

Figure 24.7 (a) Trigonal prismatic $[\text{Tc}_6\text{Cl}_{12}]^{2-}$ (b) $[\text{Tc}_8\text{Br}_{12}]^{n+}$. The bond lengths shown are for $n = 1$, i.e. $[\text{Tc}_8\text{Br}_{12}]\text{Br}\cdot 2\text{H}_2\text{O}$. The very short bonds holding together the triangular faces in (a) and the rhombohedral faces in (b) are consistent with $\text{Tc}\equiv\text{Tc}$ triple bonds.

to involve appreciable π bonding and this covalency brings with it a susceptibility to oxidation. Just as Mn^{II} hydroxide undergoes aerial oxidation to Mn^{III} so, in the presence of excess CN^- , aqueous solutions of the blue-violet $[\text{Mn}(\text{CN})_6]^{4-}$ are oxidized by air to the dark red $[\text{Mn}(\text{CN})_6]^{3-}$.

Lower oxidation states

Cyano complexes of the metals of this group in high oxidation states have already been referred to. The tolerance of CN^- to a range of metal oxidation states, arising, on the one hand, from its negative charge and, on the other, from its ability to act as a π -acceptor, is further demonstrated by the formation (albeit requiring reduction with potassium amalgam) of the M^{I} complexes, $\text{K}_5[\text{M}(\text{CN})_6]$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$). However, claims for the formation of cyano complexes with oxidation state zero are less reliable.

Reduction of $[\text{MO}_4]^-$ in hydrohalic acid by H_2 under pressure is an alternative method for preparing $[\text{Re}_2\text{X}_8]^{2-}$. In the case of technetium, however, further reduction occurs, yielding $[\text{Tc}_2\text{X}_8]^{3-}$ along with higher nuclearity clusters in which the oxidation state of the metal is below 2.⁽²⁶⁾ Chloride species include $[\text{Tc}_6\text{Cl}_{14}]^{3-}$ and $[\text{Tc}_6\text{Cl}_{12}]^{2-}$

with the trigonal prismatic structure shown in Fig. 24.7a. Bromide species⁽²⁷⁾ additionally include hexanuclear octahedral species and the octanuclear prismatic, $[\text{Tc}_8\text{X}_{12}]^{n+}$ ($n = 0, 1$) (Fig. 24.7b). Other examples of complexes in which Mn, Tc and Re are in lower oxidation states are considered in section 24.3.6 on organometallic compounds.

24.3.5 The biochemistry of manganese^(16,18)

Traces of manganese are found in many plants and bacteria, and a healthy human adult contains about 10–20 mg of Mn.

In many manganoproteins the manganese is in the II oxidation state and can often be replaced by magnesium(II) without loss of function. In other cases, where redox activity is involved, some naturally occurring forms containing either manganese or iron are known. The most important natural role of manganese, however, is in the oxidation of water in green plant photosynthesis (p. 125) where its presence in photosystemII (PSII) is essential. Here, absorbed radiation provides the energy for the oxidation

²⁷ V. I. SPITZIN, S. V. KRYUTCHKOV, M. S. GRIGORIEV and A. F. KUZINA, *Z. anorg. allg. Chem.* **563**, 136–52 (1988).

²⁶ pp. 559–63 of ref. 20.

of water, dioxygen being evolved and electrons transferred to photosystemI (PSI) where NADP is reduced. The oxidation proceeds by four 1-photon, 1-electron steps and it appears that it is the redox properties of a group of Mn atoms which provide stable stages for this stepwise oxidation. Manganese probably has two further functions:

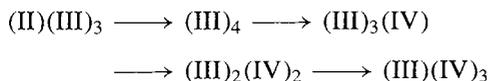
- (a) to act as a template holding two molecules of water close enough to facilitate O–O bond formation;
- (b) to make the bound water more acidic, so facilitating loss of H⁺

It is no doubt significant that the equilibrium constant for the reaction



is larger for Mn^{III} than for any other trivalent, first row transition metal ion.

Although definitive crystallographic data are lacking it seems clear that the “water oxidizing centre” (WOC) or “oxygen evolving complex” (OEC) of PSII contains four Mn atoms and it is believed that these are arranged in one of the cluster forms shown in Fig. 24.5. Physical techniques which have been used to study these proteins include esr, uv-visible spectroscopy, magnetic measurements and EXAFS. Two Mn–Mn distances, 270 and 330 pm are indicated, with *O*-, *N*- and possible *Cl*-donor atoms, giving a core of fairly low symmetry. A plausible sequence of oxidation state changes for the four Mn atoms consistent with, but by no means defined by, the available data would be:



Efforts have been made to reproduce these characteristics in model systems, and molecules with the core structures already described have been prepared. Though none as yet has shown any photoredox activity the 270 pm distance has been shown to be consistent with (μ -oxo)₂ bridges and 330 pm with μ -oxo or μ -oxo- μ -carboxylate bridges. Several mechanistic proposals have been made incorporating these features.

