METALLIC CARBONYLS AND METALLIC NITROSYLS

Introduction:

The electronic configuration of CO molecule shows that both carbon and oxygen atoms have a lone pair of electrons. Carbon atom can donate its electron pair to a transition metal atom to form OC→M coordinate bond. Hence the compounds form by combination of CO molecules, with transition metals are known as metallic carbonyls. Since the electrons supplied solely by CO molecule in the formation of OC→M bond, metal atom in carbonyl has zero oxidation state.

Carbonyls have been classified on the basis of the number of metal atoms present in the carbonyl as under.

(i) Mononuclear (or monomeric) carbonyl:

Which is having only one metal atom per molecule and having type M(CO)_y. e.g. V(CO)_6, Cr(CO)_6 etc.

(ii) Polynuclear carbonyl:

Which contain two or more metal atoms per molecule having type M_x(CO)_y. however some authors call carbonyls containing two metal atoms are called bridged carbonyl and which containing more than two metal atoms are called polynuclear carbonyls which may be homonuclear e.g. Fe_3(CO)_12 or heteronuclear e.g. MnCo(CO)_9, MnRe(CO)_10 etc.

GENERAL METHODS OF PREPARATION

Following are some of the general methods of preparation of metal carbonyls.

(i) Direct Synthesis: Only Ni(CO)_4 and Fe(CO)_5 and Co_2(CO)_8 are normally obtained by the action of CO on the finely divided metal at suitable temperature and pressure.

\[
\text{Fe} + 5\text{CO} \xrightarrow{200 \, ^\circ \text{C}, \, 100 \, \text{atm press.}} \text{Fe(CO)}_5 \\
\text{Ni} + 4\text{CO} \xrightarrow{\text{R.T.}, \, 100 \, \text{atm press.}} \text{Ni(CO)}_4 \\
2\text{Co} + 8\text{CO} \xrightarrow{200 \, ^\circ \text{C}, \, 100 \, \text{atm press.}} \text{Co}_2\text{CO}_8
\]
(ii) By carbonylating metallic salts with CO in presence of reducing agent:

Metallic carbonyls are obtained when salts like RuI₃, CrCl₃, VCl₃, CoS, Co(CO)₃, CoI₂ etc. are treated with CO in presence of suitable reducing agent like Mg, Ag, Cu, Na, H₂, AlLiH₄ etc.

\[ \text{CrCl}_3 + 5\text{CO} + \text{LiAlH}_4 \xrightarrow{115 \degree \text{C}, 70 \text{ atm press.}} \text{Cr(CO)}_6 + \text{LiCl} + \text{AlCl}_3 \]

\[ \text{RuI}_3 + 10\text{CO} + 6\text{Ag} \xrightarrow{175 \degree \text{C}, 250 \text{ atm press.}} 2\text{Ru(CO)}_5 + 6\text{AgI} \]

\[ 2\text{MnI}_2 + 10\text{CO} + 2\text{Mg} \xrightarrow{25 \degree \text{C}, 210 \text{ atm press.}} \text{Mn}_2(\text{CO})_3 + 2\text{MgI}_2 \]

\[ 2\text{CoS} + 8\text{CO} + 4\text{Cu} \xrightarrow{200 \degree \text{C}, 200 \text{ atm press.}} \text{Co}_2(\text{CO})_8 + 2\text{Cu}_2\text{S} \]

\[ 2\text{CoI}_2 + 8\text{CO} + 4\text{Cu} \xrightarrow{200 \degree \text{C}, 200 \text{ atm press.}} \text{Co}_2(\text{CO})_8 + 4\text{CuI} \]

\[ 2\text{FeI}_2 + 5\text{CO} + 2\text{Cu} \xrightarrow{200 \degree \text{C}, 200 \text{ atm press.}} \text{Fe(CO)}_5 + \text{Cu}_2\text{I}_2 \]

\[ 2\text{CoCO}_3 + 8\text{CO} + 2\text{H}_2 \xrightarrow{120-200 \degree \text{C}, 250-300 \text{ atm press.}} \text{Co}_2(\text{CO})_8 + 2\text{CO}_2 + 2\text{H}_2\text{O} \]

\[ 2\text{Cr(acac)}_3 + 12\text{CO} + 3\text{Mg} \xrightarrow{160 \degree \text{C}, 300 \text{ atm press.}} 3\text{Mg(acac)}_2 + 2\text{Cr(CO)}_6 \]

\[ \text{MoCl}_5 + 6\text{CO} + 5\text{Na} \xrightarrow{\text{in diglyme}} \text{Mo(CO)}_6 + 5\text{NaCl} \]

Sometimes CO acts as a carbonylating and reducing agent as under.

\[ \text{OsO}_3 + 5\text{CO} \xrightarrow{250 \degree \text{C}, 350 \text{ atm press.}} \text{Os(CO)}_5 + 2\text{O}_2 \]

\[ \text{Re}_2\text{O}_7 + 10\text{CO} \rightarrow \text{Re}_2(\text{CO})_{10} + 7\text{O}_2 \]

\[ \text{V(CO)}_6 \text{ is prepared by the method represented by the following equation} \]

\[ \text{VCl}_3 + 6\text{CO} + \text{Na} \xrightarrow{100 \degree \text{C}, 150 \text{ atm press.}} \text{acidification by } \text{H}_3\text{PO}_4 \xrightarrow{118 \degree \text{C}, 150 \text{ atm press.}} \text{V(CO)}_6 + 3\text{NaCl} \]

(iii) Preparation of Mo(CO)₆ and W(CO)₆ from Fe(CO)₅:

MoCl₅ and WCl₅ give the corresponding hexacarbonyls. These reactions are characterized by low yield, which can be improved by using high pressure.
MoCl₆ + 3Fe(CO)₅ $\xrightarrow{110 \, ^{0}C, \text{ether}}$ Mo(CO)₆ + 3FeCl₂ + 9CO

WCl₆ + 3Fe(CO)₅ $\xrightarrow{110 \, ^{0}C, \text{ether}}$ W(CO)₆ + 3FeCl₂ + 9CO

(iv) Preparation of Fe₂(CO)₉, and Os₂(CO)₉ from Fe(CO)₅:

When cool solution of Fe(CO)₅ and Os(CO)₅ in glacial CH₃COOH is irradiated with ultra-violet light, Fe₂(CO)₉, and Os₂(CO)₉ are obtained respectively.

Fe(CO)₅ $\xrightarrow{UV-\text{light}}$ Fe₂(CO)₉ + CO

Os(CO)₅ $\xrightarrow{UV-\text{light}}$ Os₂(CO)₉ + CO

**GENERAL PROPERTIES**

**Physical properties:**

(i) Most carbonyls are volatile solids but Fe(CO)₅, Ru(CO)₅, Os(CO)₅ and Ni(CO)₄ are liquids at ordinary temperature and quite inflammable.

(ii) Many of these decompose or melt at low temperature.

(iii) They are soluble in organic solvents. Ni(CO)₄ is insoluble in water but others react with it.

(iv) All carbonyls, except V(CO)₆, are diamagnetic substances. Metals with odd atomic number couple the odd electrons to form metal-metal bond. Probably the steric factor prevents V(CO)₆ from dimerization.

(v) All carbonyls are thermodynamically unstable with respect to oxidation in air, but their rates vary widely. CO₂(CO)₈ reacts at ordinary temp. Fe₂(CO)₉ and Ni(CO)₄ are also readily oxidized (their vapours forming explosive mixtures with air); M(CO)₆, M = Cr, Mo, W react only when heated.

**Chemical properties:**

(i) Substitution reaction:

Some or all CO groups present in carbonyl can be replaced by monodentate ligands like isocyanide (CNR), PR₃, PCl₃, py, CH₃OH etc. e.g.

