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:

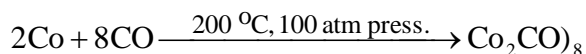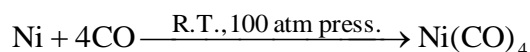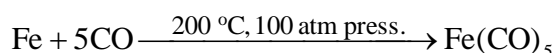Which is having only one metal atom per molecule and having type $M(CO)_y$. e.g. $V(CO)_6$, $Cr(CO)_6$ etc.

(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.
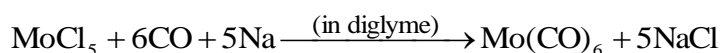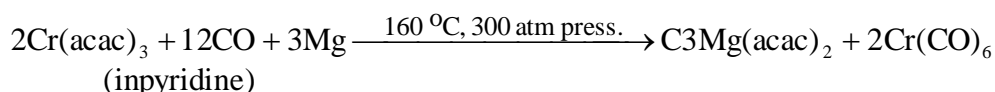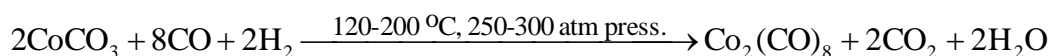
GENERAL METHODS OF PREPARATION

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.

$$Fe + 5CO \xrightarrow{\text{200 °C, 100 atm press.}} Fe(CO)_5$$

$$Ni + 4CO \xrightarrow{\text{R.T., 100 atm press.}} Ni(CO)_4$$

$$2Co + 8CO \xrightarrow{\text{200 °C, 100 atm press.}} Co_2CO)_8$$

(ii) By carbonylating metallic salts with CO in presence of reducing agent:

Metallic carbonyls are obtained when salts like RuI_3, $CrCl_3$, VCl_3, CoS, $Co(CO)_3$, CoI_2 etc. are treated with CO in presence of suitable reducing agent like Mg, Ag, Cu, Na, H_2, $AlLiH_4$ etc.

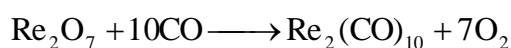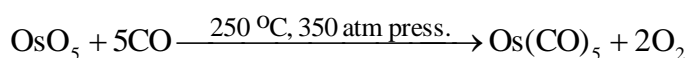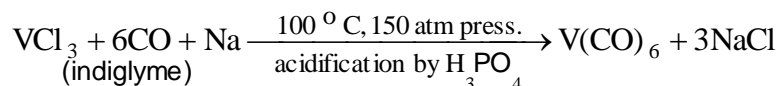$$CrCl_3 + 5CO + LiAlH_4 \xrightarrow{\text{115 }^\text{O}\text{C, 70 atm press.}} Cr(CO)_6 + LiCl + AlCl_3$$

$$RuI_3 + 10CO + 6Ag \xrightarrow{\text{175 }^\text{O}\text{C, 250 atm press.}} 2Ru(CO)_5 + 6AgI$$

$$2MnI_2 + 10CO + 2Mg \xrightarrow{\text{25 }^\text{O}\text{C, 210 atm press.}} Mn_2(CO)_5 + 2MgI_2$$
$$\text{(in diethyl ether)}$$

$$2CoS + 8CO + 4Cu \xrightarrow{\text{200 }^\text{O}\text{C, 200 atm press.}} Co_2(CO)_8 + 2Cu_2S$$

$$2CoI_2 + 8CO + 4Cu \xrightarrow{\text{200 }^\text{O}\text{C, 200 atm press.}} Co_2(CO)_8 + 4CuI$$

$$2FeI_2 + 5CO + 2Cu \xrightarrow{\text{200 }^\text{O}\text{C, 200 atm press.}} Fe(CO)_5 + Cu_2I_2$$

$$2CoCO_3 + 8CO + 2H_2 \xrightarrow{\text{120-200 }^\text{O}\text{C, 250-300 atm press.}} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

$$2Cr(acac)_3 + 12CO + 3Mg \xrightarrow{\text{160 }^\text{O}\text{C, 300 atm press.}} C3Mg(acac)_2 + 2Cr(CO)_6$$
$$\text{(inpyridine)}$$

$$MoCl_5 + 6CO + 5Na \xrightarrow{\text{(in diglyme)}} Mo(CO)_6 + 5NaCl$$

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

$$OsO_5 + 5CO \xrightarrow{\text{250 }^\text{O}\text{C, 350 atm press.}} Os(CO)_5 + 2O_2$$

$$Re_2O_7 + 10CO \longrightarrow Re_2(CO)_{10} + 7O_2$$
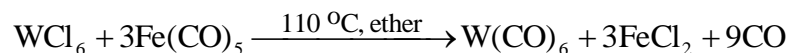
$V(CO)_6$ is prepared by the method represented by the following equation

$$VCl_3 + 6CO + Na \xrightarrow[\text{acidification by } H_3PO_4]{\text{100 }^\text{O}\text{C, 150 atm press.}} V(CO)_6 + 3NaCl$$
$$\text{(indiglyme)}$$

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

$MoCl_5$ and WCl_5 give the corresponding hexacarbonyls. These reactions are characterized by low yield, which can be improved by using high pressure.

$$MoCl_6 + 3Fe(CO)_5 \xrightarrow{110\ ^oC,\ ether} Mo(CO)_6 + 3FeCl_2 + 9CO$$

$$WCl_6 + 3Fe(CO)_5 \xrightarrow{110\ ^oC,\ ether} W(CO)_6 + 3FeCl_2 + 9CO$$
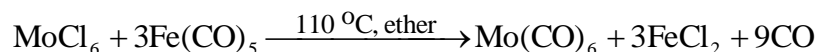
(iv) Preparation of $Fe_2(CO)_9$, and $Os_2(CO)_9$ from $Fe(CO)_5$:

When cool solution of $Fe(CO)_5$ and $Os(CO)_5$ in glacial CH_3COOH is irradiated with ultra-violet light, $Fe_2(CO)_9$, and $Os_2(CO)_9$ are obtained respectively.

$$Fe(CO)_5 \xrightarrow{UV\text{-light}} Fe_2CO)_9 + CO$$

$$Os(CO)_5 \xrightarrow{UV\text{-light}} Os_2CO)_9 + CO$$
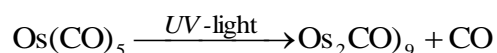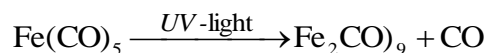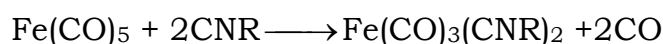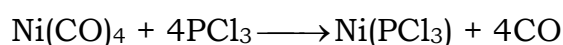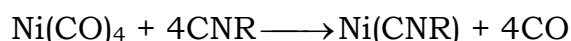
GENERAL PROPERTIES
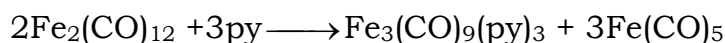
Physical properties:
(i)   Most carbonyls are volatile solids but $Fe(CO)_5$, $Ru(CO)_5$, $Os(CO)_5$ and $Ni(CO)_4$ are liquids at ordinary temperature and quite inflammable.
(ii) Many of these decompose or melt at low temperature.
(iii) They are soluble in organic solvents. $Ni(CO)_4$ is insoluble in 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. $CO_2(CO)_8$ reacts at ordinary temp. $Fe_2(CO)_9$ 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) <u>Substitution reaction:</u>

   Some or all CO groups present in carbonyl can be replaced by monodentate ligands like isocyanide (CNR), PR_3, PCl_3, py, CH_3OH etc.
  e.g.

$$Ni(CO)_4 + 4CNR \longrightarrow Ni(CNR) + 4CO$$

$$Ni(CO)_4 + 4PCl_3 \longrightarrow Ni(PCl_3) + 4CO$$

$$Fe(CO)_5 + 2CNR \longrightarrow Fe(CO)_3(CNR)_2 + 2CO$$

$$Mn_2(CO)_{10} + PR_3 \longrightarrow 2Mn(CO)_4(PR_3) + 2CO$$

$$2Fe_2(CO)_{12} + 3py \longrightarrow Fe_3(CO)_9(py)_3 + 3Fe(CO)_5$$

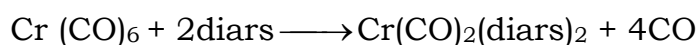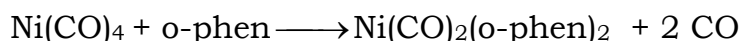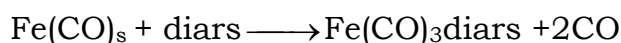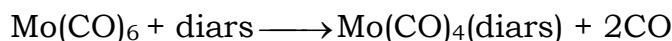$$2Fe_2(CO)_{12} + 3CH_3OH \longrightarrow Fe_3(CO)_9(CH_3OH)_3 + 3Fe(CO)_5$$
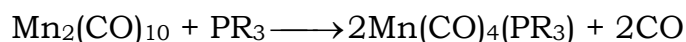
Bidentate ligands like diars, o-phen, NO_2 etc. replace at two or more CO group at a time. e.g.

$$Mo(CO)_6 + diars \longrightarrow Mo(CO)_4(diars) + 2CO$$

$$Fe(CO)_s + diars \longrightarrow Fe(CO)_3 diars + 2CO$$

$$Ni(CO)_4 + o\text{-}phen \longrightarrow Ni(CO)_2(o\text{-}phen)_2 + 2\ CO$$

$$Ni(CO)_4 + diars \longrightarrow Ni(CO)_2(diars) + 2\ CO$$

$$Cr\ (CO)_6 + 2diars \longrightarrow Cr(CO)_2(diars)_2 + 4CO$$

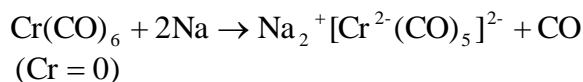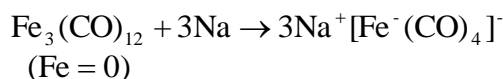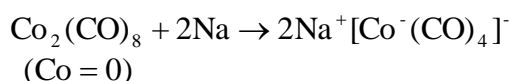$$Ni(CO)_4 + 2NO_2 \longrightarrow Ni(NO_2)_2 + 4CO$$
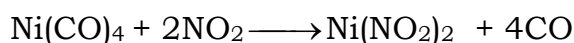
(ii) <u>Action of NaOH or Na metal:</u>

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

$$Fe(CO)_5 + 3NaOH \rightarrow Na^+[H^+Fe^{2-}(CO)_4]^- + Na_2CO_3 + H_2O$$
$$(Fe = 0)$$
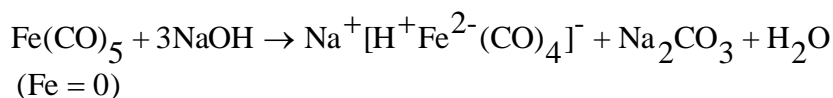
H-atom in $[H^+Fe^{2-}(CO)_4]^-$ ion is acidic which means that Fe-atom in this ion is in -2 oxidation state.

