

Table 25.7 Naturally occurring iron proteins

Name	Donor atoms. Stereochemistry of Fe	Function	Source	Approximate Mol wt	No. of Fe atoms
<i>Haem proteins</i>					
Haemoglobin	$5 \times N$ Square pyramidal	O ₂ transport	Animals	64 500	4
Myoglobin	$5 \times N$ Square pyramidal	O ₂ storage	Animals	17 800	1
Cytochromes	$5 \times N + S$ Octahedral	Electron transfer	Bacteria, plants, animals	12 400	4
<i>NHIP (non-haem iron proteins)</i>					
Transferrin		Scavenging Fe	Animals	80 000	2
Ferritin		Storage of Fe	Animals	460 000	20% Fe
Ferredoxins	$4 \times S$ Distorted tetrahedral	Electron transfer	Bacteria, plants, animals	6000–12 000	2–8
Rubridoxins	$4 \times S$ Distorted tetrahedral	Electron transfer	Bacteria	6000	1
“MoFe protein”	$4 \times S$ Distorted tetrahedral	Nitrogen fixation (see p. 1035)	In nitrogenase	220 000–240 000	24–36
“Fe protein”					

and are thought to have potential use in laser technology.⁽⁴²⁾

Lower oxidation states

With rare exceptions, such as $[\text{Fe}(\text{bipy})_3]^0$, oxidation states lower than +2 are represented only by carbonyls, phosphines, and their derivatives. These will be considered together with other organometallic compounds in Section 25.3.6.

25.3.5 The biochemistry of iron^(43–45)

Iron is the most important transition element involved in living systems, being vital to both

plants and animals. The stunted growth of the former is well known on soils which are either themselves deficient in iron, or in which high alkalinity renders the iron too insoluble to be accessible to the plants. Very efficient biological mechanisms exist to control the uptake and transport of iron and to ensure its presence in required concentrations. The adult human body contains about 4 g of iron (i.e. ~0.005% of body weight), of which about 3 g are in the form of haemoglobin, and this level is maintained by absorbing a mere 1 mg of iron per day — a remarkably economical utilization.

Proteins involving iron have two major functions:

- (a) oxygen transport and storage;
- (b) electron transfer.

Ancillary to the proteins performing these functions are others which transport and store the iron itself. All these proteins are conveniently categorized according to whether or not they contain haem, and the more important classes found in nature are listed in Table 25.7.

⁴² W. M. LAIDLAW, R. G. DENNING, T. VERBIEST, E. CHAUHARD and A. PERSOONS, *Nature* **363**, 58–60 (1993).

⁴³ J. G. LEIGH, G. R. MOORE and M. T. WILSON, *Biological Iron*, Chap. 6, pp. 181–243; A. K. POWELL, *Models for Iron Biomolecules*, Chap. 7, pp. 244–74, in ref. 10.

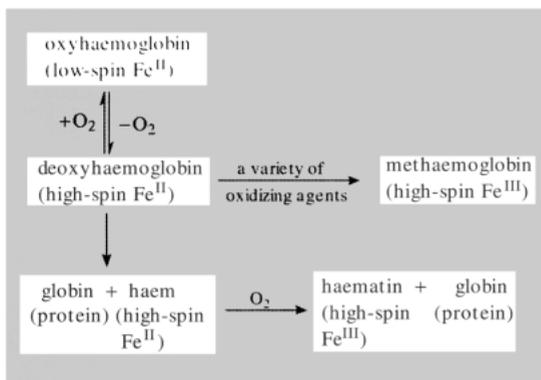
⁴⁴ R. CRICHTON, *Inorganic Biochemistry of Iron Metabolism*, Ellis Horwood, Hemel Hempstead, 1991, 212 pp.

⁴⁵ W. KAIM and B. SCHWEDERSKI, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester, 1994, 401 pp.

Haemoglobin and myoglobin

Haemoglobin (see p. 126) is the oxygen-carrying protein in red blood-cells (erythrocytes) and is responsible for their colour. Its biological function is to carry O_2 in arterial blood from the lungs to the muscles, where the oxygen is transferred to the immobile myoglobin, which stores it so that it is available as and when required for the generation of energy by the metabolic oxidation of glucose. At this point the haemoglobin picks up CO_2 , which is a product of the oxidation of glucose, and transports it in venous blood back to the lungs.†

In haemoglobin which has no O_2 attached (and is therefore known as deoxyhaemoglobin or reduced haemoglobin), the iron is present as high-spin Fe^{II} and the reversible attachment of O_2 (giving oxyhaemoglobin) changes this to diamagnetic, low-spin Fe^{II} without affecting the metal's oxidation state. This is remarkable, the more so because, if the globin is removed by treatment with HCl/acetone, the isolated haem in water entirely loses its O_2 -carrying ability, being instead oxidized by air to haematin in which the iron is high-spin Fe^{III} :



The key to the explanation lies in (a) the observation that in general the ionic radius of Fe^{II} (and also, for that matter, of Fe^{III}) decreases by roughly 20% when the configuration changes

† Human arterial blood can absorb over 50 times more oxygen than can water, and venous blood can absorb 20 times more CO_2 than water can.

from high- to low-spin (see Table 25.1), and (b) the structure of haemoglobin.

As a result of intensive study, enough is known about the structure of haemoglobin to allow the broad principles of its operation to be explained. It is made up of 4 subunits, each of which consists of a protein (globin), in the form of a folded helix or spiral, attached to 1 iron-containing group (haem). The proteins are of two types, one denoted as α consists of 141 amino acids, the other denoted as β consists of 146 amino acids. The polar groups of each protein are on the outside of the structure leaving a hydrophobic interior. The haem group, which is held in a protein "pocket" is therefore in a hydrophobic environment. Within the haem group the iron is coordinated to 4 nitrogen atoms of the planar group known as protoporphyrin IX (PIX). In the case of deoxyhaemoglobin the Fe^{II} , being high-spin, is too large to fit easily inside the hole provided by the porphyrin ring and is situated 55 pm above the ring which, in turn, is slightly bent into a domed shape, the better to accommodate the Fe^{II} . The fifth coordination site, away from the ring, is occupied by an imidazole nitrogen of a *proximal* histidine of the globin (Fig. 25.7). The vacant sixth site, below the ring, is essentially vacant, "reserved" for the O_2 but with another (*distal*) histidine restricting access. This is the so-called "tense" (deoxyT) form in which the 4 subunits of deoxyhaemoglobin are held together in an approximately tetrahedral arrangement by electrostatic $-NH_3^+ \dots \bar{O}OC-$ "salt bridges."