Ni(CO)₄ + 4CNR $\rightarrow$ Ni(CNR) + 4CO

Ni(CO)₄ + 4PCl₃ $\rightarrow$ Ni(PCl₃) + 4CO

Fe(CO)₅ + 2CNR $\rightarrow$ Fe(CO)₃(CNR)₂ + 2CO

Mn₂(CO)₁₀ + PR₃ $\rightarrow$ 2Mn(CO)₄(PR₃) + 2CO
2Fe_2(CO)_{12} + 3py → Fe_3(CO)_9(py)_3 + 3Fe(CO)_5

2Fe_2(CO)_{12} + 3CH_3OH → Fe_3(CO)_9(CH_3OH)_3 + 3Fe(CO)_5

Bidentate ligands like diars, o-phen, NO_2 etc. replace at two or more CO group at a time. e.g.

Mo(CO)_6 + diars → Mo(CO)_4(diars) + 2CO

Fe(CO)_5 + diars → Fe(CO)_3(diars) + 2CO

Ni(CO)_4 + o-phen → Ni(CO)_2(o-phen)_2 + 2CO

Ni(CO)_4 + diars → Ni(CO)_2(diars) + 2CO

Cr(CO)_6 + 2diars → Cr(CO)_2(diars)_2 + 4CO

Ni(CO)_4 + 2NO_2 → Ni(NO_2)_2 + 4CO

(ii) Action of NaOH or Na metal:

Formation of carbonylate anion (reduction). Aqueous or alcoholic solution of NaOH reacts with Fe(CO)_5 to form carbonylate anion, [HFe(CO)_4]^{-}:

Fe(CO)_5 + 3NaOH → Na^+ [H^+ Fe^{2-}(CO)_4]^{-} + Na_2CO_3 + H_2O
(Fe = 0)

H-atom in [H^+Fe^{2-}(CO)_4]^{-} ion is acidic which means that Fe-atom in this ion is in -2 oxidation state.

Na-metal in liquid NH_3 converts Fe_2(CO)_9, Co_2(CO)_8, Fe_3(CO)_{12}, Cr(CO)_6, Mn_2(CO)_{10} etc. into carbonylate anions and in these carbonyls are reduced.

Fe_2(CO)_9 + 4Na → 2Na^+ [Fe^{2-}(CO)_4]^{-} + CO
(Fe = 0)

Co_2(CO)_8 + 2Na → 2Na^+ [Co^{2-}(CO)_4]^{-}
(Co = 0)

Fe_3(CO)_{12} + 3Na → 3Na^+ [Fe^{2-}(CO)_4]^{-}
(Fe = 0)

Cr(CO)_6 + 2Na → Na^+ [Cr^{2-}(CO)_5]^{-} + CO
(Cr = 0)

Mn_2(CO)_{10} + 2Na → 2Na^+ [Mn^{2-}(CO)_5]^{-}
(Mn = 0)
(iii) Carbonyl react with halogens to form carbonyl halides shown as under.

\[
\begin{align*}
\text{Fe(CO)}_5 + X_2 & \rightarrow \text{Fe(CO)}_4 X_2 + \text{CO} \\
\text{Mo(CO)}_6 + \text{Cl}_2 & \rightarrow \text{Mo(CO)}_4 \text{Cl}_2 + 2\text{CO} \\
\text{Mn}_2(\text{CO})_{10} + X_2 \; (X=\text{Br}, \text{I}) & \rightarrow 2\text{Mn( CO)}_5 X
\end{align*}
\]

Co\(_2(\text{CO})_8\) and Ni(\text{CO})\(_4\) both get decomposed into metallic halides and CO when treated with halogens. e.g.

\[
\begin{align*}
\text{Co}_2(\text{CO})_8 + 2X_2 & \rightarrow 2\text{CoX}_2 + 8\text{CO} \\
\text{Ni( CO)}_4 + \text{Br}_2 & \rightarrow \text{NiBr}_2 + 4\text{CO}
\end{align*}
\]

(iv) **Action of NO:**

Many carbonyl react with nitric oxide to form metal carbonyl nitrosyls. e.g

\[
\begin{align*}
\text{Fe( CO)}_5 + 2\text{NO} & \xrightarrow{95^\circ \text{C}} \text{Fe( CO)}_2(\text{NO})_2 + 3\text{CO} \\
3\text{Fe}_2(\text{CO})_9 + 4\text{NO} & \rightarrow 2\text{Fe( CO)}_2(\text{NO})_2 + \text{Fe}_2(\text{CO})_5 + \text{Fe}_3(\text{CO})_12 + 6\text{CO} \\
\text{Fe}_3(\text{CO})_12 + 6\text{NO} & \xrightarrow{85^\circ \text{C}} 3\text{Fe( CO)}_2(\text{NO})_2 + 6\text{CO} \\
\text{Co}_2(\text{CO})_8 + 2\text{NO} & \xrightarrow{40^\circ \text{C}} 3\text{Co( CO)}_3(\text{NO}) + 2\text{CO}
\end{align*}
\]

Moist NO gives a blue coloured compound, Ni(NO)(OH) with Ni(\text{CO})\(_4\) while dry NO gives a blue solution of the composition, Ni(NO)(NO\(_2\))

\[
\begin{align*}
2\text{Ni( CO)}_4 + 2\text{NO} + 2\text{H}_2\text{O} & \rightarrow 2\text{Ni(NO)(OH)} + 8\text{CO} + \text{H}_2 \\
\text{Ni( CO)}_4 + 4\text{NO} & \rightarrow \text{Ni(NO)(NO}_2\) + 4\text{CO} + \text{N}_2\text{O}
\end{align*}
\]

(iv) **Action of H\(_2\):**

When Mn\(_2(\text{CO})_10\) and Co\(_2(\text{CO})_8\) react with H\(_2\), they are reduced to carbonyl hydride, Mn(\text{CO})\(_5\)H and Co(\text{CO})\(_4\)H respectively.

\[
\begin{align*}
\text{Mn}_2(\text{CO})_{10} + \text{H}_2 & \xrightarrow{200 \text{ atm. press.}} 2[\text{Mn}^-(\text{CO})_5\text{H}^+]^0 \\
\text{Co}_2(\text{CO})_8 + \text{H}_2 & \xrightarrow{165^\circ \text{C}, 200 \text{ atm. press.}} 2[\text{Co}^-(\text{CO})_4\text{H}^+]^0
\end{align*}
\]

(v) **Action of Heat:**

Different carbonyls give different product when heated shown below.
Fe(CO)₅ $\xrightarrow{250 ^\circ C}$ Fe + 5CO

3Fe₂(CO)₉ $\xrightarrow{70 ^\circ C, cool}$ 3Fe(CO)₂ + Fe₃(CO)₁₂ (in toluene)

Fe₃(CO)₁₂ $\xrightarrow{140 ^\circ C, cool}$ 3Fe + 12CO

2Co₂(CO)₈ $\xrightarrow{50 ^\circ C, inert atmosphere}$ Co₄(CO)₁₂ + 4CO

Ni(CO)₄ $\xrightarrow{180 ^\circ C}$ Ni + 4CO

3Fe₂(CO)₉ $\xrightarrow{50 ^\circ C}$ 2Fe₃(CO)₁₂ + 3CO (in toluene)

**Structure and nature of M-CO bonding in carbonyls:**

This can be explained by considering the formation of σ-bonds and π-bonds. The lone paired of electron on carbon atom would expect to form strong σ-dative bond due to electron density remain to the carbon nucleus.

**Formation of dative σ-bonds:**

It is form as a result of overlapping of empty hybrid orbital of metal atom with the filled hybrid orbital on carbon atom of CO molecule and form M←CO σ-bonds. i.e. formation of Ni←CO σ-bonds in Ni(CO)₄ takes place by the overlap between empty $sp^3$ hybrid orbital on Ni and filled $sp$ orbital on carbon atom of CO molecule. Other three Ni←CO bonds are formed in the same manner.

In the type of M(CO)₅ and M(CO)₆ carbonyls $dsp^3$ and $d^2sp^3$ hybrid orbital are used for M←CO σ-bonds. In this bond formation, metal atom acts as electron acceptor, while CO acts as electron donor.