24.3.6 Organometallic compounds

Carbonyls, cyclopentadienyls and their derivatives occupy a central position in the chemistry of this as of preceding groups, the bonding involved and even their stoichiometries having in some cases posed difficult problems. Increasingly, however, interest has focused on the chemistry of compounds involving M–C σ bonds, of which rhenium provides as rich a variety as any transition metal. It is also notable that, whereas the organometallic chemistry of manganese is largely limited to oxidation states 0, I and II, that of rhenium extends to VII.^(28,29)

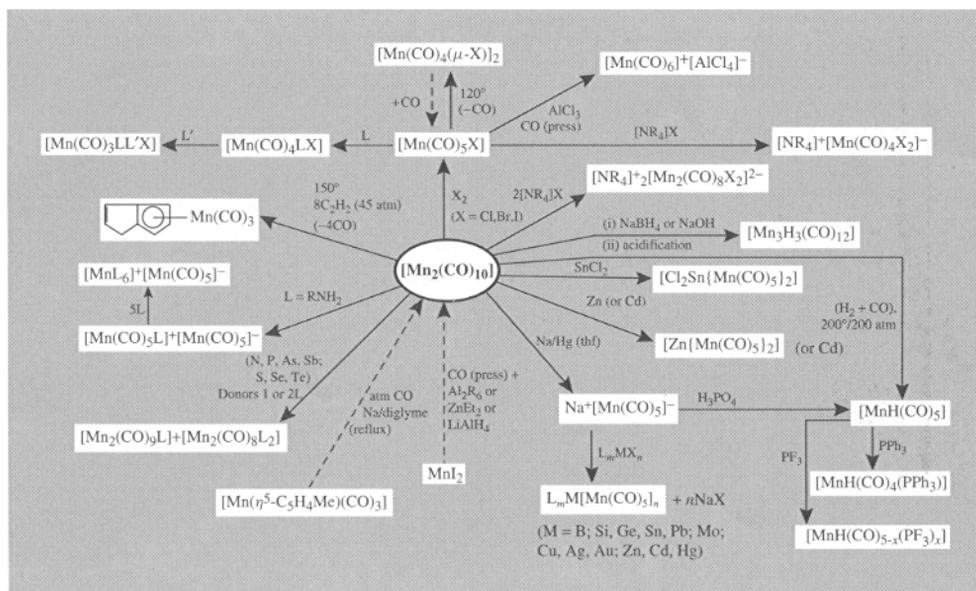
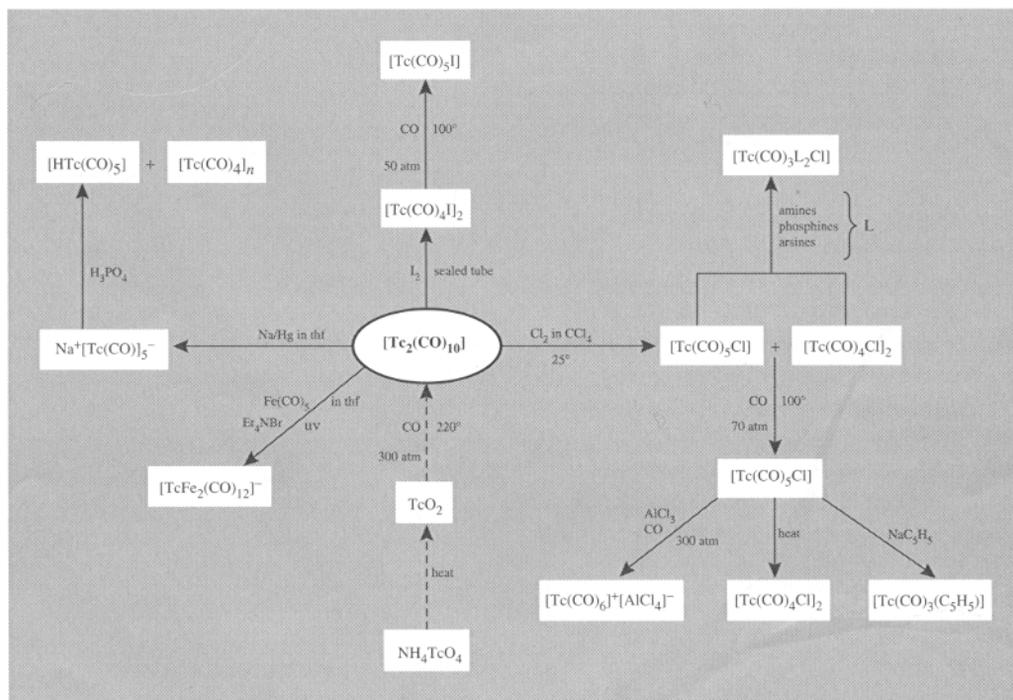
Only one well-characterized binary carbonyl is formed by each of the elements of this group. That of manganese is best prepared by reducing MnI₂ (e.g. with LiAlH₄) in the presence of CO under pressure. Those of technetium and rhenium are made by heating their heptoxides with CO under pressure. They are sublimable, isomorphous, crystalline solids: golden-yellow for [Mn₂(CO)₁₀], mp 154°, and colourless for [Tc₂(CO)₁₀], mp 160° and [Re₂(CO)₁₀], mp 177°. Their stabilities in air show a regular gradation: manganese carbonyl is quite stable below 110°C, technetium carbonyl decomposes slowly and rhenium carbonyl may ignite spontaneously. The empirical stoichiometry M(CO)₅ would imply a paramagnetic molecule with 17 valence electrons, but the observed diamagnetism (for Mn and Re) suggests at least a dimeric structure. In fact, X-ray analysis reveals the structure shown in Fig. 24.8(a) in which two M(CO)₅ groups in staggered configuration are held together by an M–M bond, unsupported by bridging ligands (cf. S₂F₁₀, p. 684).