In order that O_2 may bond to the haem, the *distal* histidine must swing away but, once the O_2 is attached, it swings back to form a hydrogen bond with the O_2 . The Fe^{II} becomes low-spin and the oxyT form, which is still domed, "relaxes" to the planar oxyR form as the now smaller Fe^{II} slips into the ring which becomes planar again. When this occurs to one of the 4 subunits of deoxyhaemoglobin the movement of the Fe, and of the histidines attached to it, is communicated through the protein chains to the other subunits. This produces a rotation and linear movement of one $\alpha\beta$ pair w.r.t. the other which, crucially,

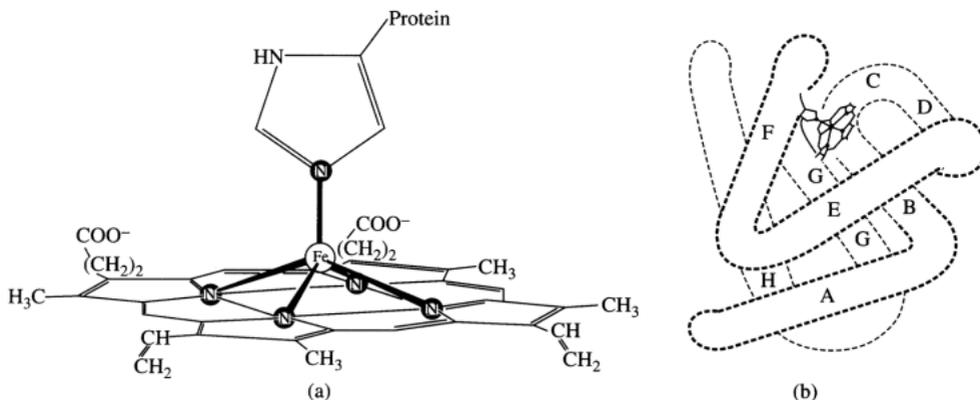


Figure 25.7 Haemoglobin: (a) The haem group, composed of the planar PIX molecule and iron, and shown here attached to the globin via an imidazole-nitrogen which completes the square pyramidal coordination of the Fe^{II} , and (b) myoglobin showing, diagrammatically, the haem group in a “pocket” formed by the folded protein. The globin chain is actually in the form of 8 helical sections, labelled A to H, and the haem is situated between the E and F sections. The 4 subunits of haemoglobin are similar.

converts the other 3 subunits to the deoxyR form, greatly increasing their affinity for O_2 . The effect of attaching one O_2 to haemoglobin is therefore to greatly increase its affinity for more.

Conversely, as O_2 is removed from oxyhaemoglobin the reverse conformational changes occur and successively decrease its affinity for oxygen. This is the phenomenon of *cooperativity*, and its physiological importance lies in the fact that it allows the efficient transfer of oxygen from oxyhaemoglobin to myoglobin. This is because myoglobin contains only 1 haem group and can be regarded crudely as a single haemoglobin subunit. It therefore cannot display a cooperative effect and at lower partial pressures of oxygen it has a greater affinity than haemoglobin for oxygen. This can be seen in Fig. 25.8 which shows that, while haemoglobin is virtually saturated with O_2 in the lungs, when it experiences the lower partial pressures of oxygen in the muscle tissue its affinity for O_2 has fallen off so much more rapidly than that of myoglobin that oxygen transfer ensues. Indeed, the actual situation is even more effective than this, because the affinity of haemoglobin for oxygen decreases when the pH is lowered (this is called the Bohr effect and arises in a complicated manner from the effect

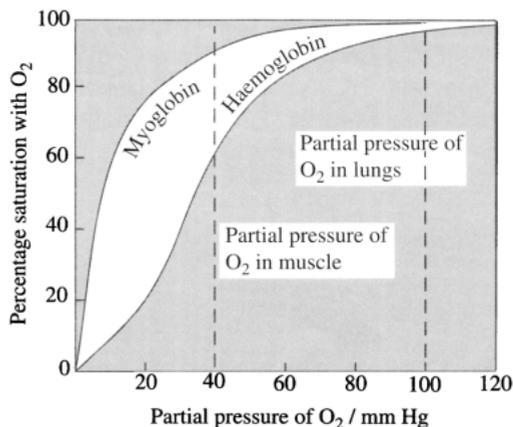


Figure 25.8 Oxygen dissociation curves for haemoglobin and myoglobin, showing how haemoglobin is able to absorb O_2 efficiently in the lungs yet transfer it to myoglobin in muscle tissue.

of pH on the salt bridges holding the subunits together). Since the CO_2 released in the muscle lowers the pH, it thereby facilitates the transfer of oxygen from the oxyhaemoglobin, and the greater the muscular activity the more the release of CO_2 helps to meet the increased demand for oxygen. Excess CO_2 is then removed from the tissue,

predominantly in the form of soluble HCO_3^- ions whose formation is facilitated by the protein chains of deoxyhaemoglobin which act as a buffer by picking up the accompanying protons.



The mode of bonding of the O_2 to Fe is important. In oxyhaemoglobin the hydrogen bonding to the *distal* histidine tilts the O_2 and produces an Fe–O–O angle of about 120° . This geometry (which hinders the formation of the Fe–O–Fe or Fe– O_2 –Fe bridge believed to be an intermediate in Fe^{II} to Fe^{III} oxidations) along with the hydrophobic environment which inhibits electron transfer, together prevent the oxidation of Fe^{II} which would destroy the haemoglobin.

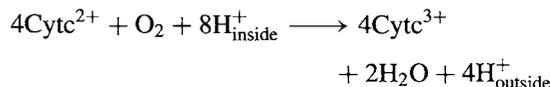
The poisoning effect of molecules such as CO and PF_3 (p. 495) arises simply from their ability to bond reversibly to haem in the same manner as O_2 , but much more strongly, so that oxygen transport is prevented. The cyanide ion CN^- can also displace O_2 from oxyhaemoglobin but its very much greater toxicity at small concentrations stems not from this but from its interference with the action of cytochrome a.

Cytochromes⁽⁴⁶⁾

The haem unit was evidently a most effective evolutionary development since it is found not only in the oxygen-transporting substances but also in electron transporters such as the cytochromes which are scattered widely throughout nature. There are three main types of cytochromes, a, b and c, members of each type being distinguished by subscripts, and their role is as intermediates in the metabolic oxidation of glucose by molecular oxygen. The iron of the haem group is attached to an associated protein by an imidazole N just as in haemoglobin and myoglobin. In most a and b cytochromes the sixth coordination site of the iron is also occupied by an imidazole N but, in type c and some type b cytochromes, it is occupied by a tightly bound

S from a methionine residue rendering these cytochromes inert not only to oxygen but also to the poisons which affect oxygen carriers. Electron transfer is effected in a series of steps, in each of which the oxidation state of the iron which is normally in a low-spin configuration oscillates between +2 and +3. Since the cytochromes are involved in the order b,c,a, the reduction potential of each step is successively increased (Table 25.8), so forming a “redox gradient”. This allows energy from the glucose oxidation to be released gradually and to be stored in the form of adenosine triphosphate (ATP) (see also p. 528).

The link with the final electron acceptor, O_2 , is the enzyme cytochrome c oxidase which spans the inner membrane of the mitochondrion. It consists of cytochromes a and a_3 along with two, or possibly three, Cu atoms. The details of its action are not fully established but the overall reaction catalysed by the enzyme is:



indicating the transport not only of electrons but also of protons across the mitochondrial membrane. As the end member of the redox gradient it differs from the other members in bonding O_2 directly and so being extremely susceptible to poisoning by CN^- .

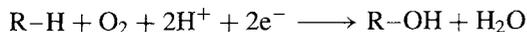
Another important group of cytochromes, found in plants, bacteria and animals is cytochrome P-450, so-called because of the absorption at 450 nm characteristic of their complexes with CO. Their function is to activate

Table 25.8 Reduction potentials of some iron proteins

Iron protein	Oxidation states of Fe	E°/V
Cytochrome a_3	$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$	0.4
Cytochrome b	$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$	0.02
Cytochrome c	$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$	0.26
Rubredoxin	$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$	–0.06
2-Fe plant ferredoxins	$\text{Fe}^{\text{III}}/\text{fractional}$	–0.40
4-Fe bacterial ferredoxins	Fractional/fractional	–0.37
8-Fe bacterial ferredoxins	Fractional/fractional	–0.42

⁴⁶ See p. 206–8 of ref. 45.