**Formation of dative π-bonds:**

This bond is formed as a result of overlapping of filled $d\pi$ orbitals or hybrid $p\pi$ orbitals of metal atom with low-lying empty $p\pi$-orbitals on CO molecule. i.e. $M \xrightarrow{\pi} CO$
i.e. Ni→CO π-bond in Ni(CO)$_4$ form by overlap between filled $dz^2$ or $dx^2-y^2$ on Ni atom and empty π* molecular orbital on CO molecule.

In M(CO)$_6$ type molecule, since $dz^2$ or $dx^2-y^2$ orbital are used for $d^2sp^3$ hybridization, M→CO π-bond form by overlapping with filled $dxy$, $dyz$ or $dxz$ orbital of M with empty π* molecular orbital on CO molecule. Out of six CO, three are linked by M←CO σ-bond and remaining three is linked by M←CO and M→CO π-bond.

The main evidence for multiple nature of M-CO bonds comes from bond lengths and vibrational spectra. As M-CO donation increases, the M-C bond becomes stronger and the C=O bond becomes weaker. Thus, the multiple bonding would result in shorter M-C bonds and longer C-O bonds as compared M-C single bonds and C=O triple bonds respectively. The C-O bond lengths are rather insensitive to bond order, the M-C bonds show appreciable shortening consistent with π-bonding concept. Some M-C distances are:

V(CO)$_6$: 2.00 ; Mo(CO)$_6$: 2.06; Cr(CO)$_6$: 1.92 ; W(CO)$_6$: 2.07
Fe(CO)$_5$: 1.80 (axial), 1.85 (trig – equatorial); Ni(CO)$_4$: 1.84

**Bridging CO groups:**

In addition to linear M-C-O groups, in some binuclear and polynuclear carbonyls the CO group is known to fulfill bridging functions.

In a terminal M-C-O group the CO donates 2 electrons to an empty metal orbital, while in bridging M(CO) M group the M-C bond is formed by sharing of one metal electron and one carbon electron.

**Effective atomic number rule (EAN):**

In the formation of M←CO bond, CO molecule electron pair to the metal atom. Thus, the metal atom is said to be have zero valency. The rule is state that “After CO groups donated a certain number of electron pairs to the zero valent metal atom through OC→M σ-bonding, the total number of electrons on metal atom including those gained from CO molecule becomes equal to the atomic number of the next inert gas”.

$$EAN = z + 2Y = G$$
Where, $z =$ total electrons of metal atom  
$Y =$ total electron donated by CO groups  
$G =$ Effective atomic number of next inert gas  

In carbonyls, CO can donate two electrons at a time, so only even number of transition metal can achieve the effective atomic number of next inert gas. e.g. for Cr(CO)$_6$,  
\[
EAN = z + 2Y = 24 + (2\times6) = 36 = \text{Ar}
\]

1) Mononuclear carbonyl having transition metal atom in even atomic number in zero oxidation state.

EAN of some mononuclear carbonyls are calculate in the following table

<table>
<thead>
<tr>
<th>Metal carbonyl</th>
<th>No. of ēs on the central metal atom = At. No.of metal = $z$</th>
<th>No. of ēs donated by CO molecule = $2Y$</th>
<th>EAN of the metal atom in carbonyl $= z + 2Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)$_6$</td>
<td>24</td>
<td>$6 \times 2 = 12$</td>
<td>$24 + 12 = 36[\text{Kr}]$</td>
</tr>
<tr>
<td>Mo(CO)$_6$</td>
<td>42</td>
<td>$6 \times 2 = 12$</td>
<td>$42 + 12 = 54[\text{Xe}]$</td>
</tr>
<tr>
<td>W(CO)$_6$</td>
<td>74</td>
<td>$6 \times 2 = 12$</td>
<td>$74 + 12 = 86[\text{Rn}]$</td>
</tr>
<tr>
<td>Fe(CO)$_5$</td>
<td>26</td>
<td>$5 \times 2 = 10$</td>
<td>$26 + 10 = 36[\text{Kr}]$</td>
</tr>
<tr>
<td>Ru(CO)$_5$</td>
<td>44</td>
<td>$5 \times 2 = 10$</td>
<td>$44 + 10 = 54[\text{Xe}]$</td>
</tr>
<tr>
<td>Os(CO)$_5$</td>
<td>76</td>
<td>$5 \times 2 = 10$</td>
<td>$76 + 10 = 86[\text{Rn}]$</td>
</tr>
<tr>
<td>Ni(CO)$_4$</td>
<td>28</td>
<td>$4 \times 2 = 8$</td>
<td>$28 + 8 = 36[\text{Kr}]$</td>
</tr>
</tbody>
</table>

2) Mononuclear carbonyl having transition metal atom in odd atomic number i.e. V(CO)$_6$ and hypothetical carbonyls Mn(CO)$_6$ and Co(CO)$_4$ etc. These carbonyls do not obey EAN rule because metal atom does not achieve next inert gas configuration.  

V(CO)$_6$: $23 + (2 \times 6) = 35$
\[ \text{Mn(CO)}_5: 25 + (2 \times 5) = 35 \]

\[ \text{Co(CO)}_4: 27 + (2 \times 4) = 35 \]

3) **Polynuclear carbonyls:** The polynuclear carbonyls obey EAN rule. Two \( \epsilon \)s each of M-M bond present in these carbonyls are included in calculating the \( \epsilon \)s per metal atom.

\[ \text{Mn}_2(\text{CO})_{10}: \begin{align*}
\epsilon & \text{s from two Mn} = 25 \times 2 = 50 \\
\epsilon & \text{s from ten CO} = 2 \times 10 = 20 \\
\epsilon & \text{s from one Mn-Mn bond} = 2 \\
\end{align*} 
\text{hence EAN of each Mn atom} = 72/2 = 36 [Kr] \]

\[ \text{Fe}_3(\text{CO})_{12}: \begin{align*}
\epsilon & \text{s from three Fe} = 26 \times 3 = 72 \\
\epsilon & \text{s from twelve CO} = 2 \times 12 = 24 \\
\epsilon & \text{s from three Fe-Fe bonds} = 6 \\
\end{align*} 
\text{hence EAN of each Fe atom} = 108/3 = 36 [Kr] \]

**18-electron rule as applied to metallic carbonyls:**

The formation of mononuclear carbonyls by transition elements with even atomic number can also be explained on the basis of 18-electron rule as shown below.

For mononuclear carbonyls, \( \text{M(CO)}_y \)

i.e. \( \text{Ni(CO)}_4: \begin{align*}
\text{No. of the valence electrons of metal atom} & = 10 \\
\text{No. of the electrons donated by CO groups} & = 8 \\
\text{Total number of electrons on the metal atom} & = 18 \\
\end{align*} \]

\( \text{Fe (CO)}_5: \begin{align*}
\text{No. of the valence electrons of metal atom} & = 8 \\
\text{No. of the electrons donated by CO groups} & = 10 \\
\text{Total number of electrons on the metal atom} & = 18 \\
\end{align*} \]

\( \text{Cr(CO)}_6: \begin{align*}
\text{No. of the valence electrons of metal atom} & = 6 \\
\text{No. of the electrons donated by CO groups} & = 12 \\
\text{Total number of electrons on the metal atom} & = 18 \\
\end{align*} \]

The formation binuclear carbonyls having metal atom with odd atomic number can also be explained on the basis of 18-electron rule as shown below for \( \text{Co}_2(\text{CO})_8 \) and \( \text{Mn}_2(\text{CO})_{10} \) carbonyls.

\( \text{Co}_2(\text{CO})_8: \begin{align*}
\text{No. of the valence electrons of two Co atoms} & = 2 \times 9 = 18 \\
\text{No. of the electrons donated by CO groups} & = 2 \times 8 = 16 \\
\text{No. of electron for Co-Co bond} & = 1 \times 2 = 2 \\
\text{Total number of electrons on two Co atoms} & = 36 \\
\text{Therefore, electrons on one Co atom} & = 36/2 = 18 \\
\end{align*} \]
Mn$_2$(CO)$_{10}$: No. of the valence electrons of two Mn atoms = 2 x 7 = 14
   No. of the electrons donated by CO groups = 2 x 10 = 20
   \[ \text{No. of electron for Mn-Mn bond} = 1 \times 2 = 2 \]
   Total number of electrons on two Mn atoms = 36
   Therefore, electrons on one Mn atom = 36/2 = 18

Here, it may be noted that though Fe has an even atomic number (i.e. 26), the formation of its binuclear carbonyl, Fe$_2$(CO)$_9$ can also accounted for by the 18-electron rule as under.