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. in to carbonylate anions and in these carbonyls are reduced.

$$Fe_2(CO)_9 + 4Na \rightarrow 2Na_2^+[Fe^{2-}(CO)_4]^{2-} + CO$$
$$(Fe = 0)$$

$$Co_2(CO)_8 + 2Na \rightarrow 2Na^+[Co^-(CO)_4]^-$$
$$(Co = 0)$$

$$Fe_3(CO)_{12} + 3Na \rightarrow 3Na^+[Fe^-(CO)_4]^-$$
$$(Fe = 0)$$

$$Cr(CO)_6 + 2Na \rightarrow Na_2^+[Cr^{2-}(CO)_5]^{2-} + CO$$
$$(Cr = 0)$$

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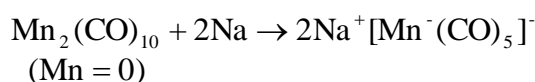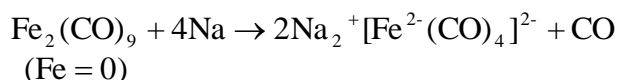
(iii) Carbonyl react with halogens to form carbonyl halides shown as under.

$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$

$$Mo(CO)_6 + Cl_2 \longrightarrow Mo(CO)_4Cl_2 + 2CO$$

$$Mn_2(CO)_{10} + X_2 \text{ (X=Br, I)} \longrightarrow 2Mn(CO)_5X$$
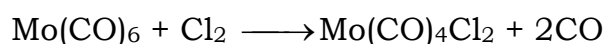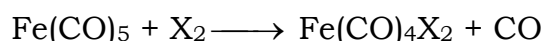
$Co_2(CO)_8$ and $Ni(CO)_4$ both get decomposed into metallic halides and CO when treated with halogens. e.g.

$$Co_2(CO)_8 + 2X_2 \longrightarrow 2CoX_2 + 8CO$$

$$Ni(CO)_4 + Br_2 \longrightarrow NiBr_2 + 4CO$$
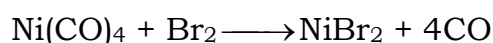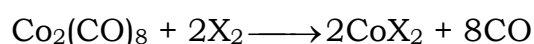
(iv) Action of NO:

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

$$Fe(CO)_5 + 2\ NO \xrightarrow{95^{O}C} Fe(CO)_2(NO)_2 + 3CO$$

$$3Fe_2(CO)_9 + 4NO \longrightarrow 2Fe(CO)_2(NO)_2 + Fe_2(CO)_5 + Fe_3(CO)_{12} + 6CO$$

$$Fe_3(CO)_{12} + 6NO \xrightarrow{85^{O}C} 3Fe(CO)_2(NO)_2 + 6CO$$

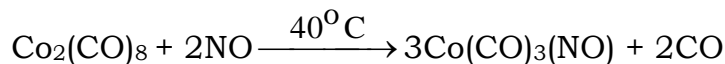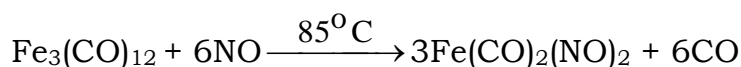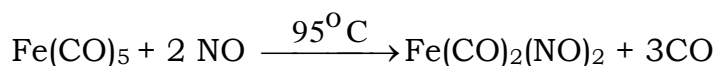$$Co_2(CO)_8 + 2NO \xrightarrow{40^{O}C} 3Co(CO)_3(NO) + 2CO$$

Moist NO gives a blue coloured compound, $Ni(NO)(OH)$ with $Ni(CO)_4$ while dry NO gives a blue solution of the composition, $Ni(NO)(NO_2)$

$$2Ni(CO)_4 + 2NO + 2H_2O \longrightarrow 2Ni(NO)(OH) + 8CO + H_2$$

$$Ni(CO)_4 + 4NO \longrightarrow Ni(NO)(NO_2) + 4CO + N_2O$$
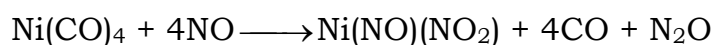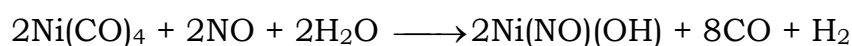
(iv) Action of H_2:

When $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ react with H_2, they are reduced to carbonyl hydride, $Mn(CO)_5H$ and $Co(CO)_4H$ respectively.

$$Mn_2(CO)_{10} + H_2 \xrightarrow{200\ atm.\ press.} 2[Mn^{-}(CO)_5 H^{+}]^0$$

$$Co_2(CO)_8 + H_2 \xrightarrow{165\ ^{O}C,\ 200\ atm.\ press.} 2[Co^{-}(CO)_4 H^{+}]^0$$
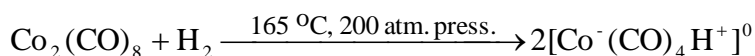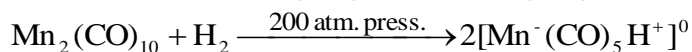
(v) Action of Heat:

Different carbonyls give different product when heated shown below.

$$Fe(CO)_5 \xrightarrow{\;250\,^{\circ}C\;} Fe + 5CO$$

$$3Fe_2(CO)_9 \xrightarrow{\;70\,^{\circ}C,\,cool\;} 3Fe(CO)_5 + Fe_3(CO)_{12}$$
$$\text{(in toluene)}$$

$$Fe_3(CO)_{12} \xrightarrow{\;140\,^{\circ}C,\,cool\;} 3Fe + 12CO$$

$$2Co_2(CO)_8 \xrightarrow{\;50\,^{\circ}C,\,inert\;atmosphere\;} Co_4(CO)_{12} + 4CO$$

$$Ni(CO)_4 \xrightarrow{\;180\,^{\circ}C\;} Ni + 4CO$$

$$3Fe_2(CO)_9 \xrightarrow{\;50\,^{\circ}C\;} 2Fe_3(CO)_{12} + 3CO$$
$$\text{(in toluene)}$$
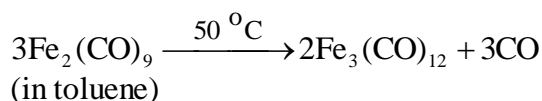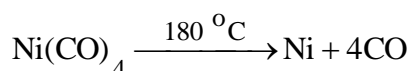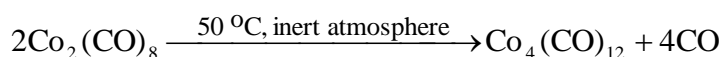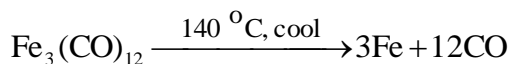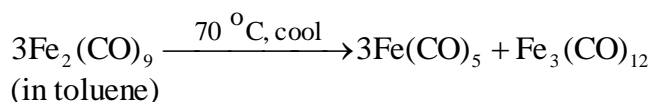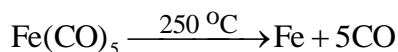
Structure and nature of M-CO bonding in carbonyls:

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.
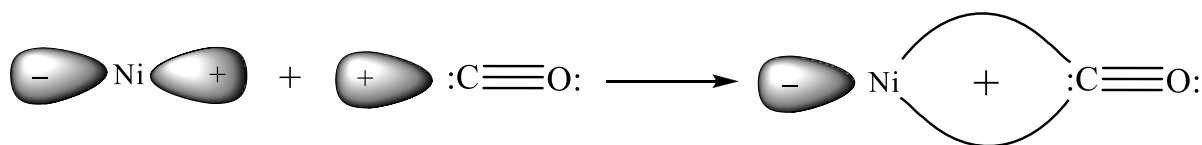
In the type of M(CO)$_5$ and M(CO)$_6$ carbonyls dsp^3 and d^2sp^3 hybrid orbital are used for M←CO σ-bonds. In this bond formation, metal atom acts as electron acceptor, while CO acts as electron donor.

