METAL CARBONYLS

Carbon monoxide possesses a unique property of unsaturation by virtue of which it may combine with a large number of metals under suitable conditions. Such compounds of carbon monoxide with metals are termed as **metallic carbonyls.**

• In carbonyls, a metal atom is directly linked to the carbon atom of a carbonyl group.
• Metal atom in carbonyls is in zero oxidation state.
• In metal carbonyls CO molecules act as neutral ligands.
• Metal carbonyls vary considerably in their properties ranging from volatile non-polar to the non-volatile electrovalent carbonyls.
Example: nickel forms volatile non-polar carbonyls whereas alkali and alkaline earth metals farm nonvolatile electrovalent carbonyls.
• The general formula of the carbonyls may be given as Mx (CO)y.
• Metal carbonyls may be regarded as parents of a number of related compounds such as metal nitrosyl carbonyl M(NO)y (CO)x and metal carbonyl hydrides, HxM(CO)y.

CLASSIFICATION

Heiber classified the metal carbonyls into two distinct groups-

(a) Mono-nuclear carbonyls : These carbonyls have the general formula M(CO)x which contain only one atom of the metal per molecule of the carbonyl. Thus, their empirical and molecular formula are identical.

Examples are $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, etc. It is important to remark that mononuclear carbonyls are generally formed by metals which possess even atomic numbers.

Characteristics of Mono-nuclear carbonyls

(i) These mononuclear carbonyls are readily soluble in organic solvents such as light petroleum, benzene, ether, etc.
(ii) These can be vaporised without decomposition.
(iii) These are more volatile than the others.

(b) Polynuclear carbonyls : These have the general formula Mx(CO)y, which contain more than one metal atom per molecule. However some carbonyls have two metal atoms as bridged carbonyls and those having more than two metal atoms as polynuclear carbonyls. Polynuclear carbonyls may be homonuclear or heteronuclear.

Characteristics Polynuclear carbonyls

(i) These are almost insoluble in organic solvents.
(ii)Many polynuclear carbonyls decompose at or below the melting point.

PREPARATION OF CARBONYLS

(a) Direct synthesis from metals and carbon monoxide

This method is limited to carbonyls of those metals which can be obtained in active form by low-temperature reduction processes.
Example,

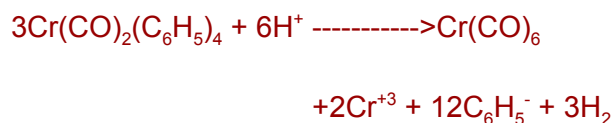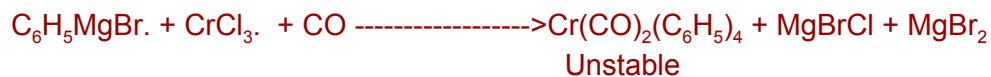(i) Nickel reacts with carbon monoxide at room temperature and normal pressure.

$$Ni + 4CO \xrightarrow{40°C} Ni(CO)_4$$

(ii) When carbon monoxide is passed over reduced iron at 180°- 220° and pressure of 50 to 200 atm. pressure, $Fe(CO)_5$ is formed.

$$Fe + 5CO \longrightarrow Fe(CO)_5$$

Rhenium, osmium and iridium carbonyl could not be prepared by direct reactions.

(b) Indirect synthesis involving the Grignard reagent

Job prepared chromium hexacarbonyl by the action of CO on a mixture of Grignard reagent and anhydrous chromium chloride in ether solution.

$$C_6H_5MgBr. + CrCl_3. + CO \longrightarrow Cr(CO)_2(C_6H_5)_4 + MgBrCl + MgBr_2$$
$$\text{Unstable}$$

$$3Cr(CO)_2(C_6H_5)_4 + 6H^+ \longrightarrow Cr(CO)_6$$

$$+2Cr^{+3} + 12C_6H_5^- + 3H_2$$

(c) Synthesis from other carbonyls

When iron pentacarbonyl is exposed to ultraviolet light, it loses carbon monoxide and forms $Fe_2(CO)_9$. This compound undergoes thermal decomposition to yield iron pentacarbonyl and trimeric tetracarbonyl.
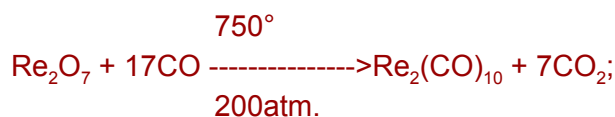
$$2Fe(CO)_5 \xrightarrow{\text{Ultraviolet}} Fe_2(CO)_9 + CO$$