Fe$_2$(CO)$_9$: No. of the valence electrons of two Fe atoms = 2 x 8 = 16
   No. of the electrons donated by CO groups = 2 x 9 = 18
   \[ \text{No. of electron for Fe-Fe bond} = 1 \times 2 = 2 \]
   Total number of electrons on two Fe atoms = 36
   Therefore, electrons on one Fe atom = 36/2 = 18

**SOME INDIVIDUAL CARBONYLS**

1. **Nickel tetra carbonyl, Ni(CO)$_4$:**

   **Preparation:**
   (i) Direct synthesis: CO is passed over reduced Ni at 60 °C

   \[ \text{Ni} + 4\text{CO} \xrightarrow{60 \, ^\circ \text{C}} \text{Ni(CO)}_4 \]

   (ii) From NiI$_2$: NiI$_2$ is heated with Co in the presence of a halogen receptor.

   \[ \text{NiI}_2 + 4\text{CO} \rightarrow \text{Ni(CO)}_4 + \text{I}_2 \]

   (iii) From nickel salt: Passing CO through alkaline suspension of NiS or Ni(CN)$_2$

   \[ \text{NiS} + 4\text{CO} \rightarrow \text{Ni(CO)}_4 + \text{S} \]

   \[ \text{Ni(CN)}_2 + 4\text{CO} \rightarrow \text{Ni(CO)}_4 + \text{C}_2\text{N}_2 \]

   **Properties:**
   (i) Colorless liquid having m.p. -25 °C and b.p. 43 °C, insoluble in water but dissolves in organic solvents. It decomposes at 180 – 200 °C.

   (ii) Action of H$_2$SO$_4$: conc. H$_2$SO$_4$ reacts with detonation

   \[ \text{Ni(CO)}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{NiSO}_4 + \text{H}_2 + 4\text{CO} \]

   (iii) Action of NO: With moist NO it gives intense blue compound Ni(NO)(OH).

   \[ 2\text{Ni(CO)}_4 + 2\text{NO} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(NO)(OH)} + 8\text{OH} + \text{H}_2 \]
(iv) Substitution reactions: see “general properties of carbonyls”.

(v) Action of heat: see “general properties of carbonyls”.

(vi) Action of Halogen: see “general properties of carbonyls”.

(vii) Action of gaseous HCl Gaseous HCl decomposes the solution of Ni(CO)$_4$, evolving H$_2$ and CO

\[
\text{Ni(CO)}_4 + 2\text{HCl}_{(g)} \rightarrow \text{NiCl}_2 + \text{H}_2 + 4\text{CO}
\]

**Uses:**

(i) Since Ni(CO)$_4$, on heating, is decomposed to metallic nickel, it is use in the production of nickel by Mond’s process.

(ii) It is also used in gas planting and as a catalyst.

**Structure:**

The vapour density and freezing point of its solution in C$_6$H$_6$ indicates that it has formula Ni(CO)$_4$. Electron diffraction studies in vapour state and X-rays studies in the solid state shows the tetrahedral structure. Ni-C bond length is 1.5 Å.

Tetrahedral shape of Ni(CO)$_4$ results from $sp^3$ hybridization of Ni-atom. Since Ni(CO)$_4$ molecule is diamagnetic, all the ten electrons present in the valence shell of Ni atom (Ni = 3$d^8$ 4$s^2$) gets paired in 3$d$ orbitals. Thus the valence shell configuration of Ni atom in Ni(CO)$_4$ molecule becomes 3$d^{10}$ 4$s^0$. OC→Ni bond results by the overlap between the empty $sp^3$ hybrid orbital on Ni atom and doubly filled $sp$ orbital on C-atom in CO molecule as shown below.

![Image of sp3 hybridization diagram]
2. Iron pentacarbonyl, Fe(CO)₅:

**Preparation:**
(i) Action of CO on iron powder at 200 °C and 100 atmosphere pressure.

\[
\text{Fe} + 5\text{CO} \rightarrow \text{Fe(CO)}_5
\]

(ii) By carbonylating FeI₂ or FeS with CO in presence of Cu-metal which acts as a reducing agent.

\[
2\text{FeS} + 10\text{CO} + 2\text{Cu} \rightarrow 2\text{Fe(CO)}_5 + \text{Cu}_2\text{S}
\]

**Properties:**
(i) Fe(CO)₅ is pale yellow liquid; b.p. 103 °C, soluble in methyl alcohol, ether, acetone and C₆H₆. It is insoluble in water.
(ii) Decomposition: At 250 °C, it decomposes to give pure Fe.

\[
2\text{Fe(CO)}_5 \rightarrow \text{Fe} + 5\text{CO}
\]

(iii) Action of ultra-violet light: When cooled solution of Fe(CO)₅ in glacial CH₃COOH is treated with ultra-violet light, Fe₂(CO)₉ is formed.

\[
2\text{Fe(CO)}_5 \rightarrow 2\text{Fe}_2(\text{CO})_9 + \text{CO}
\]

(iv) Hydrolysis: It is hydrolyzed with water and acids.

\[
\text{Fe(CO)}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + 5\text{CO} + \text{H}_2
\]

(v) Action of alkali: When heated with aqueous or alcoholic solution of NaOH, carbonylate anion, \([\text{Fe}_2(\text{CO})_4\text{H}^+]\) is formed. The hydrogen atom in this anion is acidic which means that Fe is in -2 oxidation state.

\[
\text{Fe(CO)}_5 + 3\text{NaOH} \rightarrow \text{Na}^+ [\text{Fe}^{2-}(\text{CO})_4\text{H}^+] + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

(vi) Action of NH₃: With NH₃ it gives Fe(CO)₄H₂ and carbamic acid, NH₂COOH.

\[
\text{Fe(CO)}_5 + \text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{Fe(CO)}_4\text{H}_2 + \text{NH}_2\text{COOH}
\]

(vii) Reaction with halogen: It react with halogens in non-aqueous solvent to form the stable tetra carbonyl halides, Fe(CO)₄X₂.

\[
\text{Fe(CO)}_5 + \text{X}_2 \rightarrow \text{Fe(CO)}_4\text{X}_2 + \text{CO}
\]
Structure:

The vapour density and freezing point of its C₆H₆ solution studies indicates it has formula Fe(CO)₅. Electron diffraction studies in vapour state and X-rays studies in the solid state shows that it has trigonal bipyramidal structure. Three CO groups are in the equatorial position, while among two, one is above the plane and other is below the plane, in the polar position.

There is $dsp^3$ hybridization occurs between the orbitals of Fe atom. All eight electrons of Fe atom paired in 3$d$ orbital. Fe(CO)₅ is diamagnetic. The OC→Fe bond is formed by overlapping of empty $dsp^3$ hybrid orbitals with doubly filled sp hybrid orbital on C-atom in CO molecule as shown below.

![Diagram of Fe(CO)₅ structure]

3. Chromium hexacarbonyl, Cr(CO)₆:

Preparation:

(i) By carboxylating CrCl₃ with CO in presence of a reducing agent like lithium aluminium hydride, LiAlH₄.

$$CrCl₃ + CO + LiAlH₄ \rightarrow Cr(CO)₃ + LiCl + AlCl₃$$
(ii) Br treating \( \text{CrCl}_3 \) with CO in presence of \( \text{C}_6\text{H}_5\text{MgBr} \) (Job’s Grignard reaction) under appropriate conditions. (i.e. By passing CO to 50 atm pressure and at room temperature into a suspension of \( \text{CrCl}_3 \) in either which has been treated with \( \text{C}_6\text{H}_5\text{MgBr} \) at \(-27^\circ\text{C}\)).

