

# Metal $\pi$ -Complexes



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# CARBONYLS

- Structure and bonding, vibrational spectra of metal carbonyls for bonding structural elucidation, important reaction of metal carbonyls, preparation, bonding structure.
- The p acceptor ligands possess vacant p orbitals in addition to the lone pairs of electrons. Such ligands are CO, NO,  $\text{PR}_3$ , CNR etc. These ligands donate their lone pairs to the metal atom to form a normal  $\sigma$  bond. In addition to it the vacant orbitals of ligands accept electrons from the filled metal orbitals to form a type of  $\pi$  bond.

- These ligands are thus called  $\rho$ -acid ligands or  $\pi$ -acceptor ligands or  $\pi$ -bonding ligands. The metal atoms in these complexes are in low positive, zero or negative oxidation states i.e. these ligands stabilise lower oxidation states. Thus, there is higher electron charge density on the metal in its lower oxidation states than in its higher oxidation state. Therefore, some of this excess electronic charge is transferred from metal to the vacant orbitals of the ligand by  $\pi$  bonding. S are discussed below.

# Metal Carbonyls

- The electronic configuration of CO molecule indicates that it contains a lone pair of electrons on carbon and oxygen atom each. Thus, carbon atom of CO molecule can donate its electron pair to a transition metal atom (M) to form  $\text{OC} \rightarrow \text{M}$  coordinate bond. The compounds formed by the combination of CO molecules with transition metals are called **metallic carbonyls**.

- Since the electrons forming  $OC \rightarrow M$  bond are supplied only by CO molecules, metal atom in carbonyls is said to be in zero Oxidation state. In metal carbonyls CO molecules act as neutral ligands.
- **Classification**
- **1. Mononuclear carbonyls:** These carbonyls contain only one metallic atom per molecule and have the general formula  $M(CO)_y$ . Such carbonyls are formed by the metals having even atomic number e.g.,  $Cr(CO)_6$ ,  $Fe(CO)_5$ ,  $Ni(CO)_4$ ,  $Mo(CO)_6$ ,  $W(CO)_6$  etc. Some characteristics of these carbonyls are:

# Properties

- These are generally colourless liquids or solids with low m. pts. except  $\text{V}(\text{CO})_5$  which is a black solid and  $\text{Fe}(\text{CO})_5$  which is a yellow solid.
- These are readily soluble in organic solvents like benzene, ether, light petroleum etc.
- These can be vaporised without decomposition.
- These carbonyls are more volatile than the others.

# Polymolecular carbonyls

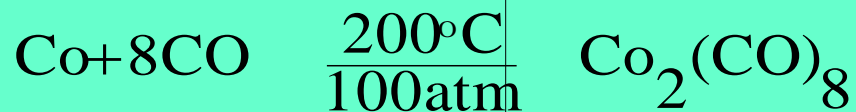
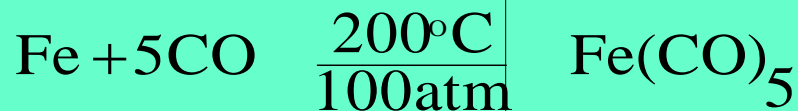
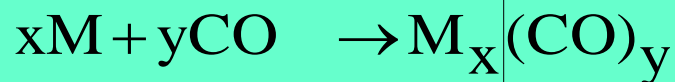
- These carbonyls contain more than one metal atom per molecule. They are represented by the general formula  $M_x(CO)_y$ .
- Some authors call the carbonyls having two metal atoms as **bridged carbonyls** and represented as  $M_2(CO)_y$  while those containing more than two metal atoms as **polynuclear carbonyls**. The polynuclear carbonyls may be of two types:

- **(a) Homonuclear carbonyls:** These carbonyls contain only one type of the metal atoms e.g.,  $\text{Fe}_3 (\text{CO})_{12}$ ,  $\text{Ru}_3 (\text{CO})_{12}$ ,  $\text{Ir}_4 (\text{CO})_{12}$  etc.
- **(b) Heteronuclear carbonyls:** These contains more than one type of metal atoms e.g.,  $\text{Mn Co} (\text{CO})_9$ ,  $\text{Mn Re} (\text{CO})_{10}$  etc.
- Some characteristics of these carbonyls are:  
These carbonyls are generally insoluble in organic solvents.  
These decompose at 'or below their melting point.



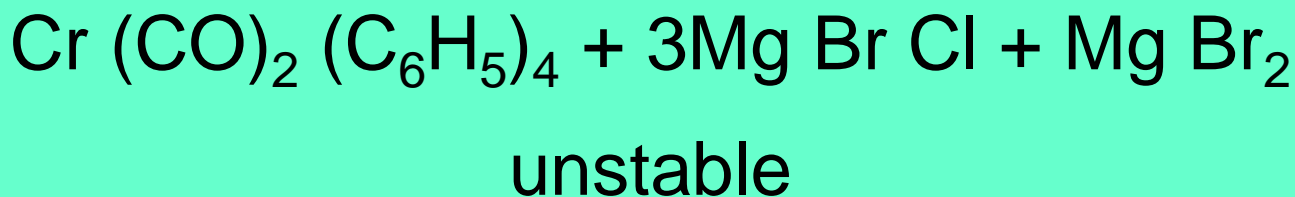
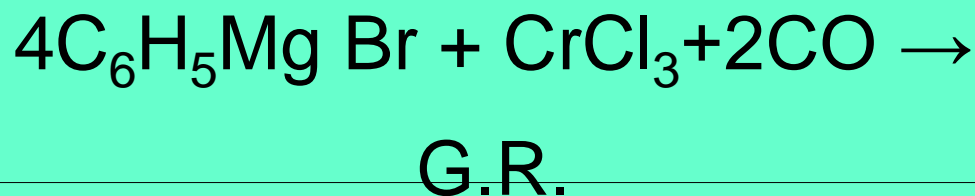
# General methods of preparation

1. **By direct synthesis:** By direct combination of CO with finely divided transition metals under suitable conditions of temperature and pressure forms carbonyls. For example:

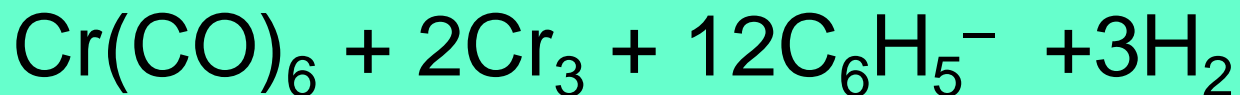
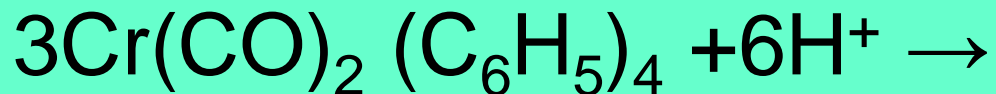


**2. By indirect synthesis involving Grignard's reagent:** Job prepared chromium hexacarbonyl  $\text{Cr}(\text{CO})_6$  by treating ethereal solution of Grignard's reagent with CO in presence of anh.  $\text{CrCl}_3$ . Similar reactions in presence of Mo (V) and W (V) chlorides gave the corresponding hexacarbonyls.

