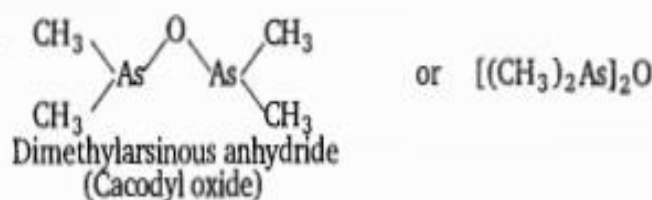


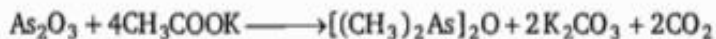
An organometallic compound is defined as one that contains at least one direct metal-carbon bond. This excludes some carbon compounds which are considered to be inorganic such as carbides, e.g., CaC_2 and cyanides e.g., NaCN . The carbon containing groups may be carbonyl, alkyl, alkene, aromatic, cyclic or heterocyclic. The various ligands that are attached to metal in organometallic compounds are summarized in Table 1.1.

There are some complexes which do not contain any $\text{M}-\text{C}$ bonds but are considered to be the members of organometallic compounds. For example, Wilkinson catalyst $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ which is used for hydrogenation of alkenes and alkynes. There is no metal-carbon bond. However, it is an organometallic compound. During catalytic cycle of hydrogenation of alkenes a stage comes when alkene is attached to the metal and forms metal-carbon bond. Due to this reason it is a member of organometallic compounds. According to leading journals of organometallic compounds, the bonding interaction is ionic or covalent, localized or delocalized between at least one carbon atom of an organic group or molecule and a main group, transition, lanthanide or actinide metal atom. Exceptionally binary metal carbonyls like $\text{Ni}(\text{CO})_4$ are considered as organometallic compounds even though CO is an inorganic compound. Similarly organic derivatives of the metalloids such as boron, silicon, germanium, arsenic and tellurium are considered to be organometallic compounds.

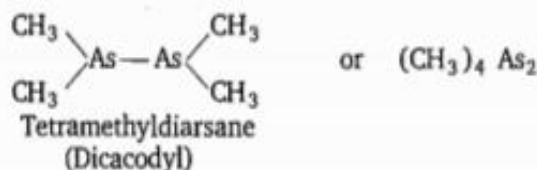
Organometallic compounds straddle both inorganic and organic chemistry. The first organometallic compound of main group elements was cacodyl oxide which has repulsive smell and is a toxic liquid.



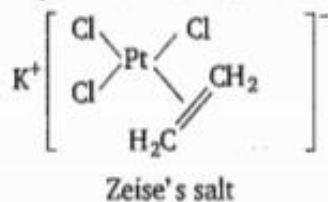
This compound was originally synthesized by heating arsenic trioxide with potassium acetate.



Dicacodyl is also considered one of the earliest organometallic compounds ever discovered. It was investigated by Edward Frankland and Robert Bunsen. It was originally made from arsenic distilled with potassium acetate.



The first organometallic compound of the transition metals was Zeise's salt, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$.



Unlike conventional transition metal complexes, the central metal atom in an organometallic compounds is often in a low oxidation state (i.e., -1, 0 or +1 or sometime + 2).

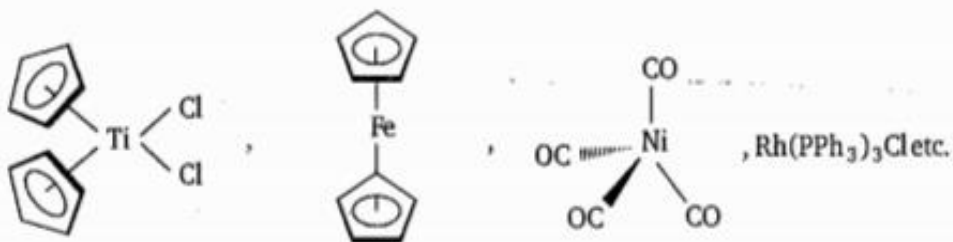
On the basis of periodic table, organometallic compounds can be classified into main group, transition metal and lanthanide/actinide organometallic compounds.

Main Group Organometallic Compounds

Examples : $\text{Na}^+\text{C}_5\text{H}_5^-$, $n\text{-BuLi}$, $\text{B}(\text{CH}_2\text{CH}_3)_3$, $\text{Li}_4(\text{CH}_3)_4$, R_4Pb ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$), RMgX ($\text{R} = \text{alkyl or aryl group, X} = \text{Cl, Br, I}$), $\text{Al}_2(\text{CH}_3)_6$ etc.

Transition Metal Organometallic Compounds :

Examples :



Organic Ligands and Nomenclature

According to IUPAC recommendation in the formulas of organometallic compounds metal is written first followed by formally anionic ligands in alphabetical order, the neutral ligands are then listed in alphabetical order based on their chemical symbol. A number of unsaturated organic ligands such as allyl, cyclopentadienyl, ethylene, benzene etc. can interact with metal in more than one mode.

Hapticity

A single organic ligand may interact with a central metal atom using one or more of its atoms simultaneously. The number of atoms in a ligand attached to the metal atom is denoted by the prefix η (the Greek letter eta) followed by a superscript indicating the number of ligand atoms attached to the metal atom. This is called hapticity. Most ligands attach through one atom only, therefore, they are called as monohapto (η^1). Cyclopentadienyl ligand, $C_5H_5^-$ or Cp, for example, can attach to metal atom through one, three or five carbon atoms. Therefore, it may act as mono (η^1)-, tri (η^3)- or pentahapto (η^5)-ligand (Fig. 1.3).

