

Coordination compounds in which carbon monoxide (CO) molecules (Carbonyl), a π -acceptor ligand are bonded directly or substantially (bridged) with transition metals in lower oxidation states (mainly 0 ^(zero), but sometimes low positive or negative) are called metal carbonyls. Metal carbonyls agree to the effective atomic no. rule, except $[V(CO)_6]$.
 e.g. $[Fe(CO)_5]$, $[Rh(CO)_5]$, $[Os_2(CO)_2]$ etc.

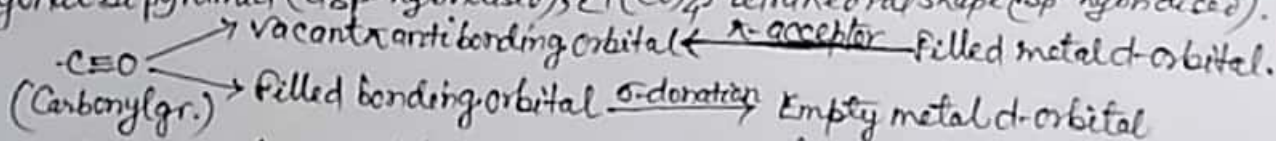
Classification of Metal Carbonyl Compounds: Metal carbonyls, $[M_x(CO)_x]$ are classified into three types, depending on the number of metal atom(s) per molecule.

1. Mononuclear Carbonyls: Metal carbonyls, $[M(CO)_x]$ containing only one metal atom per molecule are called mononuclear carbonyls. Transition metals which have an even atomic number and zero oxidation state form such carbonyls. e.g., $[Os(CO)_5]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Mo(CO)_6]$, $[Ni(CO)_4]$ etc. $[M_2(CO)_x]$ or $[MM'(CO)_x]$
2. Dinuclear Carbonyls: Metal carbonyls containing two metal atoms per molecule directly linked and CO (Carbonyl) groups bonded to terminal metal atoms with coordinate bonds are called dinuclear carbonyls. They may be homotype, e.g., $[Fe_2(CO)_9]$, $[Cr_2(CO)_{10}]$, $[Rh_2(CO)_8]$ etc. or heterotype, e.g., $[MnCo(CO)_9]$, $[MnRe(CO)_{10}]$ etc.
3. Polynuclear Carbonyls: Metal carbonyls, $[M_y(CO)_x]$ containing more than two metal atoms per molecule are called polynuclear carbonyls. Here CO (Carbonyl) groups linked with metal in terminal as well as bridge positions. e.g., $[Co_3(CO)_12]$, $[Os_3(CO)_{21}]$, $[Co_4(CO)_{16}]$, $[Fe_3(CO)_{12}]$

Methods of Preparation: A number of methods used for preparation of metal carbonyls

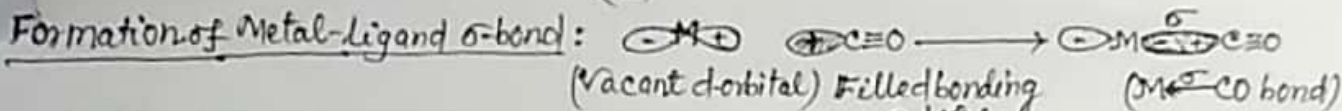
1. Mono or dinuclear metal carbonyls are generally prepared by direct interaction of finely divided metal and CO(g) at suitable temperature.
 e.g., $Ni + 4CO(g) \xrightarrow[1 \text{ atm}]{\text{Room temp.}} [Ni_2(CO)_4]$; $Fe + 5CO \xrightarrow[100 \text{ atm}]{200^\circ C} [Fe(CO)_5]$
 $2Co + 8CO(g) \xrightarrow[100 \text{ atm}]{200^\circ C} [Co_2(CO)_8]$
2. Polynuclear metal carbonyls are prepared by photo or thermal decomposition of mono dinuclear metal carbonyls.
 e.g., $2[Os(CO)_5] \xrightarrow{h\nu} [Os_2(CO)_9] + CO$
 $2[Fe(CO)_5] \xrightarrow[\text{CH}_3\text{COOH}/\Delta]{\text{Glacial}} [Fe_2(CO)_9] \longrightarrow [Fe_3(CO)_{10}]$
3. Heteronuclear metal carbonyls are prepared by interaction of two different Carbonyl Complexes. e.g. $Na[Mn(CO)_5] + [Re(CO)_5]Cl \longrightarrow [(CO)_5Mn-Re(CO)_5] + NaCl$.

Structure & Bonding of Metal Carbonyls: The structure of monocarbonyls, e.g. $[Ni(CO)_4]$, $[Fe(CO)_5]$ etc. have been studied by X-ray diffraction, Infrared spectroscopy, Electron diffraction methods. All the monocarbonyls, $[M(CO)_x]$ have linear M-CO bonds. Hexacarbonyl, $[M(CO)_6]$ have octahedral shape (d^2sp^3 hybridised), $[M(CO)_5]$ trigonal bipyramid (d^2sp^3 hybridised), $[M(CO)_4]$ tetrahedral shape (sp^3 hybridised).



