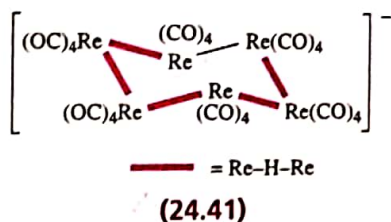## Limitations of total valence counting schemes

For some clusters such as Rh_x species, the number of electrons available may not match the number apparently required by the structure adopted. Two examples in rhodium carbonyl chemistry are $[Rh_5(CO)_{15}]^-$ and $[Rh_9(CO)_{19}]^{3-}$. The former possesses 76 valence electrons and yet has a trigonal bipyramidal Rh_5-core, for which 72 electrons are usual. However, a look at the Rh–Rh bond lengths reveals that six edges are in the range 292–303 pm, while three are 273–274 pm, indicating that the extra electrons have caused bond lengthening. In $[Rh_9(CO)_{19}]^{3-}$, 122 electrons are available but the Rh_9-core consists of two face-sharing octahedra for which 124 electrons are required by the scheme outlined above.[†] An example of an unexpected cluster structure is found for $[H_5Re_6(CO)_{24}]^-$. Rather than adopt a closed-cluster structure, the Re_6-unit in $[H_5Re_6(CO)_{24}]^-$ possesses a cyclohexane-like ring with a chair conformation (**24.41**). Each Re centre obeys the 18-electron rule (each $Re(CO)_4$ unit has $7 + (4 \times 2)$ valence electrons, two Re–Re bonds per Re provide 2 electrons, and the five H atoms with the 1– charge provide 1 electron per Re), but the preference for an open- rather than closed-cluster structure cannot be predicted.

(24.41)

These are but three examples of the limitations of electron-counting schemes. As more clusters are structurally characterized, further exceptions arise providing yet more challenges for the theorist.

Self-study exercise

X-ray crystallography confirms that $[Rh_6(P^iPr_3)_6H_{12}]^{2+}$ possesses an octahedral Rh_6-cage. Show that this cluster is 10 electrons short of the expected electron count.

24.7 Types of organometallic reactions

In this section, we introduce the main types of ligand transformations that take place at metal centres in organometallic compounds:

- ligand substitution;
- oxidative addition (including orthometallation);

[†] For detailed discussion, see: D.M.P. Mingos and D.J. Wales (1990) *Introduction to Cluster Chemistry*, Prentice Hall, Englewood Cliffs, NJ.

- reductive elimination;
- alkyl and hydrogen migration;
- β-hydrogen elimination;
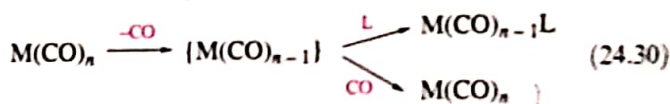- α-hydrogen abstraction.

Substitution of CO ligands

The substitution of a CO ligand by another 2-electron donor (e.g. PR_3) may occur by photochemical or thermal activation, either by direct reaction of the metal carbonyl and incoming ligand, or by first replacing a CO by a more labile ligand such as THF or MeCN. An example of the latter is the formation of $Mo(CO)_5(PPh_3)$ (eq. 24.29) which is most effectively carried out by first making the THF (**24.42**) adduct *in situ*.
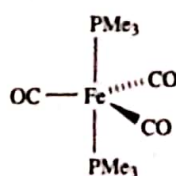

(24.42)

