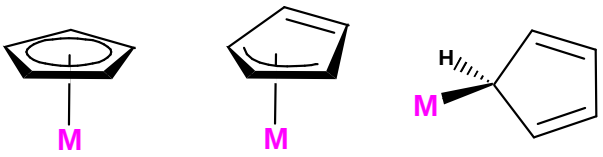
Chapter 24

Organometallic d-block

Organometallic compounds of the d-block

Compounds with element-carbon bonds involving metals from the d-block

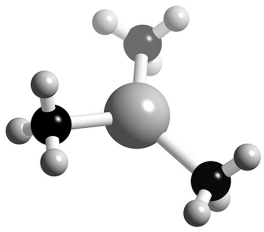
Hapticity of a ligand – the number of atoms that are directly bonded to the metal center



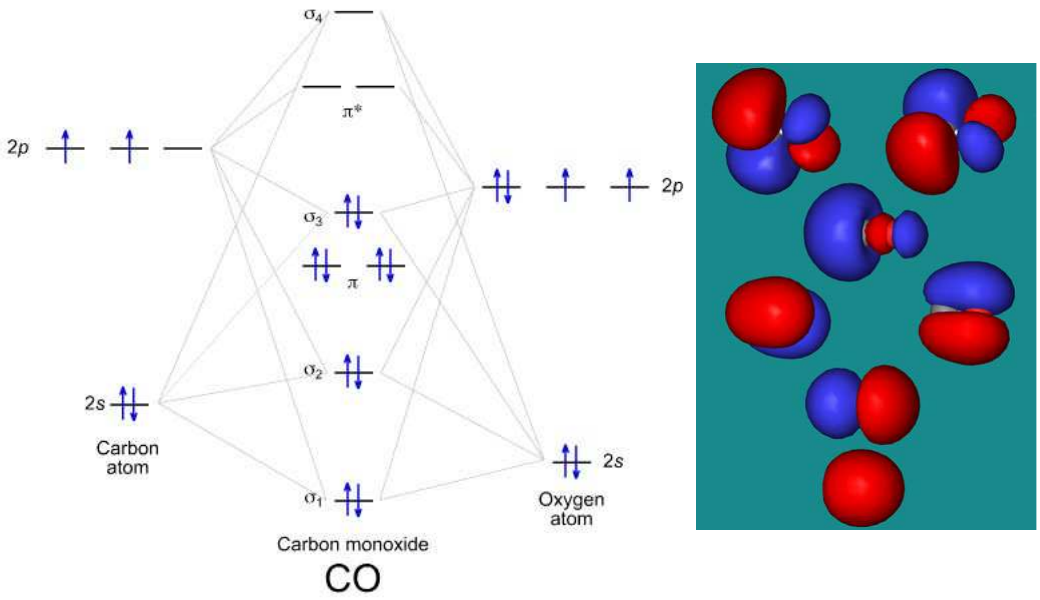
η^5 η^3 η^1

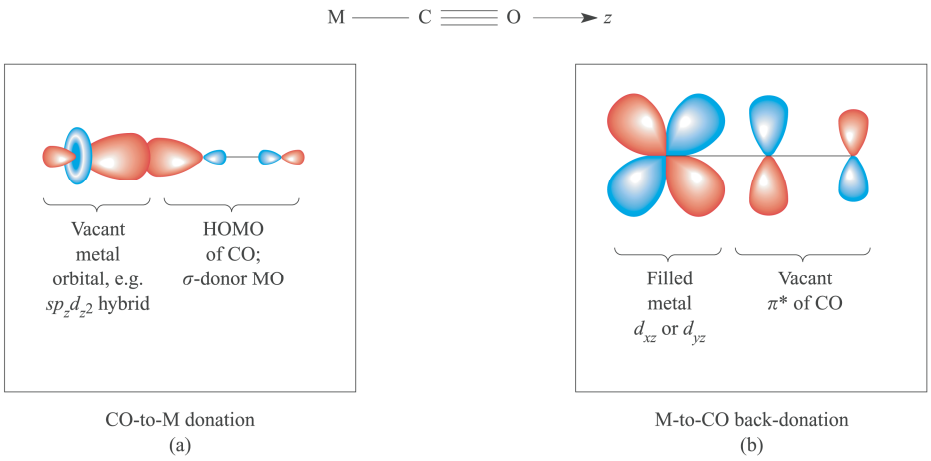
σ-bonded alkyl, aryl and related ligands

Localized 2c-2e interaction



$TiMe_3$

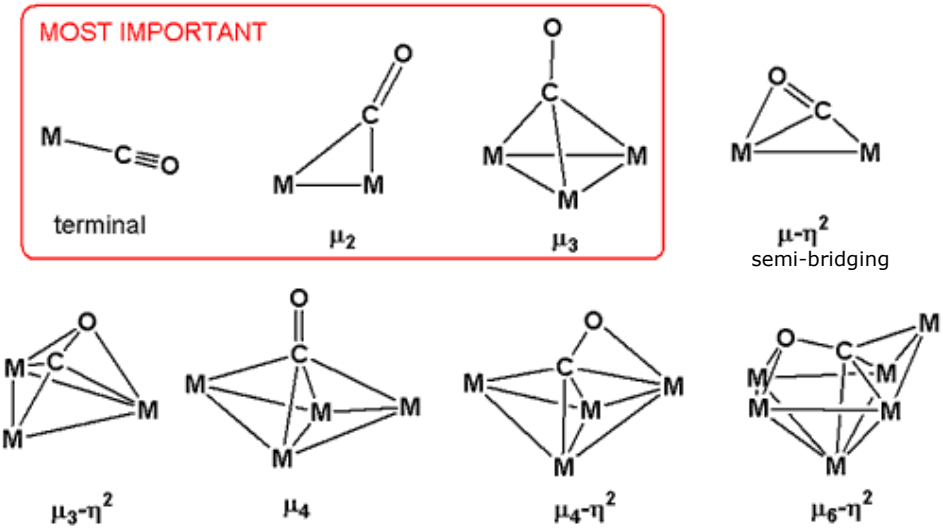




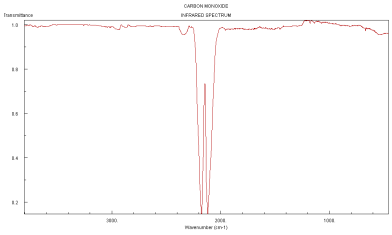
Dewar-Chatt-Duncanson model

Fig. 24.1 Components of metal−carbonyl bonding: (a) the M−CO σ-bond, and (b) the M−CO π-interaction which leads to back-donation of charge from metal to carbonyl. The orbital labels are examples, and assume that the M, C and O atoms lie on the z axis.