$$2Fe_2(CO)_9 \xrightarrow{\text{heat}} Fe(CO)_5 + [Fe(CO)_4]_3 + CO$$
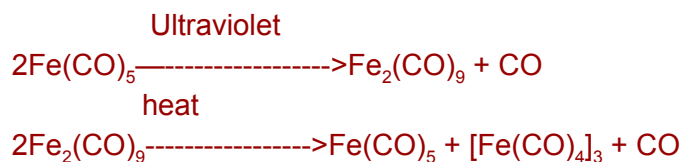
(d) Synthesis from carbonyl hydrides

When iron carbonyl hydride is oxidised by MnO_2, or H_2O_2, $[Fe(CO)_4]_3$ is formed.
Dimeric tetracarbonyl of cobalt may be obtained by heating cobalt carbonyl hydride.

(f) By treatment of oxide of metals with carbon monoxide under pressure:

Carbonyls of osmium and ruthenium are prepared by the reaction of carbon monoxide with their oxides under pressure.

$$OsO_4 + 9CO \xrightarrow[\text{50 Atm Press.}]{100°C} Os(CO)_5 + 4CO_2$$

$$Re_2O_7 + 17CO \xrightarrow[\text{200atm.}]{750°} Re_2(CO)_{10} + 7CO_2;$$

(g) Preparation of $Mo(CO)_6$ from $Fe(CO)_5$

Since CO groups present in $Fe(CO)_5$ are labile, $Fe(CO)_5$ may be used to form certain carbonyls.

$$MoCl_6 + 3Fe(CO)_5 \xrightarrow[\text{ether}]{100°} Mo(CO)_6 + 3FeCl_2 + 9\,CO$$
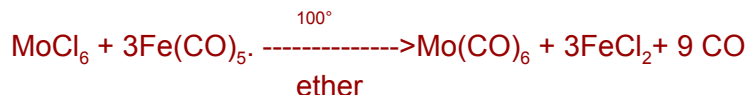
PROPERTIES OF CARBONYLS

Physical Properties

(i) The metal carbonyls are crystalline solids, except for nickel carbonyl and the pentacarbonyls of iron, ruthenium and osmium which are liquids.

(ii) Many are coloured; for example, crystals of cobalt carbonyl are orange and iron pentacarbonyl is a yellow oil, and nickel carbonyl is colourless.

(iii)Their covalent nature renders them insoluble in water. Most of them are soluble in solvents like carbon tetrachloride.

(iv) Excepting $V(CO)_6$ all the carbonyls are diamagnetic. $V(CO)_6$ is paramagnetic and its para magnetic property corresponds to the presence of one unpaired electron. The metals in carbonyls are in zero oxidation state.

Chemical Properties

Substitution reactions :

Some or all CO groups present in carbonyls can be replaced by monodentate ligands such as alkyl or aryl isocyanide (CNR), PR_3, PCl_3, Py, CH_3OH etc.
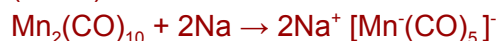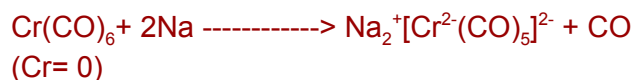For example:

$Ni(CO)_4$ + 4 CNR ------> $Ni(CNR)_4$ + 4C0

$Ni(CO)_4$ + 4 PCl_3 --------> $Ni(PCl_3)_4$ + 4CO

$Fe(CO)_5$ + 2CNR ----------> $Fe(CO)_3(CNR)_2$ + 2CO

Bidentate ligands like diars, o-phen, NO_2 etc are known to replace two or more CO groups, at a time. Example

$Mo(CO)_6$ + diars -----------> $Mo(CO)_4$ (diars) + 2CO

$Fe(CO)_5$+ diars -------------> $Fe(CO)_3$ diars + 2CO
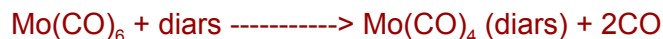
Action of NaOH or Na metal :

Formation of carbonylate anion (Reduction). Aqueous or alcoholic solution of NaOH reacts with $Fe(CO)_5$ to form carbonylate anion.

