

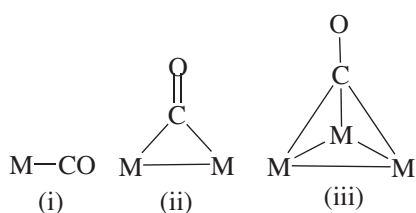
Metal Carbonyls

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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** $M_2(\mu_2\text{-CO})$, and (iii) **triply** or face **bridging** $M_3(\mu_3\text{-CO})$.



The **carbonyl stretching frequency** $\nu(\text{CO})$ decrease in the following order, $M\text{-CO} > M_2(\mu_2\text{-CO}) > M_3(\mu_3\text{-CO})$: as back donation increases with the increase of number of metal atoms.

Bond type	$\nu(\text{CO})/\text{cm}^{-1}$
M–CO	2150-1900
$M_2(\mu_2\text{-CO})$	1900-1750
$M_3(\mu_3\text{-CO})$	1750-1600

$\mu_2\text{-CO}$ ligand donates **one electron** to each of the two metal centres. $\mu_3\text{-CO}$ 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

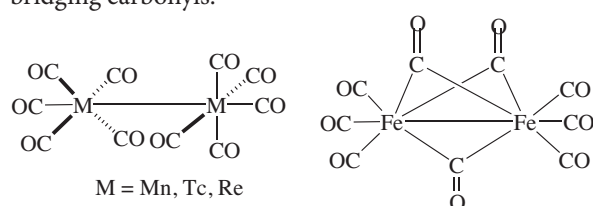
Binuclear metal carbonyls contain a M—M bond, and sometimes **bridging** carbonyl ligands. Some examples are with -

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

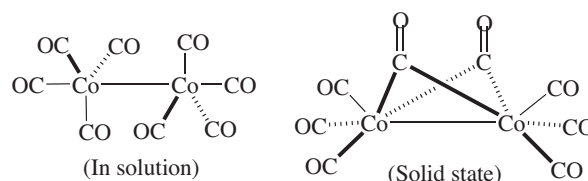
Group 8 metals - $[Fe_2(CO)_9]$

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.



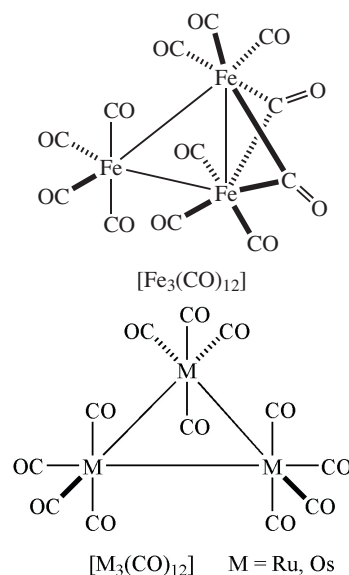
Dimerization of two 17e $[Co(CO)_4]^\cdot$ radicals gives the 18e-complex $[Co_2(CO)_8]$.



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

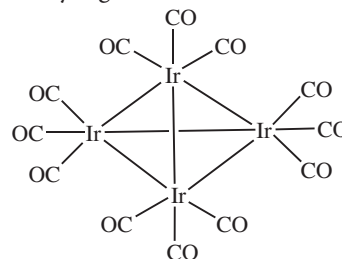
In these complexes, the metal atoms form a **triangular** arrangement. Examples include carbonyls of Group 8 metals - $[M_3(CO)_{12}]$; M = Fe, Ru, Os.



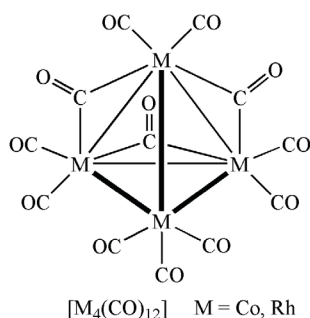
$[Fe_3(CO)_{12}]$ has two bridging carbonyls, but less reactive $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ have a strongly bonded triangular cluster with no bridging carbonyl ligands.

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

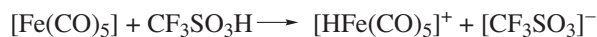


(b) Substitution with olefins

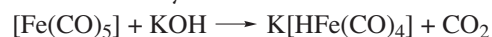


(C_4H_6 = cyclobutene and C_4H_4 = cyclobutadiene)

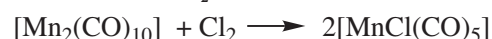
(c) Protonation with acids



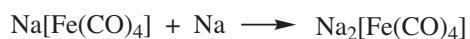
(d) Reaction with KOH (attack by OH^-), gives an anionic metal hydride



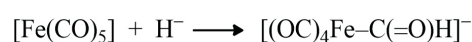
(e) Oxidation with Cl_2 gives a chloride



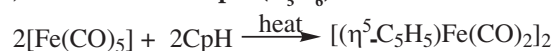
(f) Reduction with Na gives a metal carbonyl anion



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



(h) Reaction with C_5H_6 (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