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. $M \xrightarrow{\;\pi\;} CO$
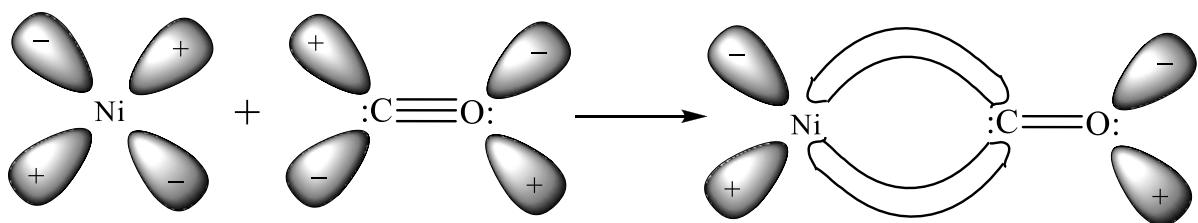
i.e. Ni→CO π-bond in Ni(CO)$_4$ form by overlap between filled dz^2 or dx^2-y^2 on Ni atom and empty π* molecular orbital on CO molecule.

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 + (2x6) = 36 = Ar

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

EAN of some mononuclear carbonyls are calculate in the following table

Metal carbonyl	No. of ēs on the central metal atom = At. No.of metal = **z**	No. of ēs donated by CO molecule = **2Y**	EAN of the metal atom in carbonyl = **z + 2Y**
$Cr(CO)_6$	24	6 x 2 = 12	24 + 12 = 36[Kr]
$Mo(CO)_6$	42	6 x 2 = 12	42 + 12 = 54 [Xe]
$W(CO)_6$	74	6 x 2 = 12	74 + 12 = 86 [Rn]
$Fe(CO)_5$	26	5 x 2 = 10	26 + 10 = 36 [Kr]
$Ru(CO)_5$	44	5 x 2 = 10	44 + 10 = 54 [Xe]
$Os(CO)_5$	76	5 x 2 = 10	76 + 10 = 86 [Rn]
$Ni(CO)_4$	28	4 x 2 = 8	28 + 8 = 36 [Kr]

2) <u>Mononuclear carbonyl having transition metal atom in odd atomic number</u> 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 x 6) = 35

$Mn(CO)_5$: $25 + (2 \times 5) = 35$

$Co(CO)_4$: $27 + (2 \times 4) = 35$

3) <u>Polynuclear carbonyl</u>: The polynuclear carbonyls obey EAN rule. Two ēs each of M-M bond present in these carbonyls are included in calculating the ēs per metal atom.

$Mn_2(CO)_{10}$: ēs from two Mn $= 25 \times 2 = 50$

ēs from ten CO $= 2 \times 10 = 20$

<u>ēs from one Mn-Mn bond $= 2$</u>

hence EAN of each Mn atom $= 72/2 = 36$ [Kr]

$Fe_3(CO)_{12}$: ēs from three Fe $= 26 \times 3 = 72$

ēs from twelve CO $= 2 \times 12 = 24$

<u>ēs from three Fe-Fe bonds $= 6$</u>

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, $M(CO)_y$
i.e. $Ni(CO)_4$: No. of the valence electrons of metal atom $= 10$

<u>No. of the electrons donated by CO groups $= 8$</u>

Total number of electrons on the metal atom $= 18$

$Fe(CO)_5$: No. of the valence electrons of metal atom $= 8$

<u>No. of the electrons donated by CO groups $= 10$</u>

Total number of electrons on the metal atom $= 18$

$Cr(CO)_6$: No. of the valence electrons of metal atom $= 6$

<u>No. of the electrons donated by CO groups $= 12$</u>

Total number of electrons on the metal atom $= 18$

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 $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ carbonyls.

$Co_2(CO)_8$: No. of the valence electrons of two Co atoms $= 2 \times 9 = 18$

No. of the electrons donated by CO groups $= 2 \times 8 = 16$

<u>No. of electron for Co-Co bond $= 1 \times 2 = 2$</u>

Total number of electrons on two Co atoms $= 36$

Therefore, electrons on one Co atom $= 36/2 = 18$

$Mn_2(CO)_{10}$: 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

No. of electron for Mn-Mn bond = 1 x 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

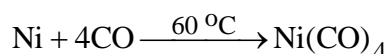No. of electron for Fe-Fe bond = 1 x 2 = 2

Total number of electrons on two Fe atoms = 36

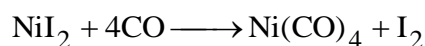Therefore, electrons on one Fe atom = 36/2 = 18

SOME INDIVIDUAL CARBONYLS
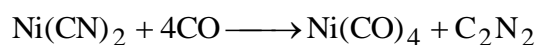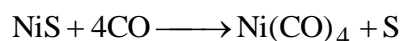
1. Nickel tetra carbonyl, $Ni(CO)_4$:

Preparation:

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

$$Ni + 4CO \xrightarrow{\;60\,^{\circ}C\;} Ni(CO)_4$$

(ii) From NiI_2: NiI_2 is heated with Co in the presence of a halogen receptor.

$$NiI_2 + 4CO \longrightarrow Ni(CO)_4 + I_2$$

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

$$NiS + 4CO \longrightarrow Ni(CO)_4 + S$$

$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + C_2N_2$$

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_2SO_4: conc. H_2SO_4 reacts with detonation

$$Ni(CO)_4 + H_2SO_4 \longrightarrow NiSO_4 + H_2 + 4CO$$
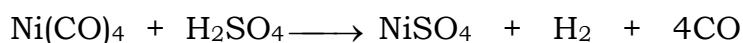
(iii) Action of NO: With moist NO it gives intense blue compound Ni(NO)(OH).

$$2Ni(CO)_4 + 2NO + 2H_2O \longrightarrow 2Ni(NO)(OH) + 8OH + H_2$$

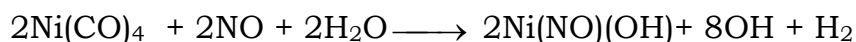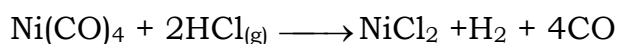(iv) Substitution reactions: see "general properties of carbonyls".

(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

$$Ni(CO)_4 + 2HCl_{(g)} \longrightarrow NiCl_2 + H_2 + 4CO$$

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_6H_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 = $3d^8\ 4s^2$) gets paired in $3d$ orbitals. Thus the valence shell configuration of Ni atom in $Ni(CO)_4$ molecule becomes $3d^{10}\ 4s^0$. 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.
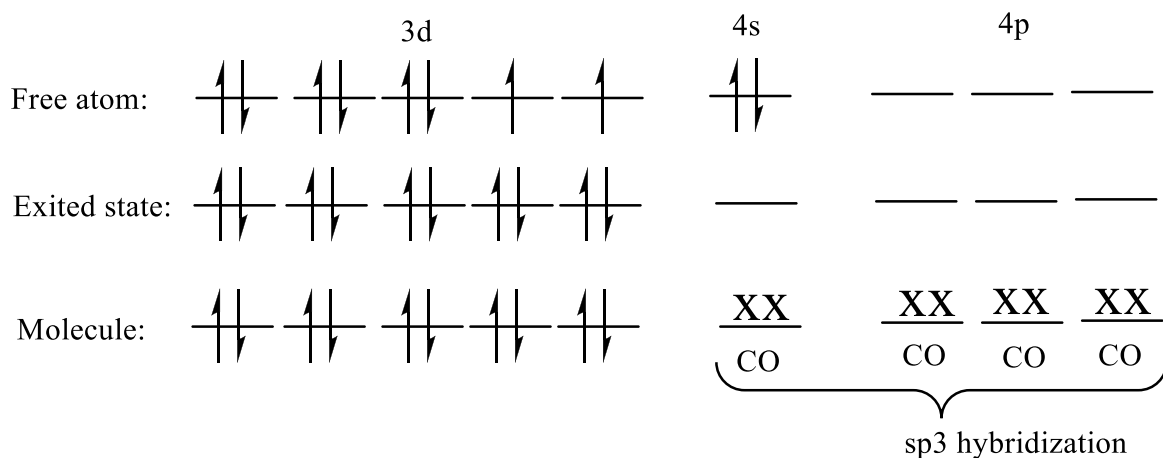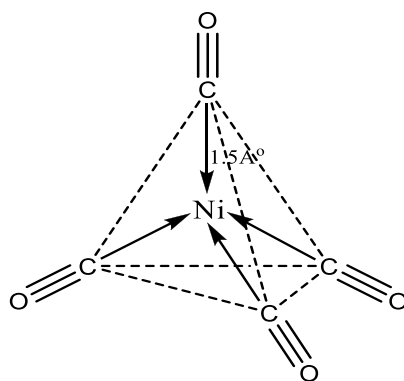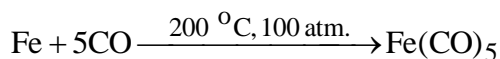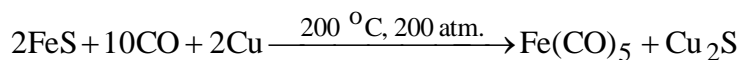
Tetrahedral structure of $Ni(CO)_4$

2. Iron pentacarbonyl, $Fe(CO)_5$:

Preparation:

(i) Action of CO on iron powder at 200 ^{0}C and 100 atmosphere pressure.

$$Fe + 5CO \xrightarrow{\;200\,^OC,\,100\,atm.\;} Fe(CO)_5$$

(ii) By carbonylating FeI_2 or FeS with CO in presence of Cu-metal which acts as a reducing agent.

$$2FeS + 10CO + 2Cu \xrightarrow{\;200\,^OC,\,200\,atm.\;} Fe(CO)_5 + Cu_2S$$

Properties:

(i) $Fe(CO)_5$ is pale yellow liquid ; b.p. 103 ^{o}C, soluble in methyl alcohol, ether, acetone and C_6H_6. It is insoluble in water.
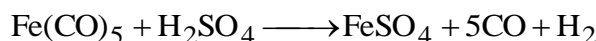
(ii) Decomposition: At 250 ^{o}C, it decomposes to give pure Fe.