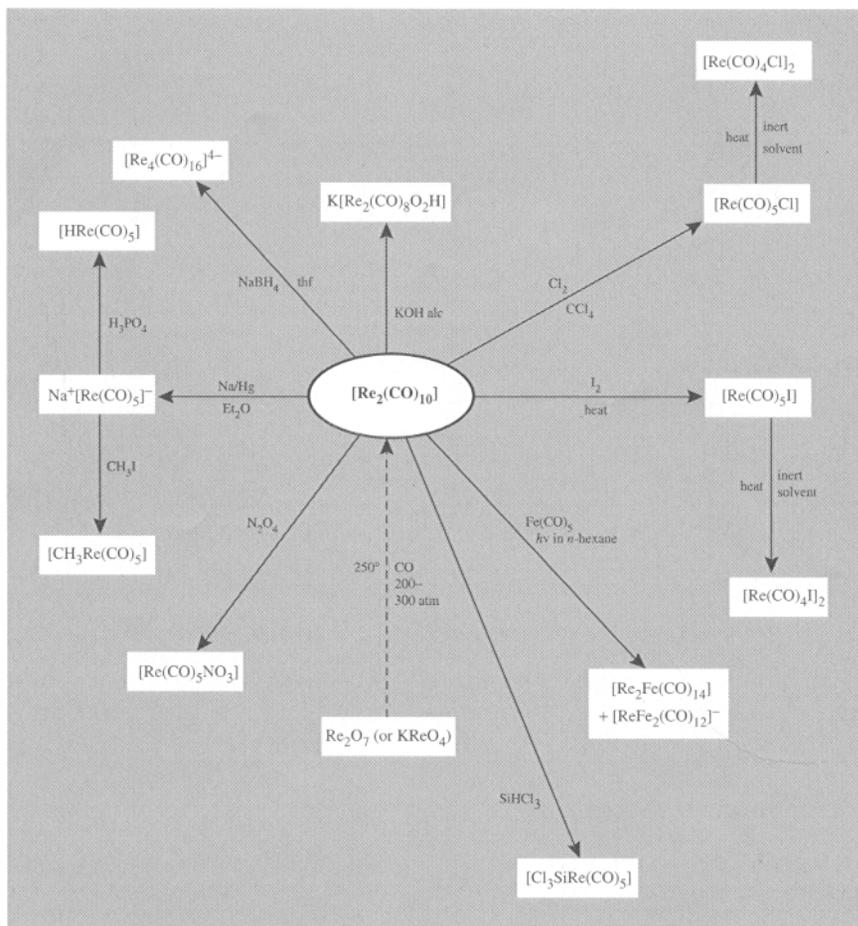
Very many derivatives of the carbonyls of Mn,⁽³⁰⁾ Tc and Re have been prepared since the parent carbonyls were first synthesized in 1949, 1961 and 1941 respectively:⁽³⁾ among the more important are the carbonylate anions,

²⁸ C. P. CASEY, *Science* **259**, 1552–8 (1993).

²⁹ W. A. HERRMANN, *Angew. Chem. Int. Edn. Engl.* **27**, 1297–313 (1988).

³⁰ C. E. HOLLOWAY and M. MELNIK, *J. Organometallic Chem.* **396**, 129–246 (1990).