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In multinuclear metal species a number of bonding modes may be adopted.



$$:\overline{M}-C\equiv\overset{+}{O}: \leftrightarrow M=C=O::$$

Free CO, υ_{CO} 2143 cm^{-1}

d(CO) = 112.8 pm

Complex	$Ni(CO)_4$	$[Co(CO)_4]^-$	$[Fe(CO)_4]^{2-}$	$[Fe(CO)_6]^{2+}$	$[Mn(CO)_6]^+$	$Cr(CO)_6$	$[V(CO)_6]^-$
$\tilde{\nu}_{CO}$ / cm^{-1}	2060	1890	1790	2204	2101	1981	1859

$\upsilon_{M\text{-}C}$ (cm^{-1})					416	441	

Table 24.1 Infrared spectroscopic data: values of $\tilde{\nu}_{CO}$ for isoelectronic sets of tetrahedral $M(CO)_4$ and octahedral $M(CO)_6$ complexes.

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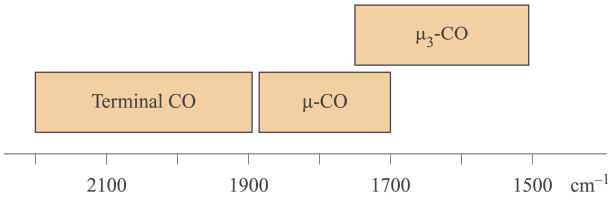


Fig. 24.2 Approximate regions in the IR spectrum in which absorptions assigned to C−O stretches observed for different carbonyl bonding modes; there is often overlap between the regions.

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Hydride ligands

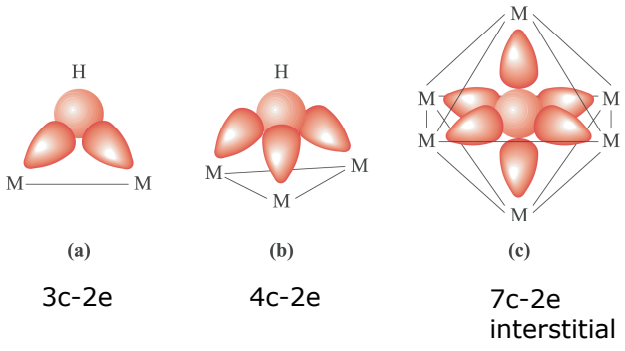
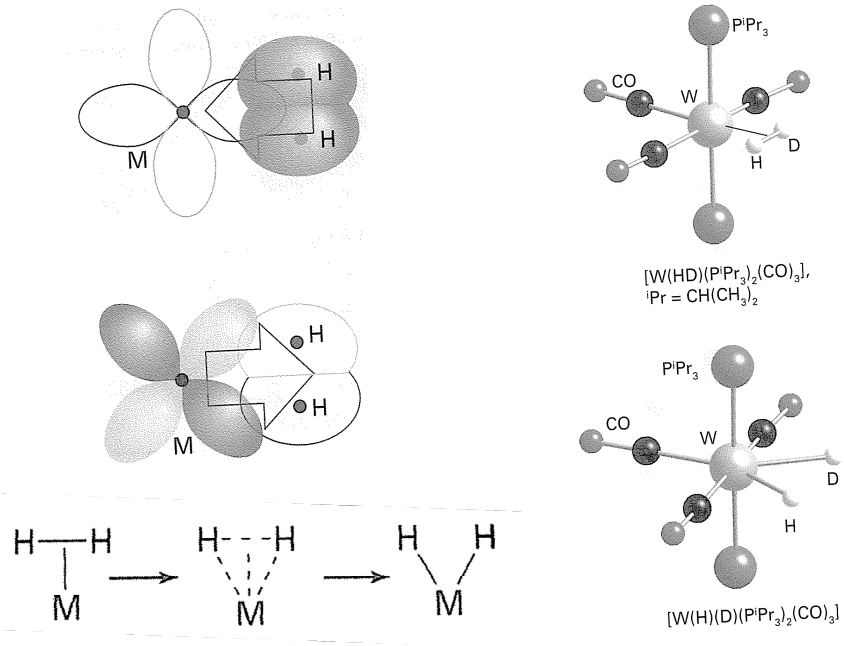


Fig. 24.3 Overlap of the H 1*s* atomic orbital with (a) two or (b) three appropriate metal hybrid orbitals to form μ-H and μ_3-H bridges. (c) For an interstitial H atom within an octahedral M_6-cage, a delocalized description involves the overlap of the H 1*s* atomic orbital with six appropriate metal orbitals to give a 7c–2e interaction.

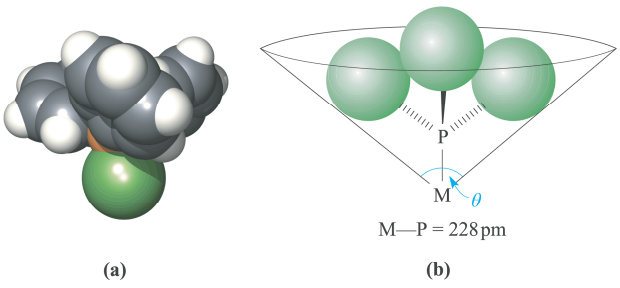
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Metal complexes with H_2



Monodentate organophosphines: σ-donor and π-acceptor

tertiary:	PR_3
secondary:	PR_2H
primary:	PRH_2



π-accepting properties:

$PF_3 > P(OPh)_3 > P(OMe)_3 > PPh_3 > P^tBu_3$

Fig. 24.4 (a) A space-filling diagram of an $FePPh_3$ unit; the phenyl groups adopt a 'paddle-wheel' arrangement. Colour code: Fe, green; P, orange; C, grey; H, white. (b) Schematic representation of the measurement of the Tolman cone angle, θ, for a PR_3 ligand; each circle represents the spatial extent of an R group.

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Ligand	Tolman cone angle / deg	Ligand	Tolman cone angle / deg
$P(OMe)_3$	107	PPh_3	145
PMe_3	118	$P(4\text{-}MeC_6H_4)_3$	145
PMe_2Ph	122	P^iPr_3	160
$PHPh_2$	126	$P(3\text{-}MeC_6H_4)_3$	165
$P(OPh)_3$	128	$P(cyclo\text{-}C_6H_{11})_3$	170
PEt_3	132	P^tBu_3	182
P^nBu_3	132	$P(2\text{-}MeC_6H_4)_3$	194
$PMePh_2$	136	$P(2,4,6\text{-}Me_3C_6H_2)_3$	212

Table 24.2 Tolman cone angles for selected phosphine and phosphite ligands.

