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Metal Carbonyls-Structure and Functions

Dr. Dinesh Chandra Sharma

Department of Chemistry, SCRS Government College, Sawai Madhopur, Rajasthan, India

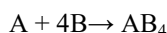
ABSTRACT: Till now, we have come across many complex compounds that contain carbonyl ligands only. These compounds are better termed as homoleptic carbonyls or metal carbonyls. Most of the transition metals are known to form homoleptic carbonyls or metal carbonyls which have simple, well-defined structures. For example tetrahedral, octahedral etc. In a metal carbonyl, the metal-carbon bond possesses both the σ and π character. The bond between the carbonyl molecule and the metal is further strengthened by the synergic effect produced by the metal-ligand bond. The two types of bonding that exist in metal carbonyls are explained below:

Structure of Metal Carbonyls:

- Due to the donation of electrons by the carbonyl molecules to the vacant orbitals of the metal, a metal-carbon σ bond is formed.
- Due to the donation of a pair of electrons from a filled d orbital metal into the vacant anti-bonding π^* orbital of carbonyl ligand, a metal-carbon π bond is formed.

Stability of Coordination Compounds:

Coordination compounds are found to dissociate in various solutions. The stability of a coordination compound in a solution mainly depends on the degree of association between the two species involved in the state of equilibrium. Quantitatively the stability of any complex is given by the magnitude of the equilibrium constant for the formation of the compound. A general example is given below:



Thus, the amount of AB_4 molecule in the solution depends upon the value of the equilibrium constant, k . This is also known as the stability constant. On the other hand, the instability constant or the dissociation constant of complexes is given by the reciprocal of the equilibrium constant of the formation reaction.

I. INTRODUCTION

In 1884, Ludwig Mond observed that the nickel valves were being eaten away by CO gas in a nickel refining industry. He heated nickel powder in a stream of CO gas to synthesize the first known metal carbonyl compound in the form of $Ni(CO)_4$.

The Mond refining process was thus born in which he proposed that the volatile $Ni(CO)_4$ compound can be decomposed to pure metal at elevated temperature. In this article, we will provide detailed information on Metal Carbonyls. This article will also discuss uses of metal carbonyls, transition metal carbonyls, synergic bond in metal carbonyls, bonding in metal carbonyls and example of metal carbonyls.

Metal carbonyl, any coordination or complex compound consisting of a heavy metal such as nickel, cobalt, or iron surrounded by carbonyl (CO) groups. Some common metal carbonyls include: tetracarbonylnickel $Ni(CO)_4$, pentacarbonyliron $Fe(CO)_5$, and octacarbonyldicobalt $Co_2(CO)_8$. In general, the metal carbonyls are produced by direct action of carbon monoxide on the finely divided metal. They are used in the preparation of metals of exceptionally high purity and as catalysts in organic syntheses.

The electronic structures of most metal carbonyls containing one metal atom per molecule (mononuclear carbonyls) bear striking resemblances to those of the noble-gas elements. For example, tetracarbonylnickel has 36 electrons (28 from the nickel atom and 8 electrons from the 4 carbonyl groups) surrounding the nickel nucleus. This number, called the effective atomic number (EAN), is also the total number of electrons in the noble-gas element krypton.

Metal carbonyls are important class of organometallic compounds that have been studied for a long time. Way back in 1884, Ludwig Mond, upon observing that the nickel valves were being eaten away by CO gas in a nickel refining industry, heated nickel powder in a stream of CO gas to synthesize the first known metal carbonyl compound in the form $\text{Ni}(\text{CO})_4$. The famous Mond refining process was thus born, grounded on the premise that the volatile $\text{Ni}(\text{CO})_4$ compound can be decomposed to pure metal at elevated temperature. Mond subsequently founded the Mond Nickel Company Limited for purifying nickel from its ore using this method.[1,2,3]

The carbonyl ligand (CO) distinguishes itself from other ligands in many respects. For example, unlike the alkyl ligands, the carbonyl (CO) ligand is unsaturated thus allowing not only the ligand to σ -donate but also to accept electrons in its π^* orbital from d_π metal orbitals and thereby making the CO ligand π -acidic. The other difference lies in the fact that CO is a soft ligand compared to the other common σ - and π -basic ligands like H_2O or the alkoxides (RO^-), which are considered as hard ligands.