**Properties:**

(i) It is colourless, insoluble crystals which sublime without decomposition and dissolve in either, \( \text{CHCl}_3 \), \( \text{CCl}_4 \), \( \text{C}_6\text{H}_6 \).

(ii) It is not attacked by air, bromine, cold aqueous alkalis. Dilute acids and conc. HCL and \( \text{H}_2\text{SO}_4 \). It is decomposed by \( \text{Cl}_2 \) and Conc. \( \text{HNO}_3 \)

(iii) It is decomposed by \( \text{F}_2 \) at \(-75^\circ\text{C}\) to form \( \text{CrF}_6 \).

(iv) Alkali metal in liquid ammonia reacts to give \( \text{Na}_2[\text{Cr(CO)}_5] \)

\[
\text{Cr(CO)}_6 + 2\text{Na (lq. NH)} \xrightarrow{\text{Cr}=0} \text{Na}_2^+[\text{Cr}^{2-} (\text{CO})_5]^{2-} + \text{CO}
\]

(v) Some carbonyls present in the \( \text{Cr(CO)}_6 \) can be replaced by pyridine (py) to get a number of compounds.

\[
\text{Cr(CO)}_6 \xrightarrow{\text{py}} \text{Cr(CO)}_4(\text{py})_2 \xrightarrow{\text{py}} \text{Cr}_2(\text{CO})_9 \xrightarrow{\text{py}} \text{Cr(CO)}_3(\text{py})_3
\]

**Structure:**

The electron diffraction studies indicate that it has octahedral. There is \( d^2sp^3 \) hybridization occurs between the orbitals of Cr atom. All the six electrons of Cr (3d\(^5\) 4s\(^1\)) paired in 3d orbitals. \( \text{Cr(CO)}_6 \) is diamagnetic. The \( \text{OC} \rightarrow \text{Cr} \) bond is formed by overlapping of empty \( d^2sp^3 \) hybrid orbitals with doubly filled \( sp \) hybrid orbital on C-atom in CO molecule as shown below.
4. Dimanganese decacarbonyl, Mn$_2$(CO)$_{10}$:

**Preparation:**
(i) By carbonylating MnI$_2$ with CO in presence of Mg (in diethyl ether) which acts as a reducing agent.

\[
2\text{MnI}_2 + 10\text{CO} + 2\text{Mg} \xrightarrow{25^\circ C, 210\text{ atm. in diethyl ether}} \text{Mn}_2(\text{CO})_{10} + 2\text{MgI}_2
\]

(ii) By carbonylating MnCl$_2$ with CO in presence of (C$_6$H$_5$)$_2$CONa.

\[
2\text{MnCl}_2 + 10\text{CO} + 4(\text{C}_6\text{H}_5)_2\text{CONa} \xrightarrow{165^\circ C, 140\text{ atm.}} \text{Mn}_2(\text{CO})_{10} + 4(\text{C}_6\text{H}_5)_2\text{CO} + 4\text{NaCl}
\]

**Properties:**

(i) It is a golden yellow crystalline substance having m.p. 155 $^\circ$C, soluble in organic solvents. It is slowly oxidized in air, especially in solution.

(ii) It reacts with halogens to formed carbonyl halides.

\[
\text{Mn}_2(\text{CO})_{10} + X_2 (X = \text{Br, I}) \rightarrow 2\text{Mn(CO)}_5X
\]

(iii) It reacts with Na-metal in liq. NH$_3$ to formed carbonylate anion.

\[
\text{Mn}_2(\text{CO})_{10} + 2\text{Na} \xrightarrow{\text{liq NH}_3} \text{2Na}^+ [\text{Mn}^-(\text{CO})_5]^- \\
(\text{Mn}=0)
\]

(iv) It react with PR$_3$ to formed Mn(CO)$_4$(PR$_3$).

\[
\text{Mn}_2(\text{CO})_{10} + \text{PR}_3 \rightarrow 2\text{Mn(CO)}_4(\text{PR}_3) + 2\text{CO}
\]
Structure:

In Mn$_2$(CO)$_{10}$, two Mn$_2$(CO)$_5$ groups are joined by Mn-Mn bond. The formation of this bond effectively adds one electron to each Mn atom. Mn(CO)$_5$ does not exist as Mn has odd atomic number, but it exists as Mn$_2$(CO)$_{10}$ (i.e. unpaired electrons of each Mn atom are used to form Mn-Mn bond). Thus, binuclear carbonyl is formed in odd atomic number of first transition series.

As shown in the structure, five terminal CO groups are joined to each Mn atom. This dimer is held together by Mn-Mn bond without helping from any bridging group.
5. Dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$:

**Preparation:**

(i) By direct combination of CO with cobalt metal

$$2\text{Co} + 8\text{CO} \xrightarrow{200 \degree \text{C,} 100 \text{ atm.}} \text{Co}_2(\text{CO})_5$$

(ii) By carbonylating $\text{CoI}_2$ or $\text{CoS}$ with CO in presence of Cu-metal or by carbonylating $\text{CoCO}_3$ with CO in presence of Cu-metal and $\text{H}_2$ both act as reducing agent.

$$2\text{CoS} (\text{or } 2\text{CuI}) + 8\text{CO} + 4\text{Cu} \xrightarrow{200 \degree \text{C,} 200 \text{ atm.}} \text{Co}_2(\text{CO})_8 + 2\text{Cu}_2\text{S} (\text{or } 4\text{CuI})$$

$$2\text{CoCO}_3 + 8\text{CO} + 2\text{H}_2 \xrightarrow{120-200 \degree \text{C,} 250-300 \text{ atm.}} \text{Co}_2(\text{CO})_8 + 2\text{H}_2\text{O}$$

**Properties:**

(i) It is orange brown crystalline substance having m.p. 51 °C. It is soluble in alcohol, ether and CCl$_4$.

(ii) It is decomposed at 50 °C in an inert atmosphere to give tetra dodecacarbonyl, $\text{Co}_4(\text{CO})_{12}$.

$$2\text{Co}_2(\text{CO})_8 \xrightarrow{50 \degree \text{C}} \text{Co}_4(\text{CO})_{12} + 4\text{CO}$$

(iii) It is converted in to deep violet basic carbonate of cobalt on exposure in air.

(iv) It reacts with $\text{H}_2$ at 165 °C and 200 atm. pressure to formed cobalt carbonyl hydride, $[\text{Co}(\text{CO})_4\text{H}^+]^0$. $[\text{Co}(\text{CO})_4\text{H}^+]^0$

$$\text{Co}_2(\text{CO})_8 + 2\text{Na} \xrightarrow{165 \degree \text{C,} 200 \text{ atm.}} [\text{Co}(\text{CO})_4\text{H}^+]^0$$

(v) It reacts with NO to give cobalt carbonyl nitrosyl, $[\text{Co}(\text{CO})_8(\text{NO})^+]^0$.

$$\text{Co}_2(\text{CO})_8 + 2\text{NO} \rightarrow [\text{Co}(\text{CO})_8(\text{NO})^+]^0 + 2\text{CO}$$

**Structure:**

Infra-red study of the solution of this compound has shown that in solution, this compound exists in two isomeric forms. One of these forms has a bridge structure while the other form has a non-bridge structure. In this
structure Co-atoms are \(d^2sp^3\) hybridized as shown below. Three \(d^2sp^3\) hybrid orbitals on each Co-atom accept a lone paired of electrons donated by the C-atom of three terminal carbonyl groups and form three Co←CO coordinate bonds. Such six bonds are formed. One \(d^2sp^3\) hybrid orbital on one Co atom (singly filled) overlap with the \(d^2sp^3\) hybrid orbital on the other Co atom (singly filled) and forms one Co-Co bond. Two \(d^2sp^3\) hybrid orbitals on each Co atom (singly filled) overlap with the appropriate orbital (singly filled) on C-atom of two bridging CO groups and form Co-Co bond. Thus, all electrons in \(\text{Co}_2(\text{CO})_8\) molecule are paired and molecule is diamagnetic.

