same product can also be prepared from $Mn(CO)_4NO$. The infrared spectra of the product was interpreted after careful annealing of the sample allowed the identification of bands split by matrix effects. $^{13}CO$ was also used, and the frequency values support a square pyramidal structure with an axial–equatorial angle of 96 ± 3°.

[279] A. Efraty and I. Feinstein, *Inorg. Chim. Acta*, 1981, **54**, L211.
[280] H. B. Bürgi, G. Anderegg, and P. Blaüenstein, *Inorg. Chem.*, 1981, **20**, 3829.
[281] J. A. Kirby, A. S. Robertson, J. P. Smith, A. C. Thompson, S. R. Cooper, and M. P. Klein, *J. Am. Chem. Soc.*, 1981, **103**, 5529.
[282] K. G. Caulton, *Coord. Chem. Rev.*, 1981, **39**, 1.
[283] M. R. Churchill, K. N. Amoh, and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 1609.
[284] G. D. Michels and H. J. Svec, *Inorg. Chem.*, 1981, **20**, 3445.
[285] S. P. Church, M. Poliakoff, J. A. Timney, and J. J. Turner, *J. Am. Chem. Soc.*, 1981, **103**, 7515.

Photolysis of a benzene solution of $Re_2(CO)_{10}$ in the presence of 3,5-di-t-butyl-*o*-benzoquinone (d.t.b.q.) produces a red colouration due to the formation of a (d.t.b.q.)$Re(CO)_4$ radical complex.[286] This has been separated by h.p.l.c. (silica column) and the elutants passed in dual-detector configuration to either an e.s.r. cavity and u.v.–visible or e.s.r.–infrared. The radical complex has considerable stability and is readily separated by this procedure from the quinone (retention times 130 and 410 s, respectively). It is suggested that the initial step of the photolysis involves the radical $Re(CO)_5$, which then complexes with (d.t.b.q.) with the loss of one carbonyl.

Photolysis of $Re_2(CO)_{10}$ in the presence of nitric oxide gives a complex mixture of five multinuclear carbonyl compounds.[287] The structures, as found by *X*-ray analysis, of two of these, $Re_3(CO)_{14}NO_2$ (72; L = $NO_2$) and $Re_3(CO)_{14}CO_2H$ (72; L = $CO_2H$), mave now been determined. The non-carbonyl ligands play similar roles in both species (72), with no involvement of metal–metal bonds.

Two products, $Mn_2(CO)_9$(butadiene) and $Mn_2(CO)_8$(butadiene), have been separated by h.p.l.c. from the photolysis of $Mn_2(CO)_{10}$ in the presence of buta-1,3-diene.[288] In one case the Mn–Mn bond is broken with $Mn(CO)_5$ and $Mn(CO)_4$ fragments joined *via* $\sigma$ and $\eta^2$ bonding, respectively, from one butadiene ligand. The second product was previously known, and has the Mn–Mn bond remaining intact with the metals each bonded $\mu^2$ to the butadiene.



(72)                                        (73)
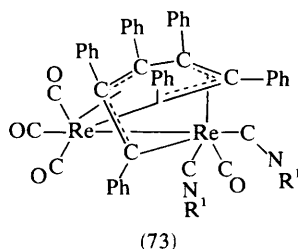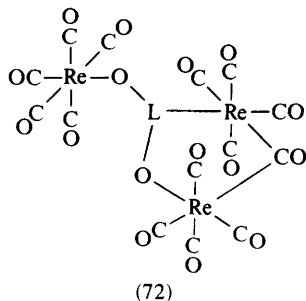
$Re_2(CO)_{10}$ reacts[289] with alkynes to give various substituted products, $Re_2(CO)_n(RC_2R)_m$, where $n,m$ = 7,2; 6,3; or 4,4. This last complex reacts readily with isocyanides to give $Re_2(CO)_4(RC_2R)_3(CNR^1)_2$, and a single-crystal *X*-ray structure (73; R = Ph, $R^1$ = $CH_2SO_2C_6H_4Me$-*p*) has been determined. Rather surprisingly this shows oligomerization of the alkynes into a chain-ligand, and the Re–Re distance of 2.83 Å is about 0.2 Å shorter than that of the parent $Re_2(CO)_{10}$ molecule. A less-dramatic bridging is found[290] for $Re_2Br_2(CO)_6(Te_2Ph_2)$, which was prepared by admixture of $Re_2Br_2(CO)_6(t.h.f.)_2$ with $Te_2Ph_2$ in toluene. Roughly octahedral *fac*-[$Re(CO)_3$] centres are bridged by bromines and the tellurium ligand, with Re–Re of 3.945 Å.