Being π -acidic in nature, CO is a strong field ligand that achieves greater d-orbital splitting through the metal to ligand π -back donation. A metal-CO bonding interaction thus comprises of a CO to metal σ -donation and a metal to CO π -back donation (Figure 8.1.18.1.1). Interestingly enough, both the spectroscopic measurements and the theoretical studies suggest that the extent of the metal to CO π -back donation is almost equal to or even greater than the extent of the CO to metal σ -donation in metal carbonyl complexes. This observation is in agreement with the fact that low valent-transition metal centers tend to form metal carbonyl complexes.

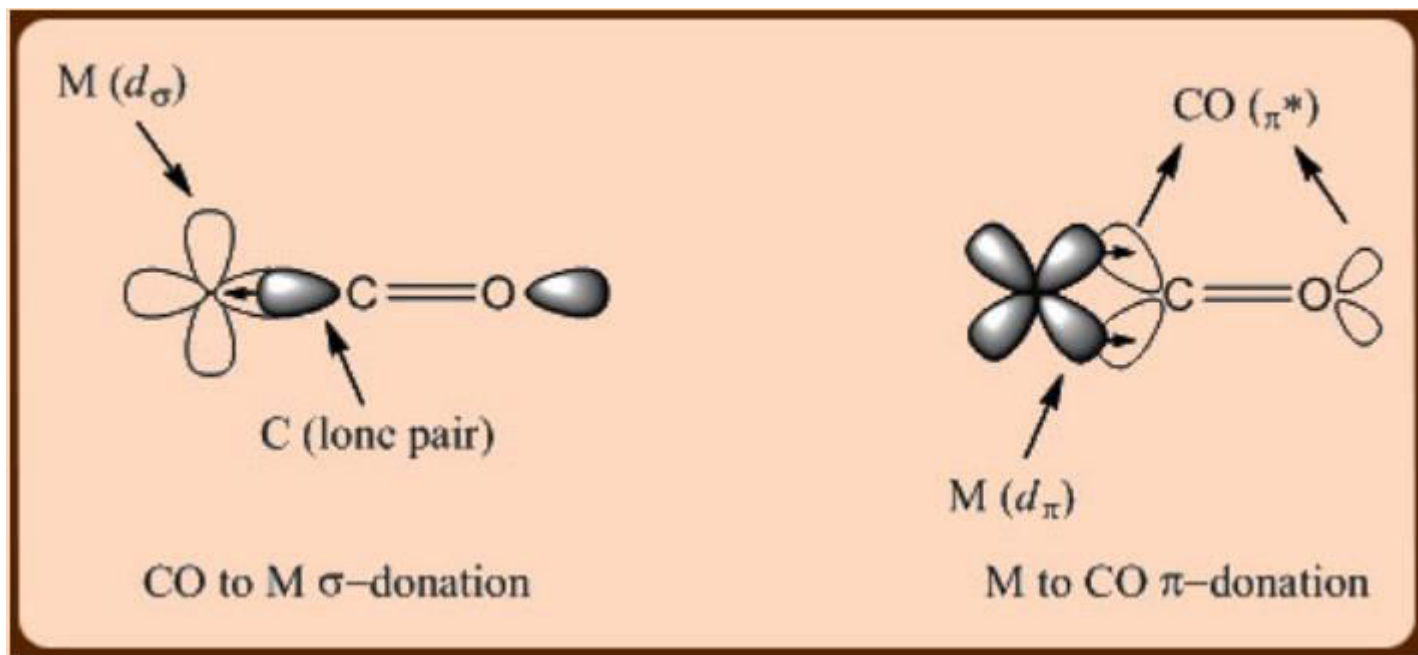


Figure : Orbital diagram showing ligand to metal forward σ -donation and the metal to ligand backward π -donation in metal-CO interaction.[5,7,8]

