

Chemistry of Metal Carbonyls of Group VIII

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Group VIII of the periodic table comprises of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt. These metals form carbonyls by reacting with CO directly or indirectly. Carbonyls of these metals have been studied extensively except carbonyls of Pd and Pt.

| | | |
|-----------|-----------|-----------|
| 26 | 27 | 28 |
| <u>Fe</u> | <u>Co</u> | <u>Ni</u> |
| 55.85 | 58.47 | 58.69 |
| 44 | 45 | 46 |
| <u>Ru</u> | <u>Rh</u> | <u>Pd</u> |
| 101.1 | 102.9 | 106.4 |
| 76 | 77 | 78 |
| <u>Os</u> | <u>Ir</u> | <u>Pt</u> |

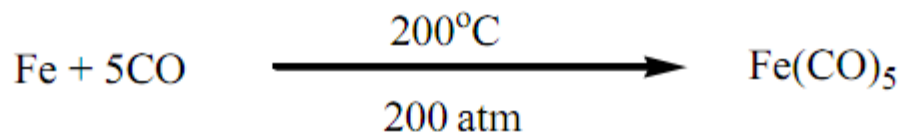
Carbonyls of Iron, Ruthenium and Osmium

Pentacarbonyliron(0), Fe(CO)₅

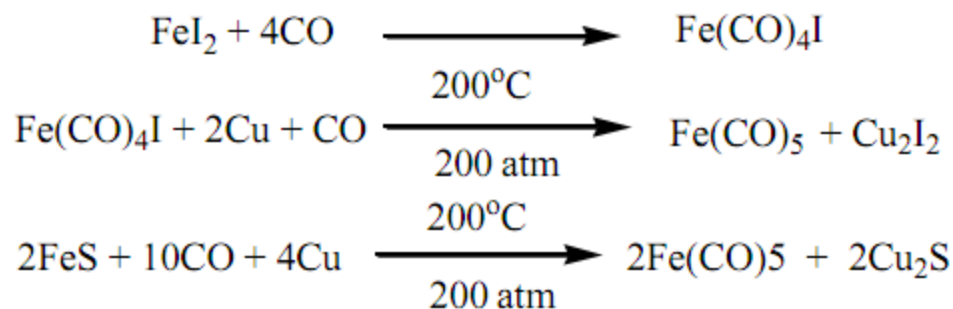
Preparation

Iron pentacarbonyl, Fe(CO)₅ can be prepared by one of the following methods.

- 1. By Direct Method:** It is prepared by the action of CO over heated iron at 200°C and 200 atm pressure.



2. **By Reaction of CO with FeI₂ or FeS:** FeI₂ and FeS react with CO at 200 atm and 200°C in the presence of Cu which act as halogen acceptor. Iron carbonyls iodide is formed as an intermediate in the first step which further reacts with CO in the presence of Cu.

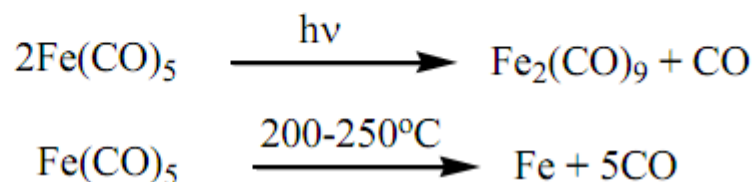


Reactivity

Iron pentacarbonyl is amber colour liquid with obnoxious odour. Its melts at -20° C, boils at 103° C and decomposes at 130° C. It is very reactive compounds and undergoes several chemical reactions. It is decomposed by light to iron monocarbonyl and carbon monoxide. It is pyrophoric in air and in an acetic acid solution; it burns to ferric oxide.

1. Action of Light and Heat

Pentacarbonyliron(o) yields enneacarbonyl when irradiated with ultraviolet radiation. It is decomposed into iron and CO at 200-250°C



2. Action of Air

Pentacarbonyliron(0) burns in air to give $\text{Fe}_2(\text{CO})_9$.

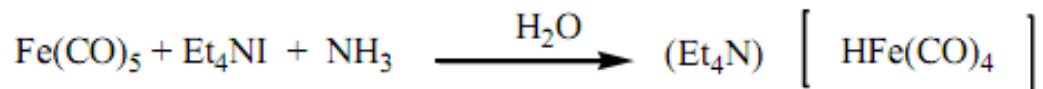


3. Reaction with ammonia

Ammonia reacts with pentacarbonyliron(0) in the presence of water to form carbonyl hydride and carbamic acid.

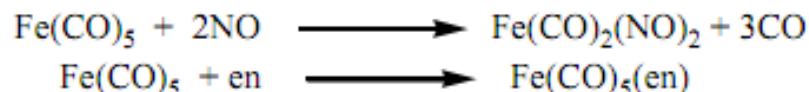


In presence of tertiary ammonium salt, NH_3 reacts with $\text{Fe}(\text{CO})_5$ to form anionic derivatives.



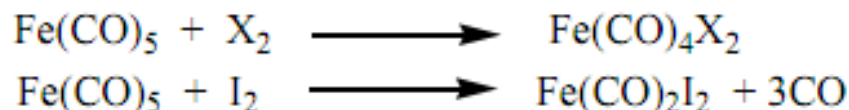
4. Reaction with Amines:

An addition product, $\text{Fe}(\text{CO})_5(\text{en})$, is formed when pentacarbonyliron(0) reacts with amines such as ethylenediamine. Pyridine (Py) reacts with $\text{Fe}(\text{CO})_5$ to yield $[\text{Fe}(\text{Py})_6]$ $[\text{Fe}_4(\text{CO})_{13}]$.



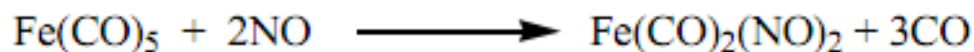
5. Reaction with Halogens:

Reaction of $\text{Fe}(\text{CO})_5$ with halogens occur in non aqueous solvent to give soluble tetracarbonyl halides, $\text{Fe}(\text{CO})_4\text{X}_2$ which lose CO spontaneously. Iodine dissolved in boiling benzene form a dicarbonyldiiodide species.

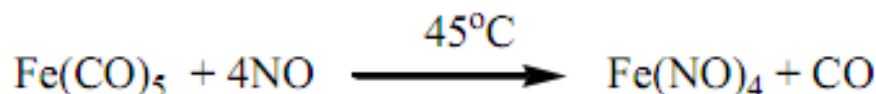


6. Reaction with NO:

Iron carbonylnitrosyl, $\text{Fe}(\text{CO})_2(\text{NO})_2$ is formed by the reaction of pentacarbonyl with NO at 95°C .



At a temperature below 45°C and high pressure NO reacts to form $\text{Fe}(\text{NO})_4$.



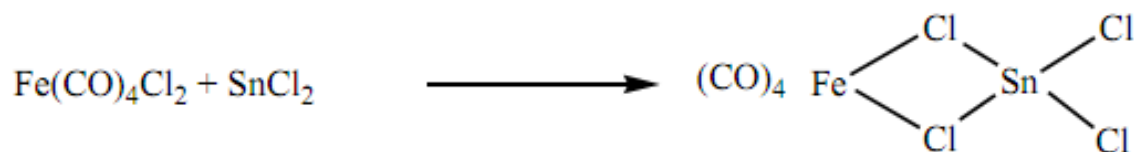
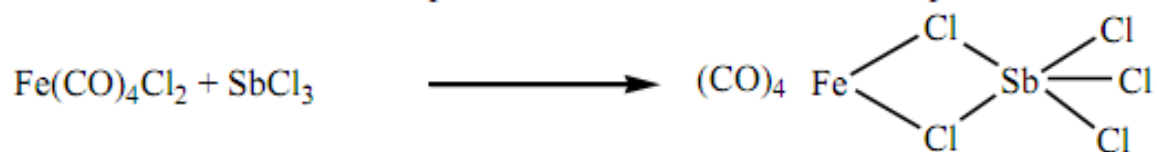
NO reacts with a solution of $\text{Fe}(\text{CO})_5$ in methanol to form $\text{Fe}(\text{CO})(\text{OH})(\text{OMe})(\text{NO})\cdot\text{MeOH}$.