$$Mo(CO)_6 \xrightarrow[-CO]{\text{in THF, } h\nu} Mo(CO)_5(THF)$$
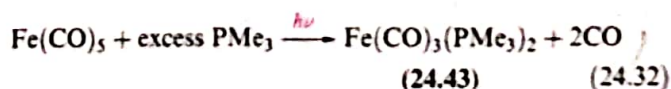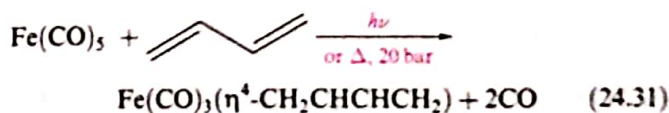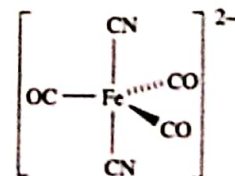$$\xrightarrow[-THF]{PPh_3} Mo(CO)_5(PPh_3) \quad (24.29)$$
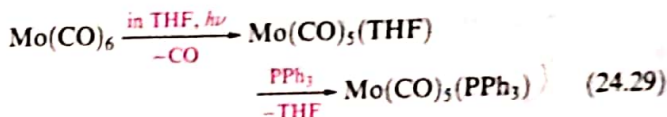
The substitution steps are *dissociative* (see Chapter 26). The outgoing ligand leaves, creating a 16-electron metal centre which is *coordinatively unsaturated*. The entry of a new 2-electron ligand restores the 18-electron count. Competition between ligands for coordination to the 16-electron centre may be countered by having the incoming ligand (L in eq. 24.30) present in excess.

$$M(CO)_n \xrightarrow{-CO} [M(CO)_{n-1}] \begin{cases} \xrightarrow{L} M(CO)_{n-1}L \\ \xrightarrow{CO} M(CO)_n \end{cases} \quad (24.30)$$

In reaction 24.31, the incoming ligand provides four electrons and displaces two CO ligands. Multiple substitution by 2-electron donors is exemplified by reaction 24.32.

$$Fe(CO)_5 + \text{(diene)} \xrightarrow[\text{or } \Delta, \text{ 20 bar}]{h\nu}$$
$$Fe(CO)_3(\eta^4\text{-}CH_2CHCHCH_2) + 2CO \quad (24.31)$$

$$Fe(CO)_5 + \text{excess } PMe_3 \xrightarrow{h\nu} Fe(CO)_3(PMe_3)_2 + 2CO \quad (24.32)$$
$$(24.43)$$
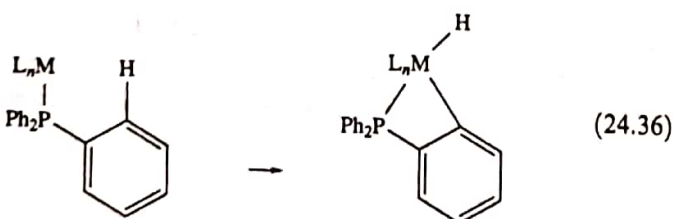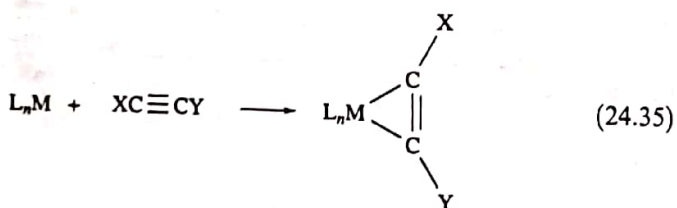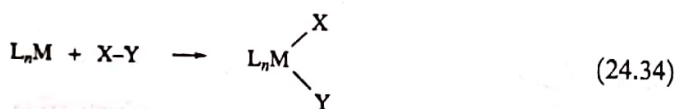

(24.43)   **(24.44)**

Mixed carbonyl/cyanido complexes of iron were described in Section 21.9. Their importance lies in their use as biomimetic models for [FeFe] and [NiFe]-hydrogenases (see Figs. 29.19 and 29.21). Photolysis of $Fe(CO)_5$ with [Et$_4$N]CN leads to substitution reaction 24.33, and introduces cyanido ligands in axial positions (structure **24.44**).

$$Fe(CO)_5 + 2[Et_4N]CN \xrightarrow{\text{in MeCN, } h\nu}$$
$$[Et_4N]_2[\textit{trans-}Fe(CO)_3(CN)_2] + 2CO$$
$$(24.33)$$
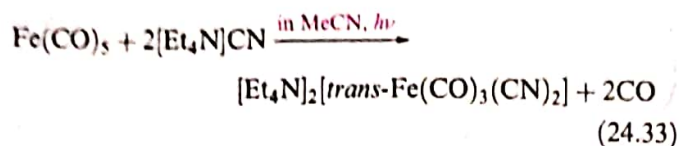
Oxidative addition

