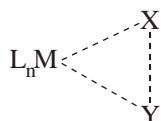


ketones; and $X-C(=O)R$ to give **acid halides**, etc.

The driving-force for these elimination processes could be the formation of stable organic molecules and/or metal complexes.

Importance of *cis* arrangement

The two groups (to be eliminated) must be in the ***cis* positions** before elimination can take place. Because, only the *cis* arrangement of ligands can form a **3 centred** transition state with the metal.



Creation of this **transition state** is crucial: as reductive elimination occurs *via* a **concerted** process, hence, all bond breaking and bond-forming occur simultaneously in a single step.

In square-planar complexes, **trans groups** must rearrange to *cis* positions before the elimination step to take place; e.g., *trans*-[PtH(CH₂CN)(PPh₃)₂] reductive eliminates MeCN, after **isomerising** it into the *cis*-isomer, *cis*-[PtH(CH₂CN)(PPh₃)₂].

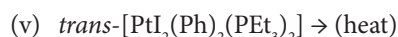
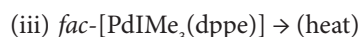
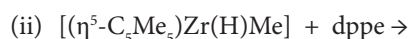
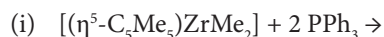
Reductive elimination is facilitated:

- (i) when the positive charge on the metal centre is increased due to the formation of a cationic complex.
- (ii) when electron density (or π -basicity) of the metal centre is reduced by dissociating a good σ -donor ligand/s.

Sometimes, reductive elimination process is accelerated by prior coordination of another ligand/s; for example, in the presence of 2 equivalents of PPh₃, $[(\eta^5-C_5Me_5)ZrMe_2]$ eliminates an ethane molecule.

Problems

1. Suggest the metal complex and the organic product(s) formed from the following reactions.



2. [TiMe₄] decomposes above -50 °C, but [TiMe₄(Me₂PCH₂CH₂PMe₂)] is stable at room temperature. Explain.

Student Corner

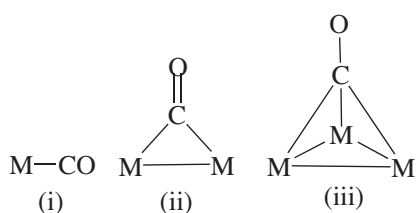
Metal Carbonyls

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Carbon monoxide is a **good π -acceptor** and the M—C bond in metal carbonyls [M(CO)_n] has a significant π character. Thus, the M—C bond is **strengthened** and the carbon oxygen bond is **weakened** with the **increase in back bonding**.

The common coordination modes of CO are; (i) **terminal**, (ii) **doubly** or edge **bridging** M₂(μ_2 -CO), and (iii) **triply** or face **bridging** M₃(μ_3 -CO).



The **carbonyl stretching frequency** $\nu(CO)$ decrease in the following order, M—CO > M₂(μ_2 -CO) > M₃(μ_3 -CO); as back donation increases with the increase of number of metal atoms.

Bond type	$\nu(CO)/cm^{-1}$
M—CO	2150-1900
M ₂ (μ_2 -CO)	1900-1750
M ₃ (μ_3 -CO)	1750-1600

μ_2 -CO ligand donates **one electron** to each of the two metal centres. μ_3 -CO ligand donates 2/3 of electron to each of the three metal centres.

Mononuclear metal carbonyls

The simplest metal carbonyls are of the type $[M(CO)_n]$, and are called **binary carbonyls** or **homoleptic carbonyls**. The stable binary carbonyls of transition metals (e.g., $[Cr(CO)_6]$, $[Fe(CO)_5]$, $[Ni(CO)_4]$) have 18 valence electrons except $[V(CO)_6]$ (17e).

Synthesis of metal carbonyls

The reductive carbonylation of metal salts in the presence of CO is the most common method of preparation. The reducing agents used are Na, Al, Mg, AlR_3 , H_2 or CO. The other method is the direct reaction of a metal with CO ligands.