In the metal carbonyl complexes, the direct bearing of the π -back donation is observed on the M-C bond distance that becomes shorter as compared to that of a normal M-C single bond distance. For example, the $\text{CpMo}(\text{CO})_3\text{CH}_3$ complex, exhibits two kind of M-C bond distances that comprise of a longer Mo- CH_3 distance (2.38 Å) and a much shorter Mo-CO distance (1.99 Å) arising out of a metal to ligand π -back donation. It becomes thus apparent that the metal-CO interaction can be easily characterized using X-ray crystallography. The infrared spectroscopy can also be equally successfully employed in studying the metal-CO interaction. Since the metal to CO π -back bonding involves a π -donation from the metal d_π orbital to a π^* orbital of a C-O bond, significant shift of the $\nu(\text{CO})$ stretching frequency towards the lower energy is observed in metal carbonyl complexes with respect to that of free CO (2143 cm^{-1}).

Preparation of metal carbonyl complexes

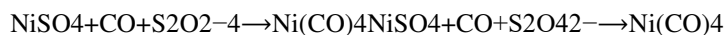
The common methods of the preparation of the metal carbonyl compounds are,

i. Directly using CO



The main requirement of this method is that the metal center must be in a reduced low oxidation state in order to facilitate CO binding to the metal center through metal to ligand π -back donation.

ii. Using CO and a reducing agent[9,10,11]



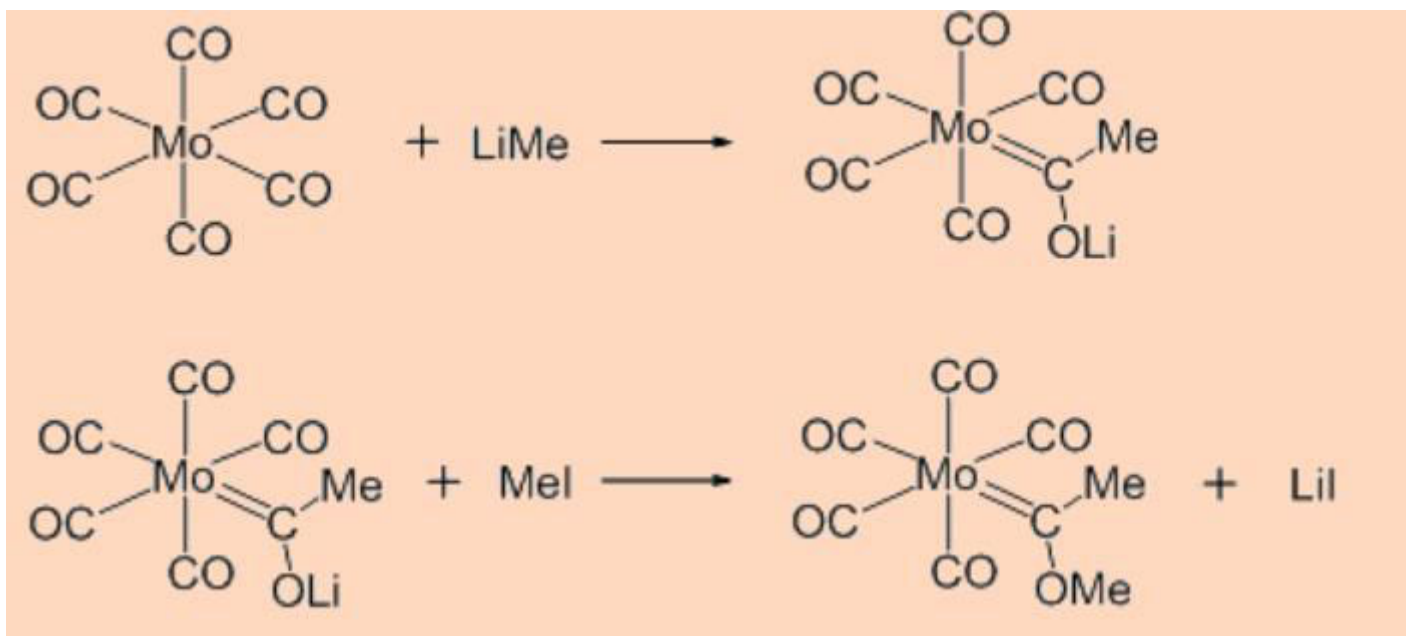
This method is commonly called reductive carbonylation and is mainly used for the compounds having higher oxidation state metal centers. The reducing agent first reduces the metal center to a lower oxidation state prior to the binding of CO to form the metal carbonyl compounds.

