Metal Carbonyls & Its Derivatives

Introduction

The coordination complexes of transition metals with carbon monoxide ligands is called metal carbonyl. Metal carbonyls of transition elements constitute another important class of organometallic compounds (compounds having at least one bond between carbon and metal). All d-block elements which contain only carbonyl ligands are called **homoleptic carbonyls**. Lone pair of electrons are available on both carbon and oxygen atoms of carbon monoxide ligand. However, the carbon atoms donate electrons to the metal, these complexes are known as carbonyls. One of the most important π- acceptor ligand is carbon monoxide.

Historical Background

Initial experiments on the reaction of carbon monoxide with metals were carried out by "Justus von Liebig" in 1834. By passing carbon monoxide over molten potassium he prepared a substance having the empirical formula KCO, which he called "Kohlenoxidkalium".

The synthesis of the first true heteroleptic metal carbonyl complex was performed by "Paul Schützenberger" in 1868 by passing chlorine and carbon monoxide over platinum black, where dicarbonyldichloroplatinum $(Pt(CO)_2Cl_2)$ was formed.

One of the founders of Imperial Chemical Industries,"Ludwig Mond", investigated in the 1890s with "Carl Langer" and "Friedrich Quincke" various processes for the recovery of chlorine. They found that the resulting gas colored the gas flame of a burner in a greenish-yellowish color; when heated in a glass tube it formed a nickel mirror. The gas could be condensed to a colorless, water-clear liquid with a boiling point of 43 °C. Thus, Mond and his coworker had discovered the first pure, homoleptic metal carbonyl, nickel tetracarbonyl $(Ni(CO)_4)$.

"Mond" and "Marcellin Berthelot" independently discovered iron pentacarbonyl,the following year. "James Dewar" and "H. O. Jones" were able to determine the structure of di-iron nonacarbonyl, In 1906, which is

produced from iron pentacarbonyl by the action of sunlight. After Mond, who died in 1909, the chemistry of metal carbonyls fell for several years in oblivion. The iron pentacarbonyl was used for the production of high-purity iron, so-called carbonyl iron, and iron oxide pigment.

In 1928, "Walter Hieber" played decisive role in the development of metal carbonyl chemistry. He systematically investigated and discovered, among other things, the "Hieber" base reaction, the first known route to metal carbonyl hydrides and synthetic pathways leading to metal carbonyls such as dirhenium decacarbonyl. "Hieber", who was the Director of the Institute of Inorganic Chemistry at the Technical University since 1934 "Munich" published in four decades 249 papers on metal carbonyl chemistry.

"Walter Reppe", An industrial chemist and later board member of the BASF, in 1930 discovered a number of homogeneous catalytic processes, such as the hydrocarboxylation, in which olefins or alkynes react with carbon monoxide and water to form products such as unsaturated acids and their derivatives.
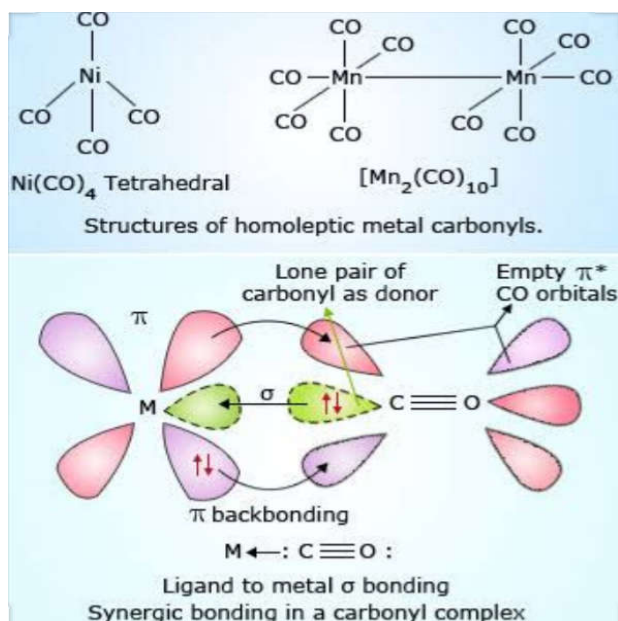
New complexes of the concept of the isolobal analogy has been found useful for the rational design. In chemistry for the development of the concept "Roald Hoffmann" was awarded with the noble prize. The concept describes metal carbonyl fragments of $M(CO)_n$ as parts of octahedral building blocks in analogy to the tetrahedral CH_3-, CH_2- or CH-fragments in organic chemistry. In his Nobel Prize lecture Hoffmann emphasized that the isolobal analogy is a useful but simple model, and in some cases does not lead to success.

Introduction:

Nomenclature and terminology:

The metal carbonyl nomenclature depends on the charge of the complex, the number and type of central atoms, the number and type of ligands and their binding modes. They occur as neutral complexes, as positively charged metal carbonyl cations or as negatively charged metal

carbonyl anion. The carbon monoxide ligand may be bound terminally to a single metal atom or bridging to two or more metal atoms. These complexes may be homoleptic, that is containing only CO ligands, such as nickel tetracarbonyl ($Ni(CO)_4$), but more commonly metal carbonyls are heteroleptic and contain a mixture of ligands. Complexes with different metals, but only one type of ligand are called **isoleptic.**

Structures of homoleptic metal carbonyls.