- (i) $CrCl_3 + Al + CO \rightarrow [Cr(CO)_6] + AlCl_3$
- (ii) $Fe + CO \rightarrow [Fe(CO)_5]$
- (iii) $CoCO_3 + H_2 + CO \rightarrow [Co_2(CO)_8]$
- (iv) $Ni + CO \rightarrow [Ni(CO)_4]$
- (v) $2[Fe(CO)_5] + h\nu \rightarrow [Fe_2(CO)_9] + CO$
- (vi) $[Fe_2(CO)_9] + h\nu \rightarrow [Fe_3(CO)_{12}]$
- (vii) $Re_2O_7 + CO \rightarrow [Re_2(CO)_{10}] + CO_2$

Polynuclear metal carbonyls

Most polynuclear metal carbonyls satisfy the 18e-rule. Some important polynuclear metal carbonyls are given below.

Binuclear metal carbonyls

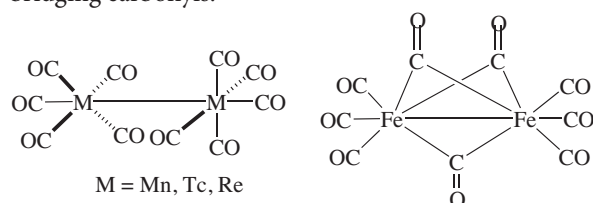
Binuclear metal carbonyls contain a M—M bond, and sometimes **bridging** carbonyl ligands. Some examples are with -

Group 7 metals - $[M_2(CO)_{10}]$; M = Mn, Tc, Re

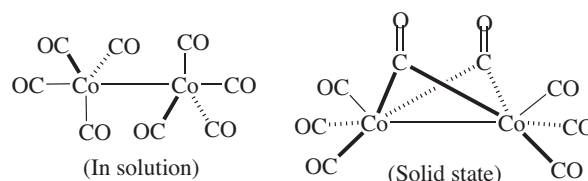
Group 8 metals - $[Fe_2(CO)_9]$

Group 9 metals - $[Co_2(CO)_8]$.

In Group 7 metal carbonyls, each metal centre is octahedral and adopts staggered conformation in the solid state. Photolysis of $[Fe(CO)_5]$ gives the binuclear complex $[Fe_2(CO)_9]$, containing a Fe—Fe bond and three bridging carbonyls.



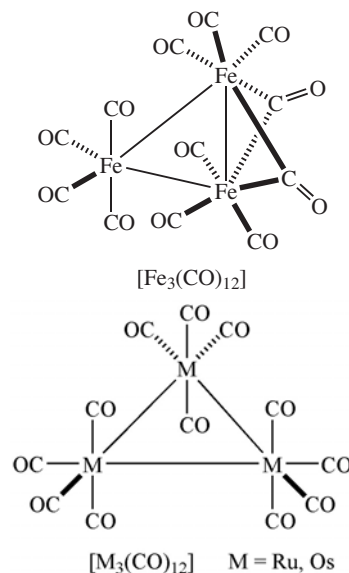
Dimerization of two 17e $[Co(CO)_4]^\cdot$ radicals gives the 18e-complex $[Co_2(CO)_8]$.



Note: In the solid state, $[Co_2(CO)_8]$ has one Co-Co bond and two bridging carbonyls; however, in solution it does not have bridging carbonyl ligands.

Trinuclear metal carbonyls

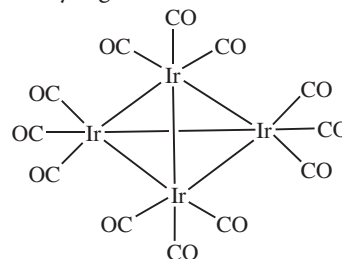
In these complexes, the metal atoms form a **triangular** arrangement. Examples include carbonyls of Group 8 metals - $[M_3(CO)_{12}]$; M = Fe, Ru, Os.



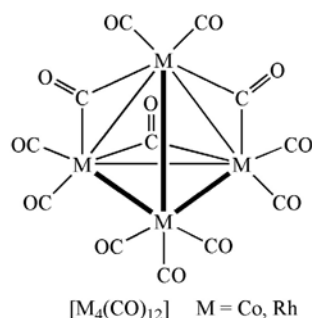
$[Fe_3(CO)_{12}]$ has two bridging carbonyls, but less reactive $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ have a strongly bonded triangular cluster with no bridging carbonyl ligands.

Tetranuclear metal carbonyls

Tetranuclear clusters of the type $[M_4(CO)_{12}]$ possess tetrahedral M_4 -framework, e.g., $[Ir_4(CO)_{12}]$ shows twelve terminal carbonyl ligands on the tetrahedral Ir_4 -unit.