7. Reaction with metallic and non metallic halides:

$\text{Fe}(\text{CO})_5$ reacts with halides such as CCl_4 , SO_2Cl_2 , SnCl_4 , SbCl_5 and CuCl_2 to form Fe(II) halides. $\text{Fe}(\text{CO})_5$ acts as a reducing agent and Fe is oxidized whereas Sn and Sb are reduced.



Reaction with SnCl_2 and SbCl_3 proceed further and additional products are formed.



Mercuric chloride reacts with $\text{Fe}(\text{CO})_5$ in acetone and yields $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$ and CO.

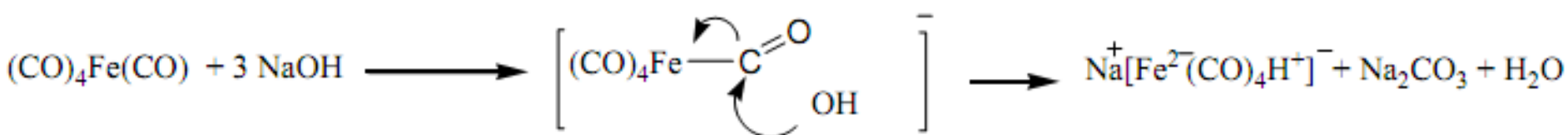


8. Hydrolysis of Fe(CO)₅:

Fe(CO)₅ is hydrolyzed by water in presence of H₂SO₄ to give FeSO₄

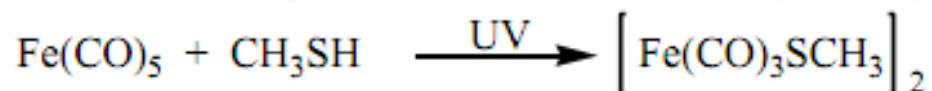
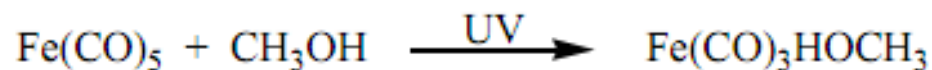


Reaction with heated NaOH forms acylat anion, $[\text{Fe}^{2-}(\text{CO})_4\text{H}^+]^-$



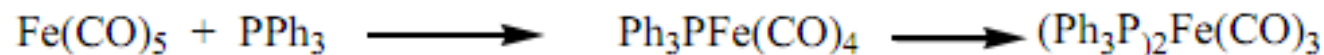
9. Reaction with alcohol and thioalcohol

Alcohols and thioalcohols react with pentacarbonyl(0) to form substituted products.



10. Reaction with triphenylphosphine

CO groups are substituted with triphenylphosphine



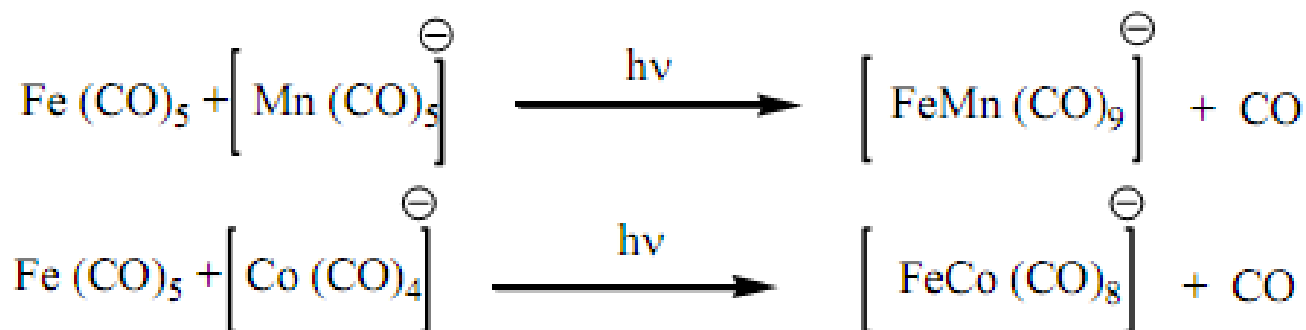
11. Action of air

$\text{Fe}(\text{CO})_5$ burns in air to form Fe_2O_3



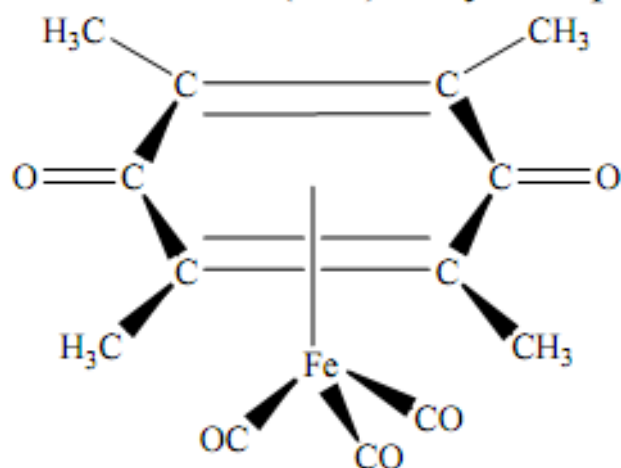
12. Action of carbonyl anion

Carbonyl anions react with pentacarbonyliron(0) to give mixed carbonyl anions.



13. Reaction with dimethylacetylene

Dimethylacetylene reacts with $\text{Fe}(\text{CO})_5$ to yield quinone derivatives.



Structure:

Vapour density and cryoscopic studies in benzene have revealed that pentacarbonyliron(0) has molecular formula $\text{Fe}(\text{CO})_5$. Electron diffraction, Raman and Infra red spectra show that $\text{Fe}(\text{CO})_5$ molecule has regular trigonal bipyramidal shape. Electron diffraction studies in vapour phase has indicated that Fe — C axial bond and Fe — C basal bond lengths are equal to 1.797 \AA and 1.842 \AA respectively. X-ray studies have shown that these bonds are almost same. Trigonal bipyramidal shape of molecule arises due to dsp^3 hybridization as shown below:

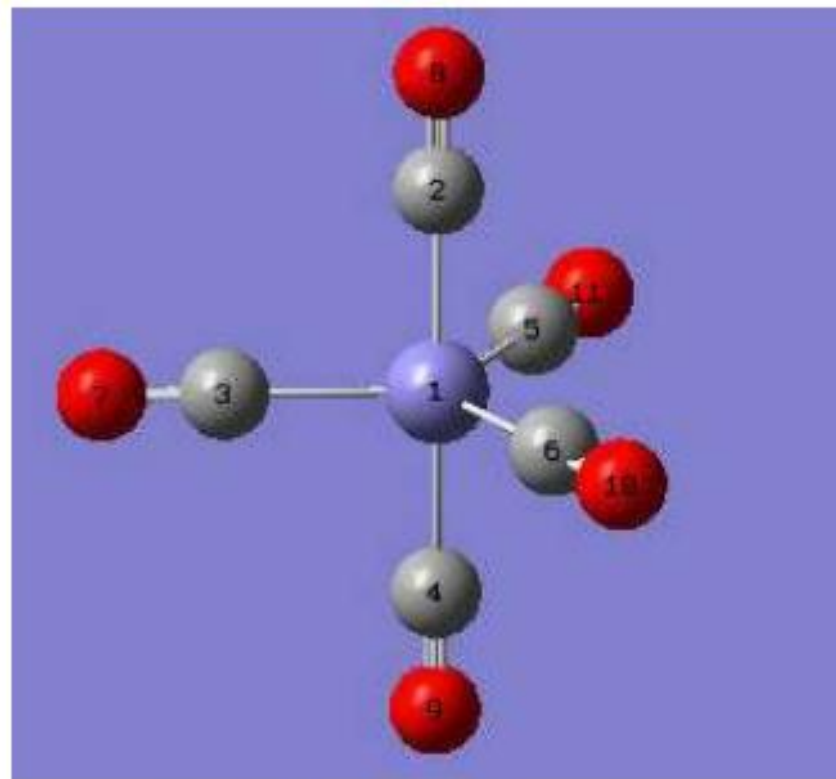
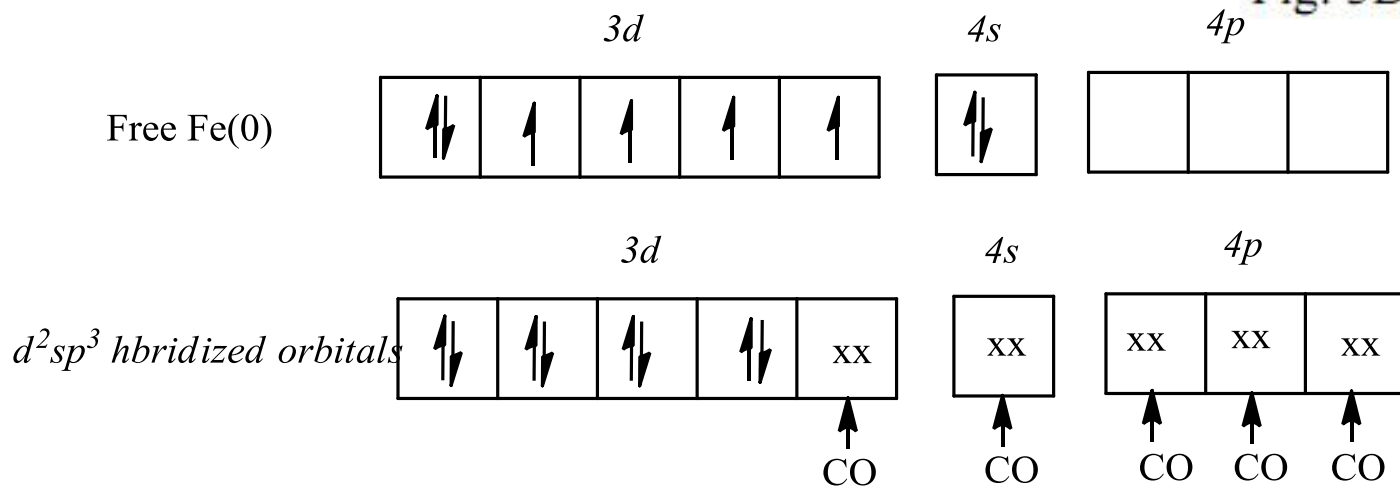


Fig: 3D view of $\text{Fe}(\text{CO})_5$



MO diagram of $\text{Fe}(\text{CO})_5$ shows that two of the five CO groups can be substituted by other ligands which indicates that two of the CO groups are bonded to the Fe differently than the other three.

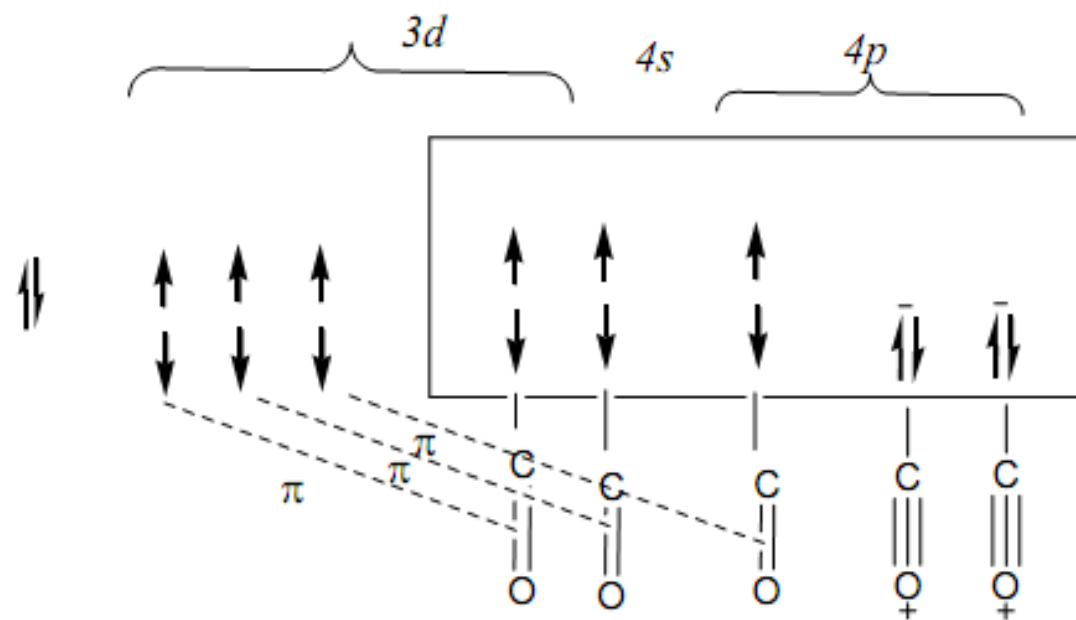


Fig: MO diagram of $\text{Fe}(\text{CO})_5$

Applications of Fe(CO)₅

1. Fe(CO)₅ is a common precursor to diverse iron compounds, including many that are useful in organic synthesis.
2. In Europe, iron pentacarbonyl was once used as an anti-knock agent in petrol in place of tetraethyl lead. Two more modern alternative fuel additives are ferrocene and methylcyclopentadienyl manganese tricarbonyl.
3. Fe(CO)₅ is used in the production of "carbonyl iron", a finely divided form of Fe, a material used in magnetic cores of high-frequency coils for radios and televisions and for manufacture of the active ingredients of some radar absorbent materials (e.g. iron ball paint).
4. It is famous as a chemical precursor for the synthesis of various iron-based nanoparticles.
5. Iron pentacarbonyl has been found to be a strong flame speed inhibitor in oxygen based flames. Few hundred ppm of iron pentacarbonyl are known to reduce the flame speed of stoichiometric methane-air flame by almost 50%. However due to its toxic nature it has not been used widely as flame retardant.
6. α -Diketones were prepared under mild conditions in high yields from aldehydes and alkyl iodides using pentacarbonyliron. (Masakazu Yamashita and Rikisaku Suemitsu New synthesis of α -diketones from aldehydes and alkyl iodides using pentacarbonyliron *Chem. Soc., Chem. Commun.*, 1977, 691 – 692)
7. Pentacarbonyliron has been shown to be useful carbonylating reagent for preparation of aldehydes, ketones, carboxylic acid derivatives and N,N'-disubstituted ureas.