π backbonding

$M \leftarrow : C \equiv O :$

Ligand to metal σ bonding
Synergic bonding in a carbonyl complex

Occurrence in nature:

Iron carbonyl clusters were also observed in Jiange H_5 chondrites identified by infrared spectroscopy. Four infrared stretching frequencies were found for the terminal and bridging carbon monoxide ligands.In the oxygen-rich atmosphere of earth metal carbonyls are subject to oxidation to the metal oxides.

Traces of the carbonyls of iron, nickel, and tungsten were found in the gaseous emanations from the sewage sludge of municipal treatment plants.The hydrogenase enzymes contain CO bound to iron. Apparently the CO stabilizes low oxidation states, which facilitates the binding of hydrogen. Carbon monoxide containing complexes are invoked for the toxicity of CO and signalling.

CLASSIFICATION OF METAL CARBONYLS:

Different types of metal carbonyls with examples are given below;

Types.   **Examples**

Mononuclear carbonyls $[Ti(CO)_6]^{-2}$, $[V(CO)_6]$, $[Cr(CO)_6]$,$[Fe(CO)_5]$, $[Ni(CO)_4]$

Dinuclear carbonyls $[Mn_2(CO)_{10}]$, $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$

Polynuclear carbonyls $[Fe_3(CO)_{12}]$, $[Co_4(CO)_{12}]$, $[Co_6(CO)_{16}]$

μ2-Bridging carbonyls $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, $[Fe_3(CO)_{12}]$, $[Co_4(CO)_{12}]$

μ3-Bridging carbonyls $[Rh_6(CO)_{16}]$ (Four triply bridged carbonyl groups)

Carbonyl hydrides $[HMn(CO)_5]$, $[HCo(CO)_4]$, $[H_2Fe(CO)_4]$

### Mononuclear (monomeric) carbonyls:

These compounds which contain only one metallic atom per molecule.

Ni(CO)$_4$, Nickel tetracarbonyl:

Preparation:

It can be prepared by passing carbon monoxide over nickel in the temperature range of 60-100°C.

$$Ni + 4CO \rightarrow Ni(CO)_4 \qquad\qquad At\ 60^0C$$

It can also be prepared by passing carbon monoxide through alkaline suspensions of nickel sulphide or nickel cyanate.

$$NiS + 4CO \rightarrow Ni(CO)_4 + S$$
$$Ni(CN)_2 + 4\ CO \rightarrow Ni(CO)_4 + C_2N_2$$
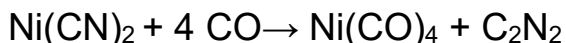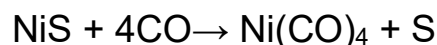
Properties:

It is a colourless liquid having melting point -25°C, boiling point 43°C and decomposition temperature in the range of 180   200°C.It is insoluble in water but dissolves in organic solvents.

It reacts with concentrated sulphuric acid along with detonation. It reacts with moist nitric oxide to give deep blue coloured compound.
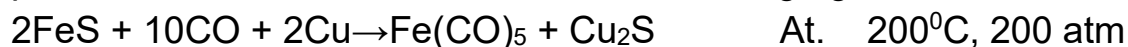
Uses:

Since $Ni(CO)_4$, on heating, decomposes to metallic nickel, it is used in the production of nickel by mond's process.It is used for plating nickel on other metals.It is used as a catalyst for synthesis of acrylic monomers in plastic industries.

Structure:
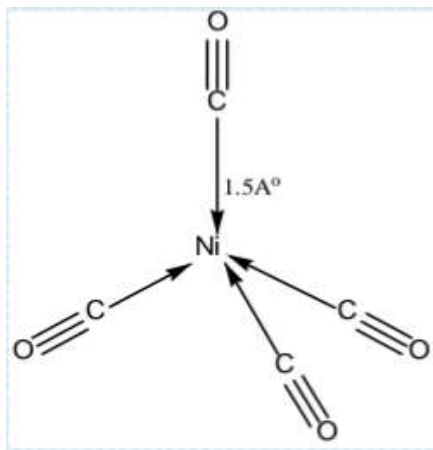
$Fe(CO)_5$, Iron pentacarbonyl:
Preparation:
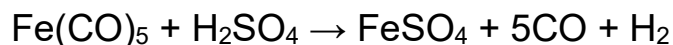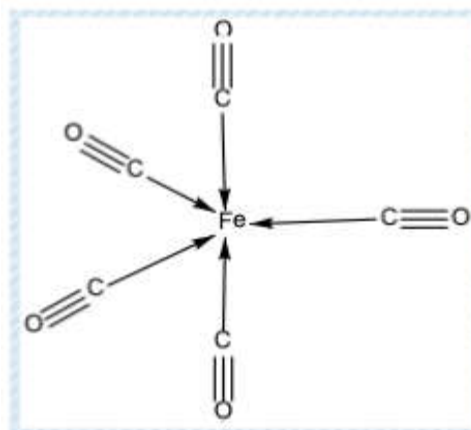It can be prepared by passing carbon monoxide over iron powder at high temperature and pressure.
$Fe + 5CO \rightarrow Fe(CO)_5$.   At. 200^0C, 100 atm
It can also be prepared by carbonylation of ferrous sulphide/iodide in presence of Cu-metal, which acts as a reducing agent.
$2FeS + 10CO + 2Cu \rightarrow Fe(CO)_5 + Cu_2S$ At. 200^0C, 200 atm
Properties:
It is a pale yellow liquid having melting point -20^oC, boiling point 103^oC and decomposition temperature around 250^oC. It is insoluble in water but soluble in glacial acetic acid, methanol, diethyl ether, acetone and benzene. Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light. It is readily hydrolysed by water and acids.