SCHEME A Some reactions of $[\text{Mn}_2(\text{CO})_{10}]$ and its derivatives.⁽³¹⁾SCHEME B Some reactions of $[\text{Tc}_2(\text{CO})_{10}]$ and its derivatives.⁽³²⁾³¹R. D. W. KEMMIT, pp. 839–51 in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford 1973.³²R. D. PEACOCK, *ibid.*, p. 899 for Scheme B, p. 953 for Scheme C and p. 954 for Scheme D.

SCHEME C Some reactions of rhenium carbonyl.⁽³²⁾

the carbonyl cations, and the carbonyl hydrides. Typical reactions are summarized in schemes A, B, C and D (this last on p. 1067).

Sodium amalgam reductions of $M_2(CO)_{10}$ give $Na^+[M(CO)_5]^-$ and, indeed, further reduction⁽³³⁾ leads to the “super reduced” species $[M(CO)_4]^{3-}$ in which the metals exhibit their lowest known formal oxidation state of -3 . On the other hand, treatment of $[M(CO)_5Cl]$ with $AlCl_3$ and CO under pressure produces $[M(CO)_6]^+AlCl_4^-$ from which other salts of the cation can be obtained.

Acidification of $[M(CO)_5]^-$ produces the octahedral and monomeric, $[MH(CO)_5]$, and a number of polymeric carbonyls have been

obtained by reduction of $[M_2(CO)_{10}]$, including interesting hydrogen-bridged complexes such as $[H_3Mn_3(CO)_{12}]$ (the first transition metal cluster in which the H atoms were located), $[H_4Re_4(CO)_{12}]$ and $[H_6Re_4(CO)_{12}]^{2-}$ (Fig. 24.8). The tendency to form high nuclearity carbonyl clusters is, however, much less evident for Mn than for Re. The largest so far obtained for Mn is the heptanuclear, $[Mn_7(\mu_3-OH)_8(CO)_8]^{34}$ but this is exceptional, there being very few others with nuclearities higher than four.⁽³⁰⁾

By contrast, the stronger M–M bonds characteristic of Re, help to provide a wider

³³ J. E. ELLIS, *Adv. Organometallic Chem.* **31**, 52 (1990).

³⁴ M. D. CLERK and M. J. ZAWOROTKO, *J. Chem. Soc. Chem. Commun.* 1607–8 (1991).