Oxidative addition reactions are very important in organometallic synthesis. Oxidative addition involves:

- the addition of a molecule XY with cleavage of the X–Y single bond (eq. 24.34), addition of a multiply-bonded species with reduction in the bond order and formation of a metallacycle (eq. 24.35), addition of a C–H bond in an *orthometallation* step (eq. 24.36) or a similar addition;
- oxidation of the metal centre by two units;
- increase in metal coordination number by 2.

$$L_nM + X-Y \longrightarrow L_nM{\overset{X}{\underset{Y}{\Big\langle}}} \qquad (24.34)$$

$$L_nM + XC\equiv CY \longrightarrow L_nM{\Big\langle}{\overset{X}{\underset{Y}{\overset{C}{\underset{C}{\|}}}}} \qquad (24.35)$$

$$(24.36)$$

Addition of O_2 to give an η^2-peroxido complex is related to reaction type 24.35. Each addition in eqs. 24.34–24.36 occurs *at a 16-electron metal centre*, taking it to an 18-electron centre in the product. Most commonly, the precursor has a d^8 or d^{10} configuration, e.g. Rh(I), Ir(I), Pd(0), Pd(II), Pt(0), Pt(II), and the metal must have an accessible higher oxidation state, e.g. Rh(III). (If the starting compound contains an 18-electron metal centre, oxidative addition cannot occur without loss of a 2-electron ligand as in reaction 24.37.)

$$Os(CO)_5 + H_2 \xrightarrow{\Delta, 80 \text{ bar}} H_2Os(CO)_4 + CO \qquad (24.37)$$
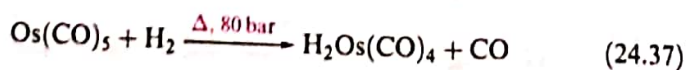
Many examples of the addition of small molecules (e.g. H_2, HX, RX) are known. The reverse of oxidative addition is *reductive elimination*, e.g. reaction 24.38, in which an acyl substituent is converted to an aldehyde.

$$H_2Co\{C(O)R\}(CO)_3 \longrightarrow HCo(CO)_3 + RCHO \qquad (24.38)$$

Oxidative addition initially gives a *cis*-addition product, but ligand rearrangements can occur and the isolated product may contain the added groups mutually *cis* or *trans*.

Alkyl and hydrogen migrations

Reaction 24.39 is an example of *alkyl migration*.
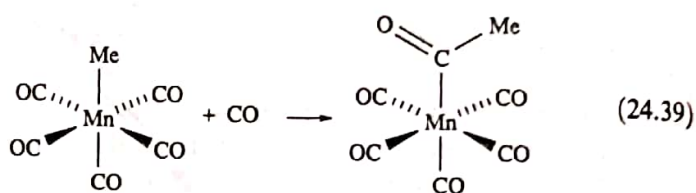
$$(24.39)$$

The reaction is also called *CO insertion* since the incoming CO molecule seems to have been inserted into the Mn–C$_{Me}$ bond: this name is misleading. If reaction 24.39 is carried out using ^{13}CO, *none* of the incoming ^{13}CO ends up in the acyl group or in the position *trans* to the acyl group; the isolated product is **24.45**.