Unlike $[\text{Ir}_4(\text{CO})_{12}]$, in the solid state, Co and Rh analogues contain three μ_2 -CO ligands. In solution, $[\text{Co}_4(\text{CO})_{12}]$ and $[\text{Rh}_4(\text{CO})_{12}]$ are fluxional.



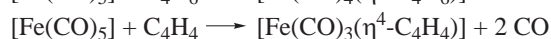
Reactions of metal carbonyls

Let us discuss some of the reactions of metal carbonyls.

(a) Substitution with PPh_3

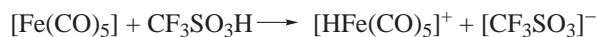


(b) Substitution with olefins



(C_4H_6 = cyclobutene and C_4H_4 = cyclobutadiene)

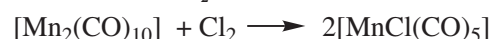
(c) Protonation with acids



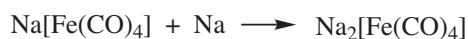
(d) Reaction with KOH (attack by OH^-), gives an anionic metal hydride



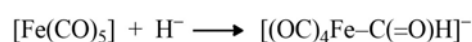
(e) Oxidation with Cl_2 gives a chloride



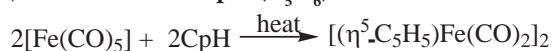
(f) Reduction with Na gives a metal carbonyl anion



(g) Addition of H^- generates a CHO group



(h) Reaction with C_5H_5 (C_5H_6)



Stretching frequencies of metal carbonyls

IR spectroscopy is an important tool for the study of metal carbonyls. The free CO has a $\nu(\text{CO})$ value of 2143 cm^{-1} . The $\nu(\text{CO})$ is proportional to the C-O bond strength and it is a measure of the extent of back bonding.

An IR spectrum can provide the following information.

- (i) *Bonding mode of CO* - whether it is terminal, doubly or triply bridging.
- (ii) *Geometry of the molecule* - the number of bands tells us the symmetry of the $\text{M}(\text{CO})_n$ fragment; for example, *cis/trans* and *fac/mer*: *trans*-complex shows only one band.
- (iii) *Electron donor and withdrawing nature of other co-ligands* - electron donors lower the CO stretching frequency.
- (iv) *Oxidation state or the charge on the complex ion* - anionic complexes show lower stretching frequencies.

The metal carbonyls $[\text{M}(\text{CO})_6]$, $[\text{M}(\text{CO})_4]$, *trans*- $[\text{M}(\text{CO})_4\text{L}_2]$ and $[\text{M}(\text{CO})_3(\text{L}_{\text{axial}})_2]$ show only one carbonyl stretching frequency whilst *fac*- $[\text{M}(\text{CO})_3\text{L}_3]$ shows two IR bands.

Problems

1. $[\text{W}(\text{CO})_6]$ reacts with two moles of PMe_3 to give an 18e-complex **X**. **X** shows only one IR band in the carbonyl region, draw the structure of **X**.
2. Draw the structure of $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2]$ which shows only one IR band in the carbonyl region.
3. Predict the product(s) of the following reactions.
 - (i) $[\text{Fe}(\text{CO})_5] + 1,3\text{-butadiene} \xrightarrow{\Delta}$
 - (ii) $[\text{W}(\text{CO})_6] + \text{MeSCH}_2\text{CH}_2\text{SMe} \xrightarrow{\Delta}$
 - (iii) $[\text{MnCl}(\text{CO})_5] + \text{NaCp} \longrightarrow$
 - (iv) $[\text{W}(\text{CO})_6] + \text{bipyridine} \xrightarrow{\Delta}$
 - (v) $[\text{W}(\text{CO})_6] + 1,3,5\text{-cycloheptatriene} \xrightarrow{\Delta}$
4. Explain the variation in $\nu(\text{CO})$ of the following compound/ions?

Compound/ions	$\nu(\text{CO})/\text{cm}^{-1}$
$[\text{Mn}(\text{CO})_6]^+$	2090
$[\text{Cr}(\text{CO})_6]$	2000
$[\nu(\text{CO})_6]^-$	1860
Free CO	2143