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π-bonded ligands

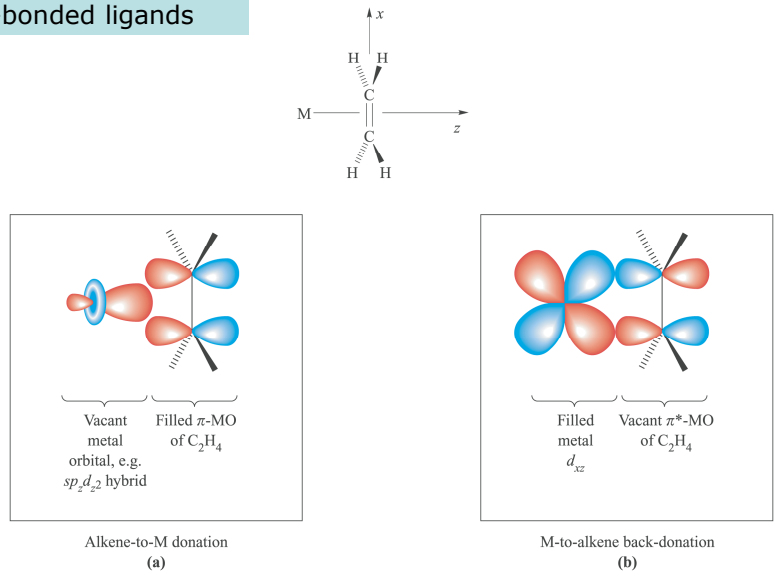


Fig. 24.5 Components of metal−alkene bonding: (a) donation of electrons from the alkene π-MO to a suitable metal *d* orbital or hybrid and (b) back-donation of electrons from metal to alkene π^* MO.

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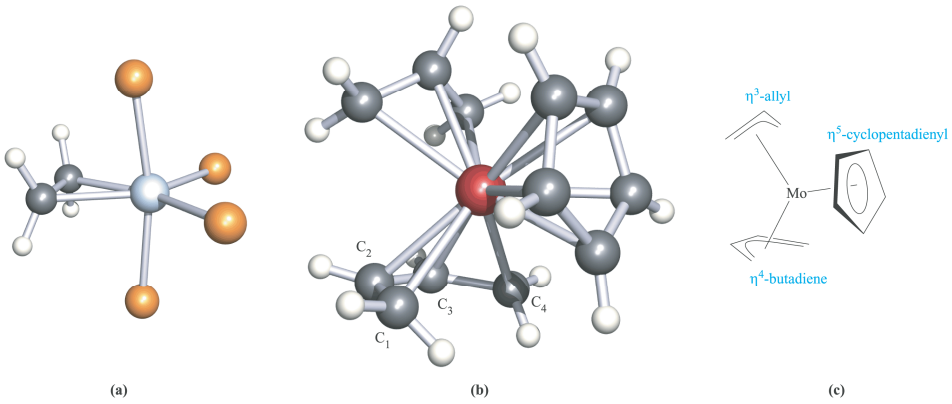
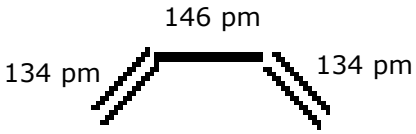
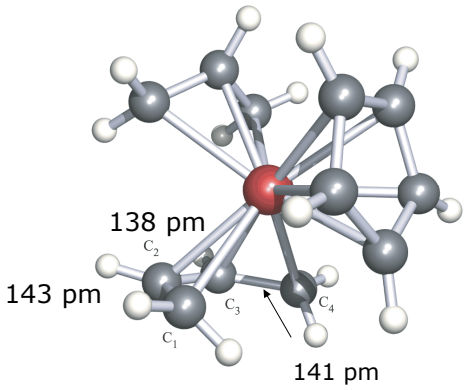


Fig. 24.6 (a) The structure (X-ray diffraction) of $Ru(\eta^2\text{-}C_2H_4)(PMe_3)_4$ illustrating the non-planarity of the coordinated ethene ligand (C−C =144 pm); only the P atoms of the PMe_3 ligands are shown [W.-K. Wong*et al*. (1984) *Polyhedron*, vol. 3, p. 1255], (b) the structure (X-ray diffraction) of $Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)$ [L.-S. Wang *et al*. (1997) *J. Am. Chem. Soc.*, vol. 119, p. 4453], and (c) a schematic representation of $Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)$. Colour code: Ru, pale grey; Mo, red; C, dark grey; P, orange; H, white.

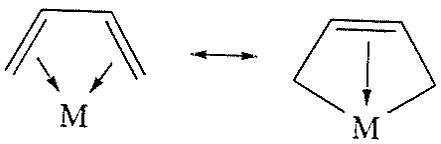
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free buta-1,3-diene

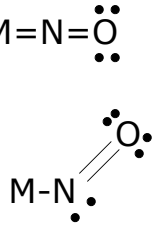


$Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)$



Nitrogen monoxide

- radical
- singly bound as nitrosyl ligand
- linear or bent (165-180°)
- donates three electrons to metal
- υ_{NO} 1525-1690 cm^{-1}



Dinitrogen

- N_2 and CO are isoelectronic, similar bonding
- Complexes of N_2 not as stable as CO

Dihydrogen

- σ-MO (electron donor orbital) and σ*-MO (acceptor)
- can weaken or cleave the H-H bond

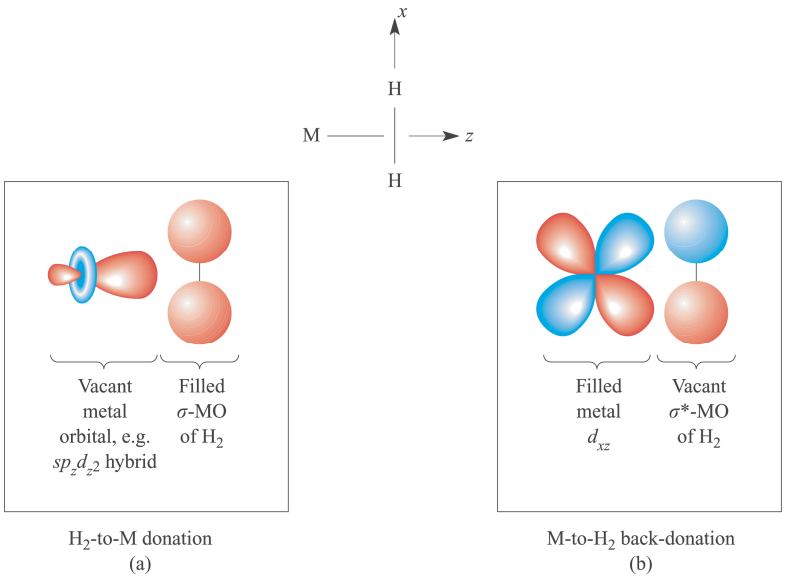


Fig. 24.9 Components of metal−dihydrogen bonding: (a) H_2-to-M donation using the H_2 σ-bonding MO and (b) M-to-H_2 back-donation into the H_2 σ*-MO. The axis set is defined in the top diagram.