Toxicity:

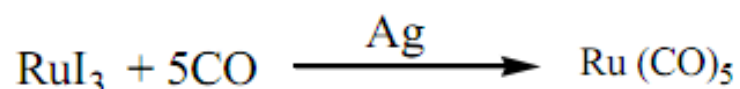
$\text{Fe}(\text{CO})_5$ is toxic, which is of concern because of its volatility (vapour pressure: 21 mmHg at 20 °C). If inhaled, iron pentacarbonyl may cause lung irritation, toxic pneumonitis, or pulmonary edema. Like other metal carbonyls, $\text{Fe}(\text{CO})_5$ is flammable.

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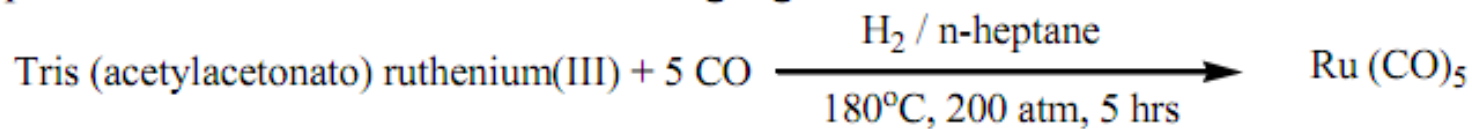
Pentacarbonylruthenium(0), $\text{Ru}(\text{CO})_5$

Pentacarbonylruthenium(0), $\text{Ru}(\text{CO})_5$ is colourless liquid and prepared as under:

1. By reducing the ruthenium salt to Ru by suitable reducing agents and reacting the Ru with CO at 200°C and 200 atm pressure.
2. RuI_3 and finely divided silver are mixed and heated with CO at 170°C and 450 atm pressure.



3. Pentacarbonylruthenium has been prepared by carbonylating acetylacetonatoruthenium(III) with CO for 5 hours at 180° C and 200 atm in the presence of H_2 which act as a reducing agent.



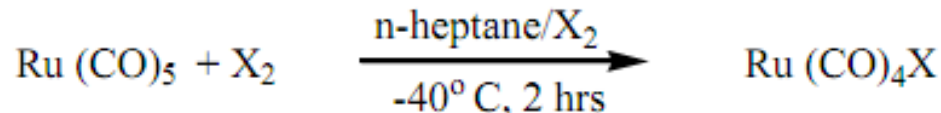
Fausto Calderazzo, and F. L'Eplattenier, **Pentacarbonyls of ruthenium and osmium. I. Infrared spectra and reactivity** *Inorg. Chem.*, 1967, 6 (6), 1220-1224.

Reactivity:

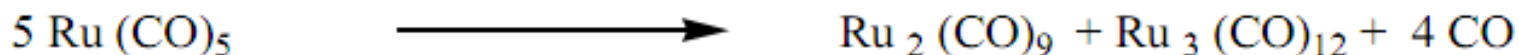
The monomeric pentacarbonyls of ruthenium, $\text{Ru}(\text{CO})_5$ and osmium, $\text{Os}(\text{CO})_5$ have been reported in the literature as volatile and colorless liquids.

Reactions of $\text{Ru}(\text{CO})_5$ with Halogens:

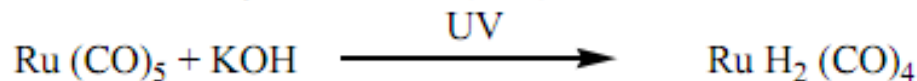
1. $\text{Ru}(\text{CO})_5$ in heptanes solution reacts with halogens at -40°C to yield halogenocarbonyls quantitatively.



2. $\text{Ru}(\text{CO})_5$ is converted to $\text{Ru}_2(\text{CO})_9$ when irradiated with UV light.
3. A mixture of $\text{Ru}_2(\text{CO})_9$ and $\text{Ru}_3(\text{CO})_{12}$ is obtained when pentacarbonylruthenium is heated at 50°C



4. $\text{Ru}(\text{CO})_5$ reacts with KOH to yield $\text{RuH}_2(\text{CO})_4$



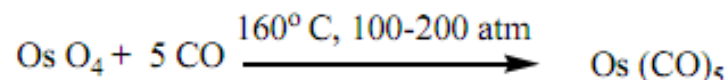
USES: Ruthenium carbonyls play an important role in different catalytic processes with carbon monoxide, e.g., the carbonylation of olefins, the formation of ethylene glycol, the synthesis and homologation of alcohol and the water gas-shift reaction.

Pentacarbonylosmium(0), Os(CO)₅

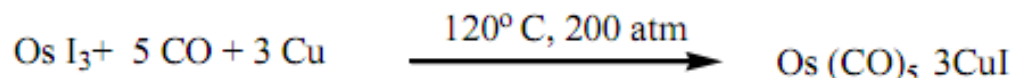
Preparation:

1. The pentacarbonylosmium is prepared by allowing OsO₄ (0.5-1 g) to react with CO at 160° C and 100-200 atm according to the method described by Hieber and Stallmann. The reaction can be run either in heptane (50 ml) or without solvents. (

W. Hieber and H. Stallmann, *Z. Elektrochem.*, **49**, 288 (1943).)



2. OsI₃ reacts with CO in the presence of Cu to yield pentacarbonylosmium at 120° C and 200 atm

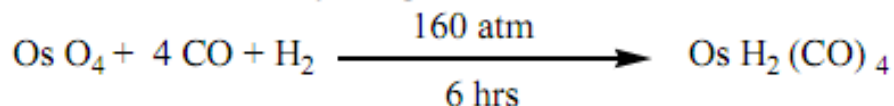


Reactivity

1. Pentacarbonylosmium reacts with molecular hydrogen at elevated temperature and pressure to give dihydridotetracarbonylosmium, OsH₂(CO)₄



2. Dihydridotetracarbonylosmium can be prepared by reacting osmium tetroxide with carbon monoxide and hydrogen in a 3 : 1 ratio in the autoclave at 180 atm.



Ruthenium dioxide hydrate (RuO₂·xH₂O) reacts with carbon monoxide at 5–20 atm to give dodecacarbonyltriruthenium, Ru₃(CO)₁₂, in an excellent yield.

Enneacarbonyliron(0), $\text{Fe}_2(\text{CO})_9$

Preparation

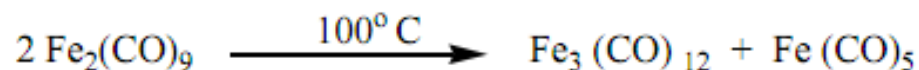
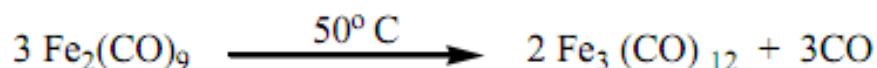
Enneacarbonyliron is prepared from pentacarbonyliron. Pentacarbonyliron is dissolved in equal volume of glacial acetic acid. Cooled solution is irradiated with mercury UV lamp of 1000 watts for six hours. Enneacarbonyliron is filtered as golden yellow fluffy crystals.



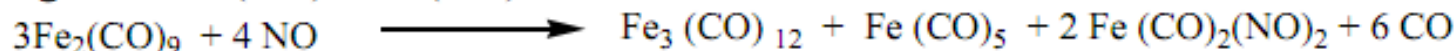
Reactivity

Enneacarbonyliron form triclinic diamagnetic crystals. It is soluble in alcohol, acetone, pyridine and toluene but insoluble in benzene, ether, water and many other organic solvent.