O₂ sufficiently to facilitate its cleavage and so catalyse the reaction,



thus making R-H water soluble and aiding its elimination. They have molecular weights in the region of 50 000 and O₂ bonds to the haem in a manner similar to that in haemoglobin but with cysteine instead of histidine in the *proximal* position. The S donor atom of the cysteine is helpful in stabilizing an Fe^{IV}=O group the oxygen of which is then inserted into the R-H bond.

Iron-sulfur proteins^(47,48)

In spite of the obvious importance and diversity of haem proteins, comparable functions, especially that of electron transfer, are performed by non-haem iron proteins (NHIP).[†] These too are widely distributed (well over 100 are now known), different types being involved in nitrogen fixation (p. 1035) and photosynthesis as well as in the metabolic oxidation of sugars prior to the involvement of the cytochromes mentioned above. The NHIP responsible for electron transfer are the iron-sulfur proteins which are of relatively low molecular weight (6000–12 000) and contain 1, 2, 4 or 8 Fe atoms which, in all the structures which have been definitely established, are each coordinated to 4 S atoms in an approximately tetrahedral manner. As a consequence of the small ligand fields associated in the tetrahedral coordination, these all contain iron in the high-spin configuration. Nearly all NHIP are notable for reduction potentials in the unusually low range –0.05 to –0.49 V (Table 25.8), indicating their ability to act as reducing agents at the low-potential end of biochemical processes.

The simplest NHIP is rubredoxin, in which the single iron atom is coordinated (Fig. 25.9a) to 4 S atoms belonging to cysteine residues in the protein chain. It differs from the other Fe-S proteins in having no labile sulfur (i.e. inorganic sulfur which can be liberated as H₂S by treatment with mineral acid; sulfur atoms of this type are not part of the protein, but form bridges between Fe atoms.)

NHIP with more than one Fe are conveniently classified as [2Fe–2S], [3Fe–4S] and [4Fe–4S] types. The first of these, the so-called plant ferredoxins act as 1-electron transfer agents and contain 2 Fe atoms joined by S bridges with terminal cysteine groups (Fig. 25.9b). The 2 Fe atoms in the oxidized form are high-spin Fe(III) but very low magnetic moments are observed because of strong spin-spin interaction via the bridging atoms. The iron centres are not equivalent however, and esr evidence suggests that in the reduced form they exist as Fe(III) and Fe(II) rather than both having a fractional oxidation state of +2.5.

The existence of [3Fe–4S] ferredoxins has been established by Mössbauer spectroscopy only comparatively recently. The cluster consists essentially of the cubane [4Fe–4S] with one corner removed, the irons being high-spin Fe(III) in the oxidized form and Fe(II) + 2Fe(III) in the reduced. The most common and most stable of the ferredoxins, however, are the [4Fe–4S] type (Fig. 25.9c). In these clusters the 4 × Fe and 4 × S atoms form 2 interpenetrating tetrahedra which together make up a distorted cube in which each Fe atom is additionally coordinated to a cysteine sulfur to give it an approximately tetrahedral coordination sphere. The cluster, like the 2-Fe dimer, acts as a 1-electron transfer agent so that an 8-Fe protein, in which there are two [4Fe–4S] units with centres about 1200 pm apart can effect a 2-electron transfer. Why 4 Fe atoms are required to transfer 1 electron is not obvious. Synthetic analogues, prepared by reacting FeCl₃, NaHS and an appropriate thiol (or still better FeCl₃, elemental sulfur and the Li salt of a thiol), have properties similar to those of the natural proteins and have been used

⁴⁷ R. CAMMACK (ed.) *Adv. Inorg. Chem.* **38**, 1992, 487 pp. Whole volume devoted to Fe-S proteins.

⁴⁸ I. BERTINI, S. CUIRLI and C. LUCHINAT, *Structure and Bonding*, **83**, 1–53 (1995).

[†] The oxygen-carrying function is performed in some invertebrates by haemerythrin which, in spite of its name, does not contain haem. It is a diiron-oxygen protein. See K. K. ANDERSON and A. GRÄLUND, *Adv. Inorg. Chem.* **43**, 359–408 (1995).

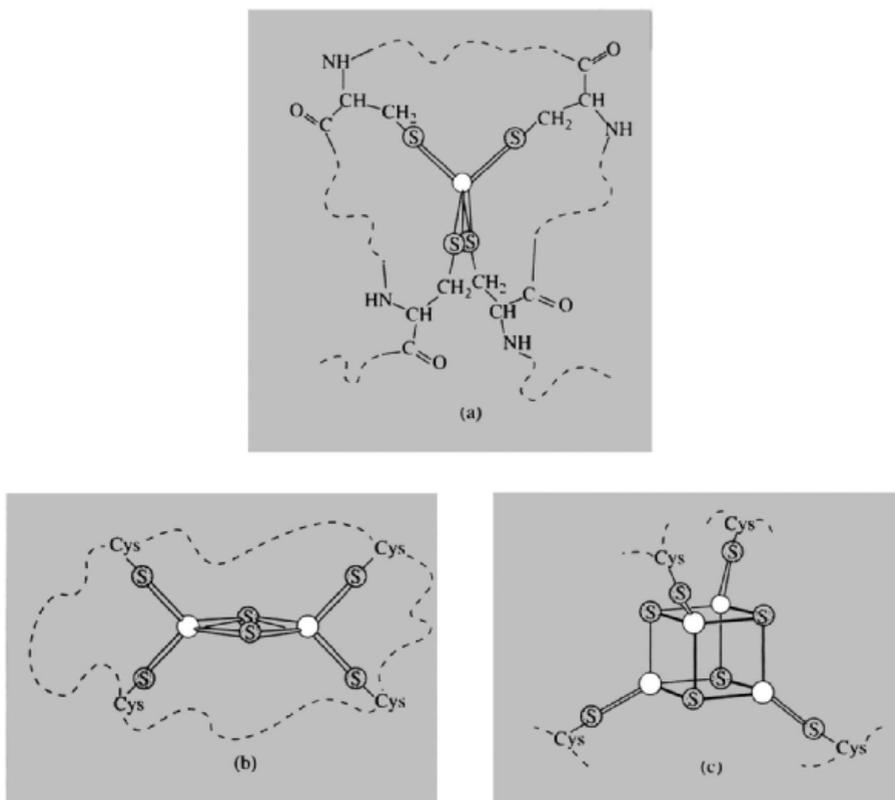
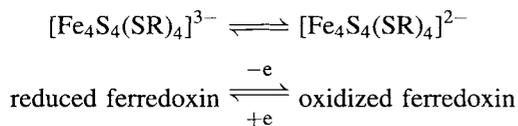


Figure 25.9 Some non-haem iron proteins: (a) rubredoxin in which the single Fe is coordinated, almost tetrahedrally, to 4 cysteine-sulfurs, (b) plant ferredoxin, $[\text{Fe}_2\text{S}_2(\text{S-Cys})_4]$, (c) $[\text{Fe}_4\text{S}_4(\text{S-Cys})_4]$ cube of bacterial ferredoxins. (This is in fact distorted, the Fe_4 and S_4 making up the two interpenetrating tetrahedra, of which the latter is larger than the former).

extensively in attempts to solve this problem.⁽⁴³⁾ The esr, electronic, and Mössbauer spectra, as well as the magnetic properties of the synthetic $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ anions, are similar to those of the reduced ferredoxins, whose redox reaction is therefore mirrored by:



This indicates a change in the formal oxidation state of the iron from +2.25 to +2.5, and mixed $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ species have been postulated. However, it appears likely that these clusters are best regarded as electronically delocalized systems in which all the Fe atoms are equivalent.