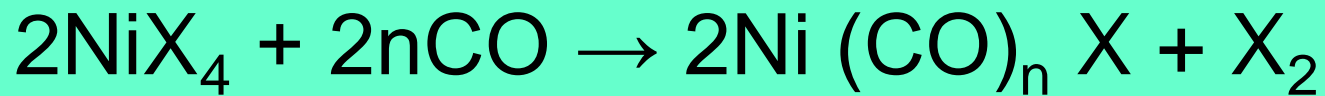
According to **Heiber**, the primary reaction is as follows:



- The unstable intermediate is decomposed in acid solution to give the hexacarbonyl.

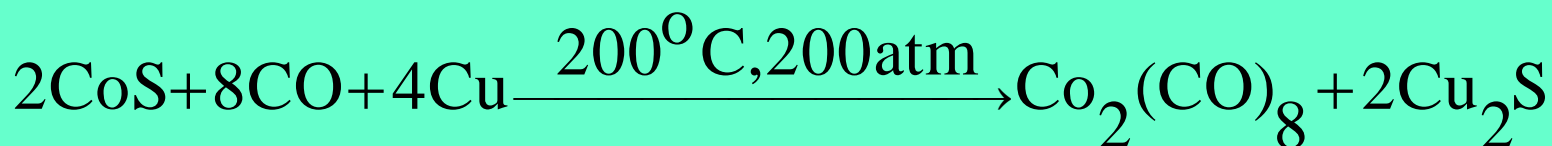
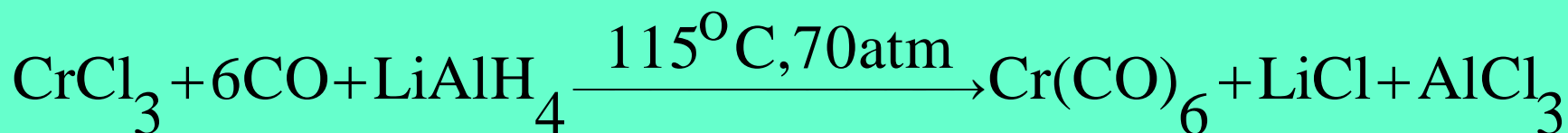
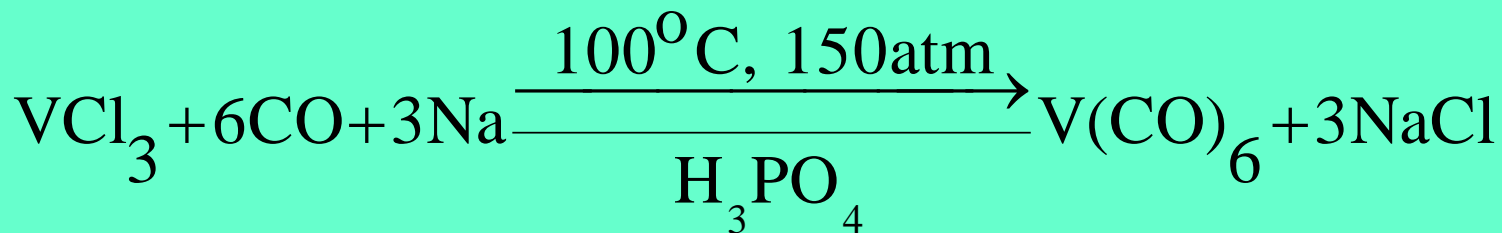


- The yield of the above reaction is low and can be improved by using high carbon monoxide pressure.
- **3. Indirect synthesis involving metal compounds:** Metal carbonyls can be prepared by the react of CO with certain metal compounds. For example:

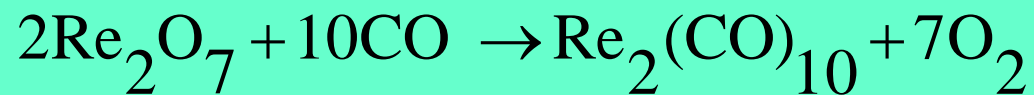
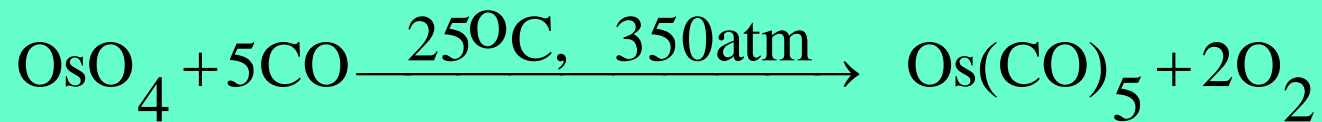


#### **4. Synthesis by carbonylating the metallic salts with CO in presence of reducing agent:**

When salts like  $\text{VCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{CoS}$ ,  $\text{CoI}_2$ ,  $\text{CoCO}_3$ ,  $\text{RuI}_3$  etc. are treated with CO (carbonylation) in presence of suitable reducing agent like Na, Mg, Ag, Au,  $\text{H}_2$ ,  $\text{LiAlH}_4$  etc., metallic carbonyls are obtained. For example,



Sometimes CO acts both as a carbonylating and reducing agent. For example, in the preparation of  $\text{Os}(\text{CO})_5$  and  $\text{Re}_2(\text{CO})_{10}$  from  $\text{OsO}_4$  and  $\text{Re}_2\text{O}_7$  respectively.

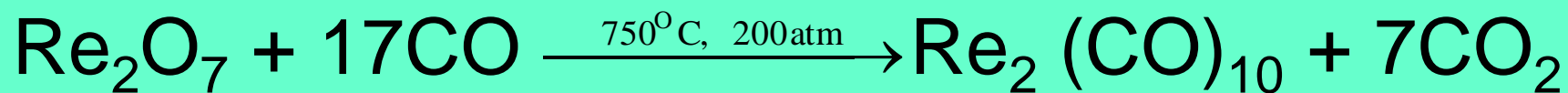
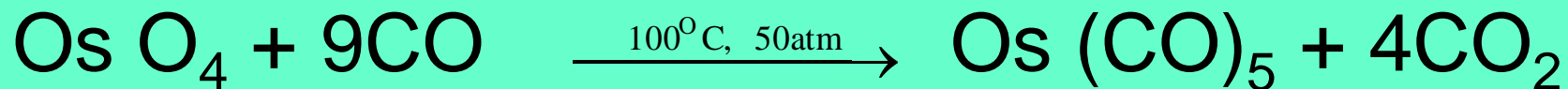


## **Synthesis from other carbonyls:**

When cooled solutions of iron and osmium pentacarbonyls in glacial acetic acid is exposed to ultraviolet light,  $\text{Fe}_3(\text{CO})_9$  and  $\text{Os}_2(\text{CO})_9$  are obtained respectively.

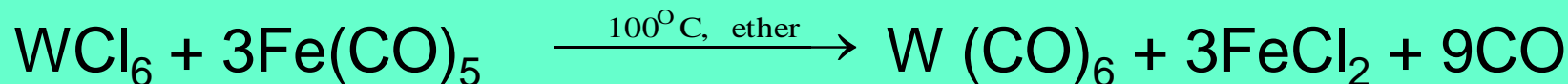
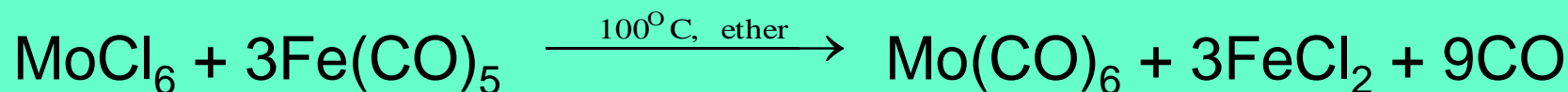


**By treating oxide of metals with CO under pressure** : Carbonyls of osmium and rhenium are prepared by this method, e.g.