$Fe(CO)_5 + H_2SO_4 \rightarrow FeSO_4 + 5CO + H_2$
Structure:

$Cr(CO)_6$, Chromium hexacarbonyl:

Preparation:

It can be prepared by carbonylation of chromium chloride with carbon monoxide using a reducing agent like lithium aluminium hydride (LAH).

$CrCl_3 + 6CO \rightarrow Cr(CO)_6$ At.   LAH, 115^0C, 70 atm

Properties:

It is a white crystalline solid melting above 150^oC and boiling at 220^oC. It is insoluble in water but soluble in ether, chloroform, carbon tetrachloride and benzene. It is not attacked by air, bromine, cold aqueous alkalis, dilute acids and concentrated hydrochloric acid as well as sulphuric acid. It is decomposed by Chlorine gas and concentrated nitric acid. It reacts with fluorine at -75^oC to form chromium hexafluoride.
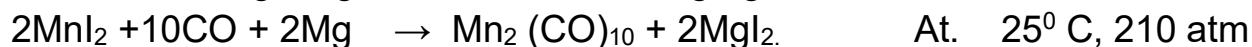
Structure:
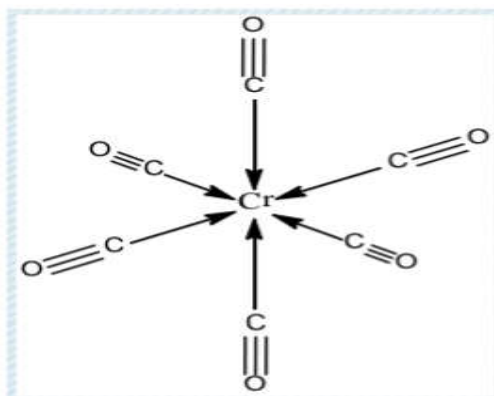
POLYNUCLEAR CARBONYLS:

These contain two or more metallic atoms per molecule and are of the type $M_x(CO)_y$. These carbonyls are also sometimes called as bridged carbonyls. Polynuclear carbonyls may be homonuclear.

**$Mn_2(CO)_{10}$, Dimanganese decacarbonyl:**

Preparation:

It can be prepared by carbonylation of manganese iodide with carbon monoxide using magnesium as a reducing agent.

$$2MnI_2 + 10CO + 2Mg \rightarrow Mn_2(CO)_{10} + 2MgI_2. \qquad \text{At. } 25^0 C, 210 \text{ atm}$$

Properties:

It forms stable golden yellow crystals having melting point of 155°C. It is oxidized by trace amount of oxygen in solution. Hence, the solution must be stored in inert atmosphere.

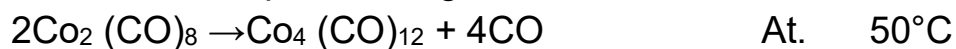**Structure:**
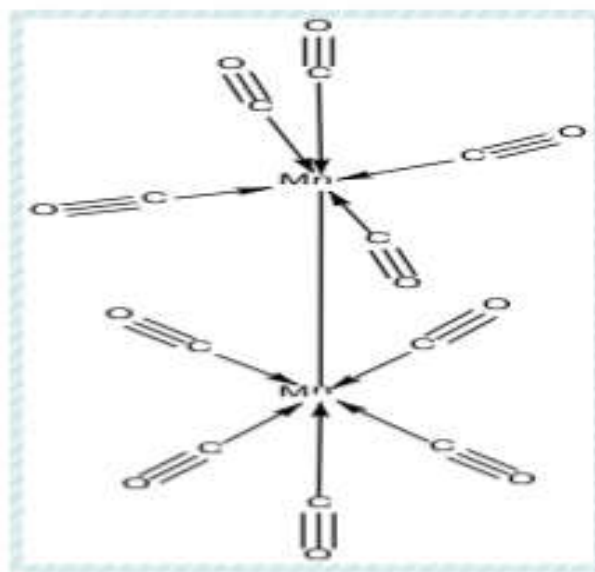
$Co_2(CO)_8$, Dicobalt octacarbonyl:

Preparation:

It can be prepared by direct combination of carbon monoxide with cobalt metal.