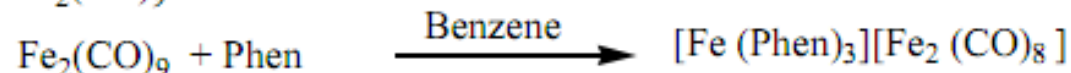
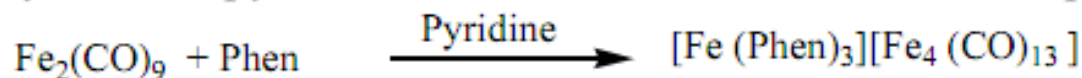
1. **Action of Heat:** On heating at 50°C , it gives $\text{Fe}_3(\text{CO})_{12}$ and CO but heating at 100°C it yields a mixture of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$



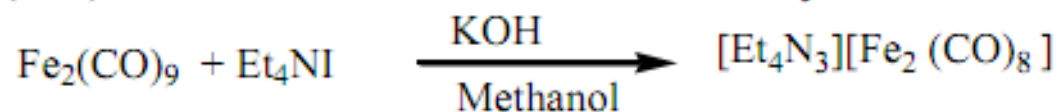
2. **Action of NO:** Enneacarbonyliron reacts with NO and yields $\text{Fe}(\text{CO})_2(\text{NO})_2$ along with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$



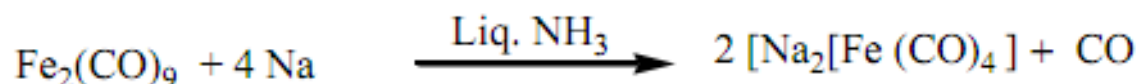
3. **Reaction with Phenanthroline:** *O*-Phenanthroline reacts with enneacarbonyliron in pyridine and benzene to form an ionic complex.



4. **Reaction with Tetraalkylammonium iodide:** Reaction of Tetraalkylammonium iodide with $\text{Fe}_2(\text{CO})_9$ in methanol in alkaline medium yields carbonylate ion.



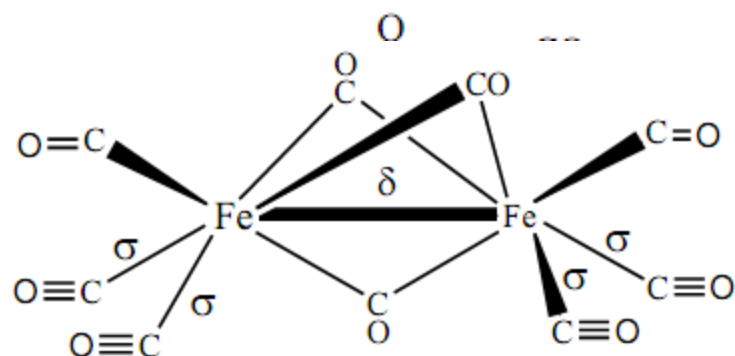
5. **Reaction with Sodium metal:** Reaction with sodium metal in liquid NH_3 yields carbonylate ion



Structure:

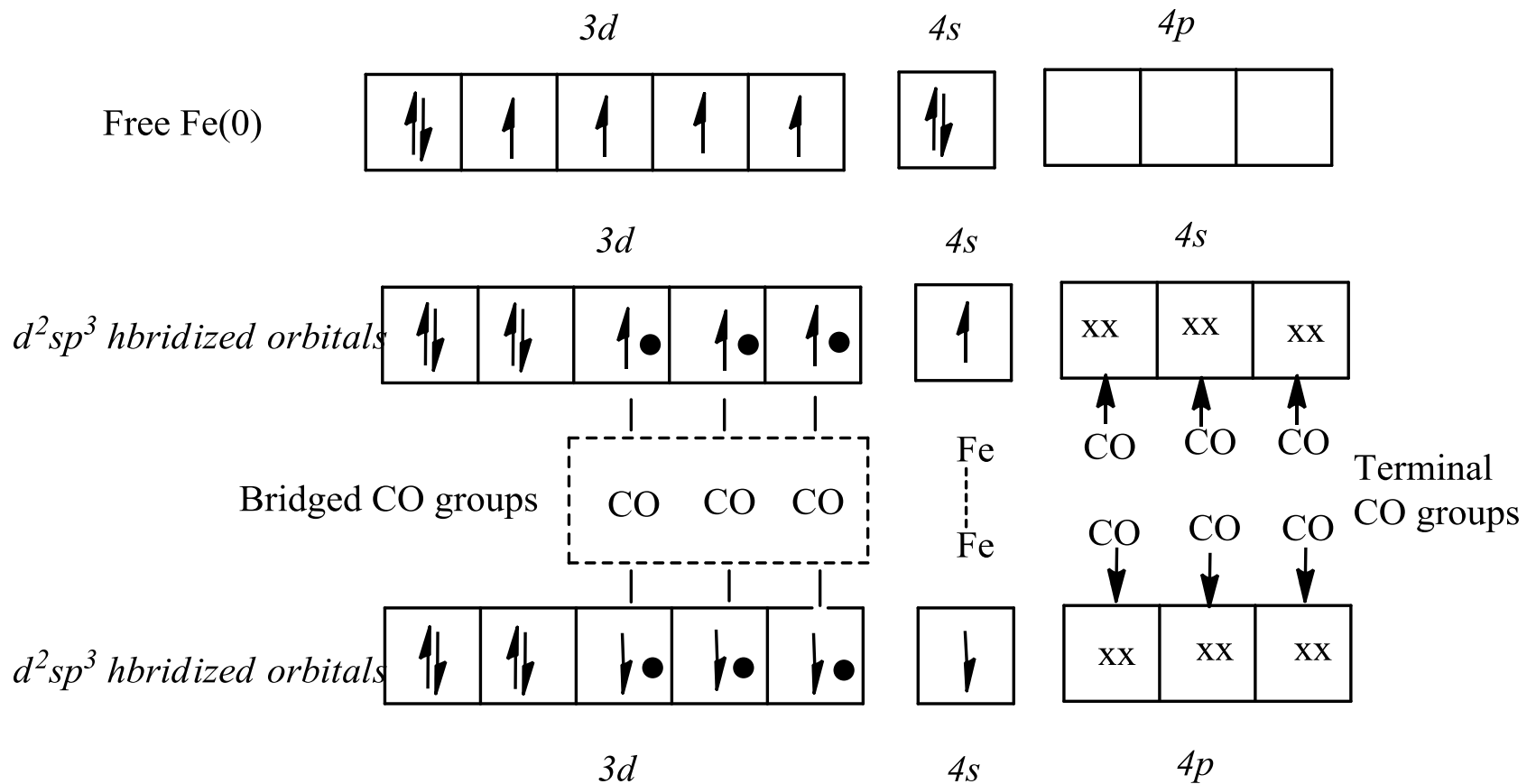
The molecular structure has been derived from the data obtained through Infra red spectra, x-ray diffraction and electron diffraction studies. Each iron atom in this molecule is attached with other Fe atom through δ -bond (Fe-C), to three bridging CO groups through a σ -bonds (Fe-C, σ -bonds) and to three terminal CO groups through Coordinate bond. Fe-Fe bond distance is found to be 2.46 \AA . The terminal C-O bond distances are smaller than the bridging C-O bond distances. Two out of the six terminal groups in this molecule form π -bond by overlapping of filled d orbitals of the metal and empty antibonding molecular orbitals of CO groups.