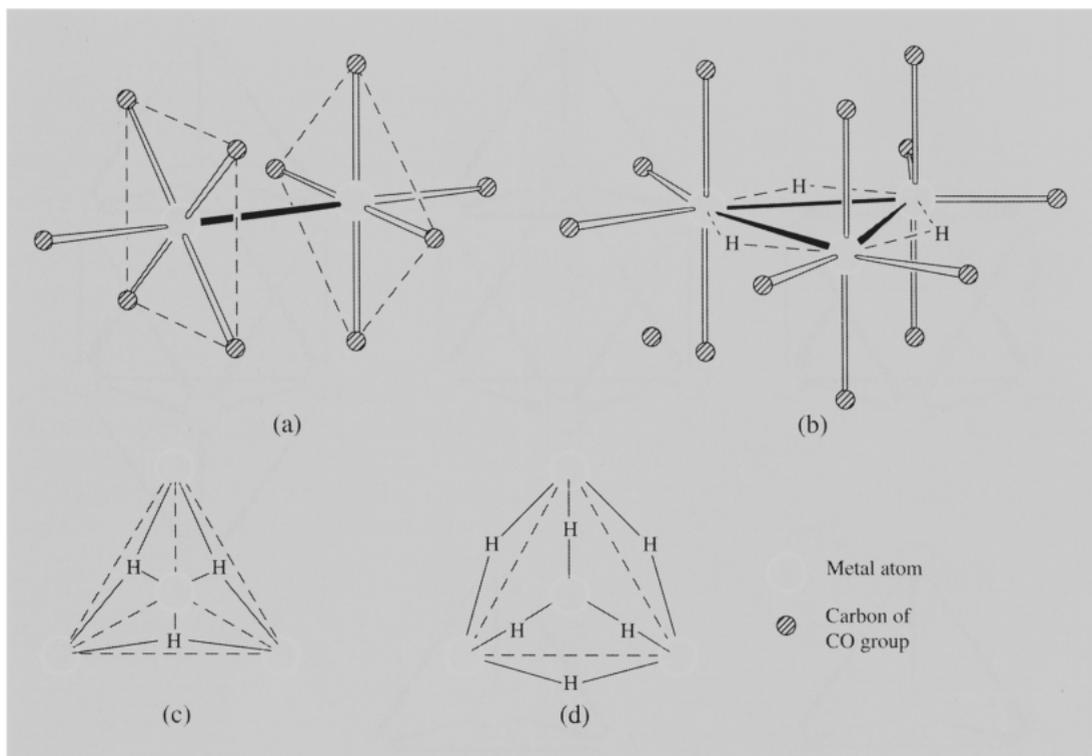


Figure 24.8 Some carbonyls and carbonyl hydrides of Group 7 metals. (a) $[M_2(CO)_{10}]$, $M = Mn, Tc, Re$ (Mn–Mn 293 pm, Tc–Tc 304 pm, Re–Re 302 pm). (b) $[H_3Mn_3(CO)_{12}]$. Mn–Mn 311 pm. (c) $[H_4Re_4(CO)_{12}]$, Re–Re 289.6–294.5 pm. (In this structure the 4 Re atoms lie at the corners of a tetrahedron, the faces of which are bridged by 4 H atoms; the molecule is viewed from above one Re which obscures the fourth H. For clarity the CO groups are not shown but 3 are attached to each Re so as to “eclipse” the edges of the tetrahedron.) (d) $[H_6Re_4(CO)_{12}]^{2-}$, Re–Re 314.2–317.2 pm. (As in (c) the 4 Re atoms lie at the corners of a tetrahedron and the CO groups have been omitted for clarity. The 3 CO groups attached to each Re are now “staggered” with respect to the edges of the tetrahedron, whilst the H atoms (6) are presumed to bridge these edges.)

variety⁽³⁵⁾ of which the carbon-centred clusters $[H_2Re_6C(CO)_{18}]^{2-}$, $[Re_7C(CO)_{21}]^{3-}$ and $[Re_8C(CO)_{24}]^{2-}$ (Fig. 24.9), obtained by the pyrolytic reduction of $Re_2(CO)_{10}$ with varying proportions of Na in thf, may be mentioned. The H atoms in the first of these clusters, though not positively located, were thought to be face-capping (i.e. μ_3). On the other hand $[Re_7HC(CO)_{21}]^{2-}$, which is obtained by treating a salt of $[Re_7C(CO)_{21}]^{3-}$ in acetone or thf with a strong acid such as HBF_4 or H_2SO_4 , exists in two isomeric forms and potential

energy computations suggest that both contain a μ -H atom and differ in the cluster edge which this bridges⁽³⁶⁾ (Fig. 24.9d and e).

When $MnCl_2$ in thf is treated with C_5H_5Na , amber-coloured crystals of manganocene, $[Mn(C_5H_5)_2]$, mp 172° , are produced. It is very sensitive to both air and water and is a most unusual compound. At room temperature it is polymeric with $Mn(\eta^5-C_5H_5)$ units linked by bridging C_5H_5 groups in a zig-zag arrangement.

³⁵ T. J. HENLY, *Coord. Chem. Revs.* **93**, 269–95 (1989).

³⁶ T. BERINGHELLI, G. D’ALFONSO, G. CIANI, A. SIRONI and H. MOLINARI, *J. Chem. Soc., Dalton Trans.*, 1281–7 (1988).