$$2Fe(CO)_5 \xrightarrow{\;250\,^OC\;} Fe + 5CO$$
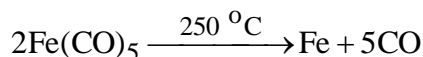
(iii) Action of ultra-violet light: When cooled solution of $Fe(CO)_5$ in glacial CH_3COOH is treated with ultra-violet light, $Fe_2(CO)_9$ is formed.

$$2Fe(CO)_5 \xrightarrow{\;UV\text{-light}\;} Fe_2(CO)_9 + CO$$
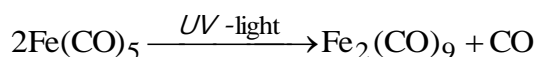
(iv) Hydrolysis: It is hydrolyzed with water and acids.

$$Fe(CO)_5 + H_2SO_4 \longrightarrow FeSO_4 + 5CO + H_2$$

(v) Action of alkali: When heated with aqueous or alcoholic solution of NaOH, carbonylate anion, $[Fe_2(CO)_4H^+]^-$ is formed. The hydrogen atom in this anion is acidic which means that Fe is in -2 oxidation state.

$$\underset{(Fe=0)}{Fe(CO)_5} + 3NaOH \longrightarrow \underset{(Fe=-2)}{Na^+[Fe^{2-}(CO)_4H^+]^-} + Na_2CO_3 + H_2O$$
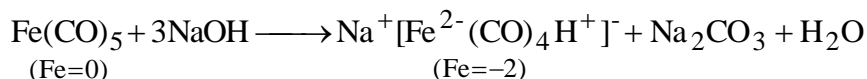
(vi) Action of NH_3: With NH_3 it gives $Fe(CO)_4H_2$ and carbamic acid, NH_2COOH.

$$Fe(CO)_5 + H_2O + NH_3 \longrightarrow Fe(CO)_4H_2 + NH_2COOH$$
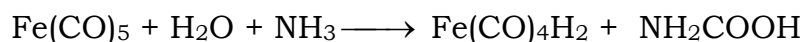
(vi) Reaction with halogen: It react with halogens in non-aqueous solvent to form the stable tetra carbonyl halides, $Fe(CO)_4X_2$.

$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$
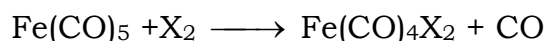
Structure:

The vapour density and freezing point of its C_6H_6 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 *dsp³* hybridization occurs between the orbitals of Fe atom. All eight electrons of Fe atom paired in *3d* orbital. $Fe(CO)_5$ is diamagnetic. The OC→Fe bond is formed by overlapping of empty *dsp³* hybrid orbitals with doubly filled *sp* hybrid orbital on C-atom in CO molecule as shown below.
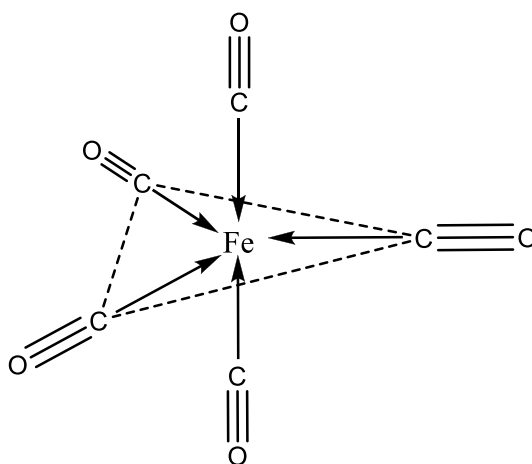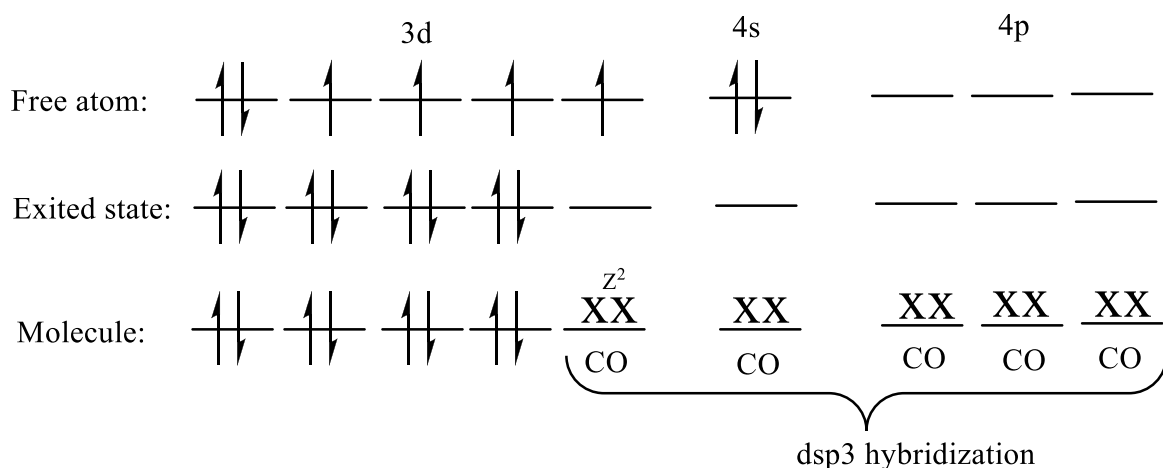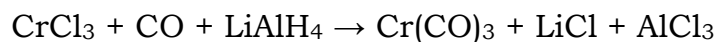

Trigonalbipyramidal structure of $Fe(CO)_5$

3. Chromium hexacarbonyl, Cr(CO)₆:

Preparation:

(i) By carbonylating $CrCl_3$ with CO in presence of a reducing agent like lithium aluminium hydride, $LiAlH_4$.

$$CrCl_3 + CO + LiAlH_4 \rightarrow Cr(CO)_3 + LiCl + AlCl_3$$

(ii) Br treating $CrCl_3$ with CO in presence of C_6H_5MgBr (Job's Grignard reaction) under appropriate conditions. (i.e. By passing CO to 50 atm pressure and at room temperature into a suspension of $CrCl_3$ in either which has been treated with C_6H_5MgBr at -27^0C).

Properties:

(i) It is colourless, insoluble crystals which sublime without decomposition and dissolve in either, $CHCl_3$, CCl_4, C_6H_6.
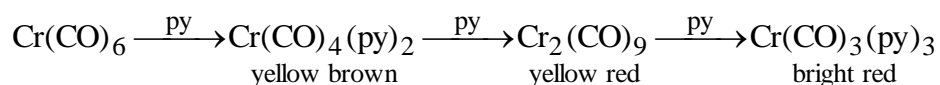
(ii) It is not attacked by air, bromine, cold aqueous alkalis. Dilute acids and conc. HCL and H_2SO_4. It is decomposed by Cl_2 and Conc. HNO_3

(iii) It is decomposed by F_2 at -75 °C to form CrF_6.

(iv) Alkali metal in liquid ammonia reacts to give $Na_2[Cr(CO)_5]$

$$\underset{(Cr=0)}{Cr(CO)_6} + 2Na \xrightarrow{\text{liq. NH}_3} Na_2{}^+[Cr^{2-}(CO)_5]^{2-} + CO$$
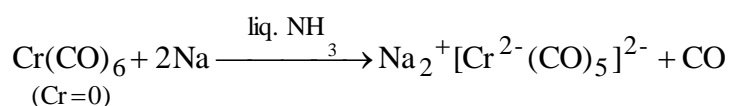
(v) Some carbonyls present in the $Cr(CO)_6$ can be replaced by pyridine (py) toget a number of compounds.

$$Cr(CO)_6 \xrightarrow{py} \underset{\text{yellow brown}}{Cr(CO)_4(py)_2} \xrightarrow{py} \underset{\text{yellow red}}{Cr_2(CO)_9} \xrightarrow{py} \underset{\text{bright red}}{Cr(CO)_3(py)_3}$$

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. $Cr(CO)_6$ is diamagnetic. The OC→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.
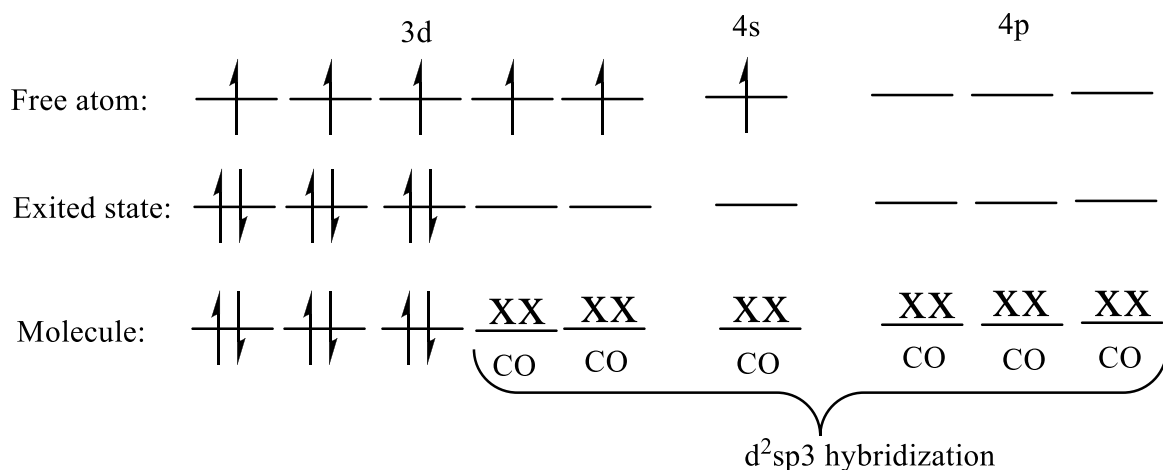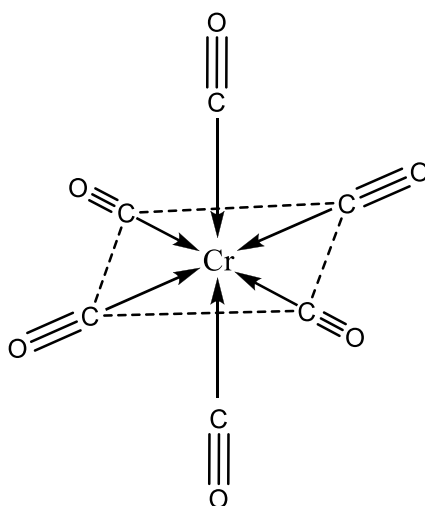
Octahedral structure of $Cr(CO)_6$