In case of non-bridge structure, Co atoms have \(dsp^3\) hybridization as shown below.
6. Di-iron nonacarbonyl, Fe₂(CO)₉:

**Preparation:**
(i) Fe(CO)₅ dissolved in glacial acetic acid is irradiated with ultraviolet light.

\[ 2\text{Fe(CO)}_5 \xrightarrow{\text{UV-light}} \text{Fe}_2\text{(CO)}_9 + \text{CO} \]

On cooling the solution, Fe₂(CO)₉ is ppted as golden yellow crystals.

**Properties:**
(i) Fe₂(CO)₉ forms golden yellow triclinic crystals in soluble in water but soluble in toluene and pyridine.

(ii) It decomposes at 100 °C. It is non-volatile when heat to 50 °C it decomposes as

\[ 3\text{Fe}_2\text{(CO)}_9 \xrightarrow{50^\circ\text{C}} 2\text{Fe}_3\text{(CO)}_{12} + 3\text{CO} \]

At 100 °C it forms Fe, Fe(CO)₅ and some Fe₃(CO)₁₂

\[ 3\text{Fe}_2\text{(CO)}_9 \xrightarrow{70^\circ\text{C,cool}} 3\text{Fe(CO)}_5 + \text{Fe}_3\text{(CO)}_{12} \]
(iii) It reacts with NO to give Fe(CO)$_2$(NO)$_2$ together with Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$.

$$3\text{Fe}_2\text{(CO)}_9 + 4\text{NO} \rightarrow \text{Fe}_3\text{(CO)}_{12} + \text{Fe}_2\text{(CO)}_5 + \text{Fe}_2\text{(CO)}_9 + 6\text{CO}$$

(iv) Fe$_2$(CO)$_9$ is react with phen in acetone or benzene solution at 80 °C to form [Fe(phen)$_3$][Fe$_2$(CO)$_8$]. In pyridine, with phen it gives [Fe(phen)$_3$][Fe$_2$(CO)$_{13}$].

(v) It reacts with Na in NH$_3$ solution give carboxylate anion.

$$\text{Fe}_2\text{(CO)}_9 + 4\text{Na}_{\text{liq. NH}} \rightarrow \text{Na}_{2}^+ [\text{Fe}^{2-}(\text{CO})_{4}]^{2-} + \text{CO}$$

**Structure:**

In the structure of Fe$_2$(CO)$_9$, doubly bridging CO groups are present in addition to that of terminal CO groups.

In Fe$_2$(CO)$_9$, three terminal CO groups are bonded to each Fe atom. The remaining three CO group are making a bridge between two Fe atom. i.e. there are three doubly bridging CO groups. Since the molecule has no unpaired electron, it is diamagnetic. There is also one Fe-Fe bond. Each Fe acquires EAN = 18.
7. Tri-iron dodecacarbonyl, Fe$_3$(CO)$_{12}$:

**Preparation:**

(i) It is obtained by heating Fe$_2$(CO)$_9$ dissolved in toluene at 70 °C

$$3\text{Fe}_2\text{(CO)}_9 \text{(toluene solution)} \xrightarrow{70^\circ \text{C, cool}} 3\text{Fe(CO)}_5 + \text{Fe}_3\text{(CO)}_{12}$$

(ii) It can be obtained by oxidation of iron carbonyl hydride, Fe(CO)$_4$H$_2$ by MnO$_2$ or H$_2$O$_2$

$$3\text{Fe(CO)}_4\text{H}_2 + 3\text{MnO}_2 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_3\text{(CO)}_{12} + 3\text{MnSO}_4 + 6\text{H}_2\text{O}$$

$$3\text{Fe(CO)}_4\text{H}_2 + 3\text{H}_2\text{O}_2 \rightarrow \text{Fe}_3\text{(CO)}_{12} + 6\text{H}_2\text{O}$$

**Properties:**

(i) It is green monoclinic crystals which is soluble in organic solvents like toluene, alcohol etc.

(ii) It reacts with pyridine and alcohol

$$3\text{Fe}_3\text{(CO)}_{12} + 3\text{py} \rightarrow \text{Fe}_3\text{(CO)}_9\text{(py)}_3 + 3\text{Fe(CO)}_5$$

$$2\text{Fe}_3\text{(CO)}_{12} + 3\text{CH}_3\text{OH} \rightarrow \text{Fe}_3\text{(CO)}_9\text{(CH}_3\text{OH)}_3 + 3\text{Fe(CO)}_5$$

(iii) It reacts with Na in NH$_3$ solution give carbonylate anion.

$$\text{Fe}_3\text{(CO)}_{12} + 6\text{Na} \xrightarrow{\text{liq. NH}} 3\text{Na}_2^+\text{[Fe}^2^-(\text{CO})_4]^{2^-}$$

(iv) It is decomposed at 140 °C to give metallic iron and CO.

$$\text{Fe}_3\text{(CO)}_{12} \xrightarrow{140^\circ \text{C}} 3\text{Fe} + 12\text{CO}$$

(v) It is react with NO at 85 °C to form iron dicarbonyl dinitrosyl, Fe(CO)$_2$(NO)$_2$

$$\text{Fe}_3\text{(CO)}_{12} + 6\text{NO} \rightarrow 3\text{Fe(CO)}_2\text{(NO)}_2 + 6\text{CO}$$

**Structure:**

A line at structure was first proposed on the basis of IR spectra, which was supported by incomplete X-Ray study. Later X-Ray study required a cyclic structure.

Each of two Fe atom is link with three terminal CO groups, also link with two bridging CO group and both Fe atoms link with third Fe atom. The remaining third Fe atom is link with four terminal CO groups and each of two Fe atoms. Fe-CO-Fe bridges are unsymmetrical.
METALLIC NITROSYL

Metal nitrosyls are coordination compounds in which NO molecule is attached as NO$^+$ ion to the metal atom or ion. In these compounds the attachment of NO$^+$ ion to the metal atom or ion takes place through N atom. In these compounds NO$^+$. In these compounds NO$^+$ ion which is called nitrosonium or nitrosyl cation acts as a ligand. The coordination compounds of transition metals containing NO$^+$ ion as ligand are metal (or metallic) nitrosyls. Examples of metal nitrosyls are given below:

(i) Metal nitrosyl carbynyls:

Important example of this type of coordination compounds are $[\text{Co}^+$(NO$^+$(CO)$_3]^0$, $[\text{Fe}^2$(NO$^+$(CO)$_2]^0$, $[\text{Mn}^3$(NO$^+$(CO)$_3]^0$, $[\text{Mn}^+$(NO$^+$(CO)$_4]^0$, $[\text{V}^-$$(NO$^+$(CO)$_5]^0$ etc.

(ii) Metal nitrosyl halides:

These compounds are represented by $[\text{Fe}^+$(NO$^+$(I)$_2]^0$, $[\text{Fe}^2$(NO$^+$(I)$_2$(CO)$_2]^0$, $[\text{Fe}^-$$(NO$^+$(I)$_2]^0$, $[\text{Fe}^2$(NO$^+$(Cl)$_2]^0$, $[\text{Co}^+$(NO$^+$(X)$_2]^0$ ($X=\text{Cl, Br, I}$), $[\text{M}^-$$(NO$^+$(Cl)$_2]^0$ ($\text{M=Mo or W}$).

(iii) Metal nitrosyl thio complexes:

These compounds are given by only Fe, Co and Ni. Examples are $\text{M}^+$(Fe$^-$(NO$^+$(S)$_2]$, $\text{M}^+$(Co$^-$(NO$^+$(S)$_2]$, $\text{M}^+$(Ni$^-$(NO$^+$(S)$_2]$. (M=Na$^+$, K$^+$, NH$_4^+$).

(iv) Metal nitrosyl cyano complexes:

Example of this type of complexes are $[\text{Mn}^+$(NO$^+$(CN)$_3]^2^-$, $[\text{Fe}^+$(NO$^+$(CN)$_5]^2^-$, $[\text{Mn}^+$(NO$^+$(CN)$_5]^3^-$, $[\text{Mo}^+$(NO$^+$(CN)$_5]^4^-$ etc. Among these complexes, pentacyano nitrosyl ferrate(II) ion, $[\text{Fe}^+$(NO$^+$(CN)$_5]^2^-$ is the most important.