4-Fe proteins are also known in which the diamagnetic, oxidized $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ can be further oxidized at high potentials of about +0.35 V (hence “high potential iron sulfur proteins”, HIPIP) to paramagnetic ($S = 1/2$), $[\text{Fe}_4\text{S}_4(\text{SR})_4]^-$ species. Structural details and, indeed, biological function are still unclear.

Other non-haem proteins, distinct from the above iron-sulfur proteins are involved in the roles of iron transport and storage. Iron is absorbed as Fe^{II} in the human duodenum and passes into the blood as the Fe^{III} protein, transferrin.⁽⁴⁹⁾ The Fe^{III} is in a distorted octahedral environment consisting of $1 \times \text{N}$, $3 \times \text{O}$ and a chelating carbonate ion which

⁴⁹ E. N. BAKER, *Adv. Inorg. Chem.* **41**, 389–463 (1994)

apparently “locks” the iron into the binding site. This has a stability constant sufficiently high for the uncombined protein to strip Fe^{III} from such stable complexes as those with phosphate and citrate ions, and so it very efficiently scavenges iron from the blood plasma. The iron is then transported to the bone marrow where it is released from the transferrin (presumably after the temporary reduction of Fe^{III} to Fe^{II} since the latter's is a much less-stable complex), to be stored as ferritin, prior to its incorporation into haemoglobin. Ferritin is a water-soluble material consisting of a layer of protein encapsulating iron(III) hydroxyphosphate to give an overall iron content of about 20%.

25.3.6 Organometallic compounds⁽⁵⁰⁾

Within the field of organometallic chemistry, iron has long held a dominant position, and the last decade has seen explosive growth in the organic chemistry of ruthenium and osmium, particularly in the cluster chemistry⁽⁵¹⁾ of osmium carbonyls. Carbonyls and metallocenes occupy dominant positions in this diverse field. Thus, although alkyls and aryls are known, they are only obtained with bulky groups which cannot undergo β -elimination (p. 925) or if the M–C σ bonds are stabilized by π -bonding ligands such as CO and P-donors.

Carbonyls (see p. 926)

Having the d^6s^2 configuration, the elements of this triad are able to conform with the 18-electron rule by forming mononuclear carbonyls of the type $\text{M}(\text{CO})_5$. These are volatile liquids which can be prepared by the direct action of CO on the powdered metal (Fe^{\dagger} and Ru) or by the action of

CO on the tetroxide (Os), in each case at elevated temperatures and pressures.

$\text{Fe}(\text{CO})_5$ is a highly toxic substance discovered in 1891, the only previously known metal carbonyl being $\text{Ni}(\text{CO})_4$. Like its thermally unstable Ru and Os analogues, its structure is trigonal bipyramidal (Fig. 25.10a) but its ^{13}C nmr spectrum indicates that all 5 carbon atoms are equivalent and this is explained by the molecules' fluxional behaviour (p. 914).

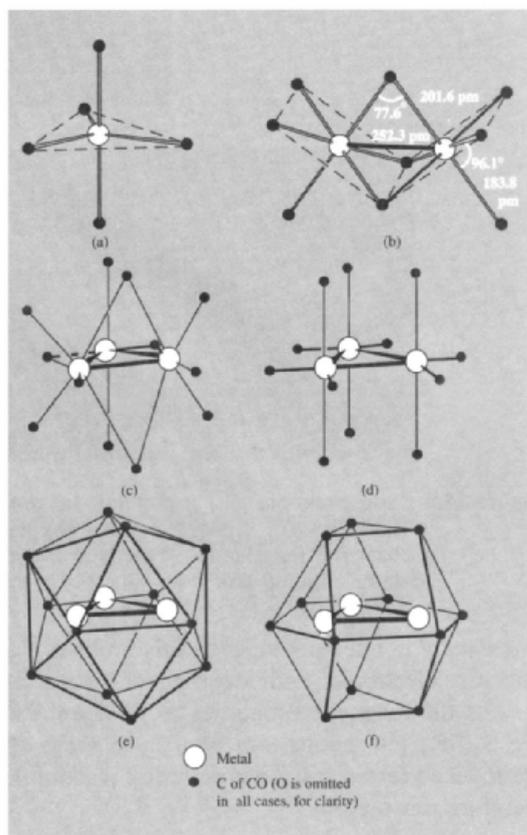


Figure 25.10 Some carbonyls of Fe, Ru and Os: (a) $\text{M}(\text{CO})_5$; $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$. (b) $\text{Fe}_2(\text{CO})_9$; $\text{Fe}-\text{Fe} = 252.3$ pm. (c) $\text{Fe}_3(\text{CO})_{12}$; $1 \text{ Fe}-\text{Fe} = 256$ pm, $2 \text{ Fe}-\text{Fe} = 268$ pm. (d) $\text{M}_3(\text{CO})_{12}$; $\text{M} = \text{Ru}, \text{Os}$, $\text{Ru}-\text{Ru} = 285$ pm, $\text{Os}-\text{Os} = 288$ pm. (e) and (f) are alternative representations of (c) and (d) emphasizing respectively the icosahedral and anti-cubeoctahedral arrangements of the CO ligands.

⁵⁰ P. L. PAUSON, Chap. 4 in *Chemistry of Iron*, pp. 73–170, Blackie, London, 1993.

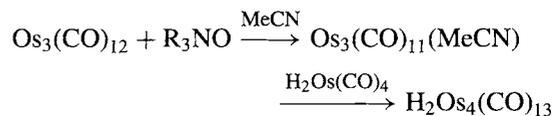
⁵¹ A. J. AMOROSO, L. H. GADE, B. F. G. JOHNSON, J. LEWIS, P. R. RAITHY and W. T. WONG, *Angew. Chem. Int. Edn. Engl.* **30**, 107–9 (1991); B. H. S. THIMMAPPA, *Coord. Chem. Revs.* **143**, 1–35 (1995).

[†] The presence of $\text{Fe}(\text{CO})_5$ in commercial cylinders of carbon monoxide at levels of 50 ppm has been reported (*Chem. in Brit.* **28**, 517 (1992)).

Exposure of $\text{Fe}(\text{CO})_5$ in organic solvents to ultraviolet light produces volatile orange crystals of the enneacarbonyl, $\text{Fe}_2(\text{CO})_9$. Its structure consists of two face-sharing octahedra (Fig. 25.10b). An electron count shows that the dimer has a total of 34 valence electrons, i.e. 17 per iron atom. The observed diamagnetism is therefore explained by the presence of an Fe–Fe bond which is consistent with an interatomic separation virtually the same as in the metal itself. It is of interest that Ru and Os counterparts of $\text{Fe}_2(\text{CO})_9$ are not only thermally less stable (the former especially so) but apparently are also structurally different, having an M–M bond supported by only 1 CO bridge. The carbonyls, which are produced along with the pentacarbonyls of Ru and Os and were initially thought to be enneacarbonyls, are in fact trimers, $\text{M}_3(\text{CO})_{12}$, which also differ structurally from $\text{Fe}_3(\text{CO})_{12}$ (Fig. 25.10c to f). This dark-green solid, which is best obtained by oxidation of $[\text{FeH}(\text{CO})_4]^-$ (see below), has a triangular structure in which two of the iron atoms are bridged by a pair of carbonyl groups, and can be regarded as being derived from $\text{Fe}_2(\text{CO})_9$ by replacing a bridging CO with $\text{Fe}(\text{CO})_4$. The Ru and Os compounds (orange and yellow respectively), on the other hand, have a more symmetrical structure in which all the metal atoms are equivalent and are held together solely by M–M bonds. It has been suggested (Johnson's Ligand Polyhedral Model⁽⁵²⁾) that the structure of the iron compound is determined not by the major bonding forces but by the interactions between the 12 CO ligands which in fact form an icosahedral array. This accommodates an Fe_3 triangle with Fe–Fe distances similar to those in the metal, but not the larger Ru_3 and Os_3 triangles which force the ligands to adopt the less dense anticubeoctahedral form. As with the mononuclear carbonyl, the ^{13}C nmr spectrum of the iron compound indicates C atom equivalence but this can be accounted for by oscillation of the Fe_3 triangle without disruption of the icosahedral

array of CO ligands.⁽⁵²⁾ In solution, a non-bridged isomer is formed, different from the Ru_3 and Os_3 carbonyls and again probably retaining the icosahedral arrangement of ligands.