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18-electron rule

•Low oxidation state organometallic complexes tend to obey the 18-electron rule.

- •Valid for middle d-block metals, and there are exceptions for early and late d-block metals.
- •16 electron complexes common for Rh(I), Ir(I), Pd(0) and Pt(0)

Rules

•Treat all ligands as neutral species to avoid assigning oxidation state to metal center.

•The number of valence electrons for a zero oxidation state metal is equal to the group number.

•1 electron donor: H*, terminal Cl*, Br*, R* (alkyl, or Ph), or RO*.

•2 electron donor: CO, PR_3, $P(OR)_3$, $R_2C{=}CR_2$ (η^2-alkene), R_2C: (carbene)

•3 electron donor: η^3-C_3H_5* (allyl radical), RC (carbyne), μ-Cl*, μ-Br*, μ-I*, μ-R_2P*

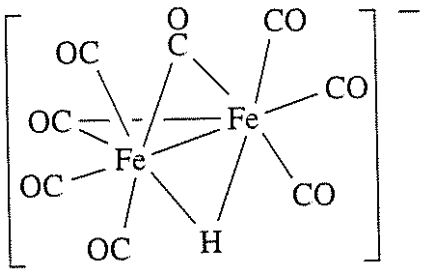
•4 electron donor: η^4-diene, η^4-C_4R_4 (cyclobutadienes)

•5 electron donor: η^5-C_5H_5*, μ_3-Cl*, μ_3-Br*, μ_3-I*, μ_3-RP*

•6 electron donor: η^6-C_6H_6 (and other η^6-arenes)

•1 or 3 electron donor: NO

18-electron rule practice

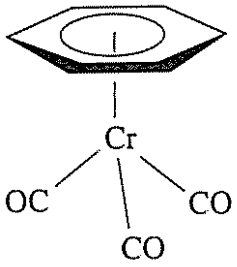


Electron count:

Fe(0) = 8 electrons
3 terminal CO = 3 × 2 electrons
2 μ-CO = 2 × 1 electron per Fe
Fe–Fe bond = 1 electron per Fe
H = $^1/_2$ electron per Fe
1– charge = $^1/_2$ electron per Fe
Total = 18 electrons per Fe

18-electron rule practice

$(\eta^6\text{-}C_6H_6)Cr(CO)_3$



Cr(0) (group 6) contributes 6 electrons

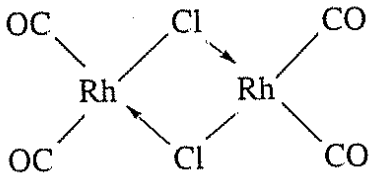
η^6-C_6H_6 contributes 6 electrons

3 CO contribute $3 \times 2 = 6$ electrons

Total = 18 electrons

18-electron rule practice

$[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$



Rh(0) (group 9) contributes 9 electrons

μ-Cl contributes 3 electrons (1 to one Rh and 2 to the other Rh)

2 CO contribute $2 \times 2 = 4$ electrons

Total per Rh = 16 electrons

Disobeys 18 electron rule

Metal carbonyls

Group number	5	6	7	8	9	10
First row metals	$V(CO)_6$ Dark blue solid; paramagnetic; dec. 343 K	$Cr(CO)_6$ White solid; sublimes *in vacuo*; dec. 403 K	$Mn_2(CO)_{10}$ Yellow solid; mp 427 K	$Fe(CO)_5$ Yellow liquid; mp 253 K; bp 376 K	$Co_2(CO)_8$ Air-sensitive, orange-red solid; mp 324 K	$Ni(CO)_4$ Colourless, volatile liquid; highly toxic vapour; bp 316 K
				$Fe_2(CO)_9$ Golden crystals; mp 373 K (dec.)	$Co_4(CO)_{12}$ Air-sensitive, black solid	
				$Fe_3(CO)_{12}$ Dark green solid; dec. 413 K	$Co_6(CO)_{16}$ Black solid; slowly dec. in air	
Second row metals		$Mo(CO)_6$ White solid; sublimes *in vacuo*	$Tc_2(CO)_{10}$ White solid; slowly dec. in air; mp 433 K	$Ru(CO)_5$ Colourless liquid; mp 251 K; dec. in air at 298 K to $Ru_3(CO)_{12} + CO$	$Rh_4(CO)_{12}$ Red solid; >403 K dec. to $Rh_6(CO)_{16}$	
				$Ru_3(CO)_{12}$ Orange solid; mp 427 K; sublimes *in vacuo*	$Rh_6(CO)_{16}$ Black solid; dec. >573 K	
Third row metals		$W(CO)_6$ White solid; sublimes *in vacuo*	$Re_2(CO)_{10}$ White solid; mp 450 K	$Os(CO)_5$ Yellow liquid; mp 275 K	$Ir_4(CO)_{12}$ Slightly air-sensitive yellow solid; mp 443 K	
				$Os_3(CO)_{12}$ Yellow solid; mp 497 K	$Ir_6(CO)_{16}$ Red solid	

Table 24.3 Neutral, low-nuclearity ($\leq M_6$) metal carbonyls of the *d*-block metals (dec. = decomposes).

