

### Metal $\pi$ -Acid Complexes:

The d-block transition metal atoms are their ability to form complexes with a variety of neutral molecules such as carbon monoxide, isocyanides, substituted phosphines, Arsines and various molecules with delocalised p $\pi$ -orbitals. In many of these complexes, the metal atoms are in low positive, zero or even negative formal oxidation states. This property is associated with the fact that these ligands have vacant orbitals in addition to lone pairs. These vacant orbitals accept electron density from filled metal orbitals to form a type of  $\pi$ -orbitals that ~~Supplement~~  $\sigma$ -bonding arising from lone pair donation. These ligands are  $\sigma$ -donor and  $\pi$ -acceptor ligands. These ligands are also called  $\pi$ -acid ligands or  $\pi$ -acceptor ligands or  $\pi$ -bonding ligands. These ligands combined with transition metals are known as  $\pi$ -acid complexes.

The compounds formed by the combination of CO molecules with transition metal atoms in low oxidation states are called metallic carbonyls. In these compounds carbonyl molecules act as a neutral ligand. The electron density is higher when metal is in their lower oxidation state. Since metal is electro positive in nature some of the excess electronic charge present on the metal atom gets transferred to the vacant  $\pi$ -orbitals of CO by forming M $\rightarrow$ CO  $\pi$ -bonds.

### Classification of carbonyls:

1. Classification based on the number of metallic bonds present in carbonyls:

- (a) Mononuclear or Monomeric carbonyls—These carbonyls have the general formula M(CO) $_x$  which contains only one atom of the metal per molecule of carbonyl. Thus their empirical and molecular formulas are identical for example Ni(CO) $_4$ , Fe(CO) $_5$ , Cr(CO) $_6$  etc. Mononuclear carbonyls are generally formed by even atomic numbers of metals. These carbonyls are readily soluble in organic solvents such as petroleum, benzene, ethers etc. They can be vaporised with decomposition.
- (b) Poly nuclear carbonyls – They have the general formulae M (CO) $_x$  having more than one metal atoms per molecule, These carbonyls may be homonuclear or heteronuclear. For examples Co $_2$ (CO) $_8$ , Fe $_2$ (CO) $_9$ , MnCo(CO) $_9$ , MnRe(CO) $_{10}$ .

(2) classification based on the structure of carbonyls:

- (a) Non - bridged carbonyls – These carbonyls do not contain any bridging carbonyl group.
- (b) Bridged carbonyls – These carbonyls contain terminal carbonyl groups along with bridging carbonyl groups and one or more carbonyl groups.

Mononuclear carbonyls always have non-bridged structure while poly-nuclear carbonyls may have non-bridged as well as bridged structure.