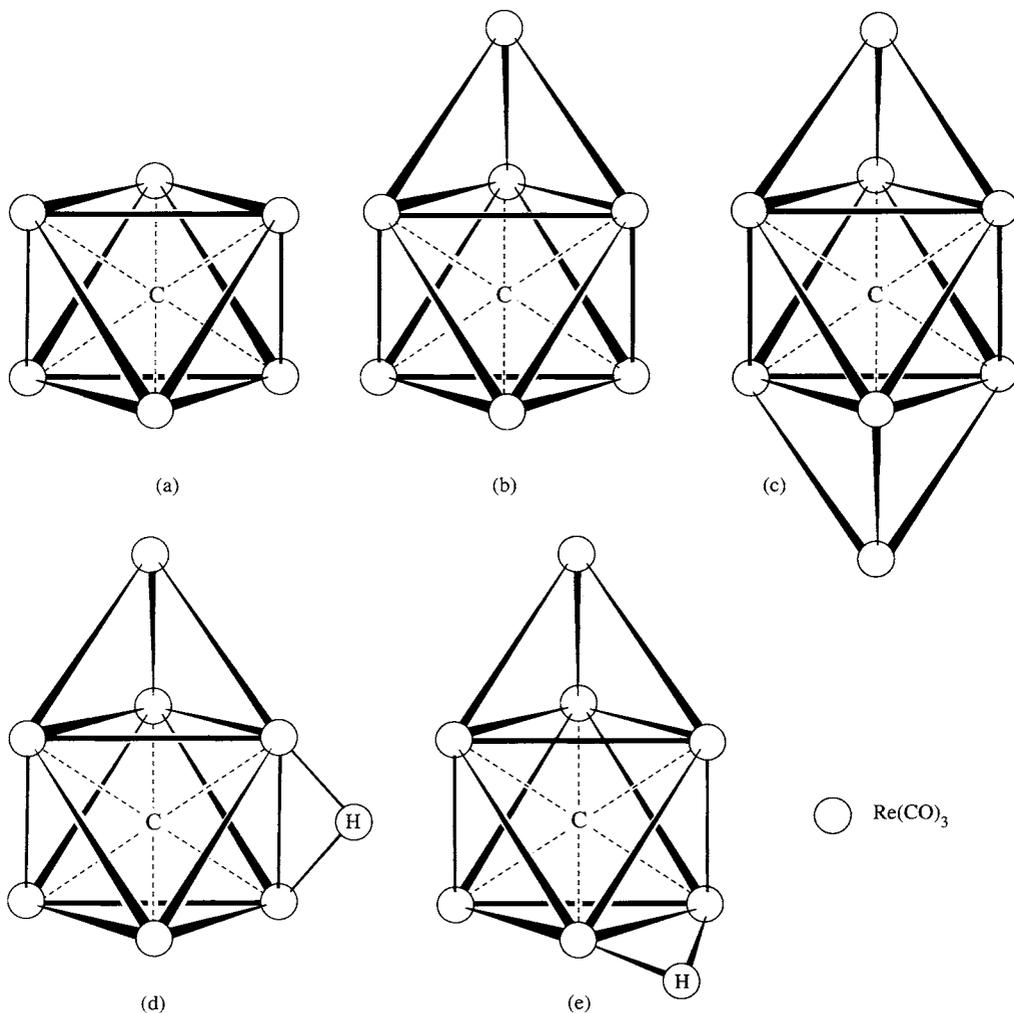
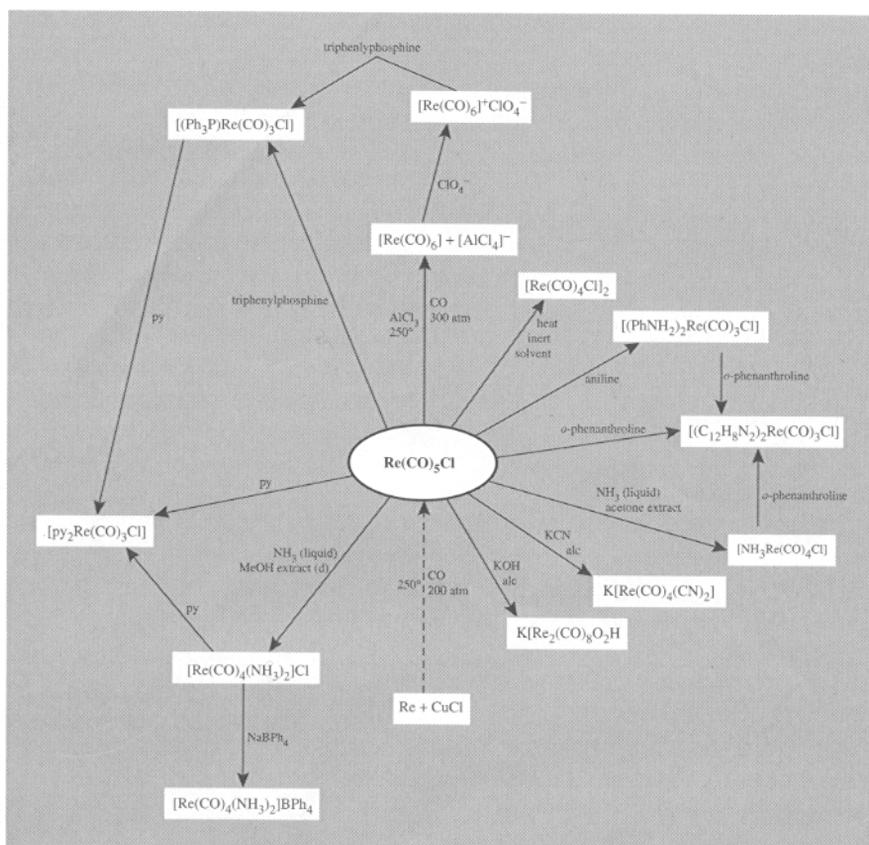


Figure 24.9 Cluster carbonyls of rhenium containing an encapsulated carbon atom. (a) Octahedral $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$. (b) Monocapped octahedral $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$. (c) *trans*-bicapped octahedral $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$. (d) and (e) isomers of $[\text{Re}_7\text{HC}(\text{CO})_{21}]^{2-}$ differing in the position of their $\mu\text{-H}$ atom.