## Preparation of Mo (CO)<sub>6</sub> and W (CO)<sub>6</sub> from Fe (CO)<sub>5</sub> :

Since CO groups present in Fe (CO)<sub>5</sub> are labile, they can be replaced by treating Fe (CO)<sub>5</sub> with Mo Cl<sub>6</sub> and WCl<sub>6</sub>.





## Colour and Melting points of some carbonyls

Carbonyls	Colour and state	Melting point/Boiling point
V (CO) <sub>6</sub>	Black crystals	Decomposes at 70°C, sublimes in vacuum
Cr (CO) <sub>6</sub>	Colourless crystals	Sublimes in vacuum
Mo (CO) <sub>6</sub>	Colourless crystals	Sublimes in vacuum
W (CO) <sub>6</sub>	Colourless crystals	Sublime in vacuum
Mn <sub>2</sub> (CO) <sub>10</sub>	Golden crystals	154 <sup>0</sup> - 150 <sup>0</sup> C
Re (CO) <sub>10</sub>	Collurless cryseals	Sublimes at 740 <sup>0</sup> C and decomposes at 177 <sup>0</sup> C
Fe (CO) <sub>5</sub>	Yellow liquid	B. P. 103 <sup>0</sup> C
Fe <sub>2</sub> (CO) <sub>9</sub>	Bronze platelets	Decomposes at 100 <sup>0</sup>
Fe <sub>3</sub> (CO) <sub>12</sub>	Dark green crystals	Decomposes at ~ 140°C
Co <sub>2</sub> (CO) <sub>8</sub>	Orange crystals	M.P. 51°C
Ni(CO) <sub>4</sub>	Colourless liquid	B.P. 43°C

# General Properties of Carbonyls

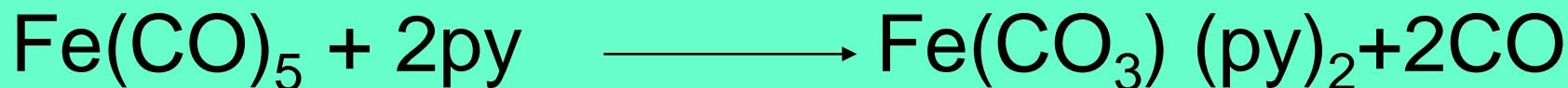
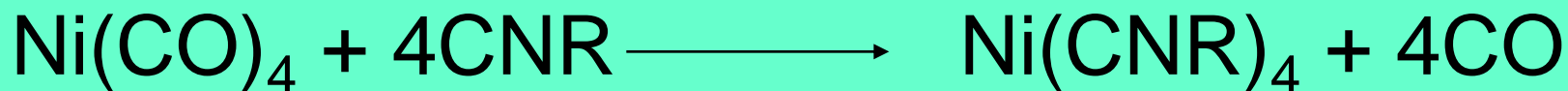
## Physical properties :

- ❖ The metal carbonyls are crystalline solids except  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Ru}(\text{CO})_5$  and  $\text{Os}(\text{CO})_5$  which are liquids of ordinary temperature.
- ❖ Generally monomeric carbonyls are colourless while polymeric are coloured and unstable as shown in Table 6.1.
- ❖ Since they are covalent in nature, most of them are soluble in organic solvents.
- ❖ They are diamagnetic in nature except  $\text{V}(\text{CO})_6$  which is paramagnetic due to the presence of one unpaired electron.

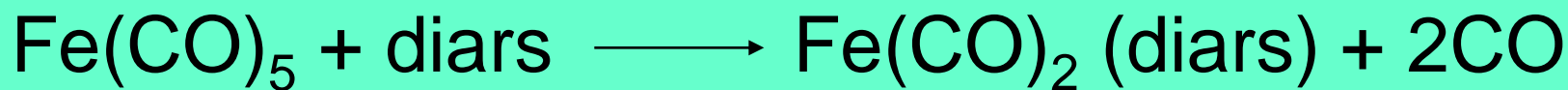
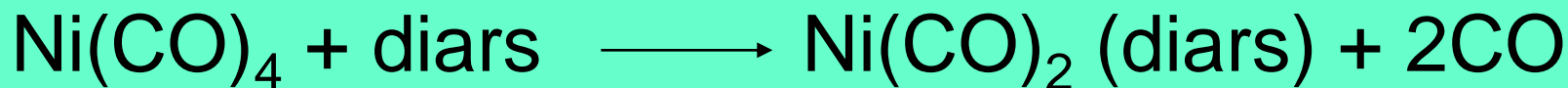
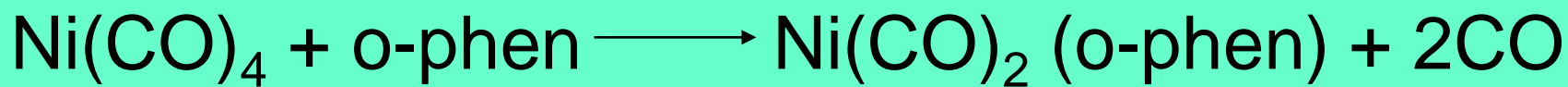
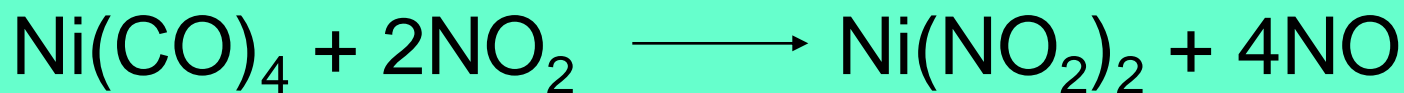
- ❖ The metals in carbonyls are in zero oxidation state.
- ❖ These are poor conductors of electricity.
- ❖ They can be sublimed or distilled at low temperature with decomposition.

## **CHEMICAL PROPERTIES:**

- ❖ **Substitution reactions** : Some or all CO groups present in the carbonyls can be replaced by monodentate ligands like py,  $\text{PCl}_3$ ,  $\text{CH}_3\text{OH}$ , alkyl or aryl isocyanide (CNR) etc. For example.