[286] K. A. M. Creber and J. K. S. Wan, *J. Am. Chem. Soc.*, 1981, **103**, 2101.
[287] B. K. Balbach, F. Helus, F. Oberdorfer, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 470.
[288] C. G. Kreiter and W. Lipps, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 201.
[289] M. J. Mays, D. W. Prest, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1981, 771.
[290] F. Calderazzo, D. Vitali, R. Poli, J. L. Atwood, R. D. Rogers, J. M. Cummings, and I. Bernal, *J. Chem. Soc., Dalton Trans.*, 1981, 1004.

$M(CO)_5X$ (M = Tc or Re, X = Cl or Br) has been prepared and shown to have identical X-ray powder photographs.[291] The anion (M = Mn or Re, X = $PR_3$) has been studied[292] by multinuclear n.m.r. ($^{31}P$, $^{55}Mn$, and $^{185,187}Re$). Useful structural correlations were made.

Electroanalytical procedures in acetonitrile solutions have been used to measure the rate constant for the conversion of *fac*-$[ReCl(CO)_3(PhMe_2P)_2]^+$ into the *mer-trans*-isomer. A value of $78 \, s^{-1}$ was obtained.[293] A similar compound, *fac*-$[MnBr(CO)_3(diphos)]$ (diphos = $Ph_2P(CH_2)_nPPh_2$, n = 1 or 2) has been used[294] as the starting material for a range of interesting transformations (Scheme 15). One of the points about these reactions is the way in which different products are obtained when using $AgClO_4$ instead of $TlPF_6$ as a halogen abstractor.
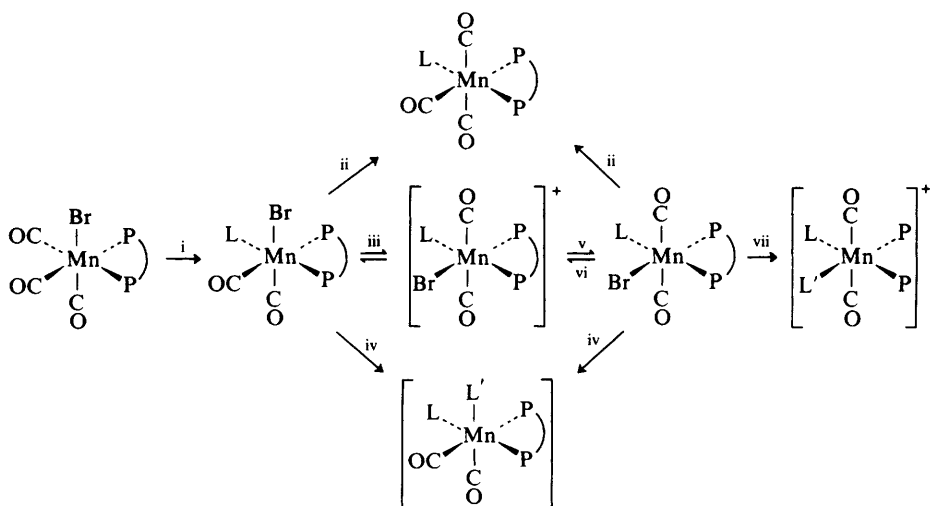


Reagents: i, L; ii, CO–$AgClO_4$; iii, $NO_2$; iv, L′–$AgClO_4$; v, $NH_2NH_2$; vi, oxidation; vii, L′–$Tl^+PF_6^-$

**Scheme 15**

$Mn_2(CO)_5(diphos)$, where diphos is as above n = 1, is known for having a rather unusual bridging carbonyl $\sigma$-bonded to one metal and $\eta$ to the other. It has since been found to be rather unreactive. However, it has now been shown[295] to be readily protonated and then is able to react with carbon monoxide to give the anion $[\{Mn(CO)_3(diphos)\}_2(\mu\text{-}H)]^+$. This shows a symmetric quintet for the bridging proton n.m.r. and has no Mn—Mn bond.

$Mn(CO)_3(py)_2(CF_3CO_2)$ and $Re(CO)_3(NHR_2)_2Br$ have both[296,297] been shown by X-ray structural methods to take the *fac* structure.

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*cis*-[MeMn(CO)$_4$($^{13}$CO)] has been studied[298] by $^{13}$C n.m.r. to determine the stereochemistry of CO insertion into the Me—Mn bond, induced by both $^{12}$CO and P(OCH$_2$)$_3$CMe. The general conclusion favours a movement of the methyl group with a consequent square-pyramidal intermediate. Another insertion type of reaction has been found[299] to occur at 5 °C over a period of two weeks for benzaldehyde left with (CO)$_5$MnSiMe$_3$. The product has been formulated as [(CO)$_5$MnCH{Ph(OSiMe$_3$)}]. The reaction was even slower when solvents were used. When the product was allowed to warm up to 80 °C, homolysis occurred with the release of Mn$_2$(CO)$_{10}$ and [CHPh(OSiMe$_3$)]$_2$. Other aldehydes were also used with *p*-methoxy- and *p*-dimethylamino-benzaldehydes giving much faster reactions but poorly defined products.