iii. From carbonyl compounds

This method involves abstraction of CO from organic compounds like the alcohols, aldehydes and CO₂.

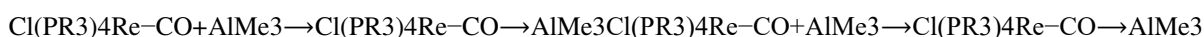
Reactivities of metal carbonyls

i. Nucleophilic attack on carbon

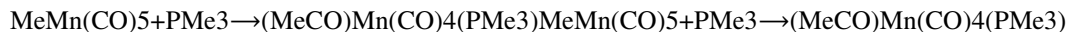


The reaction usually gives rise to carbene moiety.

ii. Electrophilic attack at oxygen



iii. Migratory insertion reaction



The metal carbonyl displays two kinds of bindings in the form of the terminal and the bridging modes. The infrared spectroscopy can easily distinguish between these two binding modes of the metal carbonyl moiety as the terminal ones show $\nu(\text{CO})$ stretching band at ca. $2100\text{--}2000\text{ cm}^{-1}$ while the bridging ones appear in the range $1720\text{--}1850\text{ cm}^{-1}$. [12,13,15]

II. DISCUSSION

The carbonyl moiety can bridge between more than two metal centers

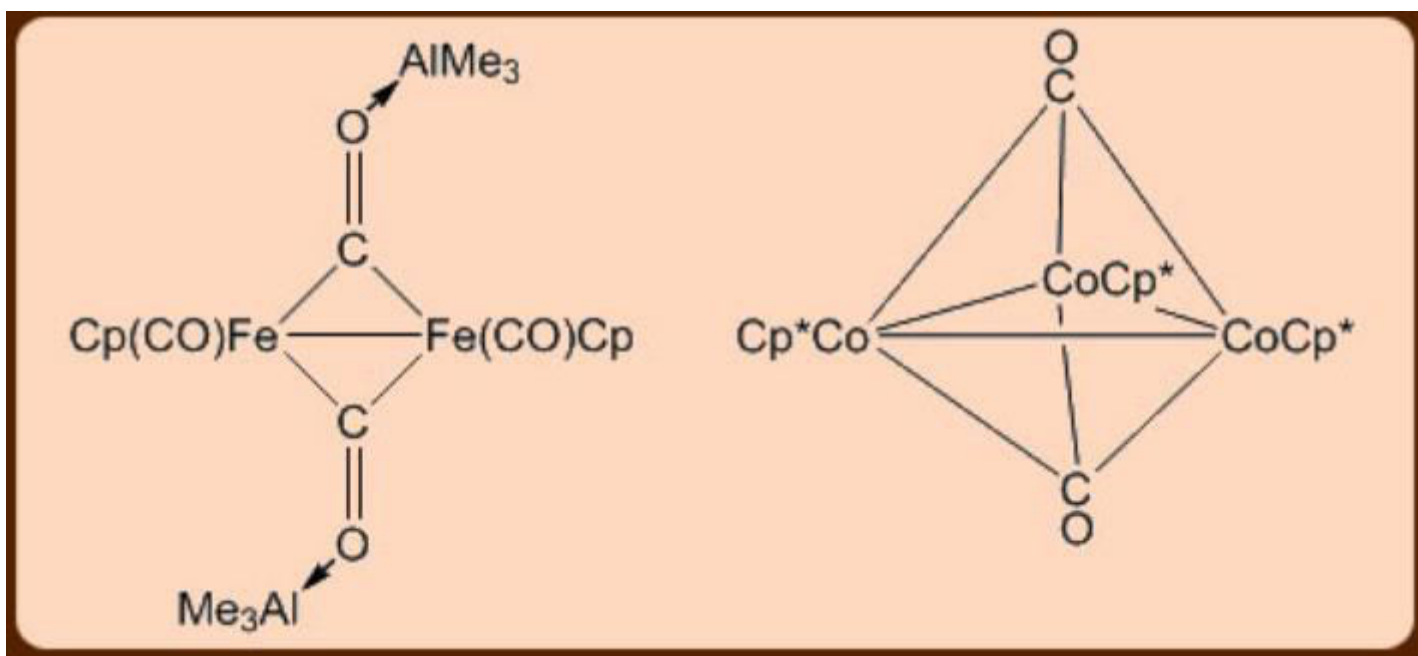


Figure : Different bridging modes of the carbonyl binding to a metal is shown.

The history of metal carbonyls goes back to 1834 when Justus von Liebig attempted initial experiments on the reaction of carbon monoxide with metals. However, it was demonstrated later that the compound he claimed to be potassium carbonyl was not a metal carbonyl at all. After the synthesis of $[\text{PtCl}_2(\text{CO})_2]$ and $[\text{PtCl}_2(\text{CO})]_2$ was reported by Schutzenberger (1868), followed by $[\text{Ni}(\text{CO})_4]$, reported by Mond (1890), Hieber prepared numerous compounds containing metal and carbon monoxide [1].