$Cr(CO)_6$+ 2Na ------------> $Na_2^+[Cr^{2-}(CO)_5]^{2-}$ + CO
(Cr= 0)
$Mn_2(CO)_{10}$ + 2Na → $2Na^+ [Mn^-(CO)_5]^-$

Action of halogens :

 Most of the carbonyls react with halogens to yield carbonyl halides.
For example:

$Fe(CO)_5 + X_2 \xrightarrow{\hspace{1cm}} Fe(CO)_4X_2 + CO$
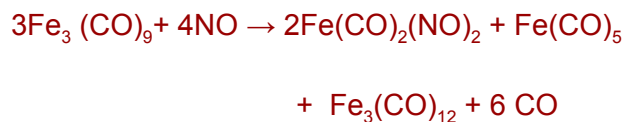
$Mo(CO)_6 + Cl_2 \rightarrow Mo(CO)_4Cl_2 + 2CO$

 Both $Co_2(CO)_8$ and $Ni(CO)_4$ are decomposed into metallic halogens and CO when treated with halogens.

Action of NO :

Many carbonyls react with nitric oxide (NO) to form metal carbonyl nitrosyls.
For example

$Fe(CO)_5 + 2\ NO \xrightarrow{\hspace{0.3cm}95°C\hspace{0.3cm}} Fe(CO)_2(NO)_2 + 3CO$

$3Fe_3(CO)_9 + 4NO \rightarrow 2Fe(CO)_2(NO)_2 + Fe(CO)_5$

$+\ Fe_3(CO)_{12} + 6\ CO$

Moist NO yields a blue-coloured compound, Ni(NO)(OH) with Ni(CO)4 while dry NO gives solution of the composition, $Ni(NO)(NO_2)$

Action of heat :

Different carbonyls yield different products when heated For example:

$Fe(CO)_5 \xrightarrow{\hspace{0.3cm}250°C\hspace{0.3cm}} Fe.\ + 5CO$

$Fe(CO)_{12} \xrightarrow{\hspace{0.3cm}140°C\hspace{0.3cm}} 3Fe + 12CO$

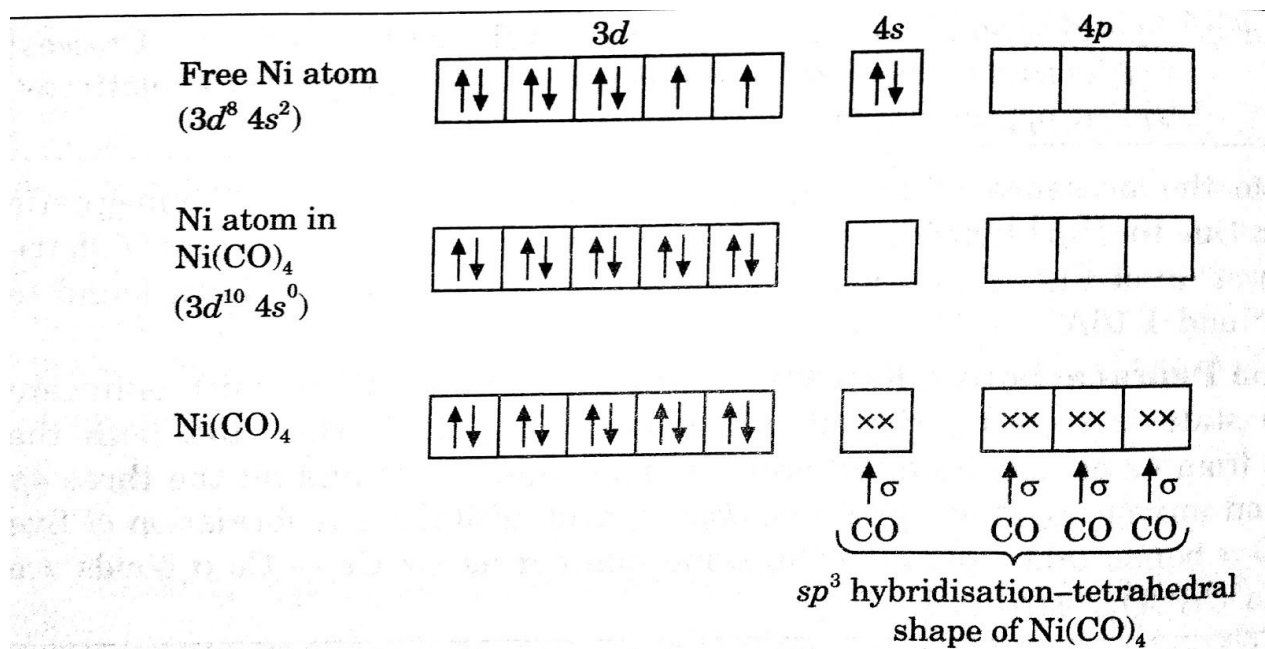$Ni(CO)_4 \xrightarrow{\hspace{0.3cm}180°\hspace{0.3cm}} Ni + 4CO$