The chemistry of these carbonyls, especially those of Os, is extensive and displays an astonishing structural diversity which has been exploited particularly by the Cambridge group of J. Lewis.⁽⁵³⁾ $\text{Os}_3(\text{CO})_{12}$ is the starting material for the preparation of other Os_3 species and for clusters of higher nuclearity.⁽⁵⁴⁾ It is itself prepared by the reaction of OsO_4 and CO under high pressure and is more stable than its Ru counterpart, which has a weaker M–M bond enthalpy (76 kJ mol^{-1} compared to 94 kJ mol^{-1} in $\text{Os}_8(\text{CO})_{12}$) and fragments rather easily. Thermolysis of $\text{Os}_3(\text{CO})_{12}$ at 200°C yields mainly $\text{Os}_6(\text{CO})_{18}$ along with smaller quantities of $\text{Os}_5(\text{CO})_{16}$, $\text{Os}_7(\text{CO})_{21}$ (Fig. 25.11) and $\text{Os}_8(\text{CO})_{23}$. By careful adjustment of conditions, thermal and photochemical methods can give good yields of selected products but more rational methods have also been developed. Nucleophilic attack, by amine oxides for instance, removes CO (as CO_2) allowing a vacant site to be filled by a donor solvent such as MeCN. The products may themselves be pyrolysed or the solvent molecules replaced by metal nucleophiles such as $\text{H}_2\text{Os}(\text{CO})_4$:



Carbonyl hydrides and carbonylate anions

The treatment of iron carbonyls with aqueous or alcoholic alkali can, by varying the conditions, be used to produce a series of interconvertible carbonylate anions: $[\text{HFe}(\text{CO})_4]^-$, $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{HFe}_3(\text{CO})_{11}]^-$ and $[\text{Fe}_4(\text{CO})_{13}]^{2-}$. Of these the first has a distorted trigonal bipyramidal structure with axial H, the second

⁵² B. F. G. JOHNSON and Y. V. ROBERTS, *Polyhedron* **12**, 977–90 (1993).

⁵³ J. LEWIS, *Chem. in Brit.* **24**(5), 795–800 (1988).

⁵⁴ A. J. DEEMING, *Adv. Organomet. Chem.* **26**, 1–96 (1986).

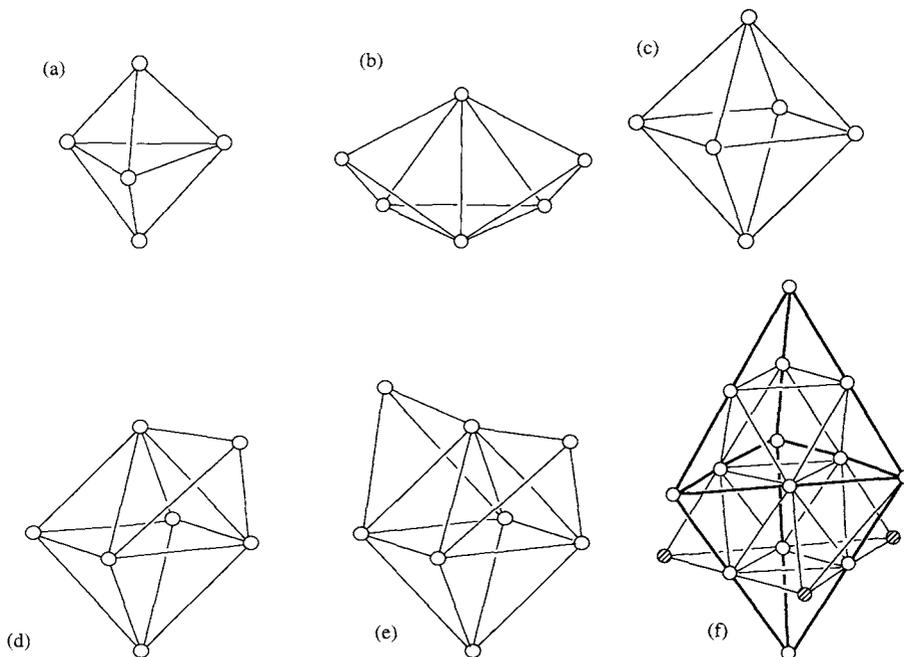


Figure 25.11 Metal frameworks of some high-nuclearity binary carbonyl and carbonylate clusters of osmium: (a) $\text{Os}_5(\text{CO})_{16}$ (trigonal bipyramid); (b) $\text{Os}_6(\text{CO})_{18}$ (bicapped tetrahedron, or capped trigonal bipyramid); (c) $[\text{Os}_6(\text{CO})_{18}]^{2-}$ (octahedron); (d) $\text{Os}_7(\text{CO})_{21}$ (capped octahedron); (e) $[\text{Os}_8(\text{CO})_{22}]^{2-}$ (bicapped octahedron); (f) $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ (3 shaded atoms cap an Os_{14} trigonal bipyramid).

is isoelectronic and isostructural with $\text{Ni}(\text{CO})_4$, the third is isoelectronic with $\text{Co}_2(\text{CO})_8$ and isostructural with the isomer containing no CO bridges, while the trimeric and tetrameric anions have the cluster structures shown in Fig. 25.12. The related ruthenium complexes $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$, are of interest as possible catalysts for the “water-gas shift reaction”.[†]

[†] Water-gas is produced by the high-temperature reaction of water and C:



and is therefore a mixture of H_2O , CO and H_2 . By suitably adjusting the relative proportions of CO and H_2 , “synthesis gas” is obtained which can be used for the synthesis of methanol and hydrocarbons (the Fischer–Tropsch process). It is this catalytically controlled adjustment:



which is the water-gas shift reaction (WGSR) (see p. 421).

Reduction of the pH of solutions of carbonylate anions yields a variety of protonated species and, from acid solutions, carbonyl hydrides such as the unstable, gaseous $\text{H}_2\text{Fe}(\text{CO})_4$ and the polymeric liquids $\text{H}_2\text{Fe}_2(\text{CO})_8$ and $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ are liberated. The use of ligand-replacement reactions to yield hydrides of higher nuclearity has already been noted.

Thermolysis of binary carbonyls or of their partially substituted derivatives, either under vacuum or in solutions, has been used to produce carbonyls and carbonylate anions with an unparalleled range of structures (Fig. 25.11). The Ru chemistry, though less well developed, mostly parallels that of Os.⁽⁵⁵⁾ These compounds are interesting not only for their catalytic potential but also for the preparative and theoretical problems they pose. Almost all these

⁵⁵ See for instance L. MA, G. WILLIAMS and J. R. SHAPLEY, *Coord. Chem. Revs.* **128**, 261–84 (1993).