(24.45)
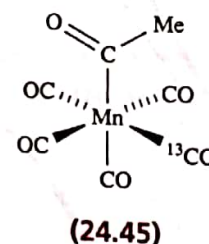
Reaction 24.39 involves the *intramolecular* transfer of an alkyl group to the C atom of a CO group which is *cis* to the original alkyl site. The incoming CO occupies the coordination site vacated by the alkyl group. Scheme 24.40 summarizes the process.
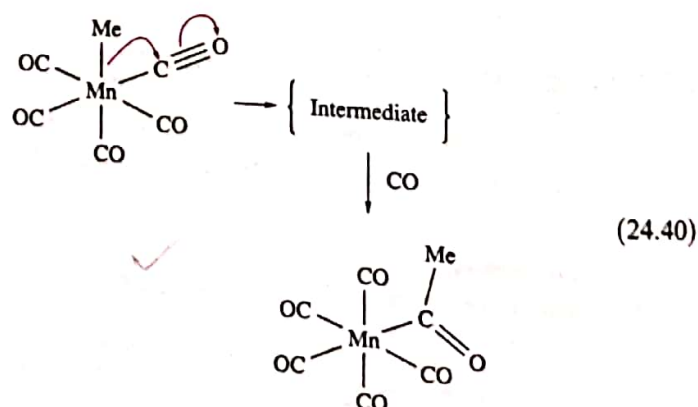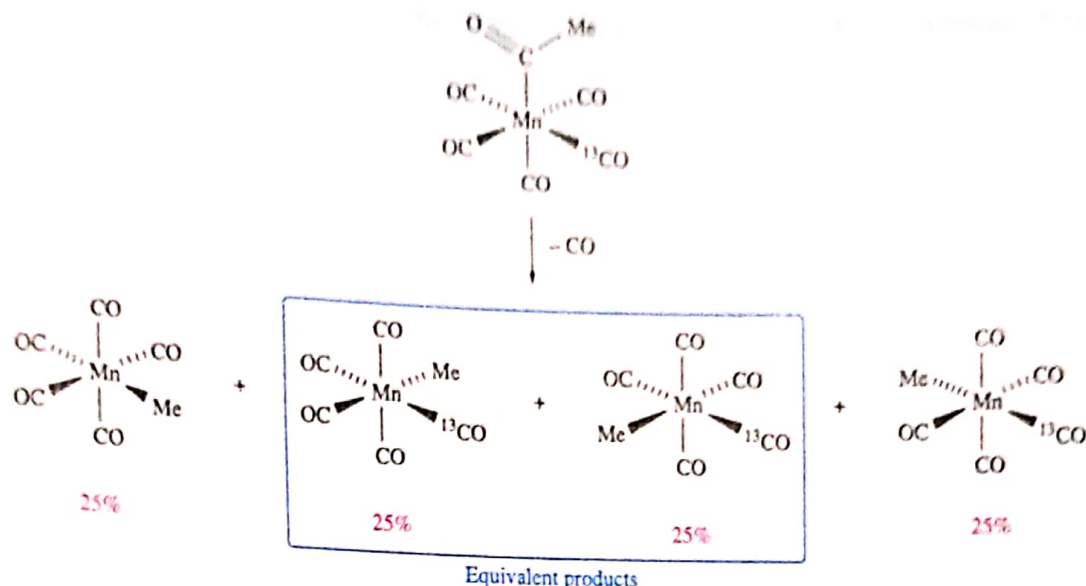

$$(24.40)$$

Fig. 24.15 The distribution of products from the decarbonylation of $Mn(CO)_4(^{13}CO)\{C(O)Me\}$ provides evidence for the migration of the Me group rather than movement of a CO molecule.

Scheme 24.40 implies that the intermediate is a coordinatively unsaturated species. In the presence of a solvent, S, such a species would probably be stabilized as $Mn(CO)_4(COMe)(S)$. In the absence of solvent, a 5-coordinate intermediate is likely to be stereochemically non-rigid (see Fig. 4.24 and discussion) and this is inconsistent with the observation of a selective *cis*-relationship between the incoming CO and acyl group. It has been concluded from the results of theoretical studies that the intermediate is stabilized by an *agostic* Mn–H–C interaction (structure **24.46**), the presence of which locks the stereochemistry of the system.[†]
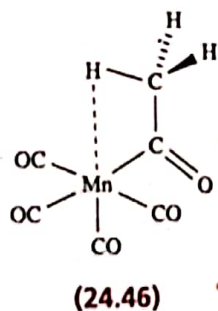

(24.46)

An *agostic* M–H–C interaction is a 3-centre 2-electron interaction between a metal centre, M, and a C–H bond in a ligand attached to M (e.g. structure **24.46**).