# **Structure and Bonding in Mononuclear Carbonyls**

The structure of mononuclear carbonyls viz. $V(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_5$ have been studied by X-ray diffraction, infrared spectroscopy and electron-diffraction. The last method has also been used for $Mo(CO)_6$ and $W(CO)_6$. All the mononuclear carbonyls have linear M-CO bonds in which CO group is linked to the metal atom through the carbon atom.

Structure of Nickel Tetracarbonyl, $Ni(CO)_4$

The vapour density of nickel carbonyl and the freezing point of its solution in benzene has shown that the molecular formula of nickel carbonyl is $Ni(CO)_4$. In this molecule Ni atom is sp^3 hybridized as shown in Fig. Here too both the electrons of 4s orbital are shifted to 3d orbitals to vacate 4s orbital. Now 4s and three 4p orbitals, on mixing together, give four sp3 hybrid orbitals. The formation of four Ni←CO sigma bond takes place in the same way as six Cr← CO sigma bonds are formed $Cr(CO)_6$ and $Fe(CO)_5$ respectively.

	3d	4s	4p

Free Ni atom
$(3d^8 \ 4s^2)$

⇅ ⇅ ⇅ ↑ ↑   ⇅   ☐ ☐ ☐

Ni atom in Ni(CO)₄
$(3d^{10} \ 4s^0)$

⇅ ⇅ ⇅ ⇅ ⇅   ☐   ☐ ☐ ☐

Ni(CO)₄

⇅ ⇅ ⇅ ⇅ ⇅   ✕✕   ✕✕ ✕✕ ✕✕

↑σ   ↑σ ↑σ ↑σ

CO   CO CO CO

sp^3 hybridisation–tetrahedral shape of Ni(CO)₄

The presence of all the paired electrons confirms the diamagnetic character of Ni(CO)₄ molecule. Due to sp3 hybridisation, Ni(CO)₄ has the expected tetrahedral shape as shown in Fig. Tetrahedral shape of the molecule has also been confirmed by the electron diffraction and infra-red studies of this compound.
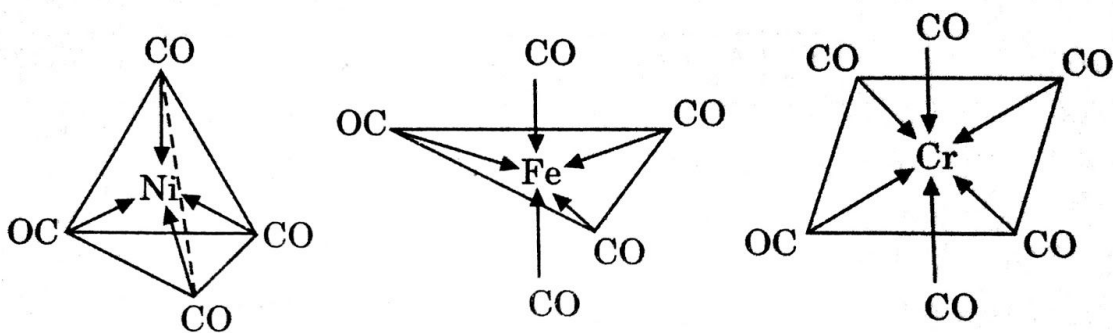
The N---C bond length in this molecule has been found to be equal to

1.50 A° which is shorter by 0.32 A° in comparison to Ni-C single bond length (=1.82 A°) found in carbonyls. TheC - O bond length in this carbonyl has been found to be equal to 1.15 A° which is larger than the C -- O bond length in CO molecule (=1.128 A).