The structure of enneacarbonyl diiron, $\text{Fe}_2(\text{CO})_9$, can be described in terms of two octahedral sharing a common face formed by the carbon atoms of the bridging carbonyls. The molecular structure in crystal has been established. Each terminal CO group contributes two electrons to the iron atom to which it is attached, and that each bridging CO group contributes one electron to the bonded metal. Three terminal CO groups provide six electrons and three bridging CO groups contribute three electrons to each metal atom making a total of nine electron. One electron is provided to each Fe by metal-metal (Fe-Fe) making a total of 10 electrons provided to Fe which is its magic number.



The structure of enneacarbonyl diiron, $\text{Fe}_2(\text{CO})_9$, can be discussed in terms of hybridization of 3d, 4s and 4p orbitals of each Fe atom which undergo d^2sp^3 hybridization. Three of the six empty d^2sp^3 hybridized orbitals on each Fe atom are occupied by six electrons donated by three terminal CO groups. A dz^2 orbital arising from the linear combination of the t_{2g} set can strongly overlap with the corresponding orbital of the other iron atom.

The hybridization scheme and MO diagram for the enneacarbonyl diiron, $\text{Fe}_2(\text{CO})_9$ is given in the figures below.



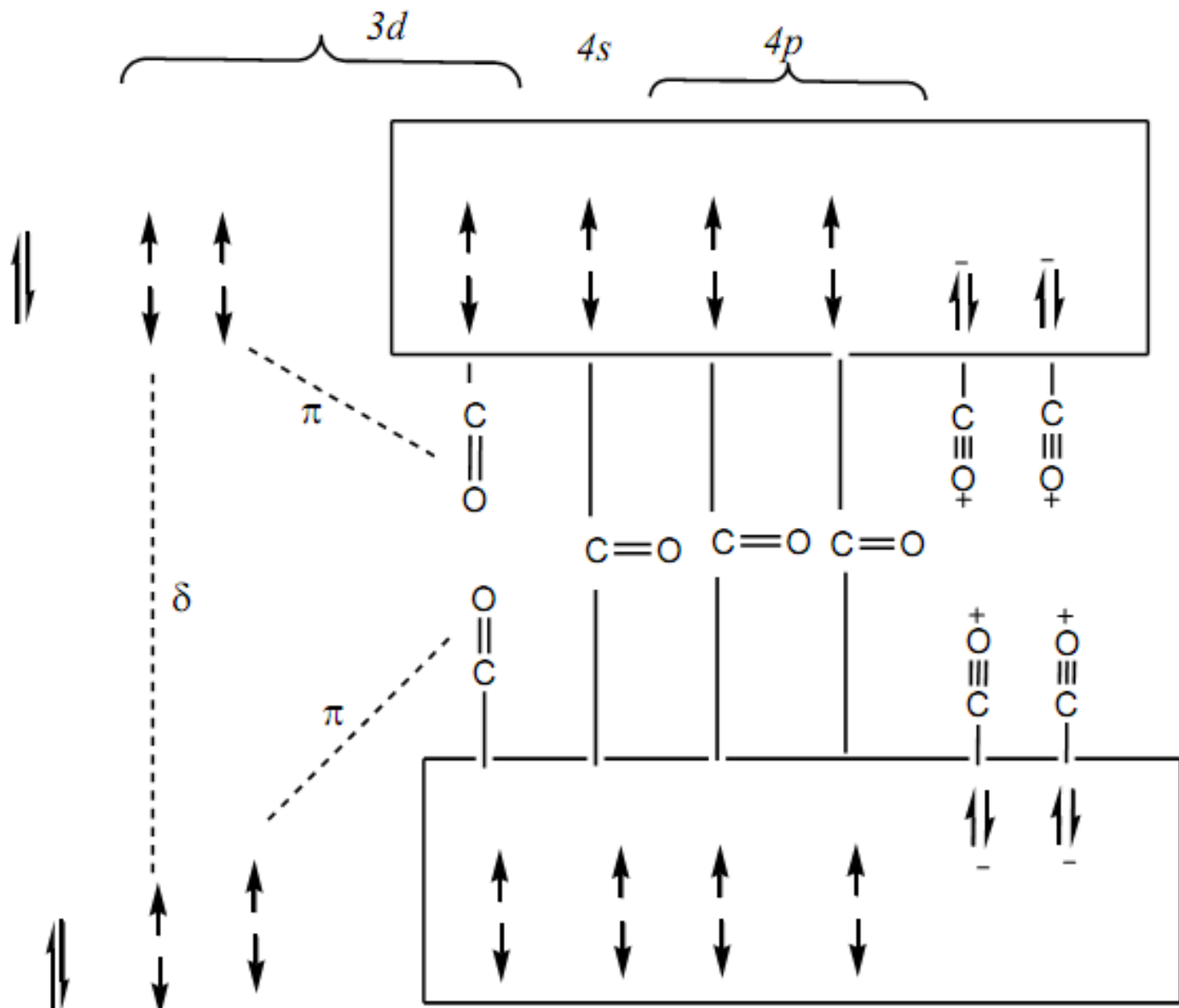
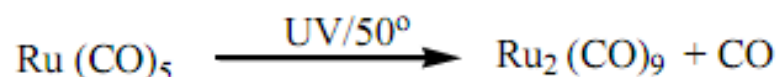


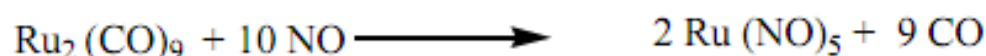
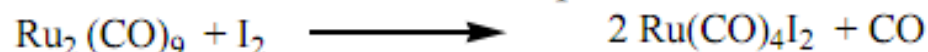
Figure: Bonding and electron distribution in $\text{Fe}_2(\text{CO})_9$

Enneacarbonyldiruthenium, $\text{Ru}_2(\text{CO})_9$ and enneacarbonyldiosmium, $\text{Os}_2(\text{CO})_9$

$\text{Ru}_2(\text{CO})_9$ is prepared by heating a solution of $\text{Ru}(\text{CO})_5$ in benzene at 50°C or by irradiating .



$\text{Ru}_2(\text{CO})_9$ reacts with iodine and NO to form respective iodide and nitrosyl.



Enneacarbonyldiosmium, $\text{Os}_2(\text{CO})_9$, is prepared by reacting CO with OsI_3 in presence of Cu



Both, $\text{Os}_2(\text{CO})_9$ and $\text{Ru}_2(\text{CO})_9$ are yellow crystalline and volatile substances

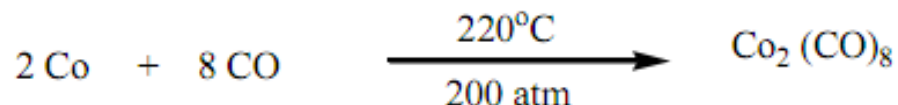
Metal carbonyls of Cobalt, Rhodium and Iridium

The carbonyls of cobalt, rhodium and iridium are well known.

Octacarbonyldicobalt, $\text{Co}_2(\text{CO})_8$

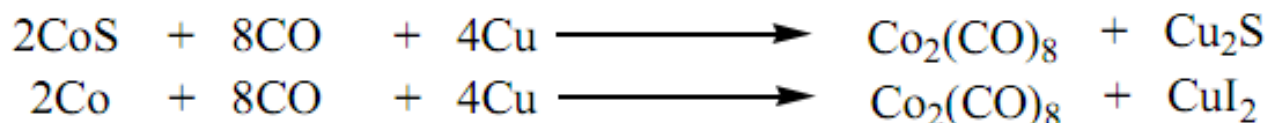
Preparation: Octacarbonyldicobalt, $\text{Co}_2(\text{CO})_8$ can be prepared by several methods as given here.