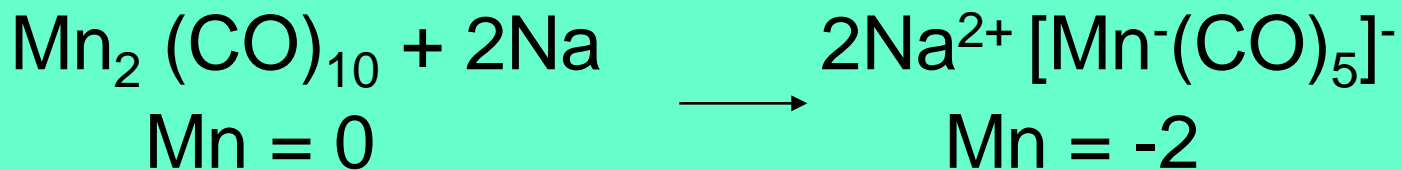
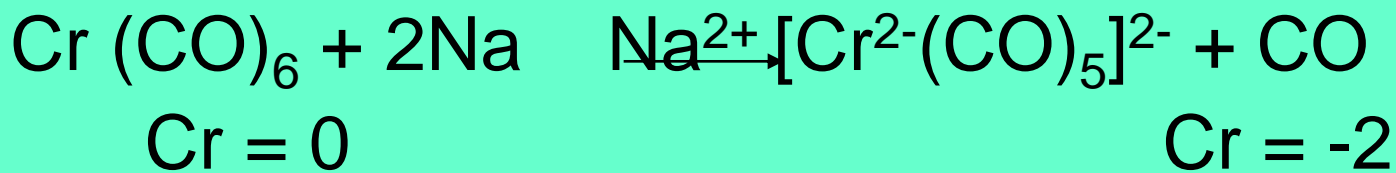


Bidentate ligands like  $\text{NO}_2$ , o-phen, diars etc. replace two or more CO groups at a time. For example :

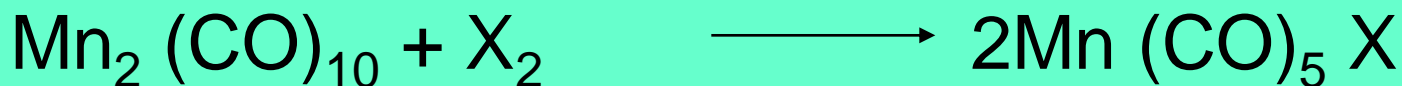
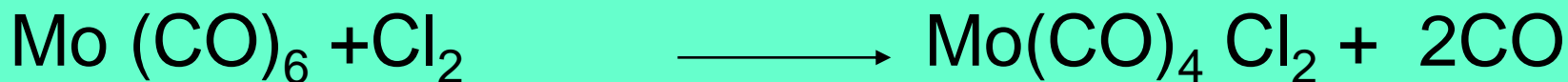


# Action of NaOH or Na metal

- ❖ Aqueous or alcoholic solution of NaOH reacts with  $\text{Fe}(\text{CO})_5$  to form carbonylate anion,  $[\text{H Fe}(\text{CO})_4]^-$
- ❖  $\text{Fe}(\text{CO})_5$  ( $\text{Fe} = 0$ ) +  $3\text{NaOH} \longrightarrow$   
 $\text{Na}^+ [\text{H}^+\text{Fe}^{2-}(\text{CO})_4]^- + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
- ❖ Na-metal in liquid  $\text{NH}_3$  converts  $\text{Cr}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Fe}(\text{CO})_{12}$  etc. into carbonylate anions and in this conversion carbonyls are reduced, e.g.,

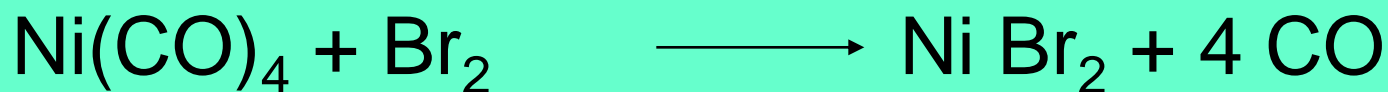


❖ **Action of halogens:** Most of the carbonyls react with halogens to form carbonyl halides. For example :

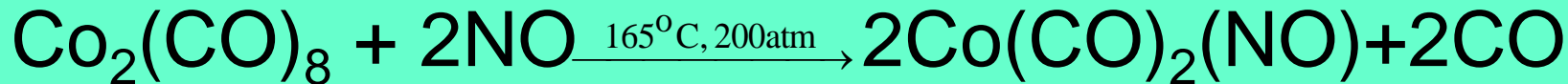
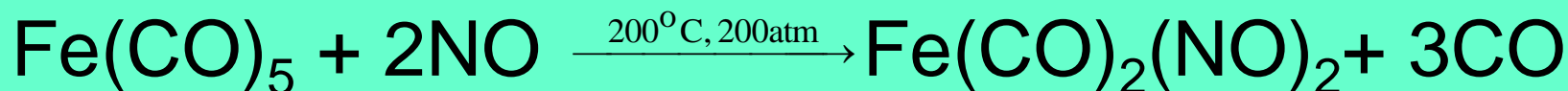


X = Br, I

- Both  $\text{Ni}(\text{CO})_4$  and  $\text{Co}_2(\text{CO})_8$  react with halogens and form metallic halides.



- ❖ **Action of NO** : Many carbonyls react with NO to form metal carbonyl nitrosyls. For example :



- ❖ **Action of  $\text{H}_2$** : When  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Co}_2(\text{CO})_8$  are treated with  $\text{H}_2$ , they are reduced to carbonyl hydrides.

# Different Metal Carbonyls

❖ **Carbonyls of VIB groups** : These form carbonyls of the type  $M(CO)_6$  where  $M = Cr, Mo$  and  $W$ . Chromium also forms  $Cr(CO)_5$ .

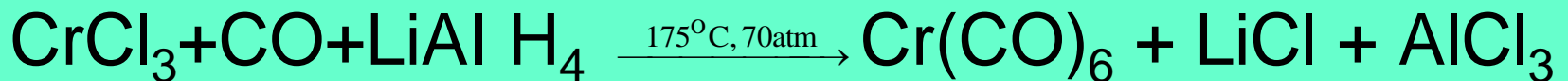
❖ **Chromium hexacarbonyl,  $Cr(CO)_6$**

## **Preparation :**

- It is prepared by Job's method by passing  $CO_2$  at 50 atm. Pressure and at room temperature into a suspension of chromic chloride in ether which has been treated with phenyl magnesium bromide at  $-70^\circ C$ .
- Chromium hexacarbonyl may be prepared by treating a solution of chromic salt dissolved in ether with  $Al(C_2H_5)_3$  and  $CO$  at high temperature and pressure.



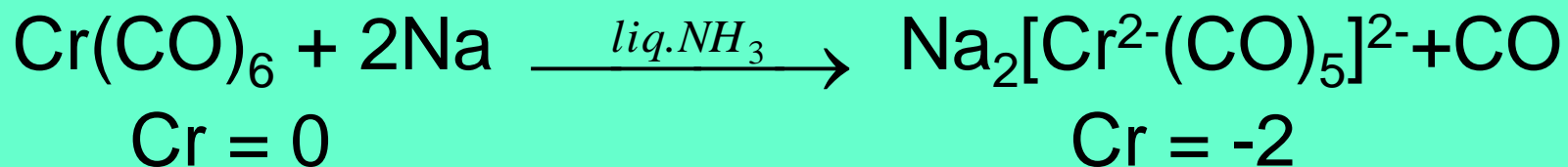
- It may also be obtained by treating chromic or chromous salt of an organic acid in pyridine solution with CO at 80-170°C and 100-300 atm. Pressure in the presence of powdered zinc or magnesium.
- It may also be prepared by treating CrCl<sub>3</sub> with CO in the presence of reducing agent like LiAlH<sub>4</sub>.



### **Properties:**

- It is a colourless crystalline solid which sublimes at 100°C.