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$$VCl_3 + Na + CO \xrightarrow[\text{in diglyme}]{420\ K,\ 150\ bar} [Na(diglyme)_2][V(CO)_6] \xrightarrow{HCl,\ Et_2O} V(CO)_6$$

$$CrCl_3 + CO + Li[AlH_4] \xrightarrow[\text{in } Et_2O]{390\ K,\ 70\ bar} Cr(CO)_6 + LiCl + AlCl_3$$

$$MoCl_5 + CO + AlEt_3 \xrightarrow{373\ K,\ 200\ bar} Mo(CO)_6 + AlCl_3 \quad (24.6)$$

$$WCl_6 + Fe(CO)_5 \xrightarrow{373\ K} W(CO)_6 + FeCl_2 \quad (24.7)$$

$$OsO_4 + CO \xrightarrow{520\ K,\ 350\ bar} Os(CO)_5 + CO_2 \quad (24.8)$$

$$Co(O_2CMe)_2{\cdot}4H_2O \xrightarrow[\text{in acetic anhydride}]{CO/H_2\ (4:1),\ 200\ bar,\ 430\ K} Co_2(CO)_8 \quad (24.9)$$

$$RuCl_3{\cdot}xH_2O + CO \xrightarrow[\text{in MeOH}]{400\ K,\ 50\ bar} Ru_3(CO)_{12} \quad (24.10)$$

$$RuCl_3{\cdot}xH_2O \xrightarrow[\text{in 2-ethoxyethanol}]{CO\ (1\ bar),\ 353\ K,\ 1h;\ 408\ K,\ 45\ min} \left\{[Ru(CO)_2Cl_2]_n \underset{}{\overset{CO}{\rightleftharpoons}} [Ru(CO)_3Cl_2]_2\right\} \xrightarrow[45\ min]{KOH,\ 348\ K} Ru_3(CO)_{12} \quad (24.11)$$

$$OsO_4 + CO \xrightarrow[\text{in MeOH}]{400\ K,\ \leq 200\ bar} Os_3(CO)_{12} \quad (24.12)$$

Metal carbonyl anions

$$Na[Ir(CO)_4] \xrightarrow[2.\ \text{Liquid } NH_3,\ 195\ K,\ \text{warm to } 240\ K]{1.Na,\ HMPA,\ 293\ K} Na_3[Ir(CO)_3]$$

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

$$Ru_3(CO)_{12} \xrightarrow{Na,\ \text{liquid } NH_3,\ \text{low T}} Na_2[Ru(CO)_4]$$

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

(R = $Me_2NCH_2CH_2NMe_2$-N,N')

$$Fe(CO)_5 \xrightarrow{Na[C_{10}H_8]} Na_2[Fe(CO)_4]$$

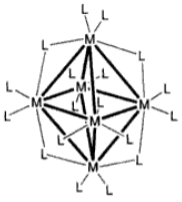
$$Mn_2(CO)_{10} + 2Na \longrightarrow 2Na[Mn(CO)_5]$$

$$Co_2(CO)_8 + 2Na \longrightarrow 2Na[Co(CO)_4]$$

$$Ru_3(CO)_{12} \xrightarrow{Na,\ THF,\ \Delta} [Ru_6(CO)_{18}]^{2-}$$

$$Os_3(CO)_{12} \xrightarrow{Na,\ diglyme,\ \Delta} [Os_6(CO)_{18}]^{2-}$$

$$Ni(CO)_4 \xrightarrow{Na[C_{10}H_8]} [Ni_5(CO)_{12}]^{2-} + [Ni_6(CO)_{12}]^{2-}$$



$[Ru_6(CO)_{18}]^{2-}$

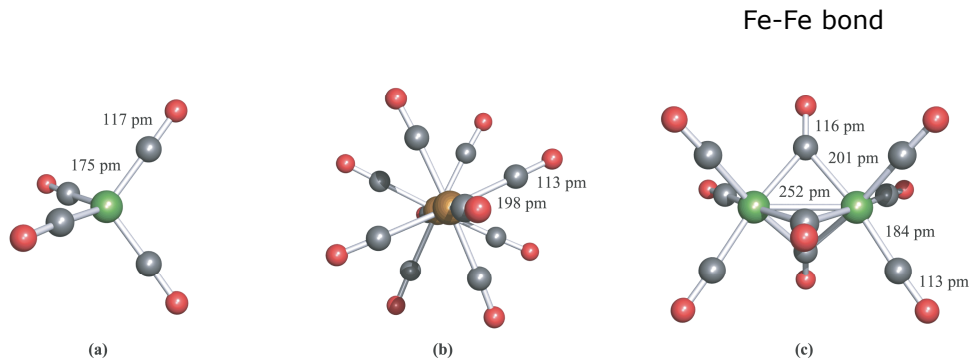


Fig. 24.10a-c The structures (X-ray diffraction) of (a) $[Fe(CO)_4]^{2-}$ in the K^+ salt [R.G. Teller *et al*. (1977) *J. Am. Chem. Soc*., vol. 99, p. 1104], (b) $Re_2(CO)_{10}$ showing the staggered configuration also adopted by $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ [M.R. Churchill *et al*. (1981) *Inorg. Chem*., vol. 20, p. 1609], (c) $Fe_2(CO)_9$ [F.A. Cotton *et al*. (1974) *J. Chem. Soc*., *Dalton Trans*., p. 800]. Colour code: Fe, green; Re, brown; Co, blue; Os, yellow; C, grey; O, red.

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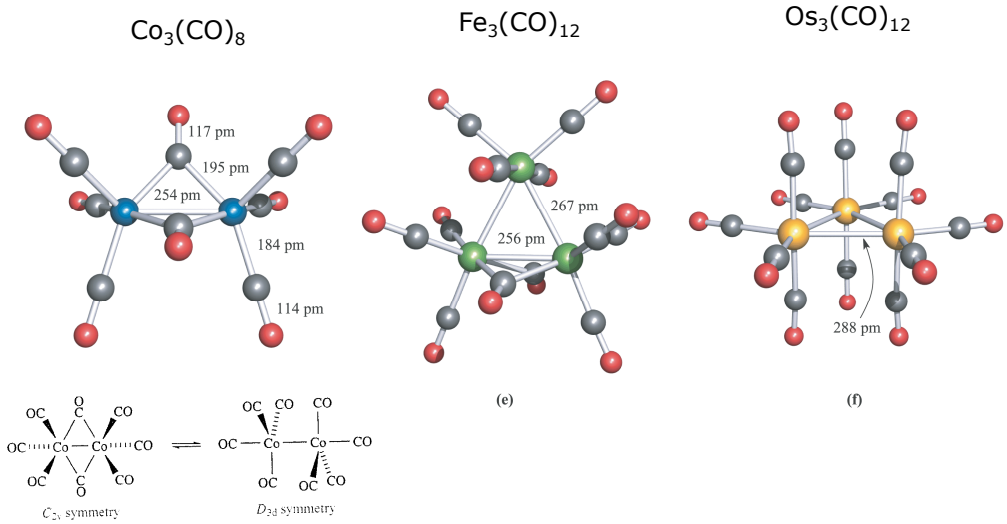


Fig. 24.10d-f The structures (X-ray diffraction) of (d) $Co_2(CO)_8$ [P.C. Leung *et al*. (1983) *Acta Crystallogr*., *Sect. B*, vol. 39, p. 535], (e) $Fe_3(CO)_{12}$ [D. Braga *et al*. (1994) *J. Chem. Soc*., *Dalton Trans*., p. 2911] and (f) $Os_3(CO)_{12}$ which is isostructural with $Ru_3(CO)_{12}$ [M.R. Churchill *et al*. (1977) *Inorg. Chem*., vol. 16, p. 878]. Colour code: Fe, green; Re, brown; Co, blue; Os, yellow; C, grey; O, red. (Continued)