At about 159°C it turns pink and adopts the “sandwich” structure, expected for $[\text{M}(\text{C}_5\text{H}_5)_2]$ compounds, and this is retained in the gaseous phase and in hydrocarbon solutions. Using substituted cyclopentadienyls a variety of analogous sandwich compounds have been prepared⁽³⁷⁾ and their magnetic properties indicate that the

high-spin (5 unpaired electrons) and low-spin (1 unpaired electron) configurations are sufficiently close together to produce an equilibrium between the two in many cases (Fig. 24.10). The spin state depends on the nature and number of substituents in the C_5 ring and also on solvent and temperature. Electron donating substituents, such as methyl, enhance the covalent character of the $\text{Mn}-\text{C}$ bonding and favour the low-spin configuration. Thus $[\text{Mn}(\eta^5\text{-C}_5\text{Me}_5)_2]$

³⁷ N. HEBENDANZ, F. H. KÖHLER, G. MÜLLER and J. REIDE, *J. Am. Chem. Soc.* **108**, 3281–9 (1986).



SCHEME D Some reactions of rhenium carbonyl chloride.

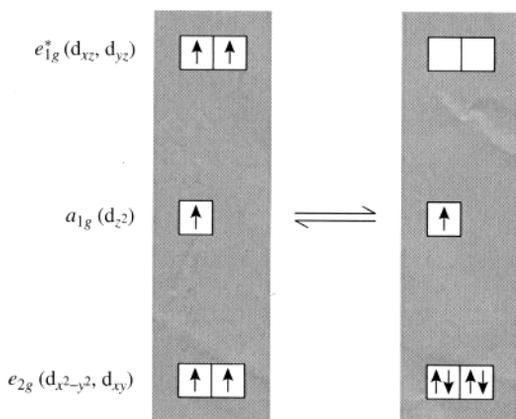


Figure 24.10 Spin equilibrium in $[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{-Me})_2]$: the orbitals shown here are the mainly metal-based orbitals in the centre of the MO diagram for metallocenes (see Fig. B, p. 939).

is exclusively low-spin, $[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]$ and other monoalkyl substituted ring systems exhibit spin-equilibria, while manganocene itself with a magnetic moment of 5.86 BM in hydrocarbon solvents at room temperature, is almost (but not entirely) high-spin.

Apart from the formation of $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)_2]$ on N_2 matrices at 20 K, Tc and Re analogues of manganocene have not been prepared. Instead, when TcCl_4 or ReCl_5 are treated with NaC_5H_5 in thf, the diamagnetic, yellow crystalline hydrides, $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}]$ are obtained (Fig. 24.11a). The protons on the cyclopentadienyl rings give rise to only one nmr signal, presumably because of rapid rotation of the rings about the metal-ring axis making the protons indistinguishable. As with Mn, however, methyl substitution has a stabilizing effect and purple $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)_2]$

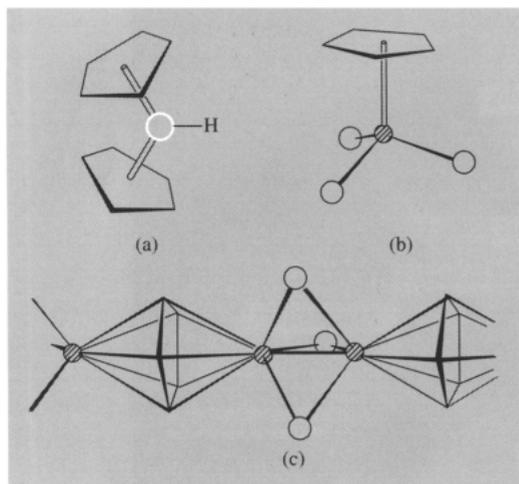


Figure 24.11 (a) $[M(\eta^5\text{-C}_5\text{H}_5)_2\text{H}]$ ($M = \text{Tc, Re}$) (b) $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)\text{O}_3]$ (The structure of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)\text{O}_3]$ is presumed to be identical but was not determined because of the lack of suitable single crystals⁽²⁹⁾. (c) Section of the linear chain $[\text{Tc}_2(\text{C}_5\text{Me}_5)\text{O}_3]_n$.

is readily obtained by photolysis of a solution of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)_2\text{H}]$ in pentane. It is low-spin at low temperatures but has a minor contribution from the high-spin configuration at room temperature.⁽³⁸⁾

Pentamethylcyclopentadienyl compounds also provide a convenient route into high-valent organorhenium chemistry.⁽²⁹⁾ Oxidation of $[\text{Re}^I(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ by H_2O_2 in a two-phase water–benzene system gives high yields of lemon yellow $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)\text{O}_3]$ (Fig. 24.11b) which, being stable in air even up to 140°C , demonstrates the remarkable stabilizing effect of oxygen on Re in high oxidation states. The same procedure⁽³⁹⁾ in the case of technetium raises its oxidation state only to 3.5, forming yellow $[\text{Tc}_2(\text{C}_5\text{Me}_5)\text{O}_3]_n$ (Fig. 24.11c) in which linear chains of Tc atoms are bridged alternately by $(\mu\text{-C}_5\text{Me}_5)$ and $(\mu\text{-O})_3$

with Tc–Tc distances respectively of 407.7(4) and the unusually short 186.7(4) pm.