Here $C \equiv O$ (Carbonyl) behaves as π -acceptor ligand. The carbonyls are highly stable at low oxidation state. Molecular orbital electronic configuration of CO:
 $(sp)^0, (d_{sp})^2, (\pi)^2 = (\pi_x^*)^2, (sp)^2, (\pi_y^*)^0 = (\pi_x^*)^0, (p_{sp})^0$.

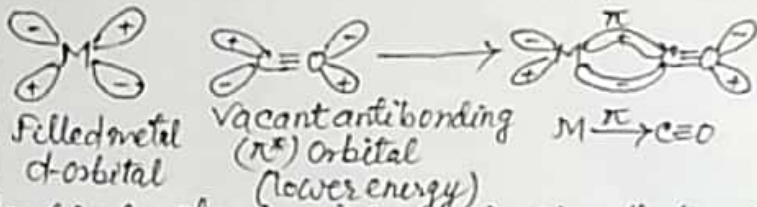
(2)



In the formation of M-CO bond, empty hybrid orbital of metal atom overlap with the filled (sp) hybrid orbital on C-atom of CO molecule. In the formation of this bond, metal atom acts as an electron pair acceptor while CO acts as an electron pair donor.

Formation of metal-ligand π -bond:

In the formation of M \rightarrow C bond, filled d-orbital of metal overlap with empty π -antibonding orbitals (π_x^* or π_y^*) on C-atom of carbonyl (CO) ligand. This bonding mechanism is synergic, since the transfer of metal electrons into -C \equiv O gr. (ligand) will tend to make, as a whole, negative and hence to enhance its basicity via the σ -orbital of C-atom. At the same time the transfer of electrons to the metal in the σ -bond tends to make, ~~as a whole, negative~~ the carbonyl ligand positive, thus increasing the acceptor strength of the π -orbital of ligand. The effect of σ -bond formation strengthens the π -bonding and vice-versa, i.e., electroneutrality in the molecule.



18-e⁻ rule: Total number of electrons in outermost orbital of metal atom and electrons donated by ligand (CO molecule) is always 18 in metal carbonyls.

Such carbonyls are more stable. This is called 18-electron rule.

e.g., $[\text{Fe}(\text{CO})_5]$: It is triangular bipyramid structure, and Fe-atom is dsp^3 hybridised. No. of electrons in outermost orbit of Fe = 8

No. of electrons donated by 5 CO (ligand molecules) = $5 \times 2 = 10$.

Total number of electrons in metal carbonyl formation = $8 + 10 = 18$.

Thus, the metal carbonyl $[\text{Fe}(\text{CO})_5]$ follows 18-e⁻ rule, and hence stable.

Structure of Polynuclear metal Carbonyls: In polynuclear carbonyls, there are M-M bonds, but in many carbonyls bridging carbonyl groups of several types are found.

Case-I When there is direct M-M bond and each metal is bonded to terminal CO groups by coordinate bond (M \leftarrow C \equiv O). e.g., $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{Fe}_2(\text{CO})_{10}]$, $[\text{Cr}_2(\text{CO})_{10}]$ etc.

Let us consider $[\text{Mn}_2(\text{CO})_{10}]$, it has D_{4h} symmetry. Two Mn-atoms are directly bonded by σ bond and five CO (ligand) bonded (terminal) to each metal atom.

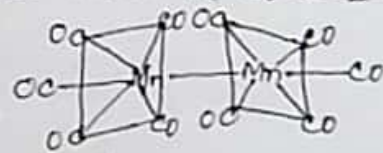
Here, valence electrons of Mn(0), $3d^5 4s^2 = 7$

No. of electrons donated by 5 CO (ligand) = $5 \times 2 = 10$

Electron from M-M bond = 1.

Total numbers of electrons of each Mn = $7 + 10 + 1 = 18$ (stable)

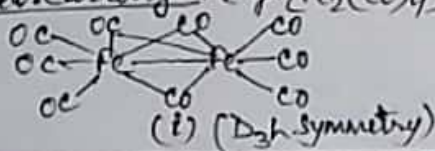
It is diamagnetic nature.



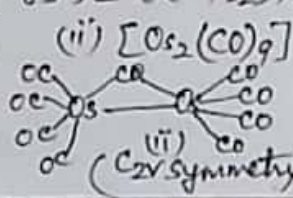
$[\text{Mn}_2(\text{CO})_{10}]$
(D_{4h} symmetry)

Case-II When both terminal and bridging carbonyl groups are present. The bridging carbonyl attached to metal by $\text{M} \leftarrow \text{C} \equiv \text{O}$. Terminal carbonyl group by $\text{M} \leftarrow \text{C} \equiv \text{O}$. e.g., $[\text{Fe}_2(\text{CO})_9]$, $[\text{Os}_2(\text{CO})_9]$, $[\text{Co}_2(\text{CO})_8]$, $[\text{M}_3(\text{CO})_{12}]$, $[\text{M}_4(\text{CO})_{12}]$, $[\text{M}_5(\text{CO})_{16}]$ etc.

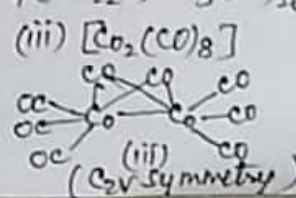
Binuclear carbonyls: e.g., $[\text{Fe}_2(\text{CO})_9]$



(i) (D_{3h} symmetry)



(ii) (C_{2v} symmetry)



(iii) (C_{2v} symmetry)