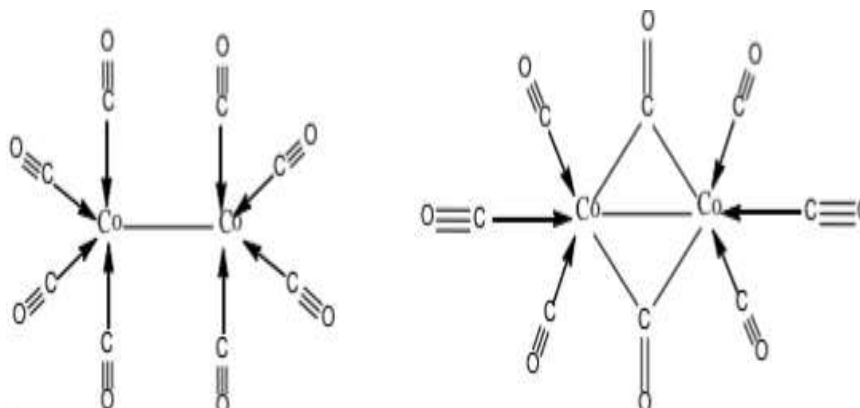$$2Co + 8CO \rightarrow Co_2(CO)_8 \qquad \text{At. } 200°C, 100 \text{ atm}$$

Properties:

It is an orange crystalline substance having melting point 51°C and turns deep violet upon exposure to air. It is soluble in alcohols, ether and carbon tetrachloride. Upon heating at 50°C it forms tetracobalt dodecacarbonyl.

$2Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4CO$ At.   50°C

Structure:

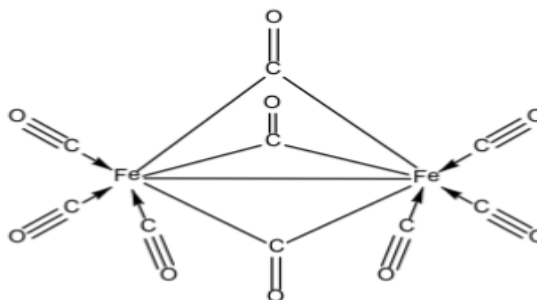
$Fe_2(CO)_9$, Diiron nonacarbonyl:

Preparation:

Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light to give golden yellow crystals.

$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$ At.   hv

Properties:

Diiron nonacarbonyl forms golden yellow triclinic crystals melting at 100°C. It is insoluble in water but soluble in toluene and pyridine.

Structure:

$Fe_3(CO)_{12}$, Triiron dodecacarbonyl:

Preparation:

It is prepared by heating diiron nonacarbonyl dissolved in toluene at $70^{\circ}C$.

$$3Fe_2(CO)_9 \rightarrow 3Fe(CO)_5 + (CO)_{12} \qquad \text{At.} \quad 70°C, \text{Toluene}$$

Properties:

It forms green monoclinic crystals which are soluble in organic solvents like toluene, alcohol etc.

It decomposes at $140^{\circ}C$ to give metallic iron and carbon monoxide.

$$Fe_3(CO)_{12} \rightarrow 3Fe + 12CO \qquad \text{At.} \quad 140°C$$

Structure:
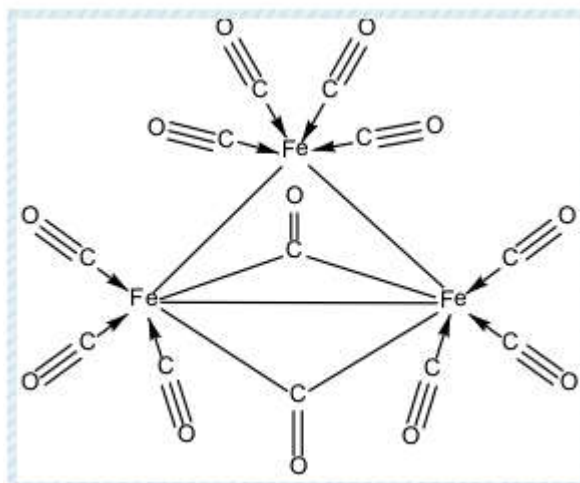
SYNTHESIS OF METAL CARBONYLS:

The general methods of preparation of metal carbonyls are given below;

Since the work of Mond and Hieber, many procedures have been developed for the preparation of mononuclear metal carbonyls as well as homo-and hetero-metallic carbonyl clusters.

Direct reaction of metal with carbon monoxid:

Nickel tetracarbonyl and iron pentacarbonyl can be prepared according to the following equations by reaction of finely divided metal with carbon monoxide.