It is to be pointed out here that, due to the formation of four OC----> M bonds, a large negative charge is accumulated on the central Ni atom. This is most unlikely. In such a situation, Pauling suggested that the double bonding takes place with the back donation of d-electron from Ni atom to CO ligands to such an extent that electroneutrality principle is obeyed. According to this principle electron pair is not shared equally between Ni and C-atoms of CO ligands but is attracted more strongly by C-atom which prevents the accumulation of negative charge on Ni-atom and is in keeping with the greater electronegativity of C-atom compared to Ni atom (C= 2.5, Ni = 1.8).

Structure and Bonding in Binuclear Carbonyls

All the binuclear carbonyls contain metal-metal bonds.

Structure of Dicobalt Octacarbonyl, $Co_2(CO)_8$

This carbonyl appears to exist in two isomeric forms. One of these forms has a bridged structure in which two CO groups bridge two Co atoms which are also linked with each other by a sigma bond (Co-Co sigma bond). Each of two Co atoms is linked to three terminal CO groups shown in Fig. The other form has a non-bridged structure with a Co-Co sigma bond linking two $Co(CO)_4$ groups Shown Fig. Thus both the structures have Co-Co sigma bonding and the diamagnetic nature of $Co_2(CO)_8$. also confirms the spin-pairing between two Co atoms, i.e. diamagnetic character of $Co_2(CO)_8$ is confirmed by the presence of Co-Co sigma bond in it. There is very little difference in energy between the two structures.
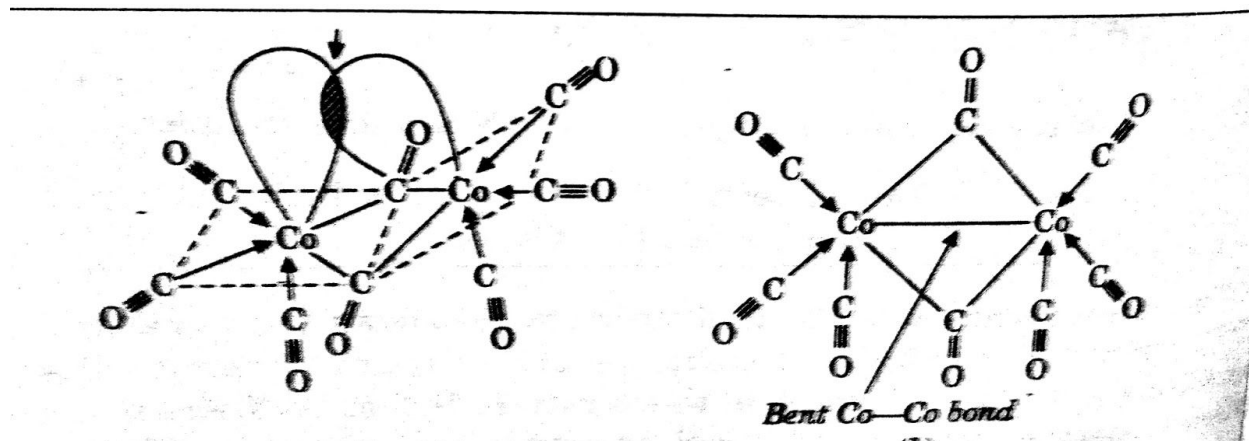

(a) Bridged structure   (b) Non-bridged structure
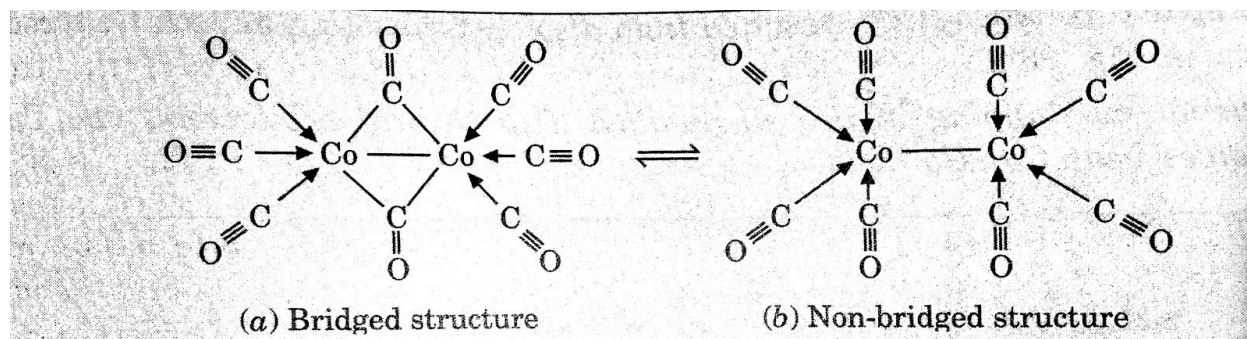
The infra-red study of the bridged structure has shown that it has two types of CO groups (i.e. terminal CO groups and bridging CO groups[>C= 0)]. Co-Co bond distance in this structure is 2.52 A°. There is infra-red evidence, showing that in solution both the structures exist in equilibrium with each other. At very low temperature the bridged structure predominates and as the temperature is raised, the non-bridged structure appears. If the temperature is increased to over 100°C, a third form appears. This third form is of uncertain structure. Bridged structure shows that coordination number of each Co-atom in the-molecule is six.