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.
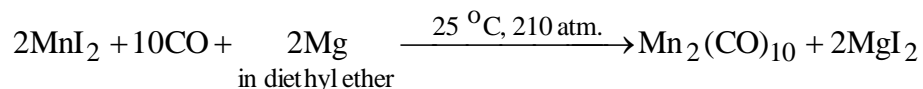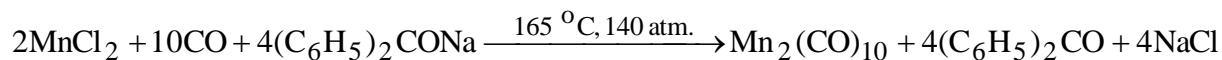
$$2MnI_2 + 10CO + \underset{\text{in diethyl ether}}{2Mg} \xrightarrow{25\,^{O}C,\,210\,atm.} Mn_2(CO)_{10} + 2MgI_2$$

(ii) By carbonylating $MnCl_2$ with CO in presence of $(C_6H_5)_2CONa$.

$$2MnCl_2 + 10CO + 4(C_6H_5)_2CONa \xrightarrow{165\,^{O}C,\,140\,atm.} Mn_2(CO)_{10} + 4(C_6H_5)_2CO + 4NaCl$$

Properties:

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

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

$$Mn_2(CO)_{10} + X_2 \ (X = Br,\ I) \rightarrow 2Mn(CO)_5X$$
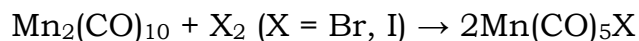
(iii) It reacts with Na-metal in liq. NH_3 to formed carbonylate anion.

$$\underset{(Mn=0)}{Mn_2(CO)_{10}} + 2Na \xrightarrow{liq\ NH_3} 2Na^+[Mn^-(CO)_5]^-$$

(iv) It react with PR_3 to formed $Mn(CO)_4(PR_3)$.

$$Mn_2(CO)_{10} + PR_3 \rightarrow 2Mn(CO)_4(PR_3) + 2CO$$
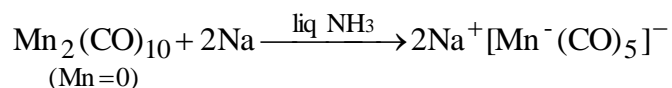
Structure:

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 exist as $Mn_2(CO)_{10}$ (i.e. unpaired electrons of each Mn atom are used to from 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.

d^2sp^3 hybridization on both Mn atom
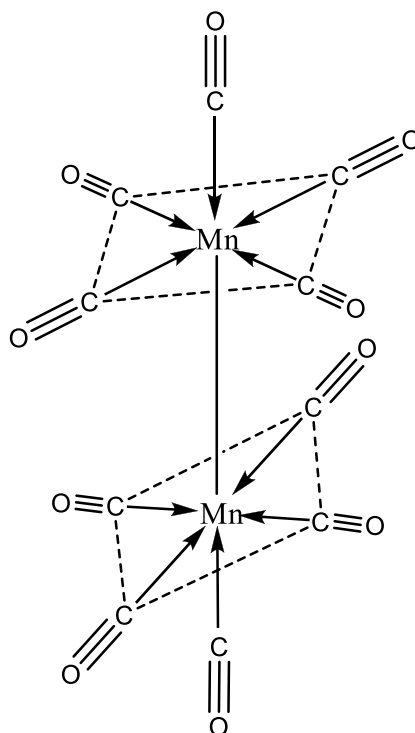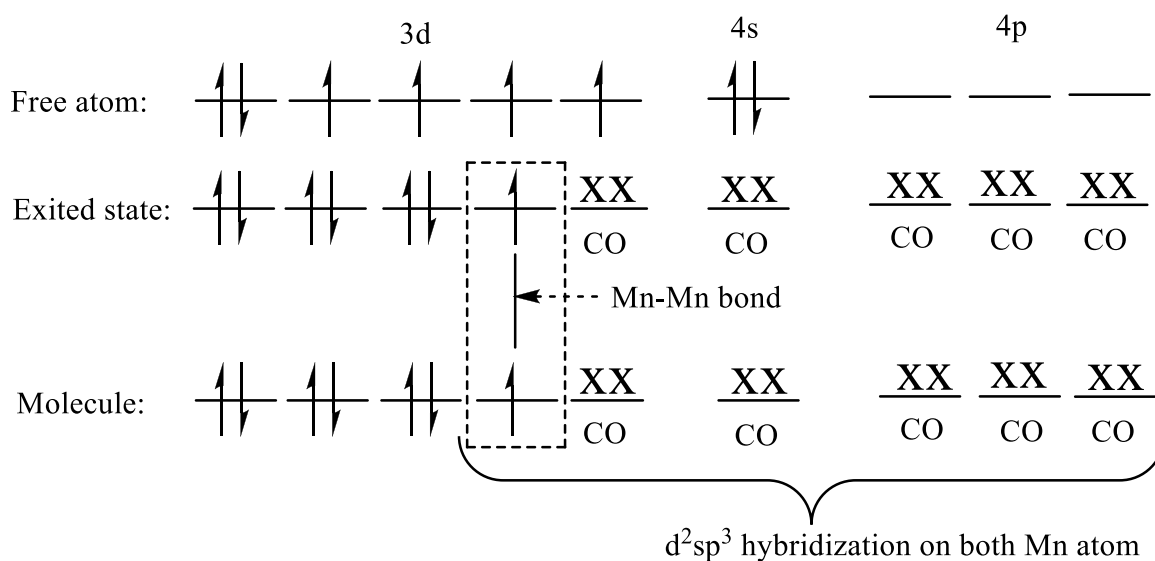
5. Dicobalt octacarbonyl, $Co_2(CO)_8$:

Preparation:

(i) By direct combination of CO with cobalt metal

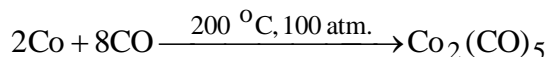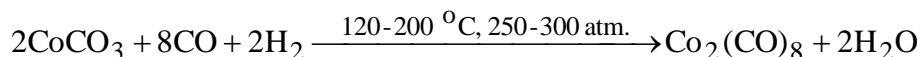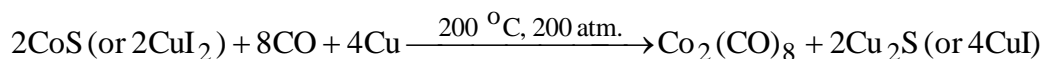$$2Co + 8CO \xrightarrow{\text{200 }^O\text{C, 100 atm.}} Co_2(CO)_5$$

(ii) By carbonylating CoI_2 or CoS with CO in presence of Cu-metal or by carbonylating $CoCO_3$ with CO in presence of Cu-metal and H_2 both act as reducing agent.

$$2CoS \text{ (or } 2CuI_2) + 8CO + 4Cu \xrightarrow{\text{200 }^O\text{C, 200 atm.}} Co_2(CO)_8 + 2Cu_2S \text{ (or } 4CuI)$$

$$2CoCO_3 + 8CO + 2H_2 \xrightarrow{\text{120-200 }^O\text{C, 250-300 atm.}} Co_2(CO)_8 + 2H_2O$$

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, $Co_4(CO)_{12}$.

$$2Co_2(CO)_8 \xrightarrow{\text{50 }^O\text{C}} Co_4(CO)_{12} + 4CO$$
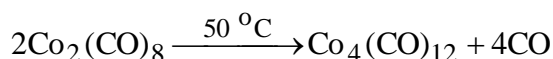
(iii) It is converted in to deep violet basic carbonate of cobalt on exposure in air.