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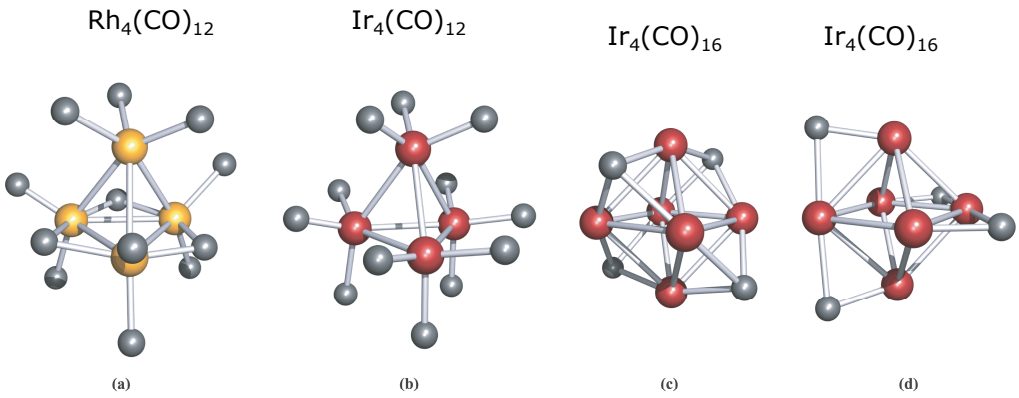


Fig. 24.11 The structures (X-ray diffraction) of (a) $Rh_4(CO)_{12}$ which is isostructural with $Co_4(CO)_{12}$ [C.H. Wei (1969) *Inorg. Chem.*, vol. 8, p. 2384], (b) $Ir_4(CO)_{12}$ [M.R. Churchill *et al.* (1978) *Inorg. Chem.*, vol. 17, p. 3528], (c) the red isomer of $Ir_6(CO)_{16}$ and (d) the black isomer of $Ir_6(CO)_{16}$ [L. Garlaschelli *et al.* (1984) *J. Am. Chem. Soc.*, vol. 106, p. 6664]. In (a) and (b), O atoms have been omitted for clarity. In (c) and (d), the terminal CO and the O atoms of the bridging CO ligands have been omitted; each Ir has two CO_{term}. Colour code: Rh, yellow; Ir, red; C, grey.

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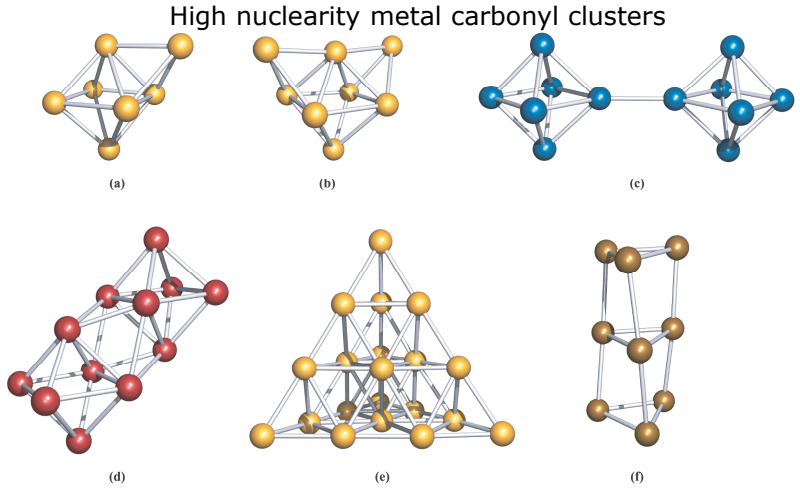


Fig. 24.12 The structures (X-ray diffraction) of the metal cores in (a) $Os_7(CO)_{21}$ [C.R. Eady *et al.* (1977) *J. Chem. Soc., Chem. Commun.*, p. 385], (b) $[Os_8(CO)_{22}]^{2-}$ in the $[(Ph_3P)_2N]^+$ salt [P.F. Jackson *et al.* (1980) *J. Chem. Soc., Chem. Commun.*, p. 60], (c) $[Rh_{12}(CO)_{30}]^{2-}$ in the $[Me_4N]^+$ salt [V.G. Albano *et al.* (1969) *J. Organomet. Chem.*, vol. 19, p. 405], (d) $[Ir_{12}(CO)_{26}]^{2-}$ in the $[Ph_4P]^+$ salt [R.D. Pergola *et al.* (1987) *Inorg. Chem.*, vol. 26, p. 3487], (e) $[Os_{20}(CO)_{40}]^{2-}$ in the $[^nBu_4P]^+$ salt [L.H. Gade *et al.* (1994) *J. Chem. Soc., Dalton Trans.*, p. 521] and (f) $[Pt_9(CO)_{18}]^{2-}$ in the $[Ph_4P]^+$ salt [J.C. Calabrese *et al.*(1974) *J. Am. Chem. Soc.*, vol. 96, p. 2614]. Colour code: Os, yellow; Rh, blue; Ir, red; Pt, brown.

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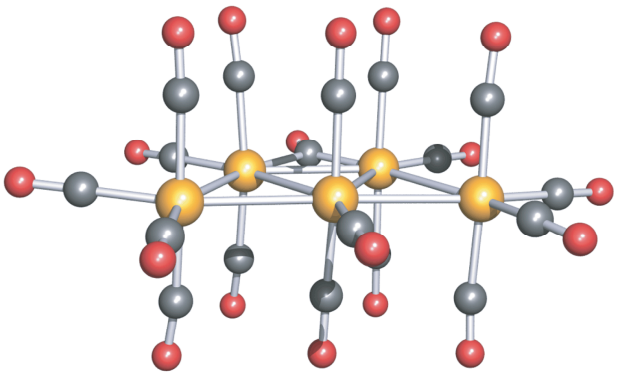


Fig. 24.13 The structure (X-ray diffraction) of $Os_5(CO)_{18}$, in which the Os atoms form a planar 'raft' [W. Wang *et al.* (1992) *J. Chem. Soc., Chem. Commun.*, p. 1737]. Colour code: Os, yellow; C, grey; O, red.