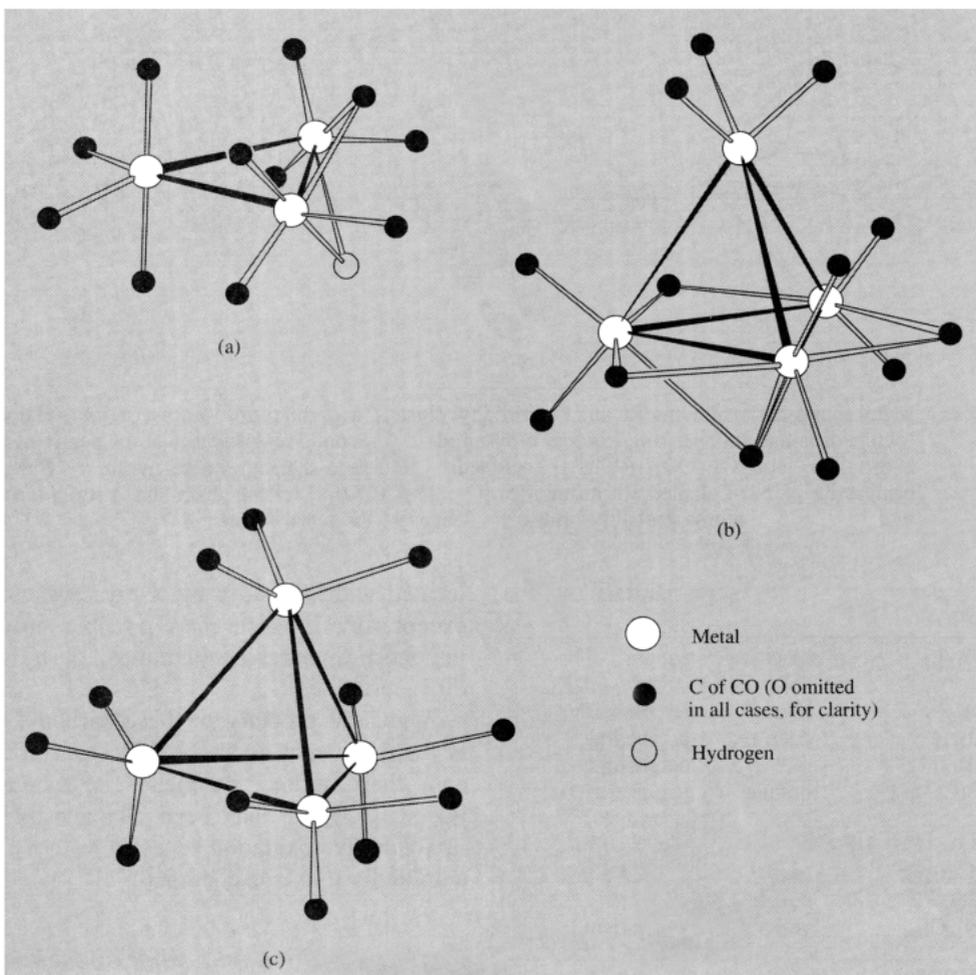


Figure 25.12 Some small carbonylate anion clusters of Fe, Ru and Os: (a) $[\text{HM}_3(\text{CO})_{11}]^-$; M = Fe, Ru. (b) $[\text{Fe}_4(\text{CO})_{13}]^{2-}$. (c) $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$. [The H atoms are not shown in (c) because this ion exists in two isomeric forms: (i) the 3 H atoms bridge the edges of a single face of the tetrahedron, and (ii) the 3 H atoms bridge three edges of the tetrahedron which do not form a face.]

polyhedral clusters are networks of triangular faces, are diamagnetic and have structures which can be rationalized by electron-counting arguments. However, in applying these rules it has to be noted that where an $\text{M}(\text{CO})_3$ group “caps” a triangular face it has no effect on the skeletal electron count of the central polyhedron. Nor do such rules predict structures *precisely*. The $[\text{H}_2\text{M}_6(\text{CO})_{18}]$, $[\text{HM}_6(\text{CO})_{18}]^-$ and $[\text{M}_6(\text{CO})_{18}]^{2-}$ clusters, for instance, while being stoichiometrically the same for M = Ru and M =

Os, and having the same essentially octahedral skeletons, nevertheless differ appreciably in the disposition of the attached carbonyl groups. The incorporation of interstitial (encapsulated) atoms such as C, H, S, N, P and, more recently, B⁽⁵⁶⁾ is a widespread and frequently stabilizing feature of these clusters. Carbido clusters are the most common the C contributing 4 electrons

⁵⁶ C. E. HOUSECROFT, D. A. MATTHEWS, A. RHEINGOLD and X. SONG, *J. Chem. Soc., Chem. Commun.*, 842–3 (1992).

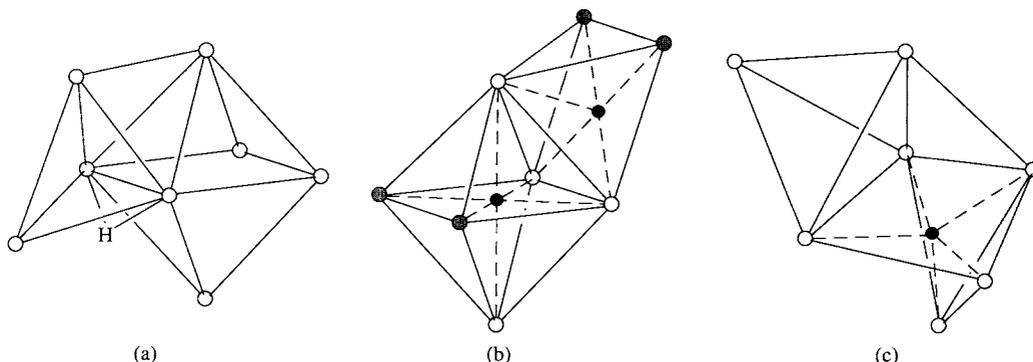


Figure 25.13 Metal frameworks of some Ru and Os carbonyl clusters with interstitial atoms. (a) $[\text{Ru}_8(\text{H})_2(\text{CO})_{21}]^{2-}$ (octahedron and face-sharing trigonal bipyramid); the second H is probably at the centre of the octahedron. (b) $[\text{Ru}_8(\text{C})_2(\text{CO})_{17}(\text{PPh}_2)_2]$ (octahedron and face-sharing square pyramid); PPh_2 ligands bridge the pairs of shaded Ru atoms. (c) $[\text{Os}_7(\text{H})_2\text{C}(\text{CO})_{19}]$ (tetrahedron and 3 irregularly spaced metal atoms); H atoms probably bridge two edges of the tetrahedron.

Table 25.9 Some metal carbonyl clusters with interstitial atoms

$[\text{Fe}_5\text{C}(\text{CO})_{15}]$	black	square pyramidal*
$[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$	black	octahedral
$[\text{Ru}_6\text{C}(\text{CO})_{17}]$	deep red	octahedral
$[\text{Ru}_6\text{H}(\text{CO})_{18}]^-$	red	octahedral
$[\text{Ru}_6(\text{H})_2\text{B}(\text{CO})_{18}]^-$	orange	trig. prism (H bridges) ⁽⁵⁵⁾
$[\text{Ru}_8\text{C}_2(\text{CO})_{17}(\text{PPh}_2)_2]$	black	Fig. 25.13b
$[\text{Ru}_8(\text{H})_2(\text{CO})_{21}]^{2-}$	black	Fig. 25.13a
$[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$	purple	bis oct.
$[\text{Os}_6\text{P}(\text{CO})_{18}\text{Cl}]$	yellow	trig. prism (Cl bridge)
$[\text{Os}_7\text{C}(\text{H})_2(\text{CO})_{19}]$	green	Fig. 25.13c
$[\text{Os}_8\text{C}(\text{CO})_{21}]$	purple	bicapped oct.
$[\text{Os}_9\text{H}(\text{CO})_{24}]$	brown	tricapped oct.
$[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$	pink-red	tetracapped oct.