(iv) It reacts with H_2 at 165 °C and 200 atm. pressure to formed cobalt carbonyl hydride, $[Co^-(CO)_4H^+]^0$. $[Co^-(CO)_4H^+]^0$

$$Co_2(CO)_8 + 2Na \xrightarrow{\text{165}^\circ\text{C, 200 atm.}} [Co^-(CO)_4H^+]^0$$
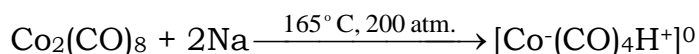
(v) It reacts with NO to give cobalt carbonyl nitrosyl, $[Co^-(CO)_8(NO)^+]^0$.

$$Co_2(CO)_8 + 2NO \rightarrow [Co^-(CO)_8(NO)^+]^0 + 2CO$$

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 hybride 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 appropriat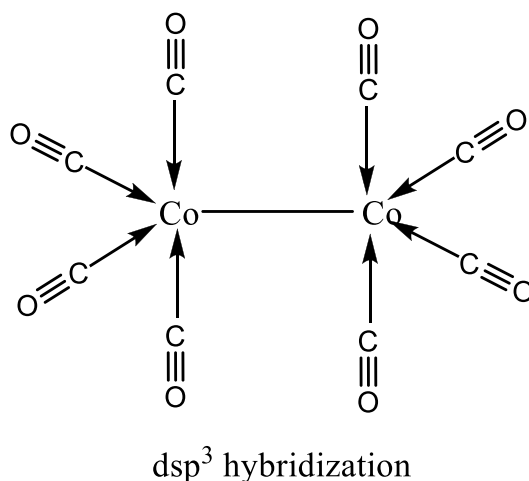e orbital (singly filled) on C-atom of two bridging CO groups and form Co-Co bond. Thus, all electrons in $Co_2(CO)_8$ molecule are paired and molecule is diamagnetic.

d²sp3 hybridization on both Co atom

d²sp³ hybridization
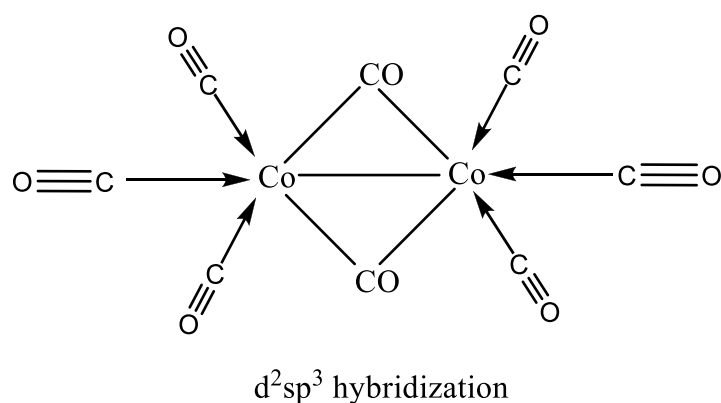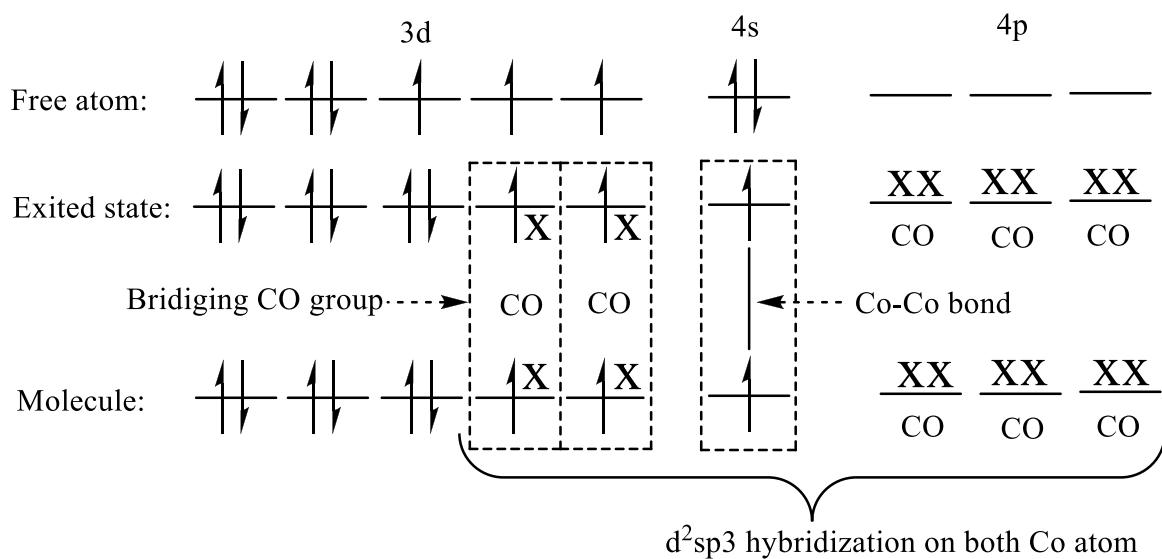
In case of non-bridge structure, Co atoms have dsp^3 hybridization as shown below.

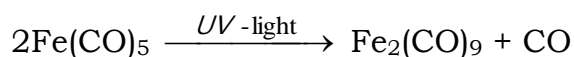|	3d	4s	4p

Free atom: ↑↓ ↑↓ ↑ ↑ ↑   ↑↓   — — —

Exited state: ↑↓ ↑↓ ↑↓ ↑↓ [↑]   XX   XX XX XX
                                CO   CO CO CO

←---- Co-Co bond

Molecule: ↑↓ ↑↓ ↑↓ ↑↓ [↑]   XX   XX XX XX
                             CO   CO CO CO

dsp^3 hybridization

$$
\begin{array}{ccc}
 & O\equiv C & O\equiv C \\
O\equiv C \rightarrow & Co - Co & \leftarrow C\equiv O \\
O\equiv C \rightarrow & & \leftarrow C\equiv O \\
 & C\equiv O & C\equiv O
\end{array}
$$

dsp^3 hybridization
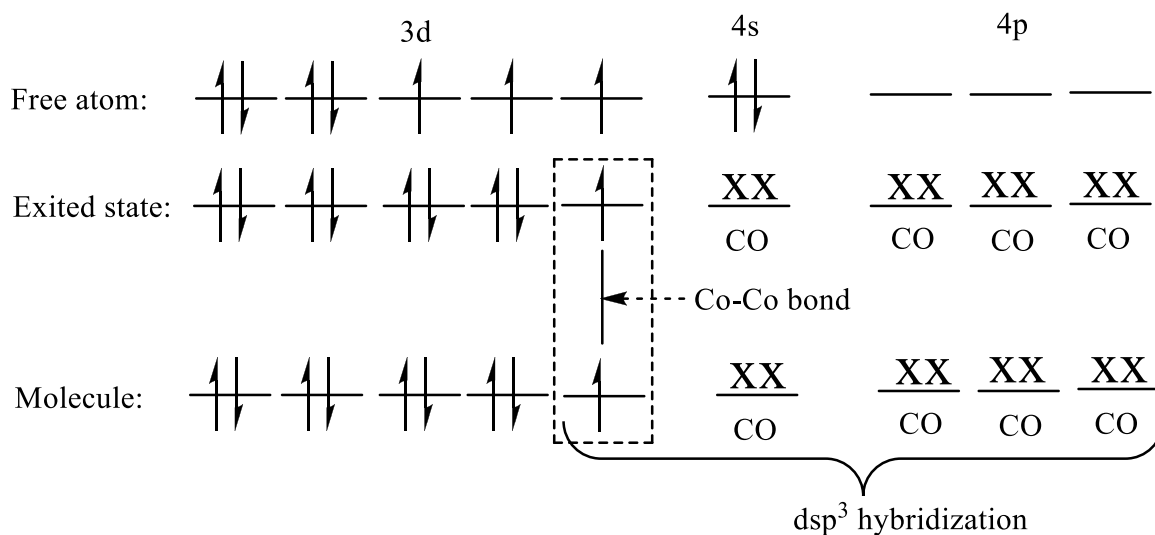
6. Di-iron nonacarbonyl, $Fe_2(CO)_9$:

Preparation:

(i) $Fe(CO)_5$ dissolved in glacial acetic acid is irradiated with ultraviolet light.

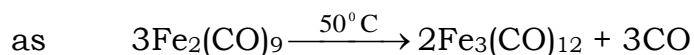$$2Fe(CO)_5 \xrightarrow{UV\text{-light}} Fe_2(CO)_9 + CO$$

On cooling the solution, $Fe_2(CO)_9$ is ppted as golden yellow crystals.

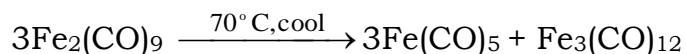**Properties:**

(i) $Fe_2(CO)_9$ forms golden yellow triclinic crystals in soluble in water but soluble in toluene and pyridine.

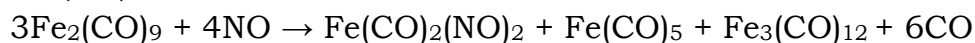(ii) It decomposes at 100 °C. It is non-volatile when heat to 50 °C it decomposes

as $3Fe_2(CO)_9 \xrightarrow{50°C} 2Fe_3(CO)_{12} + 3CO$

At 100 °C it forms Fe, $Fe(CO)_5$ and some $Fe_3(CO)_{12}$

$$3Fe_2(CO)_9 \xrightarrow{70°C,cool} 3Fe(CO)_5 + Fe_3(CO)_{12}$$

(iii) It reacts with NO to gives $Fe(CO)_2(NO)_2$ together with $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

$$3Fe_2(CO)_9 + 4NO \rightarrow Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12} + 6CO$$

(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 carbonylate anion.

$$\underset{(Fe=0)}{Fe_2(CO)_9} + 4Na \xrightarrow{\text{liq. NH}_3} Na_2{}^+[Fe^{2-}(CO)_4]^{2-} + CO$$
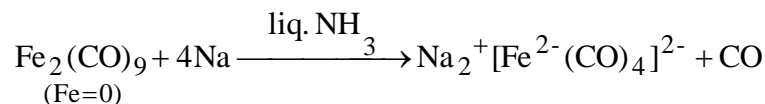
Structure:

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.
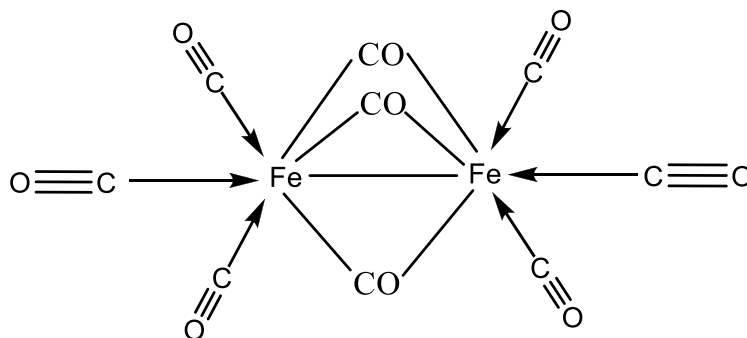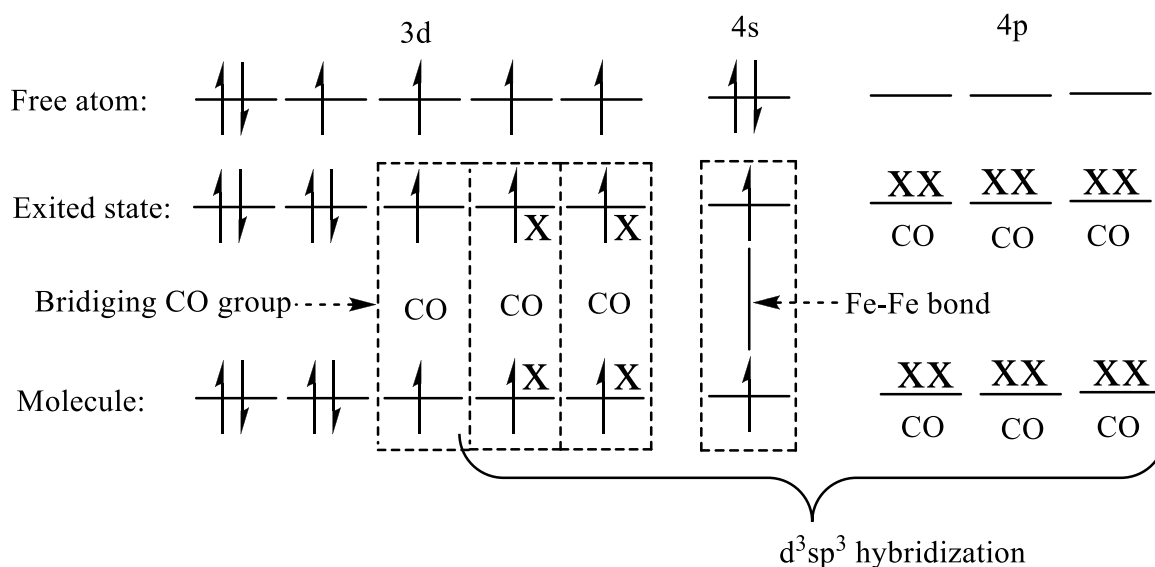
7. Tri-iron dodecacarbonyl, $Fe_3(CO)_{12}$:

Preparation:

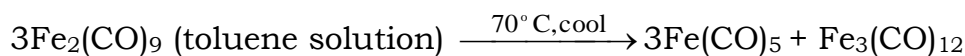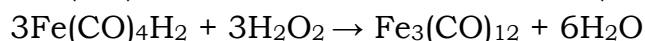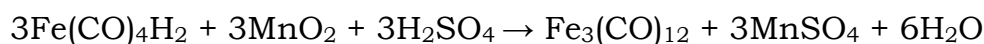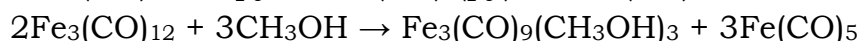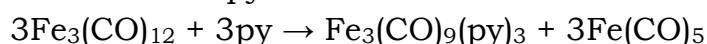(i) It is obtained by heating $Fe_2(CO)_9$ dissolved in toluene at 70 °C

$$3Fe_2(CO)_9 \text{ (toluene solution)} \xrightarrow{70°C, cool} 3Fe(CO)_5 + Fe_3(CO)_{12}$$

(ii) It can be obtained by oxidation of iron carbonyl hydride, $Fe(CO)_4H_2$ by MnO_2 or H_2O_2

$$3Fe(CO)_4H_2 + 3MnO_2 + 3H_2SO_4 \rightarrow Fe_3(CO)_{12} + 3MnSO_4 + 6H_2O$$
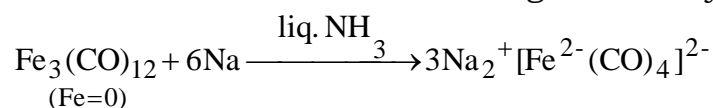$$3Fe(CO)_4H_2 + 3H_2O_2 \rightarrow Fe_3(CO)_{12} + 6H_2O$$

Properties:

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

(ii) It reacts with pyridine and alcohol

$$3Fe_3(CO)_{12} + 3py \rightarrow Fe_3(CO)_9(py)_3 + 3Fe(CO)_5$$
$$2Fe_3(CO)_{12} + 3CH_3OH \rightarrow Fe_3(CO)_9(CH_3OH)_3 + 3Fe(CO)_5$$

(iii) It reacts with Na in NH_3 solution give carbonylate anion.

$$\underset{(Fe=0)}{Fe_3(CO)_{12}} + 6Na \xrightarrow{\text{liq. } NH_3} 3Na_2^+[Fe^{2-}(CO)_4]^{2-}$$

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

$$Fe_3(CO)_{12} \xrightarrow{140\,°C} 3Fe + 12CO$$
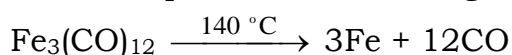
(v) It is react with NO at 85 °C to form iron dicarbonyl dinitrosyl, $Fe(CO)_2(NO)_2$

$$Fe_3(CO)_{12} + 6NO \rightarrow 3Fe(CO)_2(NO)_2 + 6CO$$
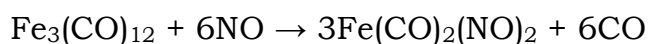
Structure:

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.
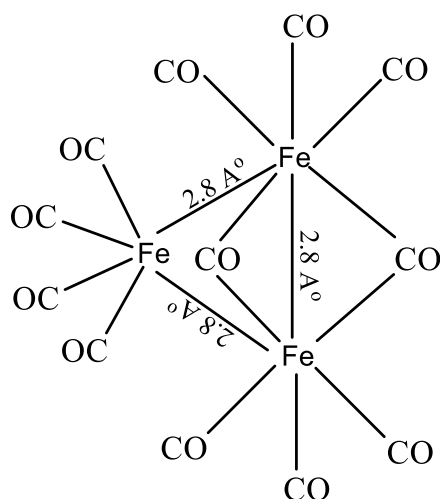
Structure of $Fe_3(CO)_{12}$

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 carbonyls:

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

(ii) Metal nitrosyl halides:

These compounds are represented by $[Fe^-(NO^+)_2I]_2$, $[Fe^{2-}(NO^+)_2(CO)_2]^0$, $[Fe^-(NO^+)_2I]^0$, $[Fe2^-(NO^+)_3Cl]^0$, $[Co^-(NO^+)_2X]^0$ (X=Cl, Br, I), $[M^-(NO^+)_2Cl_2]^0$ (M=Mo or W).

(iii) Metal nitrosyl thio complexes:

These compounds are given by only Fe, Co and Ni. Examples are $M^+[Fe^-(NO^+)_2S]^-$, $M^+[Co^-(NO^+)_2S]^-$, $M^+[Ni^-(NO^+)_2S]^-$ (M=Na$^+$, K$^+$, NH$_4$.

(iv) Metal nitrosyl cyano complexes:

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

(v) Miscellaneous metal nitrosyl complexes:

Nitrosyl complexes like $[Co^+(NO^+)(NH_3)_5]^{2+}$, $[Co^+(NO^+)(NO_2)_5]^{3-}$, $[Fe^+(NO^+)]^{2+}$, $[Ru^{2+}(NO^+)(NH_3)_4Cl]^{2+}$, $[Ru^{2+}(NO^+)Cl_5]^{2-}$, $[Fe^{2-}(NO^+)_2(PR_3)_3]^0$ etc. Among these complexes, $[Fe^+(NO^+)]^{2+}$ is the most important.

Preparation:

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

$$Fe(CO)_5 + 2NO \xrightarrow{95\,°C} Fe(CO)_2(NO)_2 + 3CO$$

$$3Fe(CO)_9 + 4NO \rightarrow 2Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12} + 6CO$$

$$Fe_3(CO)_{12} + 6NO \xrightarrow{85\,°C} 3Fe(CO)_2(NO)_2 + 6CO$$

$$Co_2(CO)_8 + 2NO \xrightarrow{40\,°C} 2Co(CO)_3(NO) + 2CO$$
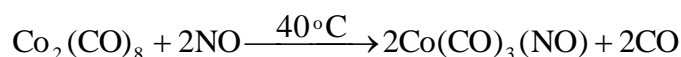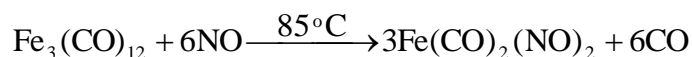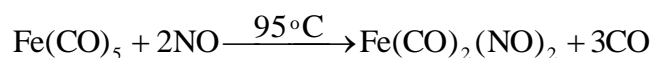
(ii) Metal nitrosyls halides can be prepared:

(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.