Rhenium has been characterized as part of a mixed-metal carbonyl cluster compound.[300] ($\mu$-H)Os$_3$Re(CO)$_{15}$(NCMe) has a *triangulo*-osmium centre with the rhenium [Re(CO)$_4$] moiety taking one of the equatorial sites. All the metals are roughly octahedral, and the (unlocated) hydrogen is inferred from bond lengths and distance to occupy a $\mu_2$-bridging site across the vector between the osmium bonded to the rhenium and that bonded to the NCMe ligand.

A range of compounds formulated Mn(CO)$_2$(MeCp)RL, [R = Me or CH$_2$Ph, L = SiPh$_3$, GePh$_3$, or GeMePh(1-naphthyl)], has been shown to be quite stable in solution.[301] The structural relationships in the various transformations have not yet been totally confirmed but it is assumed that the formation of the anion species [Mn(CO)$_2$(MeCp)L]$^-$, where L = the optically active Ge ligand, from Mn(CO)$_3$(MeCp) proceeds with retention of configuration. This anion is then alkylated by addition of RI.

Mn(CO)$_2$(t.h.f.)(Cp), produced by u.v. irradiation of the *tris*-carbonyl, reacts[302] with cyclo-octatetraene at room temperature to give Mn(CO)$_2$($\eta^2$-C$_8$H$_8$)($\eta$-C$_5$H$_5$), (74), the structure of which was found by *X*-ray diffraction procedures. The bond angles suggest octahedral site symmetry for the metal (*fac*-Cp). The tetraene ligand has only a slightly different configuration from that of the free molecule. No n.m.r. evidence could be obtained for fluxional migration of the metal group around the C$_8$ ring as the complex decomposed above *ca.* 75 °C.



(74)
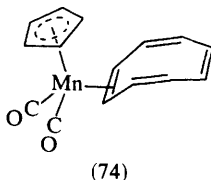
($\eta$-Cp)$_2$ReH is known to give ($\eta$-Cp)($\eta^2$-C$_5$H$_6$)Re(CO)$_2$ on photolysis with CO in light petroleum. On further photolysis, this latter compound has now been shown to revert to the hydride complex. When carried out in an Ar matrix at 14 K,

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it proved possible to obtain infrared spectra of two dicarbonyl and one monocarbonyl intermediates.[303]

CpMn(CO)$_3$ has been re-examined[304] by *X*-ray diffraction methods and the C$_5$H$_5$ ring is found to deviate quite considerably from regular pentagonal symmetry. The C—C distances range from 1.400 to 1.439 Å. Similar effects were found earlier for the rhenium compound.

The photoelectron spectra of $(\eta^3\text{-}C_3H_5\text{-}Mn(CO)_4$ and $(\eta^3\text{-}C_3H_4Me)Mn(CO)_4$ show ionizations due to the metal at around 8.04 and 8.40 eV.[305] The methyl-substituted compound causes a greater destabilization (0.55 eV) of the second $\pi$ orbital than of the HOMO (0.08 eV). Simple MO theory is in accord with this deduction, since the allyl radical HOMO has a node at the 2-position, whereas the $\pi$ orbital is at maximum electron density.

[MnPt($\mu$-CPhMe)(CO)$_2$(PR$_3$)$_2$($\eta$-C$_5$H$_5$)]$^-$ has been synthesized and shown[306] to have a bridging carbyne ligand (Mn—C = 1.829 Å, Pt—C = 1.968 Å and Mn—Pt = 2.628 Å). A double bond to the manganese and a single to the platinum are thus invoked. The electrophilic–nucleophilic nature of such carbyne (and carbene) complexes is under current debate. MO calculations[307] for CR$^+$ and the metal fragments CpMn(CO)$_2$ and Cr(CO)$_5$ have been made. The complexes contain the entity M≡CR, with donation from carbyne HOMO to metal LUMO ($\sigma$ bond) and $\pi$-bonds formed by back-donation from two metal HOMOs to two ligand LUMOs. The model supports the view that additions to such complexes are frontier-orbital controlled rather than charge-controlled. This explains how strong nucleophiles attack at the carbyne centre which is shown to be often the most negative ligand site of the complex.

Reactions at a -CS or -CSMe bridged heteronuclear (Mn, Pt) complex may help to provide experimental evidence for this debate.[308]

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