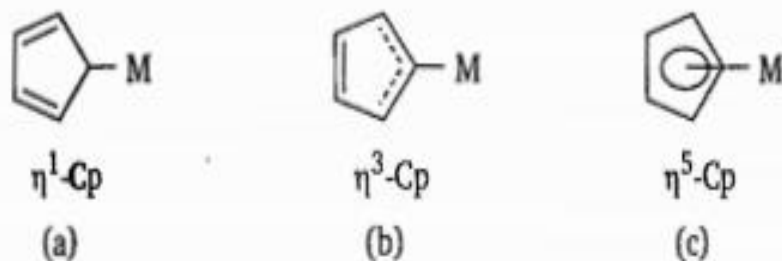


Fig. 1.3

The term hapto comes from the Greek word haptain meaning to fasten. Therefore, pentahapto means fastened in five places.

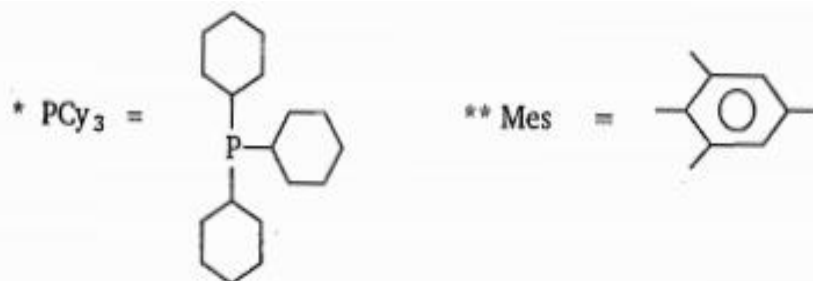
Applications of Organometallic Compounds

(1) **Organometallic Compounds as Reagents** : Some organometallic compounds especially the alkali and alkaline earth metal compounds such as *n*-BuLi, *s*-BuLi, *t*-BuLi, Grignard reagent (RMgX), Gilman's reagent (R_2CuLi) etc are used as reagents.

(2) **Organometallic Compounds as Catalysts** : The organometallic compounds are being routinely used as catalysts for the synthesis of organic compounds. Some well known organometallic homogeneous catalysts are given in Table 1.1:

Table 1.1 Homogeneous Catalysts

| Catalyst | Process |
|--|------------------------|
| $Rh(PPh_3)_3Cl$ | Hydrogenation |
| $Co_2(CO)_8$ | Hydroformylation |
| $[Rh(CO)_2I_2]^-$ | Methanol carbonylation |
| $[Ir(CO)_2I_2]^-$ | Methanol carbonylation |
| $ \begin{array}{c} PCy_3^* \\ \\ Cl \diagup Ru = \text{Ph} \\ \\ Cl \\ \\ PCy_3 \end{array} $ (Grubb's first generation catalyst) | Olefin metathesis |
| $ \begin{array}{c} Mes - N \text{---} \text{---} N - Mes^{**} \\ \\ Cl \diagup Ru = \text{Ph} \\ \\ Cl \end{array} $ (Second generation catalyst, N-heterocyclic carbene) | Olefin metathesis |



Vitamin B₁₂ (known as coenzyme B₁₂) is the only known organometallic compound in nature. It incorporates cobalt into a corrin ring and has been found to have many catalytic properties.

Organometallic Compounds as Drugs : The first organometallic compound found for anticancer activity was Cp₂TiCl₂ [Fig. 1.1(a)]. An another important organometallic compound is ferroquine (FQ) [Fig. 1.1(b)] which is used as antimalarial drug.

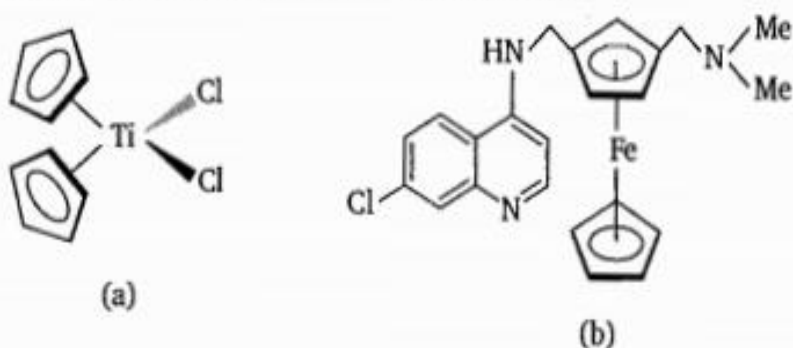


Fig. 1.1 Structure of (a) Cp₂TiCl₂ (b) Ferroquine

(3) Organometallic compounds as additives : Organometallic compounds have find applications as bulk additives for modifying the existing properties of compounds. Ferrocene is readily soluble in liquid fuels, air stable, non-toxic and usually thermally stable. Ferrocene is, therefore, added to liquid fuel to reduce carbonaceous particulate matter like soot emitted by diesel engines. The carbonaceous particulates are health hazard. Tetraethyllead [Fig. 1.2(b)] was used as antiknocking agent in the gasoline. TEL helps the gasoline to burn slowly and smoothly and prevents knocking. Combustion of TEL along with gasoline forms particles of Pb and PbO which are very harmful for health. Now, therefore methylcyclopentadienylmanganesetricarbonyl (MMT) [Fig. 1.2(c)] is used in place of TEL as anti-knocking agent.