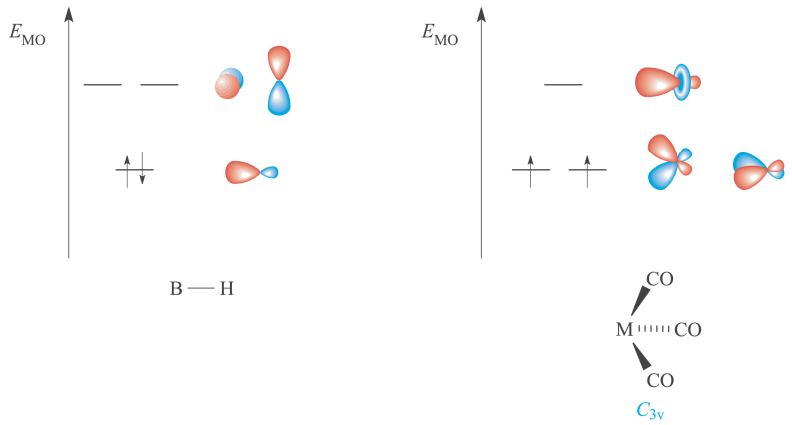
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Isolobal principle and application of Wade's rules

Two cluster fragments are isolobal if they possess the same frontier orbital characteristics: same symmetry, same number of electrons available for cluster bonding, and approximately the same energy.

Frontier MOs are close to the HOMO and LUMO

M = Fe, Ru, Os



BH and C_{3v} $M(CO)_3$ [M=Fe, Ru, Os] fragments are isolobal and their relationship allows BH units in borane clusters to be replaced by $Fe(CO)_3$, $Ru(CO)_3$ or $Os(CO)_3$

Fig. 24.14 The frontier MOs of a BH unit and a C_{3v} (i.e. 'conical') $M(CO)_3$ (M = Fe, Ru, Os) group. For the BH unit, the occupied MO is an *sp* hybrid; for $M(CO)_3$, the orbitals are represented by *pd* or *spd* hybrids. These orbitals combine with those of other cluster fragments to give cluster-bonding, non-bonding and antibonding MOs.

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Wade's rules

- A closo-deltahedral cluster cage with n vertices requires (*n*+1) pairs of electrons, which occupy (*n*+1) cluster bonding MOs.
- From a parent closo cage with n vertices, a set of more open cages (nido, arachno, and hypho) can be derived, each of which possessed (*n*+1) pairs of electrons occupying (*n*+1) cluster bonding MOs
- For a parent closo-deltahedron with *n* vertices, the related nido-cluster has (*n*-1) vertices and (*n*+1) pairs of electrons
- For a parent closo-deltahedron with *n* vertices, the related arachno-cluster has (*n*-2) vertices and (*n*+1) pairs of electrons
- For a parent closo-deltahedron with *n* vertices, the related hypho-cluster has (*n*-3) vertices and (*n*+1) pairs of electrons

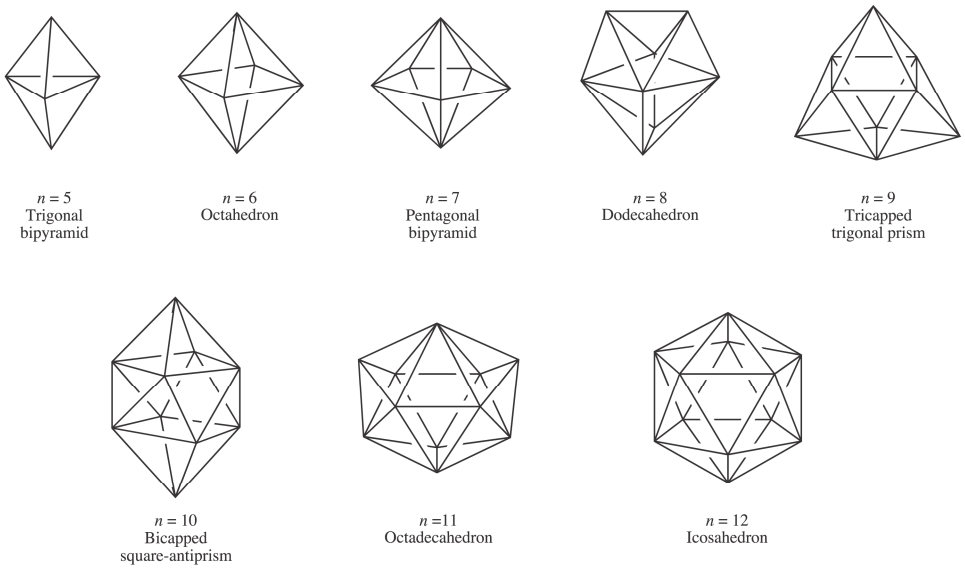


Fig. 13.27 The deltahedral cages with 5 to 12 vertices which are the parent cages used in conjunction with Wade's rules to rationalize borane cluster structures.

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Polyhedral skeletal electron pair theory (PSEPT)

- Moving to the right or left adds or removes electrons to the frontier MOs.
- Removing or adding a CO removes or adds two electrons

$$x = v + n - 12$$

where: x = number of cluster-bonding electrons provided by fragment
v = number of valence electrons from the metal atom
n = number of valence electrons provided by the ligands

Number of electrons for cluster bonding by selected fragments

Cluster fragment	Group 6: Cr, Mo, W	Group 7: Mn, Tc, Re	Group 8: Fe, Ru, Os	Group 9: Co, Rh, Ir
$M(CO)_2$	−2	−1	0	1
$M(CO)_3$	0	1	2	3
$M(CO)_4$	2	3	4	5
$M(\eta^5\text{-}C_5H_5)$	−1	0	1	2
$M(\eta^6\text{-}C_6H_6)$	0	1	2	3
$M(CO)_2(PR_3)$	0	1	2	3

Table 24.4 The number of electrons (x in equation 24.28) provided for cluster bonding by selected fragments; $\eta^5\text{-}C_5H_5 = \eta^5\text{-Cp}$.

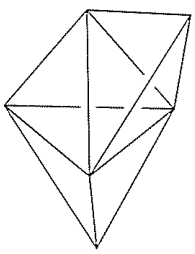
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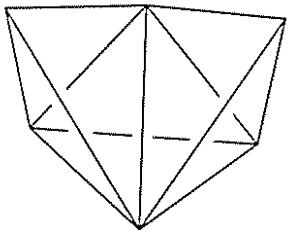
Capping Principle

Boranes tend to adopt open structures; however, capping is found in many metal cabonyls.

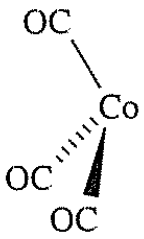
Addition of one of more capping units to a deltahedral cage requires no additional bonding electrons. A capping unit is a cluster fragment placed over the triangular face of a central cage.