- It is soluble in organic solvents such as ether, benzene, chloroform, carbon tetrachloride etc.
- It is not attacked by air, aqueous alkalies, dilute acids concentration HCl and concentration  $H_2SO_4$ . It is decomposed by chlorine or concentration  $HNO_3$ .
- When treated with sodium metal or  $NaBH_4$  in liquid  $NH_3$ , it is reduced to form carboxylate anion.



- Some CO groups of  $Cr(CO)_6$  can be replaced by pyridine.

# Chromium pentacarbonyl, $\text{Cr}(\text{CO})_5$

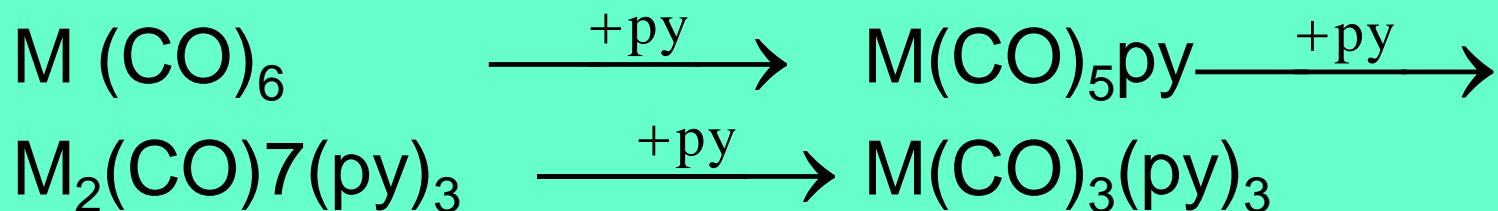
- ❖ Ultraviolet irradiation of the hexacarbonyl solution supports the existence of  $\text{Cr}(\text{CO})_5$ . It has square pyramidal structure.
- ❖ Molybdenum hexacarbonyl and Tungsten hexacarbonyl
- ❖ **Preparation:**
  - Both may be prepared by Job's method i.e., by treating  $\text{MoCl}_6$  or  $\text{WCl}_6$  with CO in presence of phenyl magnesium bromide.
  - Both may also be prepared by the action of metallic Mo or W on CO at  $225^\circ\text{C}$  and 200 atm. Pressure.

- $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  may be prepared by the action of CO on the metal in presence of sulphide of copper or iron.
- $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  may also be prepared by the action of  $\text{K}_3\text{MoCl}_9$  and  $\text{K}_3\text{WCl}_9$  with carbon monoxide.

## **Properties :**

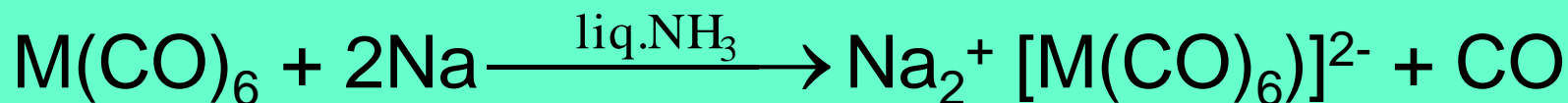
- Both are colourless crystalline solids.
- $\text{Mo}(\text{CO})_6$  sublimes at  $40^\circ\text{C}$  and boils at  $156.4^\circ\text{C}$  while  $\text{W}(\text{CO})_6$  sublimes at  $50^\circ\text{C}$  and boils at  $175^\circ\text{C}$ .
- They are soluble in organic solvents such as ether, benzene, chloroform, carbon tetrachloride etc.

- They do not react with air, aqueous alkalies acids except concentration  $\text{HNO}_3$ .
- Both are decomposed by chlorine and bromine.
- Some CO groups present in  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  are replaced by pyridine.



Where  $\text{M} = \text{Mo}$  and  $\text{W}$

- Both react with sodium metal in liquid  $\text{NH}_3$  to form ionic carbonyls.



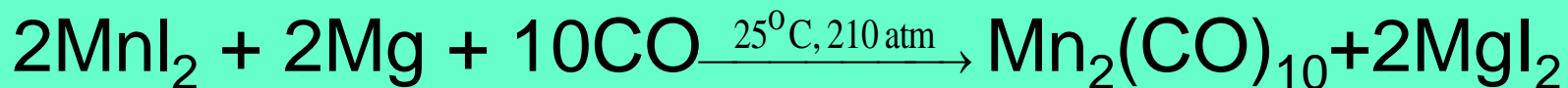
# Carbonyls of VII B group

- ❖ The form carbonyls of the general formula  $M_2(CO)_{10}$  where  $M = Mn, Tc$  and  $Re$ .

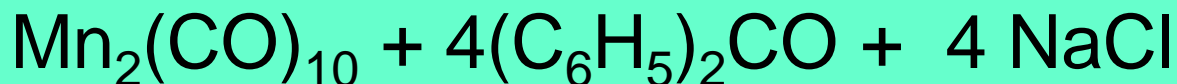
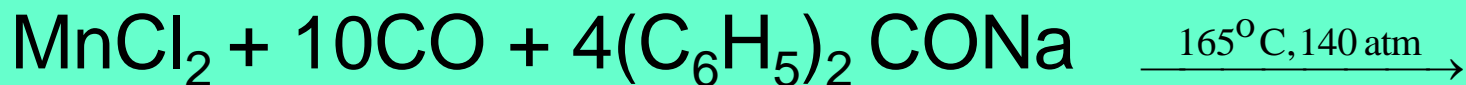
## Manganese carbonyl, $Mn_2(CO)_{10}$

### Preparation :

- By treating  $MnI_2$  and  $Mg$  with  $CO$  in ether under pressure.



- By carbonylating  $MnCl_2$  with  $CO$  in presence of  $(C_6H_5)_2CO Na$ .

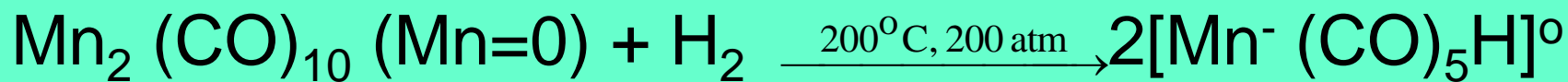


# Properties

- It is a golden yellow crystalline solid which melts at 155°C.
- It sublimes in vacuum and is soluble in organic solvents.
- **Action of halogens:** It reacts with halogens to form carbonyl halides,  $\text{Mn}(\text{CO})_5\text{X}$ .



- **Action of hydrogen:**  $\text{Mn}_2(\text{CO})_{10}$  is reduced by  $\text{H}_2$  to form carbonyl hydride.



# Technetium carbonyl, $\text{Tc}_2(\text{CO})_{10}$

❖ Higgins and co-worker in 1961 reported the formation of  $\text{Tc}_2(\text{CO})_{10}$ . It is similar to  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$ . A few iodine derivative to  $\text{Tc}_2(\text{CO})_{10}$  have also been prepared.

❖ **Rhenium carbonyl,  $\text{Re}_2(\text{CO})_{10}$**

**Preparation:** (i) By the action of rhenium heptoxide with CO at 200°C and 200 atm. Pressure.

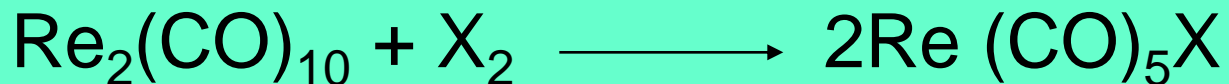


(ii) By the reaction of potassium perrhenate and rhenium hepta sulphide,  $\text{Re}_2\text{S}_7$  with CO under pressure.