$Ni + 4\ CO \rightarrow Ni(CO)_4$ (1 bar, 55°C)

$Fe + 5\ CO \rightarrow Fe(CO)_5$ (100 bar, 175°C)
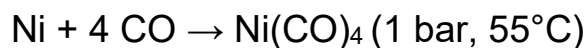
Reduction of metal salts and oxides:

Some metal carbonyls are prepared by the reduction of metal halides in the presence of high pressure of carbon monoxide. A variety of reducing agents are employed, including copper, aluminum, hydrogen, as well as metal alkyls such as triethylaluminium. Illustrative is the formation of chromium hexacarbonyl from anhydrous chromium(III) chloride in benzene with aluminum as a reducing agent, and aluminum chloride as the catalyst.

$CrCl_3 + Al + 6\ CO \rightarrow Cr(CO)_6 + AlCl_3$
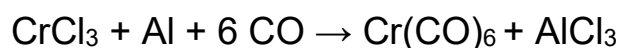
Photolysis and thermolysis:

Photolysis or thermolysis of mononuclear carbonyls generates bi- and multimetallic carbonyls such as diiron nonacarbonyl ($Fe_2(CO)_9$). On further heating, the products decompose eventually into the metal and carbon monoxide.

$2\ Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$

Salt metathesis:

Salt metathesis reaction of for example $KCo(CO)_4$ with $[Ru(CO)_3Cl_2]_2$ leads selectively to mixed-metal carbonyls such as $RuCo_2(CO)_{11}$.

$4\ KCo(CO)_4 + [Ru(CO)_3Cl_2]_2 \rightarrow 2\ RuCo_2(CO)_{11} + 4\ KCl + 11\ CO$
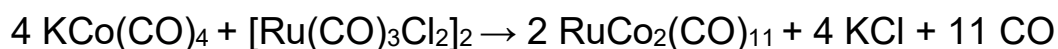
Metal carbonyl cations and carbonylates:

The synthesis of ionic carbonyl complexes is possible by oxidation or reduction of the neutral complexes. Anionic metal carbonylates can be obtained for example by reduction of dinuclear complexes with sodium.

Example is the sodium salt of iron tetracarbonylate ($Na_2Fe(CO)_4$, Collman's reagent), which is used in organic synthesis.The cationic hexacarbonyl salts of manganese, technetium and rhenium can be prepared from the

carbonyl halides under carbon monoxide pressure by reaction with a Lewis acid.

$$Mn(CO)_5Cl + AlCl_3 + CO \rightarrow Mn(CO)_6^+ + AlCl_4^-$$

The use of strong acids succeeded in preparing gold carbonyl cations such as $[Au(CO)_2]^+$, which is used as a catalyst for the carbonylation of olefins.

Reaction:

Metal carbonyls are important precursors for the synthesis of other organometalic complexes. The main reactions are the substitution of carbon monoxide by other ligands, the oxidation or reduction reactions of the metal center and reactions of carbon monoxide ligand.
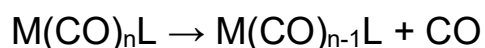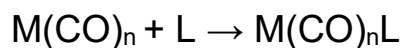
CO substitution:

The substitution of CO ligands can be induced thermally or photochemically by donor ligands. The range of ligands is large, and includes phosphines, cyanide (CN^-), nitrogen donors, and even ethers, especially chelating one. Olefins, especially diolefins, are effective ligands that afford synthetically useful derivatives. Substitution of 18-electron complexes generally follows a dissociative mechanism, involving 16-electron intermediates.

**Substitution proceeds via a dissociative mechanism:**

$$M(CO)_n \rightarrow M(CO)_{n-1} + CO$$

$$M(CO)_{n-1} + L \rightarrow M(CO)_{n-1}L$$
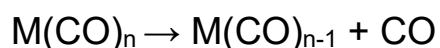
The dissociation energy is 105 kJ mol^{-1} for nickel tetracarbonyl and 155 kJ mol^{-1} for chromium hexacarbonyl. Substitution in 17-electron complexes, which are rare, proceeds via associative mechanisms with a 19-electron intermediates.

$$M(CO)_n + L \rightarrow M(CO)_nL$$

$$M(CO)_nL \rightarrow M(CO)_{n-1}L + CO$$

The rate of substitution in 18-electron complexes is sometimes catalysed by catalytic amounts of oxidants, via electron-transfer.

Reduction:

Metal carbonyls react with reducing agents such as metallic sodium or sodium amalgam to give carbonylmetalate (or carbonylate) anions.

$$Mn_2(CO)_{10} + 2\ Na \rightarrow 2\ Na[Mn(CO)_5]$$
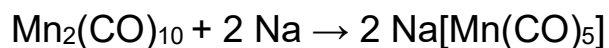
For iron pentacarbonyl, one obtains the tetracarbonylferrate with loss of CO.

$$Fe(CO)_5 + 2\ Na \rightarrow Na_2[Fe(CO)_4] + CO$$
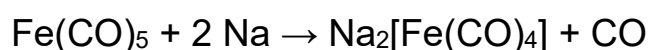
Mercury can insert into the metal-metal bonds of some polynuclear metal carbonyls.