The migration of the methyl group is reversible and the decarbonylation reaction has been studied with the ^{13}C-labelled compound; the results are shown in Fig. 24.15.
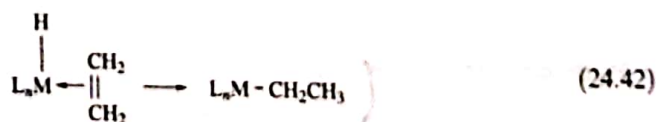
[†] For a more detailed discussion, see: A. Derecskei-Kovacs and D.S. Marynick (2000) *J. Am. Chem. Soc.*, vol. 122, p. 2078.

The distribution of the products is consistent with the migration of the Me group, and not with a mechanism that involves movement of the 'inserted' CO. The reaction products can be monitored using ^{13}C NMR spectroscopy.

The 'insertion of CO' into $M-C_{alkyl}$ bonds is well exemplified in organometallic chemistry, and one industrial example (eq. 24.41) is a step in the Monsanto process for the production of acetic acid (see Section 25.5).

$$[Rh(Me)(CO)_2I_3]^- + CO \longrightarrow [Rh(CMeO)(CO)_2I_3]^-$$
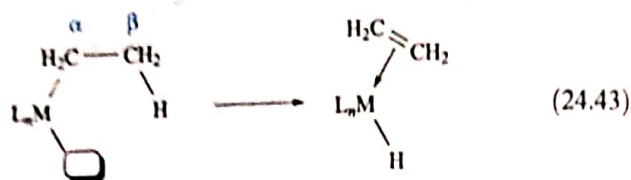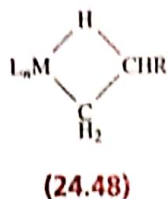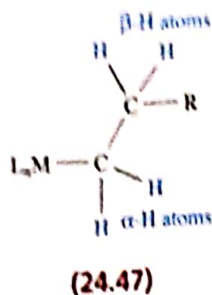(24.41)
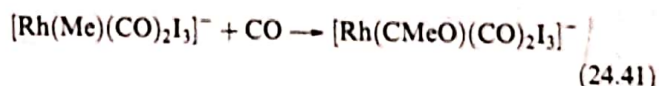
Alkyl migrations are not confined to the formation of acyl groups, and, for example, 'alkene insertion' involves the conversion of a coordinated alkene to a σ-bonded alkyl group. Equation 24.42 shows the migration of an *H atom*. Related alkyl migrations occur and result in *carbon chain growth* as exemplified in Fig. 25.16.

$$L_nM \leftarrow \begin{matrix} H \\ | \\ \| \\ \end{matrix} \begin{matrix} CH_2 \\ \\ CH_2 \end{matrix} \longrightarrow L_nM - CH_2CH_3$$
(24.42)

β-Hydrogen elimination

The reverse of reaction 24.42 is a *β-elimination* step. It involves the transfer of a β-H atom (structure **24.47**) from the alkyl group to the metal and the conversion of the σ-alkyl group to a π-bonded alkene, i.e. a C–H bond is activated. For β-elimination to occur, the metal centre must be unsaturated, with a vacant coordination site *cis* to the alkyl group (eq. 24.43). The first step is thought to

involve a cyclic intermediate **24.48** with an agostic M–H–C interaction.

(24.47)

(24.48)

$$L_nMCH_2CH_2R \longrightarrow L_nMH(\eta^2\text{-}RCH=CH_2)$$

$$\longrightarrow L_nMH + RCH=CH_2 \qquad (24.44)$$
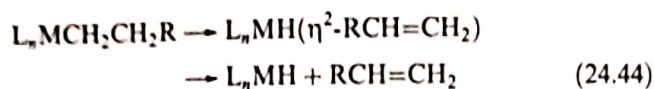
β-Elimination is responsible for the decomposition of some metal alkyl complexes (eq. 24.44), but the reaction may be hindered or prevented by:

- steric hindrance;
- having a coordinatively *saturated* metal centre as in $(\eta^5\text{-}C_5H_5)Fe(CO)_2Et$;
- preparing an alkyl derivative which does not possess a β-hydrogen atom.