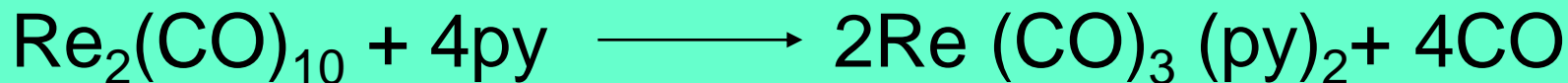
# Properties

- $\text{Re}_2(\text{CO})_{10}$  is a colourless solid.
- It sublimes at  $140^\circ\text{C}$  and melts at  $177^\circ\text{C}$ .
- It is soluble in organic solvents.
- It is not attacked by alkalies or cold and concentrated mineral acids.
- Action of halogens: It forms rhenium carbonyl halide,  $\text{Re}(\text{CO})_5\text{X}$  when treated with halogens.



where  $\text{X} =$  any halogen.

- Substitution reaction : It reacts with pyridine to form  $\text{Re}(\text{CO})_3(\text{py})_2$



# Carbonyl of VIII group

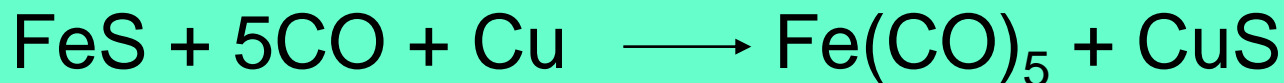
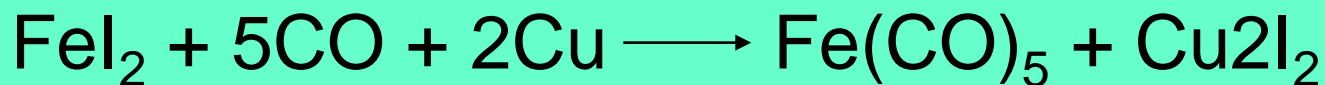
❖ **Carbonyls of Iron** : Three carbonyls of iron are known viz.  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$

■ **Iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ :**

■ It is prepared by the action of CO on iron powder at 100-200°C and 200 atm. pressure.

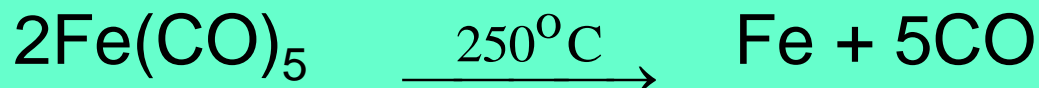


■ By the action of CO on ferrous iodide or ferrous sulphide at 100°C atm. Pressure in the presence of copper.

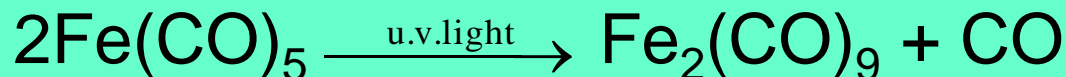


# Properties

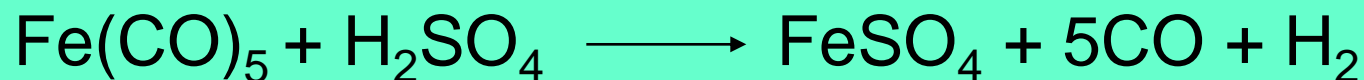
- It is a yellow liquid which boils at 103°C.
- It is soluble in methyl alcohol, ether, acetone and benzene but insoluble in water.
- It decomposes at 250°C to give iron.



- **Action of ultra-violet light:** It forms enneacarbonyl di iron (o),  $\text{Fe}_2(\text{CO})_9$  when cooled solution of  $\text{Fe}(\text{CO})_5$  in glacial acetic acid is irradiated with u.v. light.



- **Hydrolysis:** It is hydrolysed by water, acids and weak bases.



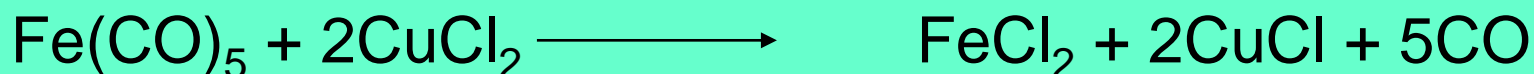
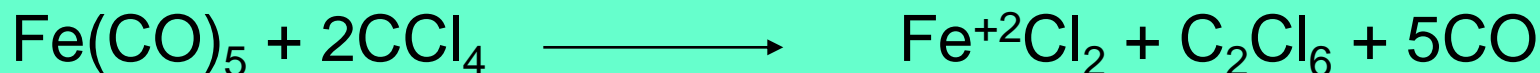
- **Reaction with halogens** : It reacts with halogens ( $X_2$ ) to form stable tetracarbonyl halides,  $Fe(CO)_4X_2$ .
- **Reaction with cyclopentadiene**: It reacts with cyclopentadiene at  $300^\circ C$  to give  $\pi$ -complex ferrocene.



- **Reaction with ethylene diamine**: It reacts with ethylene diamine to form an addition product,  $Fe(CO)_5(en)$ .



- **Reaction with halides**: With halides like  $CCl_4$ ,  $SO_2Cl_2$ ,  $SnCl_4$ ,  $SbCl_5$  and  $CuCl_2$ , it forms halides of  $Fe(II)$ . Thus, the oxidation state of  $Fe$  increases from zero to + 2. For example:



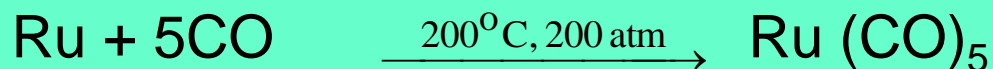
# Carbonyl of Ruthenium

- It forms three carbonyls viz.  $\text{Ru}(\text{CO})_5$ ,  $\text{Ru}_2(\text{CO})_9$  and  $\text{Ru}_3(\text{CO})_{12}$ .

- **Ruthenium pentacarbonyl,  $\text{Ru}(\text{CO})_5$ :**

- **Preparation:**

- It is prepared by the action of CO on reduced ruthenium at  $200^\circ\text{C}$  and 200 atm. Pressure.



- It is also prepared by the action of CO on  $\text{RuI}_3$  mixed with finely divided silver at  $170^\circ\text{C}$  and 450 atm. pressure.

- **Properties :**

- It is a colourless liquid having b.p.  $-22^\circ\text{C}$ .
- It is insoluble in water but soluble in chloroform, alcohol and benzene.
- It decomposes to form  $\text{Ru}_2(\text{CO})_9$  and  $\text{Ru}_3(\text{CO})_{12}$ .
- It reacts with halogens to give  $\text{Ru}(\text{CO})\text{X}_2$  and CO.

# Ruthenium enneacarbonyl, $\text{Ru}_2(\text{CO})_9$

## Preparation:

- It is prepared by irradiating pentacarbonyl to ultraviolet light.
- It is also prepared by heating solution of pentacarbonyl in benzene at  $50^\circ\text{C}$ .