$$Co_2(CO)_8 + Hg \rightarrow (CO)_4Co\text{-}Hg\text{-}Co(CO)_4$$
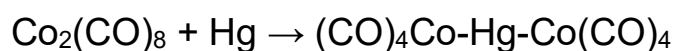
Nucleophilic attack at CO:

The CO ligand is often susceptible to attack by nucleophiles. For example, trimethylamine oxide and bistrimethylsilylamide convert CO ligands to CO_2 and CN^-, respectively. In the "Hieber base reaction", hydroxide ion attacks the CO ligand to give a metallacarboxylic acid, followed by the release of carbon dioxide and the formation of metal hydrides or carbonylmetalates. A good example of this nucleophilic addition reaction is the conversion of iron pentacarbonyl to hydridoiron tetracarbonyl anion:

$$Fe(CO)_5 + NaOH \rightarrow Na[Fe(CO)_4CO_2H]$$

$$Na[Fe(CO)_4COOH] + NaOH \rightarrow Na[HFe(CO)_4] + NaHCO_3$$
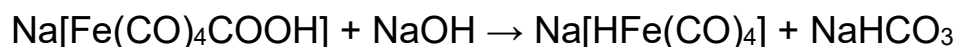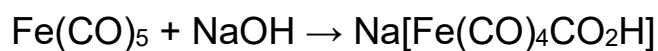
Protonation of the hydrido anion gives the neutral iron tetracarbonyl hydride.

$$Na[HFe(CO)_4] + H+ \rightarrow H_2Fe(CO)_4 + Na+$$
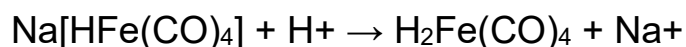
With electrophile:

Despite being in low formal oxidation states, metal carbonyls are relatively unreactive toward many electrophiles. For example, they resist attack by

alkylating agents, mild acids, mild oxidizing agents. Most metal carbonyls do undergo halogenation. Iron pentacarbonyl, for example, forms ferrous carbonyl halides:

$$Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4X_2 + CO$$
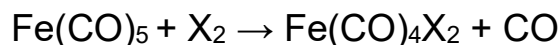
Metal-metal bonds are cleaved by halogens. Depending on the electron-counting scheme used, this can be regarded as oxidation of the metal atom:

$$Mn_2(CO)_{10} + Cl_2 \rightarrow 2\ Mn(CO)_5Cl$$
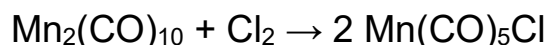
Structure and bonding:

Carbon monoxide bonds to transition metals using "synergistic π^* back-bonding.Giving rise to a partial triple bond the bonding has three components. The latter kind of binding requires that the metal have d-electrons, and that the metal is in a relatively low oxidation state (<+2) which makes the back donation process favorable. As electrons from the metal fill the π-antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened.

Infrared spectroscopy is a sensitive probe for the presence of bridging carbonyl ligands. For compounds with doubly bridging CO ligands, denoted $\mu2$-CO or often just μ-CO, vCO, vCO is usually shifted by $100-200\ cm^{-1}$ to lower energy compared to the signatures of terminal CO, i.e. in the region $1800\ cm^{-1}$. Bands for face capping ($\mu3$) CO ligands appear at even lower energies. In addition to symmetrical bridging modes, CO can be found bridge unsymmetrically or through donation from a metal d orbital to the π^* orbital of CO. The increased π-bonding due to back-donation from multiple metal centers results in further weakening of the C-O bond.

Compound:

Most metal carbonyl complexes contain a mixture of ligands. Examples include the historically important $IrCl(CO)(P(C_6H_5)_3)_2$ and the anti-knock agent $(CH_3C_5H_4)Mn(CO)_3$. The formula of many metal carbonyls can be inferred from the 18 electron rule.

PHYSICAL PROPERTIES:
State:

Majority of the metallic carbonyls are liquids or volatile solids.

Colour:

Most of the mononuclear carbonyls are colourless to pale yellow. Polynuclear carbonyls exhibit are dark in colour.

Solubility:

Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.

Toxicity:

Nickel tetracarbonyl exhibits strongest inhalation toxicity. These compounds are carcinogenic over long-term exposure.Due to low melting points and poor thermal stability, they show toxicity related to the corresponding metal and carbon monoxide. Exposure to these compounds can cause damage to lungs, liver, brain and kidneys.

Magnetic Property:

All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic.In case of dinuclear metal carbonyls formed by metals with odd atomic number, the unpaired electrons are utilized for the formation of metal-metal bonds.

Thermal Stability:

Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.Thermodynamic Stability:Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates. $Co_2(CO)_8$ and $Fe_2(CO)_9$ are oxidized by air at room temperature while chromium and molybdenum hexacarbonyls are oxidized in air when heated.

CHEMICAL PROPERTIES:

The metal carbonyls give a variety of chemical reactions.