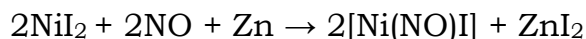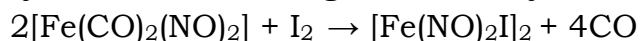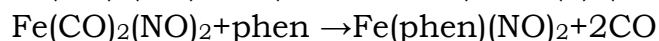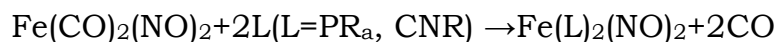$CoX_2 + 4NO + Co \rightarrow 2[Co(NO)_2X]$

$2NiI_2 + 2NO + Zn \rightarrow 2[Ni(NO)I] + ZnI_2$

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

$2[Fe(CO)_2(NO)_2] + I_2 \rightarrow [Fe(NO)_2I]_2 + 4CO$

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.,

$Fe(CO)_2(NO)_2 + 2L(L=PR_a, CNR) \rightarrow Fe(L)_2(NO)_2 + 2CO$

$Fe(CO)_2(NO)_2 + phen \rightarrow Fe(phen)(NO)_2 + 2CO$

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

$2[Fe(CO)2(NO)_2] + I_2 \rightarrow [Fe(NO)_2I]_2 + 4CO$
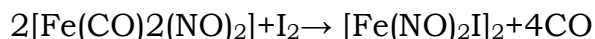
Properties of metal nitrosyl halides:

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

$[Fe(NO)_2X]_2 + 2L \rightarrow 2[Fe(NO)_2XL]$
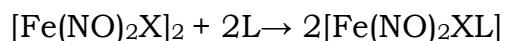
(ii) Iron nitrosyl halide, $[Fe(NO)_2I]_2$ reacts with K_2S and CH3CI to form dark red compounds which have the composition, $K_2[Fe(NO)_2S]_2$ and $[Fe(NO)_2(SCH_3)]_2$ and are called Roussin's salts. In these compounds, Fe is in -1 oxidation state.

$$[Fe(NO)_2I] \xrightarrow[-2KI]{+K_2S} K_2[Fe(NO)_2S]_2 \xrightarrow[\text{-2KCl}]{+CH_3Cl} [Fe(NO)_2(SCH_3)]_2$$
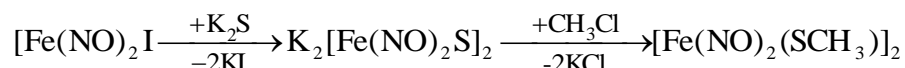
SOME METALLIC NITROSYLS

Now let us make study of sodium nitroprusside, $Na_2[Fe^{2+}(CN)_5(NO^+)]$ and nitroso ferrous sulphate, $FeSO_4NO$ 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 $Na_4[Fe^{2+}(CN)_6]$

$Na_4[Fe^{2+}(CN)_6] + NaNO_2 + H_2O \rightarrow Na_2[Fe^{2+}(CN)_5(NO^+)] + 2NaOH + NaCN$

(ii) by passing nitric oxide (NO) into acidified solution of $Na_4[Fe(CN)_6]$.

$2Na_4[Fe(CN)_6] + H_2SO_4 + 3NO \rightarrow 2Na_2[Fe(NO)(CN)_5] + 2NaCN + Na_2SO_4 + $
$1/2\ N_2 + H_2O$

Properties:

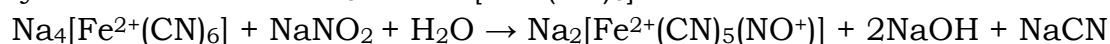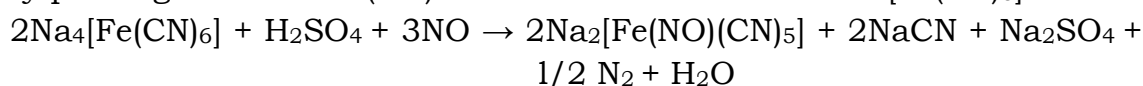(i) Sodium nitroprusside forms beautiful ruby red rhombic crystals which are soluble in water.

(ii) When freshly prepared sodium nitroprusside is added to a solution containing sulphide ion (i.e. Na_2S but not H_2S), 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.
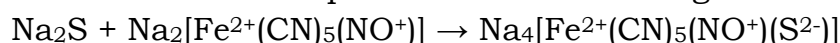
$Na_2S + Na_2[Fe^{2+}(CN)_5(NO^+)] \rightarrow Na_4[Fe^{2+}(CN)_5(NO^+)(S^{2-})]$
(Violet or purple colour)

(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.

$Na_2SO_3 + Na_2[Fe(CN)_5(NO)] \rightarrow Na_4[Fe(CN)_5(NO)(SO_3)]$
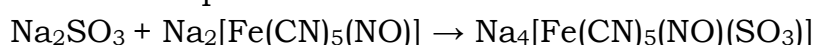
(iv) With silver nitrate a flesh coloured $Ag_2[Fe(CN)_5(NO)]$ is produced.

$2AgNO_3 + Na_2[Fe(CN)_5(NO)] \rightarrow Ag_2[Fe(CN)_5(NO)] + 2NaNO_3$
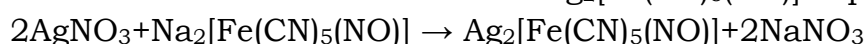
(v) Aldehydes and ketones containing CH_3-CO-R group give deep red colour with sodium nitroprusside and excess of NaOH.

(vi) It is converted into sodium ferrocyanide, $Na_4[Fe(CN)_6]$ on treatment with an alkali.

$6Na_2[Fe(CN)_5(NO)] + 14NaOH \rightarrow 5Na_4[Fe(CN)_6] + Fe(OH)_2 + 6NaNO_3 + 6H_2O$
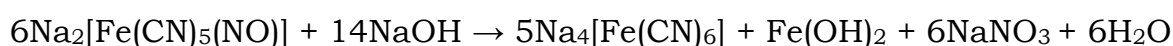
According to another view NO^+ groups present in nitroprusside is oxidized to NO_2 and thus a nitro complex is obtained.

$Na_2[Fe(CN)_5(NO)] + 2NaOH \rightarrow Na_4[Fe(CN)_5(NO_2)] + H_2O$
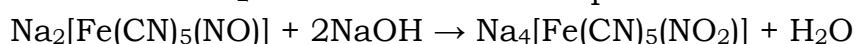
(vii) $[Fe(CN)_5(NO)]^{2-}$ ion has diamagnetic character. Its diamagnetic character confirms the fact that NO is present as NO^+ ion in this complex ion.

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 $[Fe(CN)_5(NO)]$ is 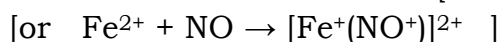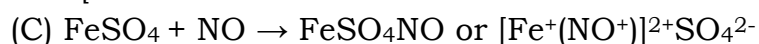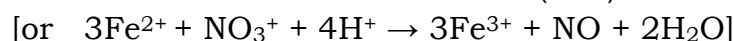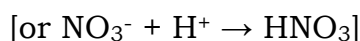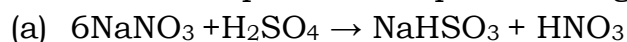-2. In other words, the formula of sodium nitroprusside is $Na_2[Fe^{2+}(CN)_5 (NO^+)]$. $[Fe^{2+}(CN)_5(NO^+)]^{2-}$ has octahedral structure with Fe^{2+} ion located at the centre of the octahedron.

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, FeSO₄NO or [Fe⁺(NO⁺)]SO₄:

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_2SO_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) $6NaNO_3 + H_2SO_4 \rightarrow NaHSO_3 + HNO_3$
   [or $NO_3^- + H^+ \rightarrow HNO_3$]

(b) $6FeSO_4 + 2HNO_3 + 3H2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$
   [or $3Fe^{2+} + NO_3^+ + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$]

(C) $FeSO_4 + NO \rightarrow FeSO_4NO$ or $[Fe^+(NO^+)]^{2+}SO_4^{2-}$
   [or $Fe^{2+} + NO \rightarrow [Fe^+(NO^+)]^{2+}$]

In aqueous solution $[Fe^+(NO^+)]^{2+}$ ion is better expressed as $[Fe(NO)(H_2O)_5]^{2+}$. 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_3^- 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 $(sp)^2{}_O, (\sigma sp^b)^2, (\pi_y{}^b)^2 = (\pi_z{}^b)^2, (sp)^2{}_N, (\pi_y{}^*)^1 = \pi_z{}^*)^0, (\sigma sp^*)^0$ [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 carbonyls. 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 $M^-\leftarrow NO^+$. 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 carbonyls.

On the basis of molecular orbital theory, the hybrid orbital on N-atom containing a lone pair [i.e. $(sp)^2_N$ 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 $ON^+\rightarrow M^-$ σ-bond. Now the empty $\pi_x{}^*$ or $\pi_y{}^*$ molecular orbital can overlap with the filled d-orbitals (d_{xy}, d_{yz}, d_{zx} orbitals in octahedral case and dx^2-y^2 and dz^2 orbitals in tetrahedral case) to form $M^-\leftarrow NO^+$ 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 $1.67A^0$) 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) $[Co^-(CO)_3(NO^+)]^0$: ēs from Co^- = 27 + 1 = 28
                     ēs from 3 CO = 2 x 3 = 6
                     <u>ēs from NO^+ = 1 x 2 = 2</u>
               hence EAN of each Co atom = 36 [Kr]

(ii) $[Fe^{2-}(CO)_2(NO^+)_2]^0$: ēs from Fe^{2-} = 26 + 2 = 28
                     ēs from 2 CO = 2 x 2 = 4
                     <u>ēs from NO^+ = 2 x 2 = 4</u>
               hence EAN of each Fe atom = 36 [Kr]

(iii) $[Fe^{2-}(NO^+)_2(Pr_3)_2]^0$: ēs from Fe^{2-} = 26 + 2 = 28
                     ēs from NO^+ = 2 x 2 = 4
                     <u>ēs from 2 Pr_3 = 2 x 2 = 4</u>
               hence EAN of each Fe atom = 36 [Kr]

(iv) $[Mn^{3-}(CO)(NO^+)_3]^0$: ēs from Mn^{3-} = 25 + 3 = 28
                     ēs from CO = 1 x 2 = 2
                     <u>ēs from 3 NO^+ = 3 x 2 = 6</u>
               hence EAN of each Fe atom = 36 [Kr]

THE END