## Properties:

- It is yellow crystalline solid which is volatile.
- With iodine, it forms  $\text{Ru}(\text{CO})_2\text{I}_2$ .
- With NO, it gives  $\text{Ru}(\text{NO})_5$ .
- Ruthenium dodecacarbonyl,  $\text{Ru}_3(\text{CO})_{12}$

## Preparation :

- By heating  $\text{Ru}(\text{CO})_5$  at  $50^\circ\text{C}$ .

- By exposing  $\text{Ru}(\text{CO})_5$  to ultra violet light. It is a green crystalline solid.

## **Carbonyl of Rhodium:**

- It forms two carbonyls viz.  $\text{Rh}_2(\text{CO})_8$  and  $\text{Rh}_4(\text{CO})_{11}$ .

## **Rhodium octacarbonyl, $\text{Rh}_2(\text{CO})_8$ .**

### **Preparation :**

- It is prepared by the action of CO on metallic rhodium under high pressure.
- It may also be prepared by the action of CO on rhodium tri iodide at  $100^\circ\text{C}$  and high pressure in presence of halogen acceptor such as metallic copper.

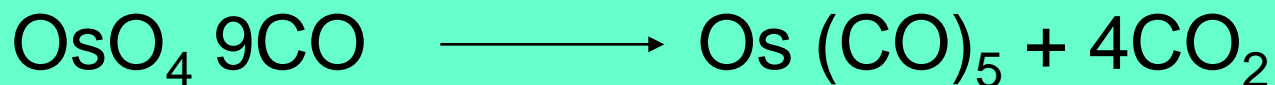
# Carbonyl of osmium

- It forms two carbonyls viz.  $\text{Os}(\text{CO})_5$  and  $\text{Os}_2(\text{CO})_9$ .

## Osmium pentacarbonyl, $\text{Os}(\text{CO})_5$

### Preparation :

- It is obtained by the action of CO on  $\text{OsI}_3$  at  $120^\circ\text{C}$  and 200 atm. Pressure in presence of copper.
- It is also obtained by the action of CO on  $\text{OsO}_4$  at  $100^\circ\text{C}$  atm. pressure.



- It is a colourless liquid having m.p.  $-150^\circ\text{C}$



# Osmium enanea carbonyl, $\text{Os}_2(\text{CO})_9$

- **Preparation** : It is obtained by the action of CO on osmium tri iodide in presence of copper.

## Properties:

- It is yellow crystalline solid.
- It sublimes without decomposition and melts at  $224^\circ\text{C}$ .
- It is more stable towards heat than  $\text{Ru}_2(\text{CO})_9$ .

## Carbonyl of Iridium :

- It forms two carbonyls viz,  $\text{Ir}_2(\text{CO})_8$  and  $\text{Ir}_4(\text{CO})_{12}$ .

## Iridium octacarbonyl, $\text{Ir}_2(\text{CO})_8$ :

- **Preparation**: It is prepared by reacting  $\text{K Ir}_2 \text{Br}_6$  or  $\text{K Ir}_2 \text{I}_6$  with CO at  $200^\circ\text{C}$  and 200 atm.

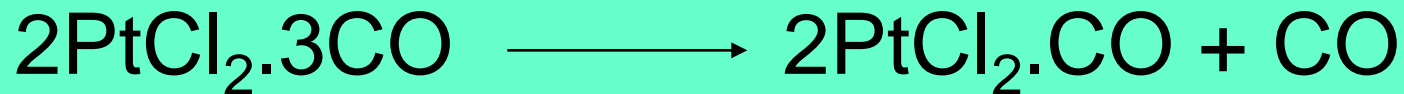
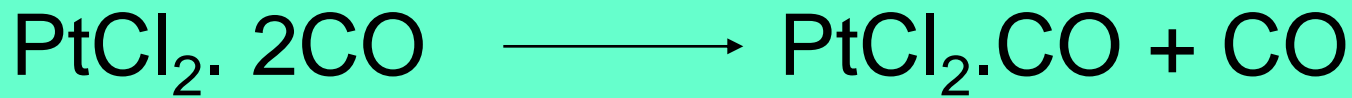
# Properties

- It is a yellow crystalline solid.
- It decomposes at 200°C.
- Chemically it is inert.

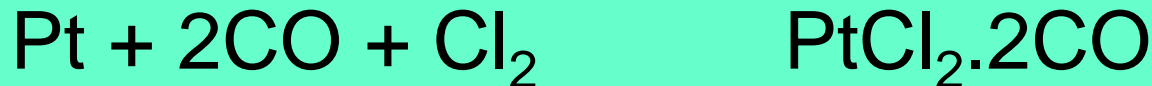
## Carbonyls of Platinum

### Preparation:

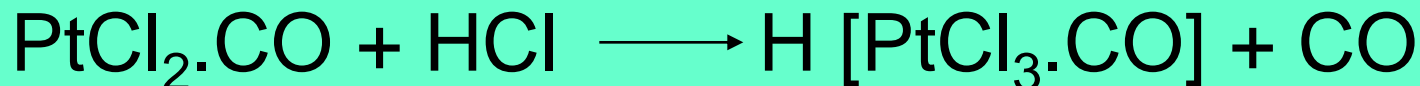
- When CO is passed over platinous chloride at 250°C, a mixture of  $\text{PtCl}_2 \cdot 2\text{CO}$  and  $2\text{PtCl}_2 \cdot 3\text{CO}$  is obtained.
- $3\text{PtCl}_2 + 5\text{CO} \xrightarrow{250^\circ\text{C}} \text{PtCl}_2 \cdot 2\text{CO} + 2\text{PtCl}_2 \cdot 3\text{CO}$
- Pure  $\text{PtCl}_2 \cdot \text{Co}$  is obtained by subliming the higher carbonyl chloride through a tube heated to 250°C.



- $\text{PtCl}_2 \cdot 2\text{CO}$  is also obtained by heating Pt foil or sponge at 240-250°C with CO and  $\text{Cl}_2$ .



- These carbonyls are easily decomposed by water and hydrochloric acid.



# Structures of Metallic Carbonyls

- ❖ **Effective atomic number rule or EAN rule:**  
The most satisfactory formula of carbon monoxide is : C :: O :
- ❖ From the above structure of carbon monoxide, it seems that the lone pair of electrons on the carbon atom can be used to form a dative bond with certain metals ( $M \leftarrow C=O$ ). In the formation of  $M \leftarrow C=O$  bonds, the electrons are denoted by carbon monoxide molecules and the metal atoms thus said to have zero oxidation state. The number of carbon monoxide molecules which can combine with one metal atom is controlled by the tendency of the metal atom to acquire the effective atomic number of the next inert gas. This is given for stable monomeric carbonyls.

$$\text{E.A.N.} = m + 2y = G.$$

where

$m$  = atomic number of the metal M.

$y$  = number of CO molecules in one molecule of carbonyl  $M(\text{CO})_y$

$G$  = atomic number of the next inert gas

**(a) Mononuclear carbonyls having metallic atom even atomic number :** The metals having even atomic number obey EAN rule and hence form mononuclear carbonyls as shown in Table.