3. By the Direct action of CO on cobalt



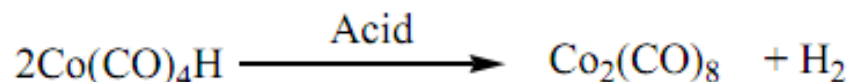
4. By the action of CO on cobalt salt:

Cobalt salts such as sulfides and iodides are reduced in presence of copper and CO reacts with cobalt to form carbonyls



5. By the action of acids on cobalt carbonyl hydride

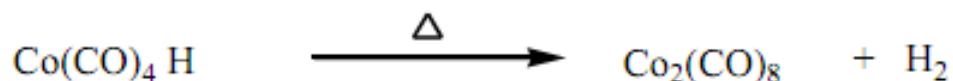
Cobalt carbonyl hydride reacts with acids to form cobaltcarbonyl and hydrogen is collected



6. By thermal decomposition of cobalt carbonyl hydride

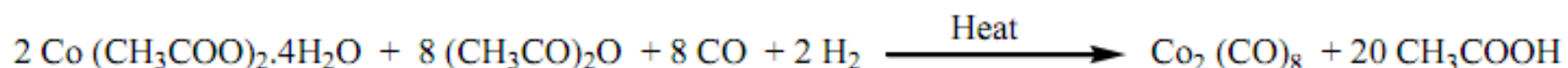
6. By thermal decomposition of cobalt carbonyl hydride

Cobalt carbonyl hydride is cooled to -78°C and then allowed to warm up to -30°C . The hydrogen liberated is pumped off leaving behind cobalt carbonyl hydride.



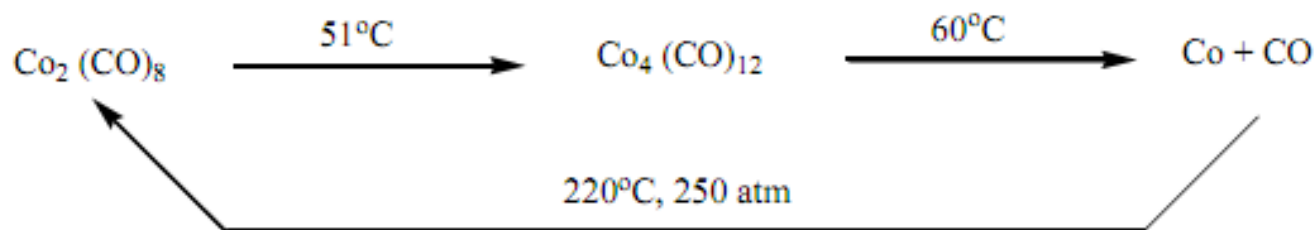
7. By treating cobalt(II)acetate with CO in presence of acetic anhydride and H₂

Cobalt(II)acetate is heated with CO and H₂ in presence of acetic anhydride and H₂ in acetic acid.



Reactivity: Cobalt carbonyl is obtained as orange, transparent and air sensitive crystals having m.p of 51°C . It is soluble in organic solvents like alcohol and CS_2 but insoluble in water. It is reactive compound and reacts with several reagents.

1. **Decomposition:** Cobalt carbonyl decomposes at its melting point to yield $\text{Co}_4(\text{CO})_{12}$ which decomposes to give CO



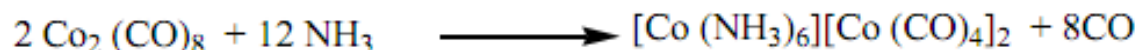
Halogen also decomposes $\text{Co}_2(\text{CO})_8$ to CoX



2. Heating causes decarbonylation and formation of the tetrahedral cluster:



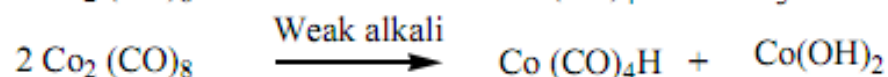
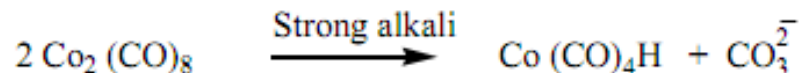
3. **Disproportionation reaction:** Strong bases having N and oxygen donor atoms disproportionate $\text{Co}_4(\text{CO})_{12}$.



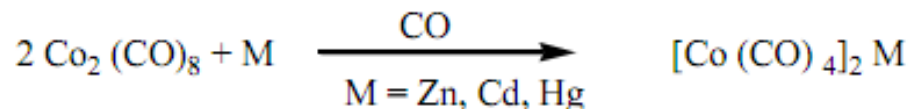
However with isocyanides, phosphorous, arsines and stibine disproportionation reactions give penta coordinated cobalt(I) compounds.



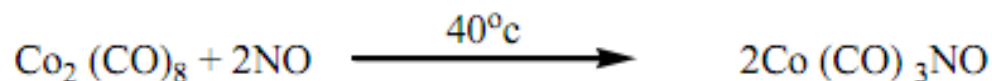
4. **Reactions with alkali:** $\text{Co}_2(\text{CO})_8$ reacts with alkali to give carbonyl hydrides.



5. **Reactions with Zn, Cd and Hg:** Zn, Cd and Hg react with $\text{Co}_2(\text{CO})_8$ in presence of CO to form metal derivatives.



6. **Reactions with NO:** $\text{Co}_4(\text{CO})_{12}$ reacts with NO to give substituted products.



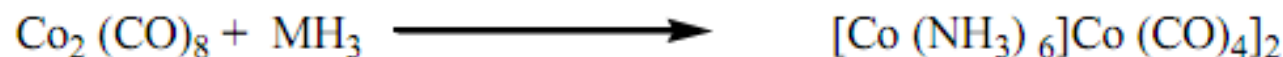
7. **Reactions with thioalcohols:** Reaction of $\text{Co}_2(\text{CO})_8$ with thioalcohols yields $\text{Co}(\text{CO})_3\text{SC}_6\text{H}_5$.



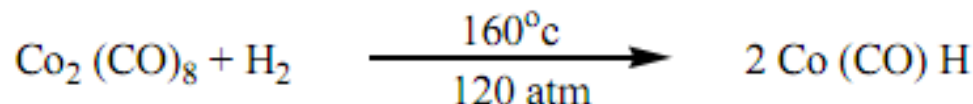
8. **Reactions with Methanol:** Methanol reacts with $\text{Co}_2(\text{CO})_8$ to substitute three CO groups



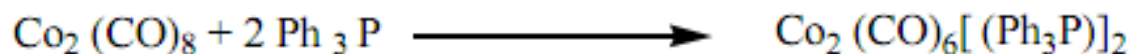
9. **Reactions with NH_3 :** Ammonia reacts with octacarbonyldicobalt to form anionic species.



10. **Formation of carbonyl hydrides:** $\text{Co}_2(\text{CO})_8$ is treated with H_2 at 160°C and 120 atm to get carbonyl hydrides.