Compounds with at least one bond between carbon and metal are known as organometallic compounds [2]. Very strictly speaking, the carbon in organometallic compounds should be organic. Metal carbonyls are the transition metal complexes of carbon monoxide, containing a metal-carbon bond. These metal-carbon bonded complexes are such important players of organometallic chemistry that it cannot afford to keep the metal carbonyls out of the team just because of the definition. The metal carbonyls offer a very facile route to the synthesis of many other organometallic compounds.

A lone pair of electrons are available on both carbon and oxygen atoms of a carbon monoxide ligand. However, as the carbon atoms donate electrons to the metal, these complexes are named carbonyls. A variety of such complexes, such as mononuclear, polynuclear, homoleptic and mixed ligands, are known. These compounds are widely studied due to their ability to release carbon monoxide [3], their industrial importance, their catalytic properties [4] and their structural interest [5]. Carbon monoxide is one of the most important π -acceptor ligands. Because of its π -acidity, carbon monoxide can stabilize the zero formal oxidation state of metals in carbonyl complexes. [17,18,19]

III. RESULTS

Metal carbonyls absorb strongly at 2170–1700 cm^{-1} .⁵³ When the carbon of the carbon monoxide is associated with only one metal, absorption usually occurs at 2170–1900 cm^{-1} . The CO frequency shows variation with the number and availability of electrons in the rest of the molecule. The CO frequency and bond order are lowered when the ligand is an electron donor. In complexes with strong electron donors the frequency may fall below 1900 cm^{-1} .