Each of the Co atoms is d^2sp^3 hybridised as shown in Fig. The Co-Co bond is bent which arises due to the unusual overlapping of two singly-filled d^2sp^3 hybrid orbitals. One of these two singly-filled d^2sp^3 hybrid orbitals is from one Co atom while the other similar hybrid orbital is from the other Co atom.
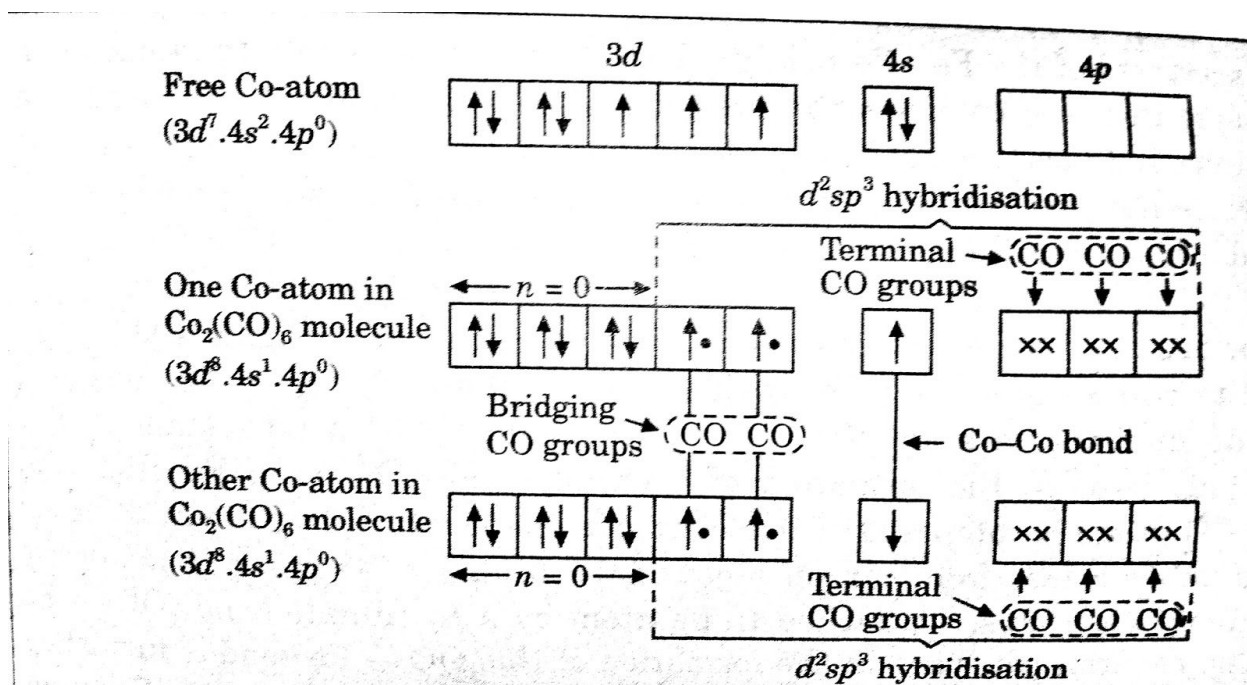
The structure of $Co_2(CO)_8$ resulted from d^2sp^3 hybridisation of each Co atom is shown in Fig.

Unusual overlapping of two singly-filled d^2sp^3 hybrid orbitals on two C atoms gives bent Co-Co bond.

Bent Co—Co bond

Structure of $Co_2(CO)_8$