Manganese(II) forms alkyls with a distinct tendency to polymerize. Thus the bright orange $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ is a polymer in which each Mn attains tetrahedral coordination, being doubly bridged to each adjacent metal by two CH_2SiMe_3 groups (each Mn–C–Mn bridge is best regarded as a three-centre, two-electron bond). Red-brown $\text{Mn}(\text{CH}_2\text{CMe}_3)_2$ is similarly bridged but, for no obvious reason, is only tetrameric, a terminal ligand being attached to each of the two outer Mn atoms which are therefore only 3-coordinate.

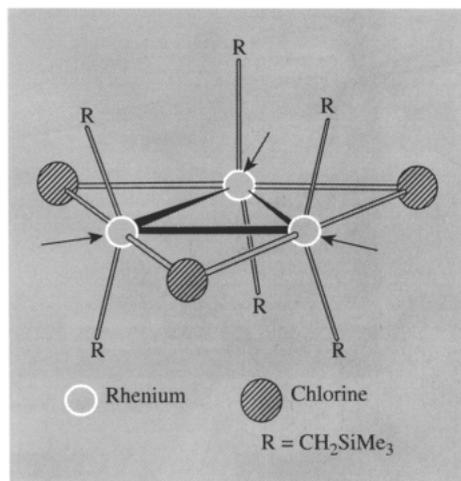


Figure 24.12 Rhenium clusters: $[\text{Re}_3\text{Cl}_3\text{R}_6]$; arrows indicate vacant coordination sites where further ligands can be attached.

The simplest of the σ -bonded Re–C compounds is the green, paramagnetic, crystalline, thermally unstable ReMe_6 , which, after WMe_6 , was only the second hexamethyl transition metal compound to be synthesized (1976). It reacts with LiMe to give the unstable, pyrophoric, $\text{Li}_2[\text{ReMe}_8]$, which has a square-antiprismatic structure, and incorporation of oxygen into the coordination sphere greatly increases the stability, witness $\text{Re}^{\text{VI}}\text{OMe}_4$, which is thermally stable up to 200°C , and $\text{Re}^{\text{VII}}\text{O}_3\text{Me}$, which is stable in air. The interaction of $[\text{ReCl}_4(\text{thf})_2]$

³⁸ J. A. BANDY, F. G. N. CLOKE, G. COOPER, J. P. DAY, R. B. GIRLING, R. G. GRAHAM, J. C. GREEN, R. GRINTER and R. N. PERUTZ, *J. Am. Chem. Soc.* **110**, 5039–50 (1988).

³⁹ B. KANELAKOPOULOS, B. NUBER, K. RAPTIS and M. L. ZIEGLER, *Angew. Chem. Int. Edn. Engl.* **28**, 1055 (1989).

with (o-tolyl)MgBr in thf yields the dark red, paramagnetic tetraaryl, $[\text{Re}(\text{2-MeC}_6\text{H}_4)_4]^{(40)}$. This highly air-sensitive compound, if treated with PMe_2R ($\text{R} = \text{Me, Ph}$), is converted into the thermally stable and rather inert benzyne, $[\text{Re}(\eta^2\text{-C}_6\text{H}_3\text{Me})(\text{PMe}_2\text{R})_2(\text{2-MeC}_6\text{H}_4)_2]^{(41)}$.

A whole series of alkyl cluster compounds $\text{Re}_3\text{Cl}_3\text{R}_6$ has been prepared by reacting Re_3Cl_9 with a large excess of RMgCl in

thf. The blue diamagnetic trimethylsilylmethyl complex (Fig. 24.12) is best known. A red isomer has been obtained in which the Cl bridges have exchanged positions with three of the terminal alkyls, and it is also possible to replace the Cl bridges by CH_3 to produce, $[\text{Re}_3(\mu\text{-CH}_3)_3(\text{CH}_2\text{SiMe}_3)_6]$. Adducts, $[\text{Re}_3\text{Cl}_3(\text{CH}_2\text{SiMe}_3)_6\text{L}_3]$ ($\text{L} = \text{CO, H}_2\text{O}$) can be obtained, but phosphines tend to cause cleavage of the Re_3 ring instead of forming adducts.

⁴⁰ P. SAVAGE, G. WILKINSON, M. MOTEVALLI and M. B. HURSTHOUSE, *J. Chem. Soc., Dalton Trans.*, 669–73 (1988).

⁴¹ J. ARNOLD, G. WILKINSON, B. HUSSAIN and M. B. HURSTHOUSE *J. Chem. Soc., Chem. Commun.* 704–5 (1988).