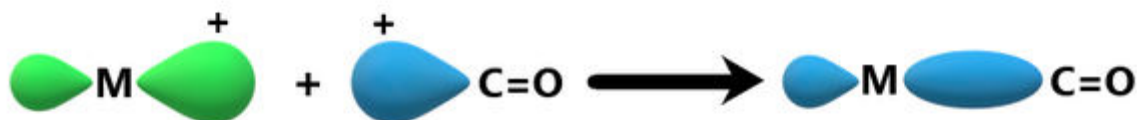
Bridging carbonyl compounds, where the carbon is associated with two metal atoms, usually absorb at 1900–1700 cm^{-1} .⁵³

Metal carbonyl compounds can generally be used as valid precursors in the preparation of metallic nanoparticles. Moreover, when they possess a mixed metal composition, a retention of their atomic ratio may be envisaged, as carbonyl clusters are molecular compounds of specific composition. For instance, in 2006, THF solutions of the already known homoleptic $[\text{Co}_3\text{Ru}(\text{CO})_{12}]^{4-}$ ⁴⁶ have been deposited into mesoporous silica matrixes via impregnation techniques,⁴⁷ and subsequently thermally decomposed to obtain bimetallic nanoparticles.⁴⁸ The already low oxidation states of the metals in the carbonyl cluster precursor are essential to avoid further reducing atmosphere during the thermal treatment. Notably, while the pure unsupported $[\text{Co}_3\text{Ru}(\text{CO})_{12}]^{4-}$ cluster starts to degrade at 150 °C and it is fully decomposed at 220 °C, when it is incorporated inside mesoporous silica its stability is significantly enhanced, as the full degradation temperature raises by over 100 °C. The obtaining of bimetallic nanoparticles was confirmed by magnetic measurements. In fact, the $[\text{Co}_3\text{Ru}(\text{CO})_{12}]^{4-}$ species is diamagnetic, however a rapid increase of magnetization was observed after decomposition, consistent with the formation of the ferromagnetic Co_3Ru nanoparticles. However, segregated Co and Ru nanoparticles were observed before formation of the final alloy with the same composition as the original cluster. Metal–carbonyl compounds that release carbon monoxide in a controlled manner have been shown to exert some interesting therapeutic effects.¹¹⁰ Carbon monoxide-releasing molecules can induce blood vessel dilation, and act as cardio- and cytoprotectants. Carbon monoxide is naturally generated in living organisms and has been shown to induce vasodilation, and possess anti-inflammatory and antiapoptotic properties. Several carbon monoxide-releasing molecules, based on metals such as manganese, iron, cobalt, nickel, and ruthenium, have been studied.[20,21,22]

IV. CONCLUSIONS

Bonding in Metal Carbonyl is achieved by the formation of both σ and π bonds. Thus the formation of metal carbonyl consists of two steps:

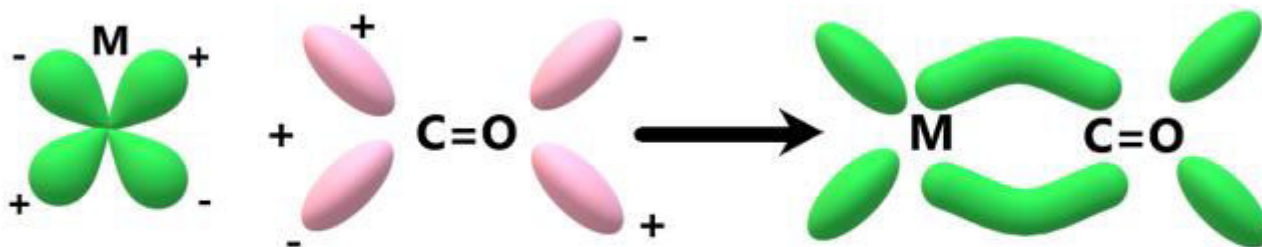
- Formation of bond: This bond is formed due to the donation of electrons by the carbonyl molecules in the vacant orbitals of the metal. This results in the overlap of the non-bonding orbitals of the Carbon atom with the vacant orbitals of the metal atom.