Examples of σ-bonded alkyl groups that cannot undergo β-elimination because they lack a β-H atom are Me, CH_2CMe_3, CH_2SiMe_3 and CH_2Ph. Thus, methyl derivatives cannot decompose by a β-elimination route and are usually more stable than their ethyl analogues. This does not mean that methyl derivatives are necessarily stable. The coordinatively unsaturated $TiMe_4$ decomposes at 233 K, but the stability can be increased by the formation of 6-coordinate adducts such as $Ti(bpy)Me_4$ and $Ti(Me_2PCH_2CH_2PMe_2)Me_4$.

α-Hydrogen abstraction

Early *d*-block metal complexes containing one or two α-hydrogen atoms (see **24.47**) may undergo *α-hydrogen abstraction* to yield *carbene* (alkylidene, **24.49**) or *carbyne* (alkylidyne, **24.50**) complexes. The solid state structure of the product of reaction 24.45 confirms differences in the Ta–C bond lengths: 225 pm for Ta–C$_{alkyl}$ and 205 pm for Ta–C$_{carbene}$.

$$L_nM=CR_2 \qquad\qquad L_nM\equiv CR$$

(24.49)   (24.50)

(24.45)
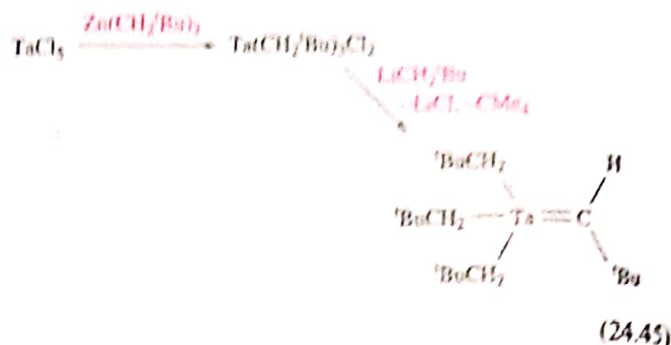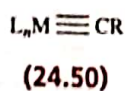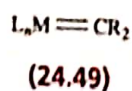
Abstraction of a second α-H atom gives a carbyne complex (e.g. reaction 24.46). Other routes to carbenes and carbynes are described in Section 24.12.

$$WCl_6 \xrightarrow[-CMe_4, \ LiCl]{LiCH_2CMe_3} W(\equiv CCMe_3)(CH_2CMe_3)_3 \quad (24.46)$$

Summary

A basic knowledge of the reaction types described in this section allows us to proceed to a discussion of the chemistry of selected organometallic complexes and (in Chapter 25) catalysis. Oxidative additions and alkyl migrations in particular are very important in the catalytic processes used in the manufacture of many organic chemicals. Selected important organometallic compounds used as catalysts are summarized in Box 24.2.

24.8 Metal carbonyls: selected reactions

The degradation of $Ni(CO)_4$ or $Fe(CO)_5$ to the respective metal and CO is a means of manufacturing high-purity nickel and iron. The thermal decomposition of $Ni(CO)_4$ is used in the Mond process to refine nickel (see eq. 21.4). Iron powder for use in magnetic cores in electronic components is produced by thermally decomposing $Fe(CO)_5$. The Fe particles act as nucleation centres for the production of particles up to 8 μm in diameter.

Reactions 24.18–24.23 illustrated conversions of neutral carbonyl compounds to carbonylate anions. Reduction by Na is typically carried out using Na/Hg amalgam. With Na in liquid NH_3, highly reactive anions can be formed (eqs. 24.47–24.50).

$$Cr(CO)_4(Me_2NCH_2CH_2NMe_2\text{-}N,N')$$

$$\xrightarrow{Na,\ liquid\ NH_3} Na_4[Cr(CO)_4] \qquad (24.47)$$

$$M_3(CO)_{12} \xrightarrow[low\ temp.]{Na,\ liquid\ NH_3} Na_2[M(CO)_4]$$

$$M = Ru, Os \qquad (24.48)$$

$$Ir_4(CO)_{12} \xrightarrow{Na,\ THF,\ CO\ (1\ bar)} Na[Ir(CO)_4] \qquad (24.49)$$