*corresponding Ru and Os compounds are red and orange respectively.

to the formal electron count and originating possibly from the solvent or, more often, from cleavage of a CO ligand. This is especially true for Ru where the formation of carbido clusters is a general consequence of thermolysis. Some illustrative examples of these compounds are listed in Table 25.9.

The encapsulated atom usually occupies the centre of the polyhedron of metals (or its base in the case of square pyramids). Its position can be

located with precision by X-ray crystallography except for H, when it is possible only under the most favourable conditions, or by neutron diffraction.

A general property of these carbonyl clusters is their tendency to behave as electron "sinks", and their redox chemistry is extensive.⁽⁵⁷⁾ $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{n-}$ has been characterized in no less than five oxidation states ($n = 0-4$); though admittedly this is exceptional.

Carbonyl halides and other substituted carbonyls

Numerous carbonyl halides, of which the best known are octahedral compounds of the type $[\text{M}(\text{CO})_4\text{X}_2]$ are obtained by the action of halogen on $\text{Fe}(\text{CO})_5$, or CO on MX_3 ($\text{M} = \text{Ru}, \text{Os}$). Stepwise substitution of the remaining CO groups is possible by X^- or other ligands such as N, P and As donors.

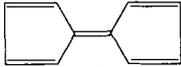
Direct substitution of the carbonyls themselves is of course possible. Besides Group 15 donor ligands, unsaturated hydrocarbons give especially interesting products. The iron carbonyl acetylenes provided early examples of the use of carbonyls in organic synthesis. From them a wide variety

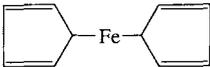
⁵⁷ S. R. DRAKE, *Polyhedron* 9, 455-74 (1990).

of cyclic compounds can be obtained as a result of condensation of coordinated acetylenes with themselves and/or CO. The complexes involving the acetylenes alone are usually unstable intermediates which are only separable when bulky substituents are incorporated on the acetylene. More usually, complexes of the condensed cyclic products are isolated. These ring systems include quinones, hydroquinones, cyclobutadienes and cyclopentadienones, the specific product depending on the particular iron carbonyl used and the precise conditions of the reaction.

Ferrocene and other cyclopentadienyls

Bis(cyclopentadienyl)iron, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$, or, to give it the more familiar name coined by M. C. Whiting, “ferrocene”, is the compound whose discovery in the early 1950s utterly transformed the study of organometallic chemistry.⁽²⁾ Yet the two groups of organic chemists who independently made the discovery, did so accidentally. P. L. Pauson and T. J. Kealy (*Nature* **168**, 1039 (1951)) were attempting to synthesize ful-

valene, , by reacting the Grignard reagent cyclopentadienyl magnesium bromide with FeCl_3 , but instead obtained orange crystals (mp 173°C) containing Fe^{II} and analysing for $\text{C}_{10}\text{H}_{10}\text{Fe}$. In a paper submitted simultaneously (*J. Chem. Soc.* 632 (1952)), S. A. Miller, T. A. Tebboth and J. F. Tremaine reported passing cyclopentadiene and N_2 over a reduced iron catalyst as part of a programme to prepare amines and they too obtained $\text{C}_{10}\text{H}_{10}\text{Fe}$.[†]

The initial structural formulation was , but the correct formulation, an unprecedented “sandwich” compound, was soon to follow. For this and for subsequent independent work in this field, G. Wilkinson and

E. O. Fischer shared the 1973 Nobel Prize for Chemistry.

The structure of ferrocene and an MO description of its bonding have already been given (p. 937). The rings are virtually eclipsed as they are in the analogous ruthenocene (light-yellow, mp 199°C) and osmocene (white, mp 229°C).

This is also the case in the decamethylmetallocenes of Ru and Os but not in the iron analogue which has a staggered conformation, presumably due to steric crowding around the smaller metal.

$[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2]$ satisfy the 18-electron rule (p. 1134) and are stable to air and water but are readily oxidized. From ferrocene the blue-green, paramagnetic ferricinium ion, $[\text{Fe}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)_2]^+$, is produced whereas the Ru and Os monocations are unstable, oxidizing further to $[\text{M}^{\text{IV}}(\eta\text{-C}_5\text{H}_5)_2]^{2+}$ or dimerizing to $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}^{\text{III}}\text{-M}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)_2]^{2+}$. The decamethylferricinium salt, $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2][\text{tcne}]$, (tcne = tetracyanoethylene) is a dark green crystalline material consisting of linear chains of alternating anions and cations.⁽⁵⁸⁾ It has the astonishing property of being a 1D molecular ferromagnet (with a saturation magnetisation greater than that of metallic iron itself on a molar basis), although the mechanism by which this originates is not yet settled.

The most notable chemistry of the biscyclopentadienyls results from the aromaticity of the cyclopentadienyl rings. This is now far too extensively documented to be described in full but an outline of some of its manifestations is in Fig. 25.14. Ferrocene resists catalytic hydrogenation and does not undergo the typical reactions of conjugated dienes, such as the Diels–Alder reaction. Nor are direct nitration and halogenation possible because of oxidation to the ferricinium ion. However, Friedel–Crafts acylation as well as alkylation and metallation reactions, are readily effected. Indeed, electrophilic substitution of ferrocene occurs with such facility compared to, say, benzene (3×10^6 faster) that some explanation is called for. It has been suggested that,

[†] In retrospect it seems likely that ferrocene was actually first prepared as volatile yellow crystals in the 1930s by chemists at Union Carbide who passed dicyclopentadiene through a heated iron tube, but the significance was not then realized.

⁵⁸ J. S. MILLER and A. J. EPSTEIN, *Chem. Brit.* **30**(6), 477–80 (1994).