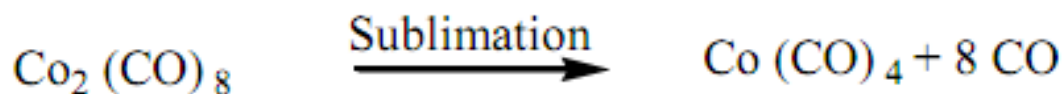
11. **Substitution of triphenylphosphine:** Two CO groups of $\text{Co}_2(\text{CO})_8$ are replaced by PPh_3 in reaction between triphenylphosphine and $\text{Co}_2(\text{CO})_8$



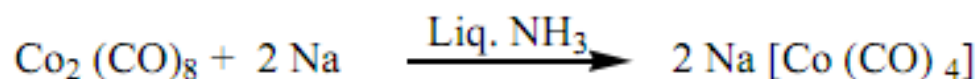
- 12. Substitution of Isocyanides:** Isocyanides reacts with $\text{Co}_2(\text{CO})_8$ to replace six CO groups.



- 13. Sublimation:** $\text{Co}_2(\text{CO})_8$ sublimes on a probe at -196°C to give paramagnetic $\text{Co}(\text{CO})_4$



- 14. Action of sodium metal:** Sodium metal reacts with $\text{Co}_2(\text{CO})_8$ in liquid ammonia to form anionic species

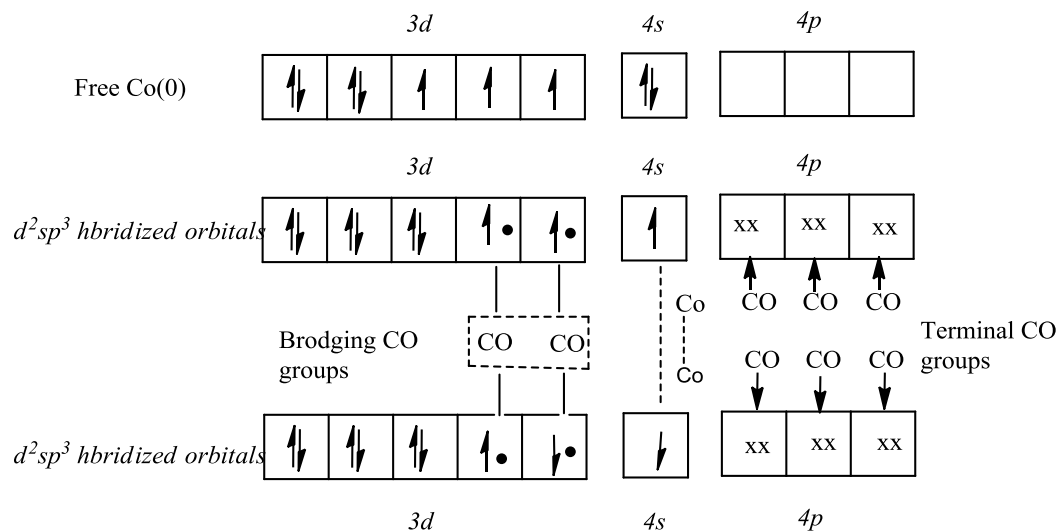
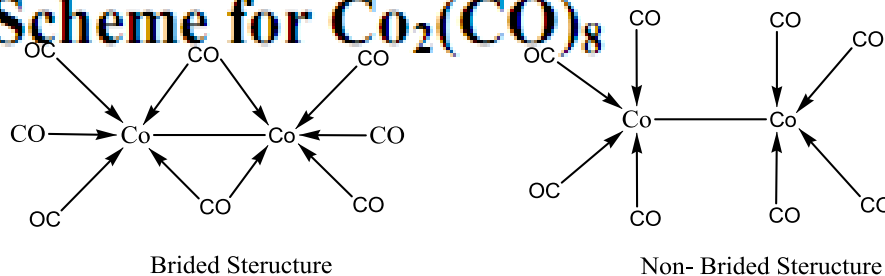


Structure:

Dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$:

This carbonyl exists 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 to each other through Co-Co σ -bond. Each of two Co atom is bonded to three terminal CO groups.

Hybridization Scheme for $\text{Co}_2(\text{CO})_8$



The other form has a non bridged structure with a Co-Co σ -bond linking two $\text{Co}(\text{CO})_4$ groups. Both the structures have Co-Co σ -bonding and the diamagnetic nature. The IR spectrum of the bridged structure has confirmed that it has two types of CO groups, i.e., terminal and bridging. Co-Co bond length is 2.52 \AA . Both the structures exist in equilibrium in solution. Bridged structure predominates at very low temperature and non-bridged structure is dominant at higher temperature. At a temperature higher than 100°C a third isomeric of uncertain structure is also found.

Each of the Co atom is d^2sp^3 hybridized as shown in the figure above. Co-Co σ -bond is slightly bent which arises due to unusual overlap of singly filled d^2sp^3 hybridized orbital on each Co atom.

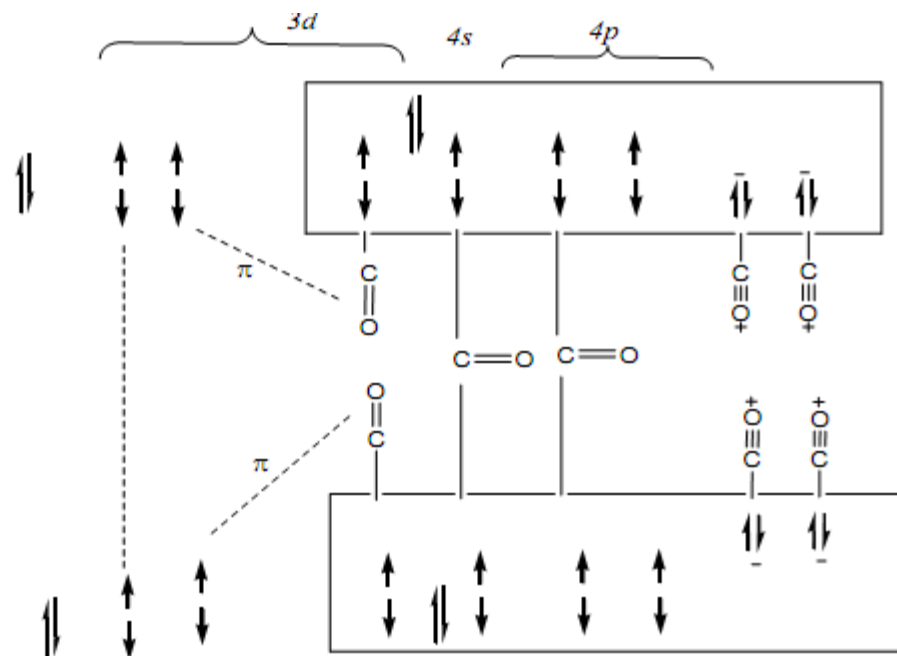
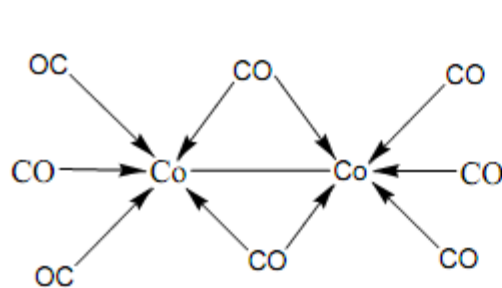
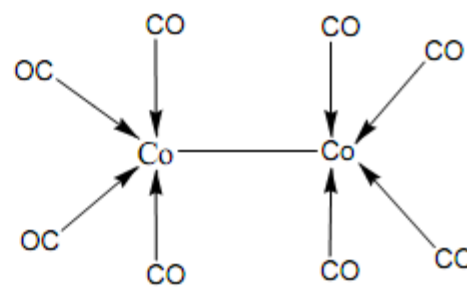


Fig: MO diagram of $\text{Co}_2(\text{CO})_8$



Bridged Structure



Non- Brided Structure