Ligand substitution reactions:

Substitution of carbon monoxide ligand by various mono dentate and bidentate ligands can be carried out using thermal and photochemical reactions. Monodentate ligands like isocyanides(CNR), cyanide (CN-), phosphine (PR_3) and ethers can partially or completely replace the carbonyl group.

$Fe (CO)_5 + 2CNR \rightarrow Fe(CO)_3(CNR)_2 + 2CO$
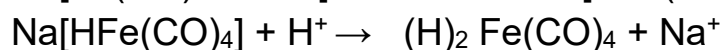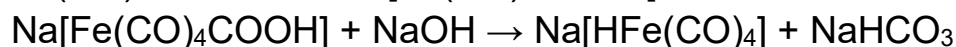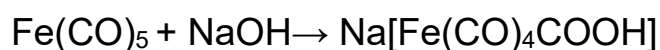
$Ni(CO)_4 + 4CNR \rightarrow Ni(CNR)_4 + 4CO$
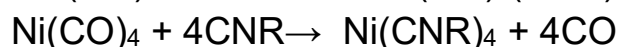
Reaction with metallic sodium:

Metallic sodium and its amalgam can be used to reduce the metal carbonyls.

$Cr(CO)_6 + 2 Na \rightarrow Na_2 [Cr(CO)_5] + CO$

$Mn_2 (CO)_{10} + 2 Na \rightarrow 2 Na[Mn(CO)_5] + CO$
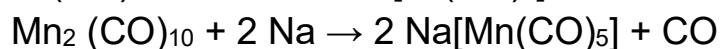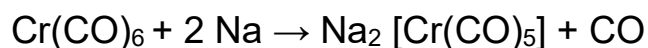
In the above two reactions, the Cr and Mn atoms in their zero oxidation states are reduced to -2 and -1 oxidation states respectively.

Reaction with sodium hydroxide:

The reaction of sodium hydroxide with metal carbonyls results in nucleophilic attack by hydroxide ion on the carbonyl group to give a metal carboxylic acid complex. Upon further action with sodium hydroxide, the carboxylic acid gives up carbon dioxide to form a hydrido anion. The protonation of this anion results in the formation of iron tetracarbonyl hydride as shown below:

$Fe(CO)_5 + NaOH \rightarrow Na[Fe(CO)_4COOH]$

$Na[Fe(CO)_4COOH] + NaOH \rightarrow Na[HFe(CO)_4] + NaHCO_3$

$Na[HFe(CO)_4] + H^+ \rightarrow (H)_2 Fe(CO)_4 + Na^+$

The above reaction is known as Heiber base reaction.

Reaction with halogens:

Most of the metal carbonyls react with halogens to give carbonyl halides.

$Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4 X_2 + CO$

$Mo(CO)_6 + Cl_2 \rightarrow Mo(CO)_4 Cl_2 + 2CO$
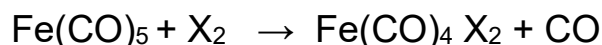
Reaction with hydrogen:

Some of the carbonyls can be reduced by hydrogen to give carbonyl hydrides

$Co_2(CO)_8 + H_2 \rightarrow 2[Co(CO)_4H]$ At. 165^0C, 200 atm

$Mn_2(CO)_{10} + H_2 \rightarrow 2[Mn(CO)_5H]$ At.   200 atm
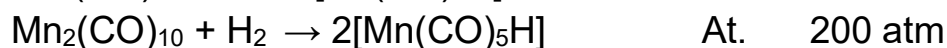
Reaction with nitric oxide:

A good number of metal carbonyls react with nitric oxide to give carbonyl nitrosyls.

$Fe(CO)_5 + 2NO \rightarrow Fe(CO)_2(NO)_2 + 3CO$ At. 95^0C

$Co_2(CO)_8 + 2NO \rightarrow 2Co(CO)_3(NO) + 2CO$ At. 40^0C
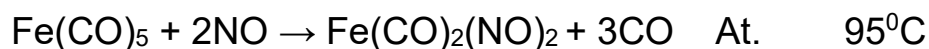
The reaction between iron pentacarbonyl and nitric oxide involves replacement of three carbonyl groups by two nitric oxide molecules. Electronically, this is equivalent as nitric oxide is a three electron donor ligand whereas carbon monoxide is a two electron donor.

Analytical characterization:

Apart from X-ray crystallography, important analytical techniques for the characterization of metal carbonyls are infrared spectroscopy and 13C-NMR spectroscopy. Infrared active vibrational modes, such as CO-stretching vibrations are often fast compared to intramolecular processes, whereas NMR transitions occur at lower frequencies and thus sample structures on a time scale that, it turns out, is comparable to the rate of intramolecular ligand exchange processes.

Iron pentacarbonyl Iron pentacarbonyl exhibits only a single 13C-NMR signal owing to rapid exchange of the axial and equatorial CO ligands by Berry pseudorotation.

Infrared spectra:

An important technique for characterizing metal carbonyls is infrared spectroscopy. The C-O vibration, typically denoted vCO, occurs at 2143

cm^{-1} for CO gas. The energies of the vCO band for the metal carbonyls correlates with the strength of the carbon-oxygen bond, and inversely correlated with the strength of the π-backbonding between the metal and the carbon.