(v) Miscellaneous metal nitrosyl complexes:

Nitrosyl complexes like $[\text{Co}^+$(NO$^+$(NH$_3$)$_3]^2^-$, $[\text{Co}^+$(NO$^+$(NO$_2$)$_3]^3^-$, $[\text{Fe}^+$(NO$^+$(NO)$_2]^2^-$, $[\text{Ru}^+$(NO$^+$(NH$_3$)$_3$Cl]$^2^+$, $[\text{Ru}^+$(NO$^+$(Cl)$_5]^2^-$, $[\text{Fe}^+$(NO$^+$(PR$_3$)$_3]^0$ etc. Among these complexes, $[\text{Fe}^+$(NO$^+$(NO)$_2]^2^-$ is the most important.
Preparation:

(i) Metal nitrosyl carbonyls can be obtained by the action of NO on metal carbonyls, e.g.,

\[ \text{Fe(CO)}_3 + 2\text{NO} \xrightarrow{95^\circ C} \text{Fe(CO)}_2(\text{NO})_2 + 3\text{CO} \]

\[ 3\text{Fe(CO)}_3 + 4\text{NO} \rightarrow 2\text{Fe(CO)}_2(\text{NO})_2 + \text{Fe(CO)}_5 + \text{Fe}_3(\text{CO})_{12} + 6\text{CO} \]

\[ \text{Fe}_3(\text{CO})_{12} + 6\text{NO} \xrightarrow{85^\circ C} 3\text{Fe(CO)}_2(\text{NO})_2 + 6\text{CO} \]

\[ \text{Co}_2(\text{CO})_8 + 2\text{NO} \xrightarrow{40^\circ C} 2\text{Co(CO)}_3(\text{NO}) + 2\text{CO} \]

(ii) Metal nitrosyls halides can be prepared:

(a) By the action of NO on metal halides in the presence of a suitable metal (e.g. Co, Zn etc.) which acts as a halogen acceptor, e.g.

\[ \text{CoX}_2 + 4\text{NO} + \text{Co} \rightarrow 2[\text{Co(NO)}_2\text{X}] \]

\[ 2\text{NiI}_2 + 2\text{NO} + \text{Zn} \rightarrow 2[\text{Ni(NO)}_2\text{I}] + \text{ZnI}_2 \]

(b) By the action of halogen on nitrosyl carbonyls, e.g.,

\[ 2[\text{Fe(CO)}_2(\text{NO})_2] + \text{I}_2 \rightarrow [\text{Fe(NO)}_2\text{I}]_2 + 4\text{CO} \]

Properties of metal nitrosyl carbonyls:

(i) Substitution reactions: In metal carbonyl nitrosyls, NO\(^+\) ions are more firmly attached with the metal ion than the CO groups. It is for this reason that when metal carbonyl nitrosyls are treated with ligands like PR\(_3\), CNR, phen etc., it is only CO groups that are replaced by these ligands, e.g.,

\[ \text{Fe(CO)}_2(\text{NO})_2 + 2\text{L}(\text{L}=\text{PR}_3, \text{CNR}) \rightarrow \text{Fe(L)}_2[\text{NO}]_2 + 2\text{CO} \]

\[ \text{Fe(CO)}_2(\text{NO})_2 + \text{phen} \rightarrow \text{Fe(phen)(NO)}_2 + 2\text{CO} \]

(ii) Action of halogens: Many metal carbonyl nitrosyls, when treated with halogens, are converted into metal nitrosyl halides, e.g.,

\[ 2[\text{Fe(CO)}_2(\text{NO})_2] + \text{I}_2 \rightarrow [\text{Fe(NO)}_2\text{I}]_2 + 4\text{CO} \]

Properties of metal nitrosyl halides:

(i) Metal nitrosyl halides react with other ligands to form mono-nuclear complexes, e.g.,

\[ [\text{Fe(NO)}_2\text{X}]_2 + 2\text{L} \rightarrow 2[\text{Fe(NO)}_2\text{XL}] \]

(ii) Iron nitrosyl halide, [Fe(NO)]_2I\(_2\) reacts with K\(_2\)S and CH\(_3\)Cl to form dark red compounds which have the composition, K\(_2\)[Fe(NO)]\(_2\)S\(_2\) and [Fe(NO)]\(_2\)(SCH\(_3\))\(_2\) and are called Roussin’s salts. In these compounds, Fe is in -1 oxidation state.

\[ [\text{Fe(NO)}_2\text{I}]_2 + \text{K}_2\text{S} \xrightarrow{-2\text{KI}} \text{K}_2[\text{Fe(NO)}_2\text{S}]_2 \quad \text{and} \quad [\text{Fe(NO)}_2(\text{SCH}_3)]_2 \]
SOME METALLIC NITROSYLS

Now let us make study of sodium nitroprusside, Na$_2$[Fe$^{2+}$(CN)$_5$(NO$^-$)] and nitroso ferrous sulphate, FeSO$_4$NO or [Fe$^+(NO^-)$]SO$_4$ which are important metallic nitrosyls.

1) Sodium nitroprusside, Na$_2$[Fe$^{2+}$(CN)$_5$(NO$^-$)]:

**Preparation:** It is prepared
(i) By the action of NaNO$_3$ on Na$_4$[Fe$^{2+}$(CN)$_6$]

Na$_4$[Fe$^{2+}$(CN)$_6$] + NaNO$_2$ + H$_2$O → Na$_2$[Fe$^{2+}$(CN)$_5$(NO$^-$)] + 2NaOH + NaCN

(ii) by passing nitric oxide (NO) into acidified solution of Na$_4$[Fe(CN)$_6$].

2Na$_4$[Fe(CN)$_6$] + H$_2$SO$_4$ + 3NO → 2Na$_2$[Fe(NO)(CN)$_5$] + 2NaCN + Na$_2$SO$_4$ + 1/2 N$_2$ + H$_2$O

**Properties:**
(i) Sodium nitroprusside forms beautiful ruby red rhombic crystals which are soluble in water.

(ii) When freshly prepared sodium nitroprusside is added to a solution containing sulphide ion (i.e. Na$_2$S but not H$_2$S), a purple or violet colour is produced. The production of this colour is due to the formation of Na$_4$[Fe$^{2+}$(CN)$_5$(NO$^-$)(S$^{2-}$)]. The production of this purple or violet colour is used to confirm the presence of S$^{2-}$ ion in a given mixture.

Na$_2$S + Na$_2$[Fe$^{2+}$(CN)$_5$(NO$^-$)] → Na$_4$[Fe$^{2+}$(CN)$_5$(NO$^-$)(S$^{2-}$)]

(Violet or purple colour)

(iii) Alkali sulphites give a rose red colour due to the formation of Na$_4$[Fe(CN)$_5$(NO)(SO$_3$)]. This reaction can be used to distinguish sulphites from thiosulphates which do not show this reaction.

Na$_2$SO$_3$ + Na$_2$[Fe(CN)$_5$(NO)] → Na$_4$[Fe(CN)$_5$(NO)(SO$_3$)]

(iv) With silver nitrate a flesh coloured Ag$_2$[Fe(CN)$_5$(NO)] is produced.

2AgNO$_3$ + Na$_2$[Fe(CN)$_5$(NO)] → Ag$_2$[Fe(CN)$_5$(NO)] + 2NaNO$_3$

(v) Aldehydes and ketones containing CH$_3$-CO-R group give deep red colour with sodium nitroprusside and excess of NaOH.

(vi) It is converted into sodium ferrocyanide, Na$_4$[Fe(CN)$_6$] on treatment with an alkali.

6Na$_2$[Fe(CN)$_5$(NO)] + 14NaOH → 5Na$_4$[Fe(CN)$_6$] + Fe(OH)$_2$ + 6NaNO$_3$ + 6H$_2$O

According to another view NO$^+$ groups present in nitroprusside is oxidized to NO$_2$ and thus a nitro complex is obtained.