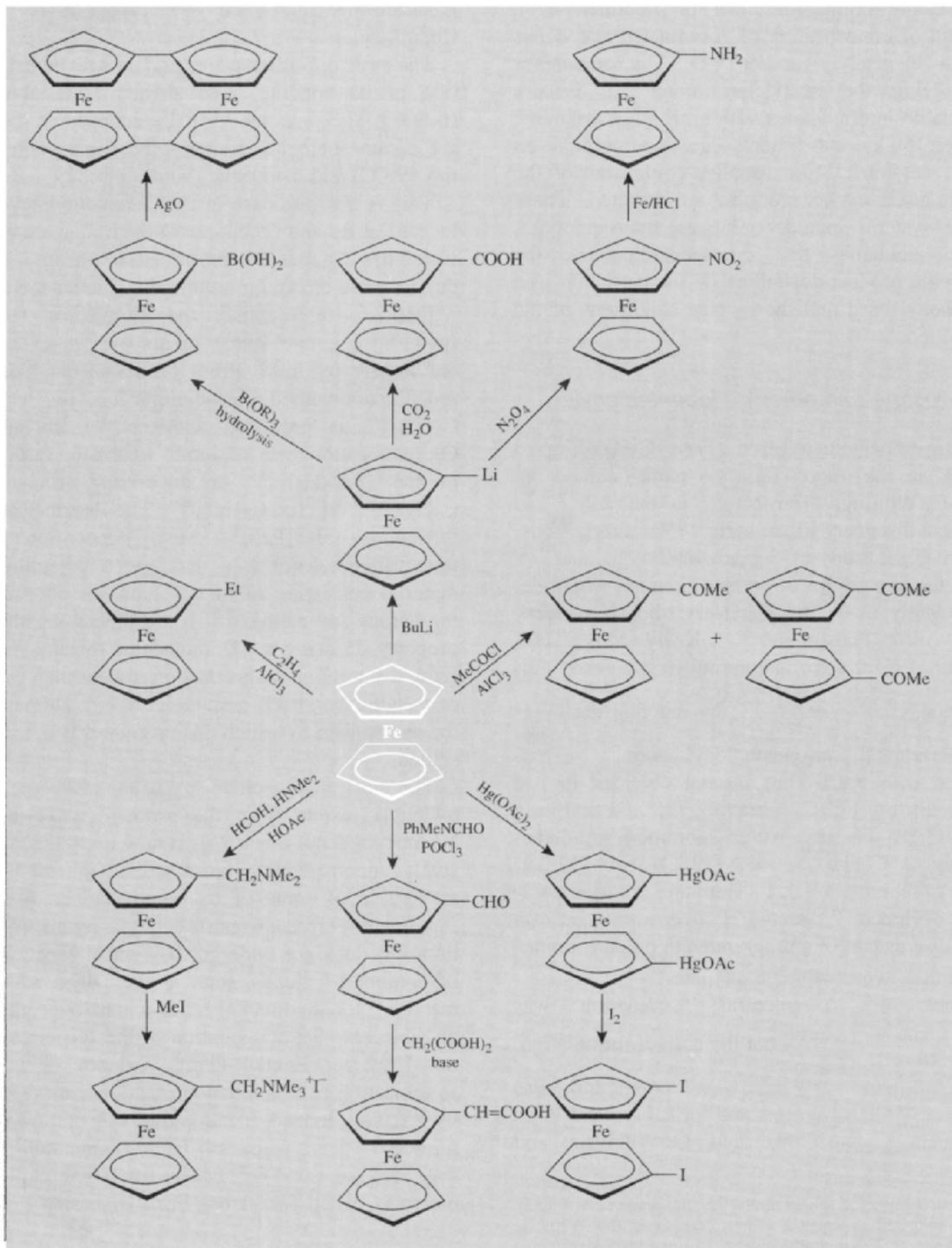
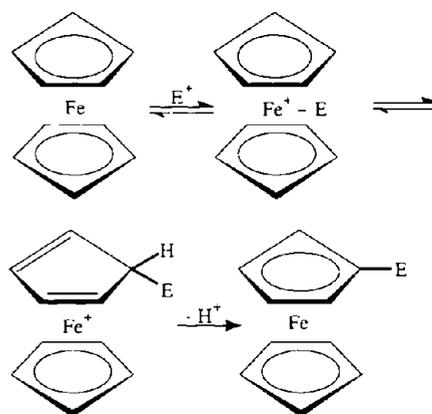


Figure 25.14 Some reactions of ferrocene.

in general, electrophilic substituents (E^+) interact with the metal atom and then transfer to the C_5H_5 ring with proton elimination. Similar reactions are possible for ruthenocene and osmocene but usually occur less readily, and it appears that reactivity decreases with increasing size of the metal (see adjacent Scheme).

Many interesting cyclopentadienyl iron carbonyls have been prepared, the best known being the purple dimer, $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ (Fig. 25.15a), prepared by reacting $Fe(CO)_5$ and dicyclopentadienyl at $135^\circ C$ in an autoclave. Diamagnetism and an Fe-Fe distance of only 249 pm indicate the presence of an Fe-Fe bond. Prolonged reaction of the same reactants produces the very dark green, tetrameric cluster compound, $[Fe(\eta^5-C_5H_5)(CO)_4]$ (Fig. 25.15b), which involves CO groups which are triply bridging and so give rise to an exceedingly low (1620 cm^{-1}) ν_{CO} absorption. $[Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2]$ (Fig. 25.15c) is also of note as



Scheme

an early example of a fluxional organometallic compound. The 1H nmr spectrum consists of only two sharp lines, one for each ring. A single line is expected for the pentahapto ring since all its protons are equivalent, but it is clear that some averaging process must be occurring for the

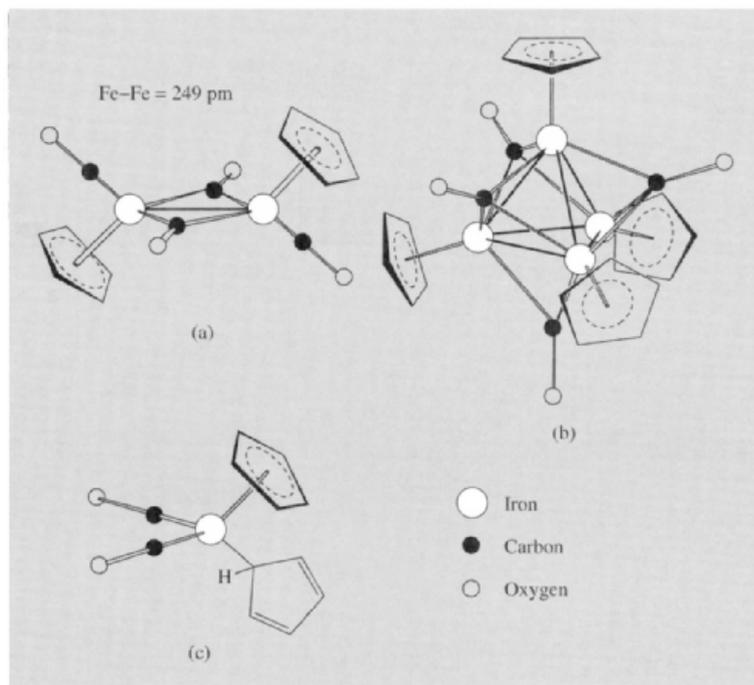


Figure 25.15 Some cyclopentadienyl iron carbonyls: (a) $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, (b) $[(\eta^5-C_5H_5)Fe(CO)_4]_4$ and (c) $[(\eta^1-C_5H_5)(\eta^5-C_5H_5)Fe(CO)_2]$.

non-equivalent protons of the monohapto ring to produce just one line. It is concluded that the point of attachment of the monohapto ring to the metal must change repeatedly and rapidly ("ring whizzing") thus averaging the protons.

Although the cyclopentadienyls dominate the "aromatic" chemistry of this group, bis(arene) compounds are also well established. They are able to satisfy the 18-electron rule as the dications, $[M(\text{arene})_2]^{2+}$ or by the two rings adopting different bonding modes; one η^6 the other η^4 .

Other aspects of the organometallic chemistry of this triad have been referred to in Chapter 19 but for fuller details more extensive reviews should be consulted.^(50,59)

⁵⁹G. WILKINSON, F. G. A. STONE and E. W. ABEL (eds.), *Comprehensive Organometallic Chemistry*, Vol. 4, Pergamon Press, Oxford, 1982, Iron, pp. 243–649, Ruthenium, pp. 650–965, Osmium, pp. 967–1064. E. W. ABEL, F. G. A. STONE and G. WILKINSON, (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 7, Iron, Ruthenium and Osmium, 1995.