# Mononuclear carbonyls of metal atoms having even atomic number

Metal carbonyl	At. No. of the metal (m)	No. of electron donated by CO molecules (2y)	E.A.N. (m+2y)	At. no. of next inert gas (G)
Cr (CO) <sub>6</sub>	24	2 x 6 = 12	24 + 12 = 36	Kr (36)
Fe (CO) <sub>5</sub>	26	2 x 5 = 10	26 + 10 = 36	Kr (36)
Ni (CO) <sub>4</sub>	28	2 x 4 = 8	28 + 8 = 36	Kr (36)
Mo (CO) <sub>6</sub>	42	2 x 6 = 12	42 + 12 = 54	Xe (54)
Ru (CO) <sub>5</sub>	44	2 x 5 = 10	44 + 10 = 54	Xe (54)
W (CO) <sub>6</sub>	74	2 x 6 = 12	74 + 12 = 86	Rn (86)
Os (CO) <sub>4</sub>	76	2 x 5 = 10	76 + 10 = 86	Rn (86)

On the basis of EAN it can be explained why Ni atom does not form hexacarbonyl, Ni (CO)<sub>6</sub>. It is because of the fact that EAN of Ni atom in Ni (CO)<sub>6</sub> would be equal to  $28 + 2 \times 6 = 40$  which is not the atomic number of any of the inert gases.

**(b) Mononuclear carbonyls have the metallic atom with odd atomic number:** The metal atoms having odd atomic number do not obey EAN rule and hence can not form mononuclear carbonyls. For example, some hypothetical carbonyls are given in the table.

# Hypothetical mononuclear carbonyls having atom with odd atomic number

<b>Metal carbonyl</b>	<b>At. No. of the metal (m)</b>	<b>No. of electron donated by CO molecules (2y)</b>	<b>E.A.N. (m+2y)</b>	<b>At. no. of next inert gas (G)</b>
<b>V (CO)<sub>6</sub></b>	<b>23</b>	<b>2 x 6 = 12</b>	<b>23 + 12 = 35</b>	<b>Kr (36)</b>
<b>Mn (CO)<sub>6</sub></b>	<b>25</b>	<b>2 x 5 = 10</b>	<b>25 + 10 = 35</b>	<b>Kr (36)</b>
<b>Co (CO)<sub>4</sub></b>	<b>27</b>	<b>2 x 4 = 8</b>	<b>27 + 8 = 35</b>	<b>Kr (36)</b>



**(C) Polynuclear carbonyls:** Sidgwick and Bailey have shown that for polynuclear carbonyls of the type  $M_x (CO)_y$ , the general formula is :

$$G = \frac{xm + 2y}{x} = x-1$$

where

G = The atomic number of the next inert gas

x = The number of metal atoms

m = The atomic number of the metal

y = The number of CO molecules in one molecule of the carbonyl

**Co<sub>2</sub>(CO)<sub>8</sub> :**

Electrons from 2Co atoms =  $2 \times 27 = 54$

Electrons from 8CO molecules =  $2 \times 8 = 16$

Electrons from one Co-Co bond =  $1 \times 2 = 02$

**Fe<sub>2</sub>(CO)<sub>9</sub> :**

Electrons from 2Fe atoms =  $2 \times 26 = 52$

Electrons from 9CO molecules =  $2 \times 9 = 18$

Electrons from one Fe-Fe bond =  $1 \times 2 = 02$

**Fe<sub>3</sub>(CO)<sub>12</sub> :**

Electrons from 3Fe atoms =  $3 \times 26 = 78$

Electrons from 12CO molecules =  $2 \times 12 = 24$

Electrons from one 3Fe-Fe bonds =  $2 \times 3 = 06$

# 18-Electrons rule in metal carbonyls

- The formation of mononuclear carbonyls by transition metals can also be explained on the basis of 18 electron rule. According to this rule a metal atom with even atomic number combines with a such number of CO molecules so that the valence-shell  $(n-1) d, ns, np$  of the metal atom acquires 18 electrons as shown in table.

# Formation of mononuclear carbonyls with metals having even at no. on the basis of 18-electron rule

Carbonyls	No. of the valence electrons on the metal atom	No. of electrons donated by CO molecules (y)	Total no. of electrons on the metal atoms (x + y)
$\text{Cr}(\text{CO})_6$ (Cr = $3d^5, 4s^1$ )	6	$2 \times 6 = 12$	$6 + 12 = 18$
$\text{Fe}(\text{CO})_5$ (Fe = $3d^6, 4s^2$ )	8	$2 \times 5 = 10$	$8 + 10 = 18$
$\text{Ni}(\text{CO})_4$ (Ni = $3d^8, 4s^2$ )	10	$2 \times 4 = 8$	$10 + 8 = 18$



$$2\text{Mn} = 2 \times 7 = 14 \bar{e}s$$

$$10\text{CO} = 2 \times 10 = 20 \bar{e}s$$

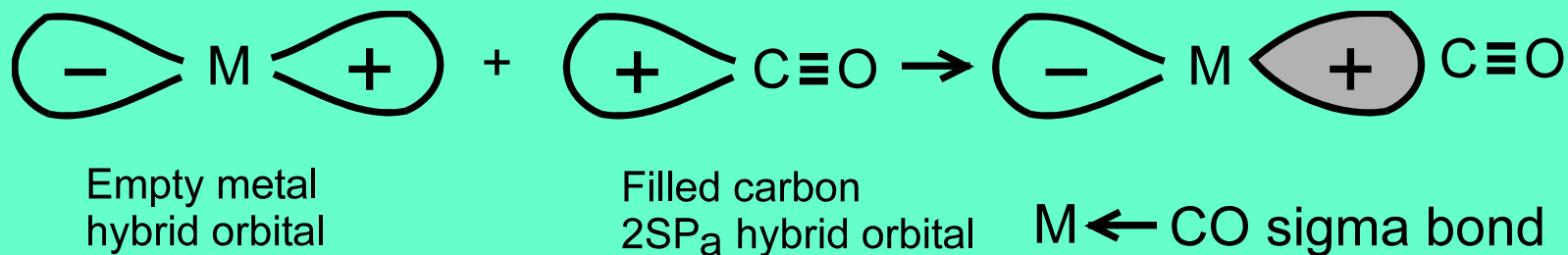
$$\text{Mn} - \text{Mn} \text{ bond} = 02 \bar{e}s$$

# Molecular orbital approach

- The nature of bond present in metal carbonyls can be explained on the basis of molecular orbital theory as shown below:
  - Mononuclear carbonyls : These carbonyls have linear M – CO bond in which CO molecule is attached with metal atom through C atom. The C atom undergoes sp hybridization to form two hybrid orbitals which are denoted as  $Sp_a$  and  $SP_b$ . Now configurations of C and O atoms may be written as below:



- Thus, the total number of bonding and antibonding electrons are 6 and zero respectively, the bond order of the molecule will be  $6-0/2 = 3$ . Hence the number of bonds between C and O atoms in CO molecule is 3 *i.e.*, one  $\sigma$  and two  $\pi$ .
- The bond formation between metal atom and CO molecule occurs as follows:
  - (a) An empty metal  $\sigma$  orbital overlaps with filled carbon  $\sigma$  orbital to form  $M \rightarrow C = O$  bond as shown in Fig.



(b) A filled d orbital of the metal overlaps with empty antibonding  $\pi$  orbital of the carbon atom to form  $M \leftarrow CO$  dative  $\pi$  bond as shown in Fig.