Na$_2$[Fe(CN)$_5$(NO)] + 2NaOH → Na$_4$[Fe(CN)$_5$(NO$_2$)] + H$_2$O

(vii) [Fe(CN)$_5$(NO)]$^{2-}$ ion has diamagnetic character. Its diamagnetic character confirms the fact that NO is present as NO$^+$ ion in this complex ion.

**Structure:**

[Fe(CN)$_5$(NO)]$^{2-}$ was formerly supposed to contain Fe(+3) ion but Pauling in 1931 and Sidgwick in 1934 suggested that the odd electron of NO group enters the valence-shell of Fe (+3) ion making Fe in +2 oxidation state. Thus NO radical acquires one positive charge and gets coordinated to Fe(+2) ion as
NO\(^+\) radical. This view is supported by the fact that Na\(_2\)[Fe(CN)\(_5\)](NO)] is diamagnetic where as K\(_3\)[Fe(CN)\(_6\)] is paramagnetic. Thus in [Fe(CN)\(_5\)](NO)]\(^2-\) there are total three positive charges (Fe = +2, NO = +1) and five negative charges due to the presence of five CN groups. Hence total charges acquired by [Fe(CN)\(_5\)](NO)]\(^2-\) is -2. In other words, the formula of sodium nitroprusside is Na\(_2\)[Fe\(^{2+}\)(CN)\(_5\)](NO\(^+\)]. [Fe\(^{2+}\)(CN)\(_5\)](NO\(^+\)]\(^2-\) has octahedral structure with Fe\(^{2+}\) ion located at the centre of the octahedron.

**Uses:**

It is use as a reagent in qualitative analysis for the detection of sulphides, sulphites, aldehydes and ketones containing CH\(_3\)-CO-R group.

2) Nitroso ferrous sulphate, FeSO\(_4\)NO or [Fe\(^+(NO^+)\)]SO\(_4\):

When, to the aqueous solution of a metallic nitrate (say NaNO\(_3\)) is added freshly prepared solution of FeSO\(_4\) and a few drops of conc. H\(_2\)SO\(_4\) along the sides of the test tube, a brown ring of nitroso ferrous sulphate, [Fe\(^+(NO^+)\)]SO\(_4\) is obtained at the junction of the two liquids in the test tube. The formation of nitroso ferrous sulphate takes place through the following equations:

(a) \(6\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_3 + \text{HNO}_3\)

\[\text{or } \text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3\]

(b) \(6\text{FeSO}_4 + 2\text{HNO}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}\)

\[\text{or } 3\text{Fe}^{2+} + \text{NO}_3^- + 4\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{NO} + 2\text{H}_2\text{O}\]

(C) \(\text{FeSO}_4 + \text{NO} \rightarrow \text{FeSO}_4\text{NO or } [\text{Fe}^+(\text{NO}^+)]^{2+}\text{SO}_4^{2-}\)

\[\text{or } \text{Fe}^{2+} + \text{NO} \rightarrow [\text{Fe}^+(\text{NO}^+)]^{2+}\]

In aqueous solution [Fe\(^+(NO^+)\)]\(^2+\) ion is better expressed as [Fe(NO)(H\(_2\)O)\(_5\)]\(^2+\). It is a paramagnetic substance corresponding to the presence of three unpaired electrons, since solution magnetic measurements give 3.90 B.M. as the value of its magnetic moment. This value supports the fact that Fe is in +1 oxidation state in this complex ion i.e. it is a high spin complex of Fe (+1) (3d\(^7\) system) with NO\(^+\). The complex has N—O stretching frequency at 1745 cm\(^{-1}\) which indicates the presence of strong π-bonding and the intense brown colour strongly suggests Fe\(^+\)—NO\(^+\) charge transfer.

The formation of [Fe\(^+(NO^+)\)]\(^2+\) ion has been utilized in the detection of NO\(^-\) ion in a given inorganic salt.

**Structure and nature of M—NO bonding in nitrosyls:**

According to Coulson the molecular orbital configuration of NO molecule is (sp)\(^2\)\(_O\), (osp\(^b\))\(^2\), (\(\pi_y\))\(^2\)=π\(_z\))\(^2\), (sp)\(^2\)\(_N\), (\(\pi_y^*\))\(^1\)=π\(_x^*\))\(^0\), (osp\(^*\))\(^0\) [in getting this configuration x-axis has been assumed to be the molecular axis and sp hybrid orbital have been obtained by the combination of 2s and 2p\(_x\) orbital]. Now when NO molecule coordinates with metal atom to form metallic nitrosyls, the single electron present in \(\pi_y^*\) molecular orbital is transferred to metal atom M so that NO molecule is converted into NO\(^+\) cation (called nitrosonium or nitrosyl cation) and M atom becomes M\(^-\) ion. Each of the atoms viz. N and O in NO\(^+\) ion contains one lone pair of electrons in (sp)\(_O\) and (sp)\(_N\) hybrid orbital
respectively. Now since NO$^+$ ion is iso-electronic with CO molecule, this ion co-ordinates with M$^-$ ion as a two-electron donor in metal nitrosyls in the same way as CO co-ordinates to M atom in metal carboxyls. Note that, NO molecule is a three-electron-donor. Since O-atom is more electronegative than N-atom, it is N-atom of NO$^+$ ion which coordinates to M$^-$ ion metal nitrosyls. In other wards we say that coordination of NO$^+$ ion to M$^-$ ion metal nitrosyl takes place through the lone pair residing in $(sp)^n$ hybrid orbital on N-atom. The coordinate bond formed in metal nitrosyls can be shown as M$^-$←NO$^+$. Thus, we see that the nature of bonding between NO$^+$ and M$^-$ in nitrosyls is the same as that between CO molecule and M atom in carboxyls.

On the basis of molecular orbital theory, the hybrid orbital on N-atom containing a lone pair [i.e. $(sp)^2N$ lone pair] overlaps with a suitable vacant hybrid orbital on M$^-$ ion ($sp^3$ in tetrahedral or $d^2sp^3$ in octahedral case) to form ON$^+$$→$$M^-$ σ-bond. Now the empty π* or πy* molecular orbital can overlap with the filled d-orbitals (dxy, dyz, dzx orbitals in octahedral case and dx$^2$-y$^2$ and dz$^2$ orbitals in tetrahedral case) to form M$^-$←NO$^+$ π-bond. This type of overlap transfers some charge from M$^-$ ion to NO$^+$ ion. Structural studies have shown that the M—N bond in nitrosyls is extremely short (= 1.57 to 1.67Å$^0$) indicating substantial double bond character.

**Effective atomic number (EAN) rule as ap| metallic nitrosyls:**

Metallic nitrosyls also obey the EAN shown below for certain nitrosyls. In these cases, NO (assumed to be a unipositive ion, NO$^+$ and hence acts as an electron donor. Metal atoms are, therefore, in negative o state.

(i) $[$Co(CO)$_3$(NO$^+$)$]$:$  ēs from Co$^-$ = 27 + 1 = 28
ēs from 3 CO = 2 x 3 = 6
ēs from NO$^+$ = 1 x 2 = 2
hence EAN of each Co atom = 36 [Kr]

(ii) $[$Fe$_2$(CO)$_2$(NO$^+$)$_2]$:$  ēs from Fe$^{2+}$ = 26 + 2 = 28
ēs from 2 CO = 2 x 2 = 4
ēs from NO$^+$ = 2 x 2 = 4
hence EAN of each Fe atom = 36 [Kr]

(iii) $[$Fe$_2$(NO$^+$)$_2$(Pr$_3$)$_2]$:$  ēs from Fe$^{2+}$ = 26 + 2 = 28
ēs from NO$^+$ = 2 x 2 = 4
ēs from 2 Pr$_3$ = 2 x 2 = 4
hence EAN of each Fe atom = 36 [Kr]

(iv) $[$Mn$_3$(CO)(NO$^+$)$_3]$:$  ēs from Mn$^{3+}$ = 25 + 3 = 28
ēs from CO = 1 x 2 = 2
ēs from 3 NO$^+$ = 3 x 2 = 6
hence EAN of each Fe atom = 36 [Kr]

THE END