Chapter 2

Metal Carbonyls and Clusters

Metal Carbonyls :

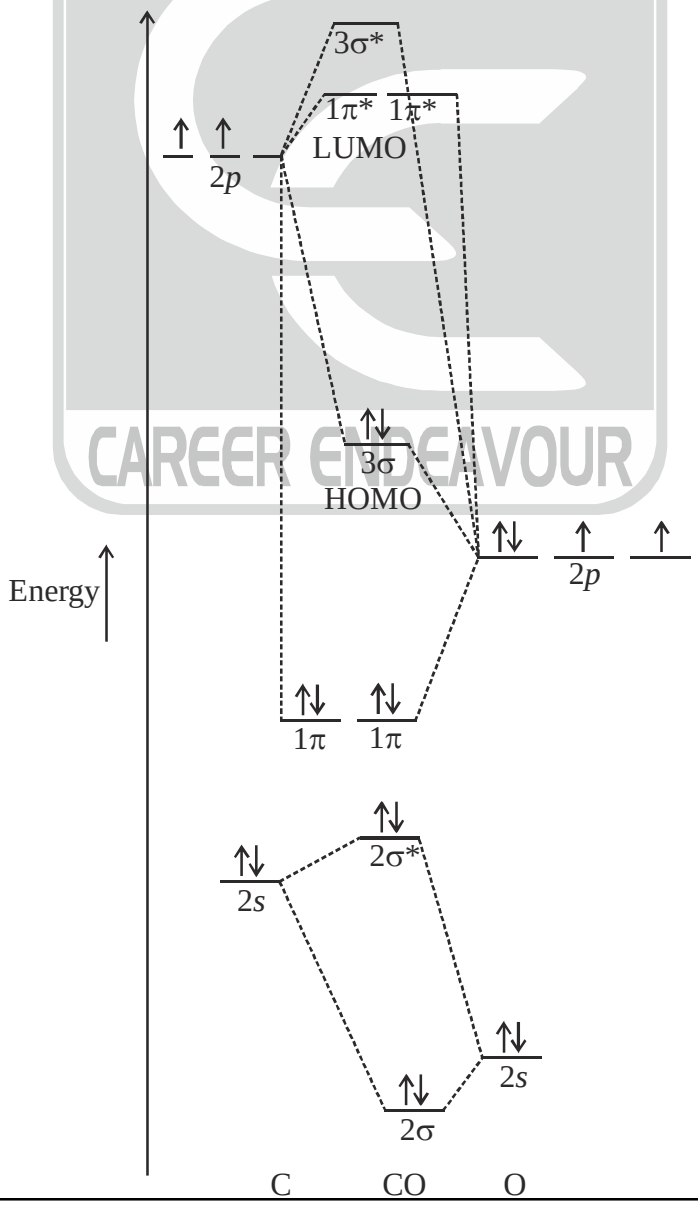
Metal carbonyls are those compounds which contain carbonyl (CO) as a ligand bonded to metal. Some properties of metal carbonyls are

(1) This CO group is a weak σ donor and strong π acceptor.

$$M \xleftarrow[\sigma \text{ bond}]{} CO$$

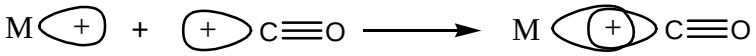
(2) Metal should be in low oxidation state CO stablises low oxidation state

MOLECULAR ORBITAL DIAGRAM OF CO

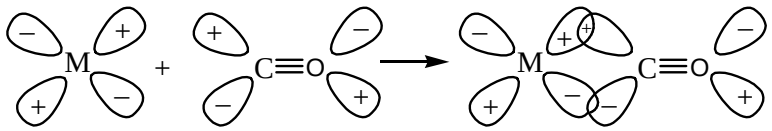


BONDING IN METAL CARBONYLS :

(1) σ- Bond :



(2) π- Back Bonding : π back bonding utilises in filled d orbital of metal & empty π* orbital of CO

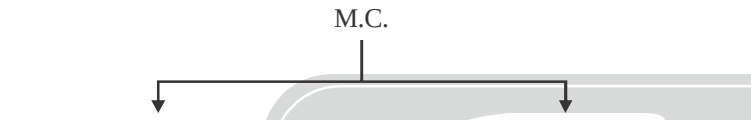


π-bond

This type of bonding where both π and σ bond help (reinforce) each other is called synergistic bonding during σ-bond formation CO donates electron density to the metal. As a result of which –ve charge on the metal increases. Metal can remove this excess electron density by π back bonding from a filled d-orbital of metal to empty π* orbital of CO.

CLASSIFICATION OF METAL CARBONYLS:

1. On the basis of ligand present in metal carbonyls they can be classified as



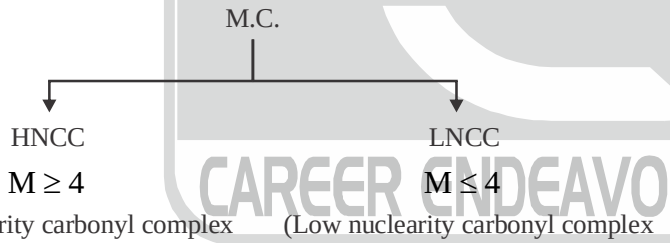
Homoleptic : Complex containing only carbonyl as a ligand)

e.g. $Rh_6(CO)_{16}$, $Mn_2(CO)_{10}$, $W(CO)_6$ etc.

Heteroleptic : $M + CO's$ + other ligands.

e.g. $Fe(CO)_3(PPh_3)_2$, $Ni(CO)_3(PPh_3)$, $W(CO)_3(PPh_3)$ etc.

2. On the basis of metal present in metal carbonyls, they can be classified as



M = 4 is a border line case.

SPECTRAL PROPERTY OF METAL CARBONYLS:

I.R. SPECTROSCOPY OF METAL CARBONYLS:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ cm^{-1}$$

Where k is the stiffness (strength) of the bond, whereas μ is reduced mass and $\mu = \frac{m_1 m_2}{m_1 + m_2}$

It is clear from above equation that $\nu \propto \sqrt{k}$ and $\nu \propto \frac{1}{\sqrt{\mu}}$

$\nu_{C\equiv 0}$ (free) $2143\ cm^{-1}$

$\nu_{(CO)^+} = 2184\ cm^{-1}$

ν_{C-O} (terminal) $= 2120 - 1850\ cm^{-1}$