COORDINATION COMPOUNDS

BONDING IN METAL CARBONYLS

❖ ORGANO METALLIC COMPOUNDS

Introduction

Organometallic compounds are characterized by the direct bonding of carbon atoms from organic groups, typically alkyl or aryl, to metal atoms. Additionally, compounds featuring elements like boron, phosphorus, silicon, germanium, and antimony bonded to organic groups are also considered organometallic. Numerous organometallic compounds serve as significant reagents in the synthesis of organic compounds.

Classification of Organometallic Compounds

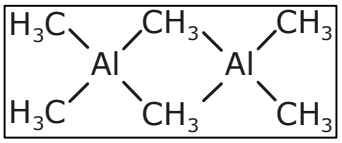
Organometallic compounds are classified in three classes.

(i) **Sigma bonded organometallic compounds:** In these complexes, a sigma bond connects the metal atom and the carbon atom of the ligand.

For Examples:

(a) Grignard reagents, R – Mg – X where R is an alkyl or aryl group and X is a halogen.

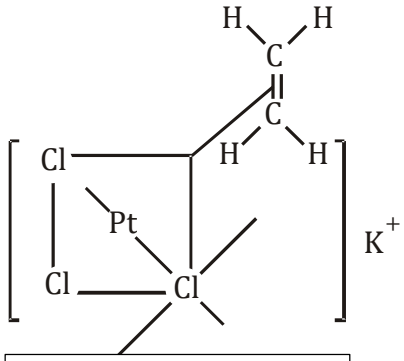
(b) Zinc compounds of the formula R_2Zn such as $(C_2H_5)_2Zn$. (Isolated by Frankland). Other similar compound is $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$, $Pb(CH_3)_4$ etc.



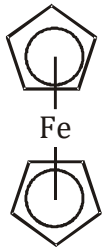
$Al_2(CH_3)_6$ is a dimeric compound and has a structure similar to diborane, (B_2H_6). It is an electron deficient compound and two methyl groups act as bridges between two aluminum atoms.

(ii) **Pi-bonded organometallic compounds:** These are compounds formed by metals and alkenes, alkynes, benzene, and other ring compounds. In such complexes, a bond is established between the metal and ligand, involving the π-electrons of the ligand.

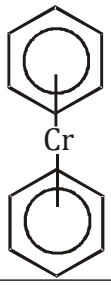
Three notable examples include Zeise's salt, ferrocene, and benzene chromium. These are shown below.



Zeise's Salt
$K\{PtCl_3(\eta^2 - C_2H_4)\}$



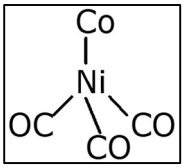
Ferrocene
$Fe(\eta^5 - C_5H_5)_2$



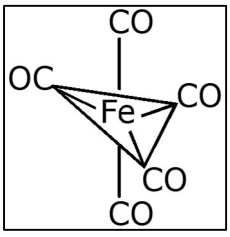
Dibenzene chromium
$Cr(\eta^6 - C_6H_6)_2$

The indication of the number of carbon atoms bonded to the metal in these compounds is denoted by the Greek letter η (eta) followed by a numerical value. The prefixes η^2, η^5, and η^6 signify that the compound has 2, 5, and 6 carbon atoms bonded to the metal, respectively.

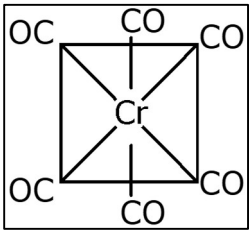
(iii) **Sigma and Pi bonded organometallic compounds:** Belonging to this category are metal carbonyl compounds, which are created through the interaction of metal and carbon monoxide. These compounds exhibit both σ- and π-bonding. Typically, the oxidation state of metal atoms in these compounds is zero. Carbonyls can exist as mononuclear, bridged, or polynuclear entities.

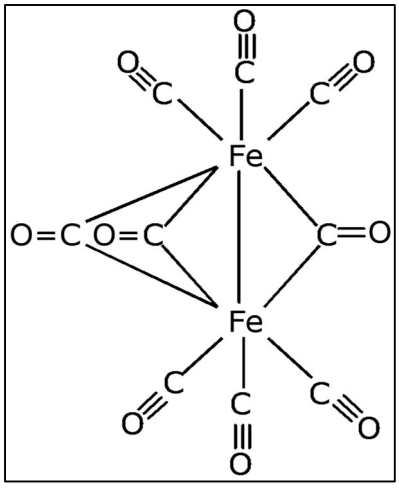


Tetracarbonyl nickel(0)
$Ni(CO)_4$



Pentacarbonyl iron(0)
$Fe(CO)_5$

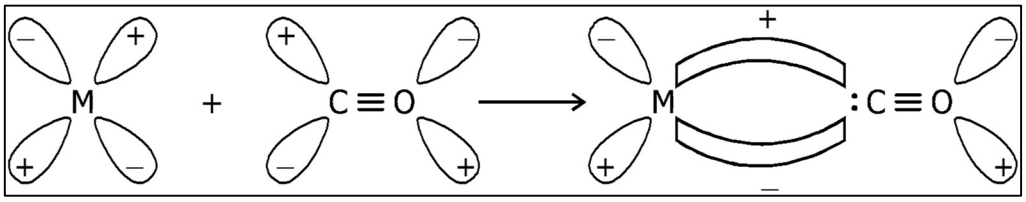




Hexacarbonyl chromium(0)
$Cr(CO)_6$

In a metal carbonyl, the bond between the metal and carbon involves both σ- and π-character. The σ-bond forms when an empty hybrid orbital of the metal atom overlaps with an orbital on the carbon atom of carbon monoxide, which contains a lone pair of electrons.

The creation of a π-bond occurs when a filled orbital of the metal atom overlaps with an empty antibonding π* orbital of the carbon atom in carbon monoxide. This overlapping process is also referred to as the back donation of electrons from the metal atom to carbon.



The π-overlap is perpendicular to the nodal plane of σ-bond.

In olefinic complexes, the electrons in the bonding π-orbital are contributed to both the vacant orbital of the metal atom and simultaneously to the back bonding p-orbital of the olefin.