The number of observable IR transitions (but not the energies) can thus be predicted. For example, the CO ligands of octahedral complexes, e.g. $Cr(CO)_6$, transform as a1g, eg, and t1u, but only the t1u mode (anti-symmetric stretch of the apical carbonyl ligands) is IR-allowed. Spectra for complexes of lower symmetry are more complex. For example, the IR spectrum of $Fe_2(CO)_9$ displays CO bands at 2082, 2019, 1829 cm^{-1}. The number of IR-observable vibrational modes for some metal carbonyls.

Nuclear magnetic resonance spectroscopy:

Metal carbonyls are often characterized by 13C NMR spectroscopy. To improve the sensitivity of this technique, complexes are often enriched 13CO. Typical chemical shift range for terminally bound ligands is 150 to 220 ppm. Bridging ligands resonate between 230 and 280 ppm. The 13C signals shift toward higher fields with an increasing atomic number of the central metal.

The activation energy of ligand exchanges processes can be determined by the temperature dependence of the line broadening.

Mass spectrometry:

Mass spectrometry provides information about the structure and composition of the complexes. Spectra for metal polycarbonyls are often easily interpretable, because the dominant fragmentation process is the loss of carbonyl ligands (m/z= 28).

$$M(CO)_n^+ \rightarrow M(CO)_{n-1} + CO$$
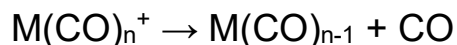
Electron ionization is the most common technique for characterizing the neutral metal carbonyls. Neutral metal carbonyls can be converted to charged species by derivatization, which enables the use of electrospray ionization, instrumentation for which is often widely available. For example,

treatment of a metal carbonyl with alkoxide generates an anionic metallaformate that is amenable to analysis by ESI-MS;

$$L_nM(CO) + RO^- \rightarrow [L_nM-C(=O)OR]^-$$
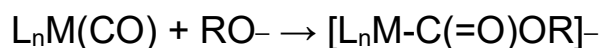
Some metal carbonyls react with azide to give isocyanato complexes with release of nitrogen. By adjusting the cone voltage and/or temperature, the degree of fragmentation can be controlled. The molar mass of the parent complex can be determined, as well as information about structural rearrangements involving loss of carbonyl ligands under ESI-MS conditions.

Mass spectrometry combined with infrared photodissociation spectroscopy can provide vibrational informations for ionic carbonyl complexes in gas phase.

Applications:

Metallurgical uses:

Metal carbonyls are used in several industrial processes. Perhaps the earliest application was the extraction and purification of nickel via nickel tetracarbonyl by the Mond process (see also carbonyl metallurgy).

Carbonyl iron is used inter alia for the preparation of inductors, pigments, as dietary supplements, in the production of radar-absorbing materials in the stealth technology, and in thermal spraying.

Catalysis:

Metal carbonyls are used in a number of industrially important carbonylation reactions. In the oxo process, an olefin, dihydrogen, and carbon monoxide react together with a catalyst (e.g. dicobalt octacarbonyl) to give aldehydes. Illustrative is the production of butyraldehyde;

$$H_2 + CO + CH_3CH=CH_2 \rightarrow CH_3CH_2CH_2CHO$$
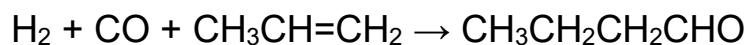
Butyraldehyde is converted on an industrial scale to 2-ethylhexanol, a precursor to PVC plasticizers, by aldol condensation, followed by hydrogenation of the resulting hydroxyaldehyde. The "oxo aldehydes"

resulting from hydroformylation are used for large-scale synthesis of fatty alcohols.

Hydroformulation mechanism:

Another important reaction catalyzed by metal carbonyls is the hydrocarboxylation. The example below is for the synthesis of acrylic acid and acrylic acid esters.

Hydrocarboxylation of acetylene with an alcohol:

Also the cyclization of acetylene to cyclooctatetraene uses metal carbonyl catalysts;

In the Monsanto and Cativa processes, acetic acid is produced from methanol, carbon monoxide, and water using hydrogen iodide as well as rhodium and iridium carbonyl catalysts, respectively. Related carbonylation reactions afford acetic anhydride.

CO-releasing molecules (CO-RMs):

Carbon monoxide-releasing molecules are metal carbonyl complexes that are being developed as potential drugs to release CO. At low concentrations, CO functions as a vasodilatory and an anti-inflammatory agent. CO-RMs have been conceived as a pharmacological strategic approach to carry and deliver controlled amounts of CO to tissues and organs.

Application

Metal carbonyl complexes are of great interest last 10 years and many people studies have been done on these molecules. The successful development on the metal carbonyl and their products has demonstrated by the various examples of the recent literature. The metal carbonyl complexes are usually stabilized by the metal centers in the low oxidation states. Metal carbonyls are used in a number of industrially important carbonylation reactions.