Rationalize why $Os_6(CO)_{18}$ adopts the following structure instead of an octahedral cage

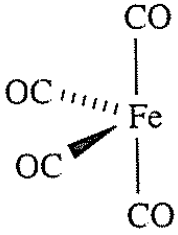




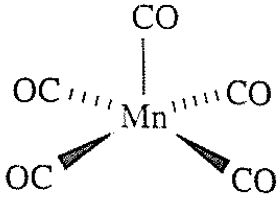
Isolobal pairs of metal carbonyls and hydrocarbon fragments



and CH (provides three orbitals and three electrons)



and CH_2 (provides two orbitals and two electrons)



and CH_3 (provides one orbitals and one electron)

Mingos cluster valence electron count

Each low oxidation state metal cluster possesses a characteristic number of valence electrons.

Cluster framework	Diagrammatic representation of the cage	Valence electron count
Triangle		48
Tetrahedron		60
Butterfly or planar raft of four atoms		62
Square		64

A difference of two between valence electron counts corresponds to a 2 e- reduction (adding two electrons) or oxidation (removing two electrons).

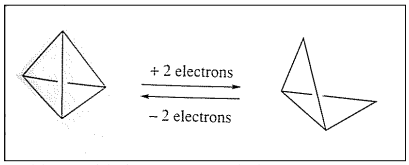


Table 24.5a Characteristic total valence electron counts for selected low oxidation state metal clusters.

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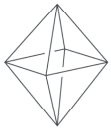
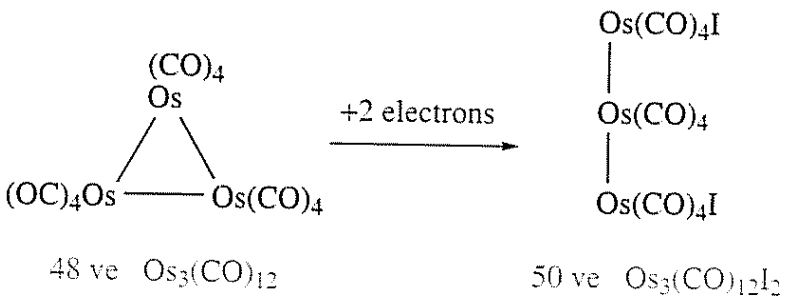
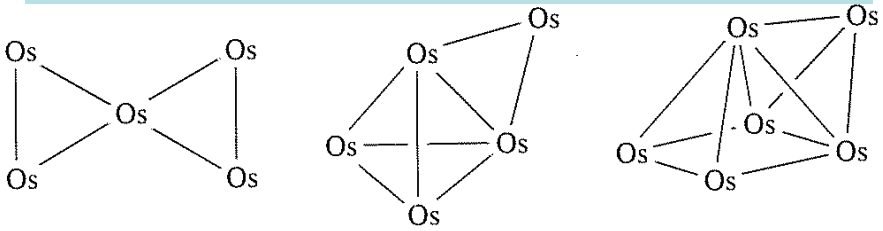
Cluster framework	Diagrammatic representation of the cage	Valence electron count
Trigonal bipyramid		72
Square-based pyramid		74
Octahedron		86
Trigonal prism		90

Table 24.5b Characteristic total valence electron counts for selected low oxidation state metal clusters. (Continued)

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Condensed cages

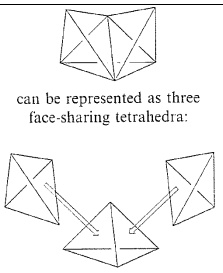


Total valence electron count for a condensed structure is equal to the total number of electrons required by the sub-cluster units minus the electrons associated with the shared unit.

18 electrons for shared M atom; 34 electrons for shared M-M edge; 48 electrons for a shared M_3 face.

$Os_6(CO)_{18}$ Three face-sharing tetrahedra
Valence electron count = 3*60 = 180
Subtract 48 for each shared face = 180-(2*48) = 84
The number of valence electrons available
= 6*8 + 18*2 = 84

→ The observed structure is consistent with the number of valence electrons available



Applications as catalysts

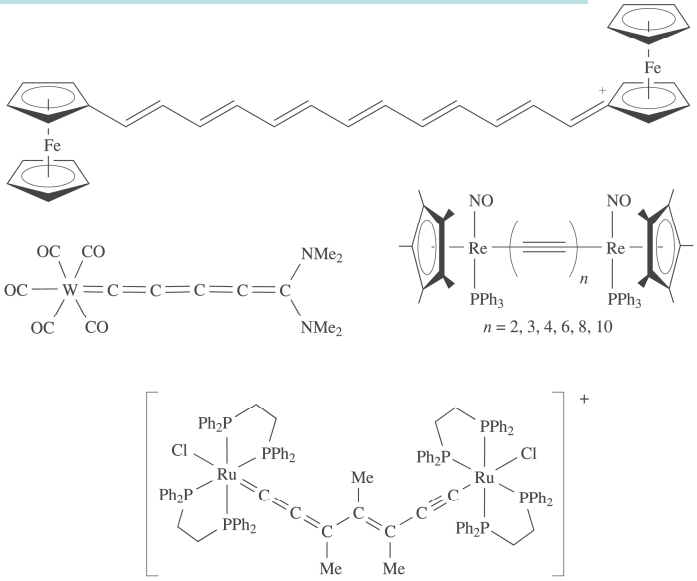
Homogeneous catalyst	Catalytic application
$RhCl(PPh_3)_3$	Alkene hydrogenation
cis-$[Rh(CO)_2I_2]^-$	Monsanto acetic acid synthesis; Tennessee–Eastman acetic anhydride process
$HCo(CO)_4$	Hydroformylation; alkene isomerization
$HRh(CO)_4$	Hydroformylation (only for certain branched alkenes)†
$HRh(CO)(PPh_3)_3$	Hydroformylation
$[Ru(CO)_2I_3]^-$	Homologation of carboxylic acids
$[HFe(CO)_4]^-$	Water–gas shift reaction
$(\eta^5\text{-}C_5H_5)_2TiMe_2$	Alkene polymerization
$(\eta^5\text{-}C_5H_5)_2ZrH_2$	Hydrogenation of alkenes and alkynes
$Pd(PPh_3)_4$	Many laboratory applications including the Heck reaction

† $HRh(CO)_4$ is more active than $HCo(CO)_4$ in hydroformylation, but shows a lower regioselectivity (see **equation 27.5** and discussion).

Box 24.3 Homogeneous catalysts.

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Molecular Wires



Box 24.4 Molecular wires.

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