Formation of σ bond

- Formation of bond due to back bonding: This bond is formed due to the donation of pair of electrons from the filled d-orbitals of the metal atom to the vacant π^* (π antibonding) orbitals of the Carbonyl ligand or

molecule. As electrons from the metal fill the π -antibonding orbital of CO, they then weaken the carbon-oxygen bond compared with the free carbon monoxide, while the metal-carbon bond is strengthened. This bond is formed due to back bonding as the metal atom donates a pair of electrons from its filled d-orbitals to the empty π -antibonding orbitals of the CO ligand. This type of bonding is also known as synergic bonding.

Formation of π bond

Bonding in Metal Carbonyls

The carbon monoxide ligand is a unique ligand which is different from other ligands. The bond between transition metals and metal carbonyls is achieved by “synergistic π star back-bonding.” The bonding is partially similar to the triple bond. The carbonyl (CO) ligand is unsaturated, i.e. it not only donates electrons to form σ -bond but also accepts electrons in its π^* orbital from d_{π} metal orbitals. Thus the CO ligand behaves as an acidic ligand.

Properties of Metal Carbonyls

The important properties of metal carbonyls are discussed below in the article:

- Metal carbonyls exist as solids at standard temperature and pressure i.e. at room temperature and standard atmospheric pressure (STP).
- They are toxic in nature and can be fatal if inhaled as the carbonyl ion in the metal carbonyl binds with the haemoglobin in the blood to form carboxyhaemoglobin which hinders the oxygen binding capacity of haemoglobin in the blood cells.
- They are volatile in nature as they have low melting points.
- They are soluble in both polar and non-polar solvents.
- On heating, they decompose to the respective metal and carbon monoxide.
- Both metal and Carbonyl ions are responsible for the reactivity of the metal carbonyls.
- They are carcinogenic in nature.

Types of Metal Carbonyls

Metal carbonyls can be classified into various types:

Based on Types of Ligands

- Homoleptic Metal Carbonyls: In homoleptic carbonyls, only one type of ligands i.e. CO ligands are present. They are represented using the general formula $M_x(CO)_y$
- Heteroleptic Metal Carbonyls: Heteroleptic carbonyls contain CO ligands along with other types of ligands such as -Cl, -Br, -I, etc. They are represented using the $M_xL_m(CO)_y$ general formula.

Based on The Number of Metal Centres Involved in Forming The Complex

- Mononuclear metal carbonyl: These metal carbonyls have only one metal centre. The general formula of mononuclear metal carbonyls is $M(CO)_x$
- Polynuclear metal carbonyl: These metal carbonyls have two or more metal centres. The general formula of mononuclear metal carbonyls is $M_xN_y(CO)_z$

Uses of Metal Carbonyls

- Nickel carbonyl is used to produce pure Nickel using the Mond process.
- Iron carbonyls are used to prepare dietary supplements.

- They are used in organic synthesis and as catalysts.
- They are being used as drugs to release CO.
- They are also used to create aldehydes.

Metal Carbonyls Organometallics

These compounds have at least one metal-carbon bond and the carbon atom is a part of an organic group. Some common examples of organometallics are Grignard Reagent – RMgX, Gilman Reagent – R₂CuLi, Dimethylmagnesium – Me₂Mg, Triethylborane – Et₃B, Ferrocene, Cobaltocene. These compounds are very important in the field of chemistry.

Properties of Organometallics

The properties of Organometallic compounds are:

- Most of them exist in a solid state.
- Some of them may be present in both liquid and gaseous states.
- Organometallics formed by electropositive elements such as lithium, aluminium can be flammable in nature.
- They are very toxic and volatile in nature.
- They are not soluble in water but in ethers.
- They are very reactive in nature.
- They have high electronegativity.

Uses of Organometallics

The uses of Organometallic compounds are:

- They are used as reagents in organic reactions.
- They are used in the treatment of syphilis.
- Grignard reagent which is an organometallic is widely used in organic chemistry.
- Cis-Platin is used as an anti-cancer drug.
- They are used as additives.[21,22]

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