

⇒ Organometallic Compounds?

Those compounds in which the central metal atom is linked directly with the carbon atom of the organic ligand are called organometallic compounds or organometallics. In short, organometallics contain at least one M-C direct bond, may be ionic or covalent. The metal atom may be a main group elements (Gr. 1, 2, 13), transition metals, Lanthanides or actinides. The organic ligands may be alkyl, aryl, allyl, alkene, alkyne etc. However, organoboron, organosilicon, organo-arsenic, carbonyl, nitrosyl <sup>etc also</sup> are included in organometallics. Although carbides & cyanides, which contain M-C bonds are not organometallics. Some examples of organometallics are:

$\text{CH}_3\text{Li}$  (Methyl Lithium),  $\text{Mg}^{2+}(\text{C}_5\text{H}_5^-)_2$  (Magnesium cyclopentadienide),  $\text{Be}(\text{CH}_3)_2$  (Dimethyl beryllium),  $\text{R-C}\equiv\text{C-Na}^+$  (Sodium alkynide),  $\text{R-Mg-X}$  (Grignard reagent),  $(\eta^5\text{C}_5\text{H}_5)_2\text{Fe}$  (Ferrocene) etc.

⇒ Classification of Organometallic Compounds: Organometallic compounds may be classified in a number of ways: 1. On the basis of M-C bond nature: M-C bond may be ionic, covalent ( $\sigma$ - or  $\pi$ -bonded), electron deficient/bridged multicentred, so organometallics are classified as follows:

(i) Ionic Organometallics: The organometallic compounds formed by high electro positive metals, e.g. alkali, alkaline earth metals, lanthanides and actinides are essentially ionic. In these compounds, C-atom is negatively charged, i.e.  $\text{M}^+-\text{C}^-$  bond present. However, Li-C, Mg-C & Be-C have greater covalent character due to polarising power of cations.

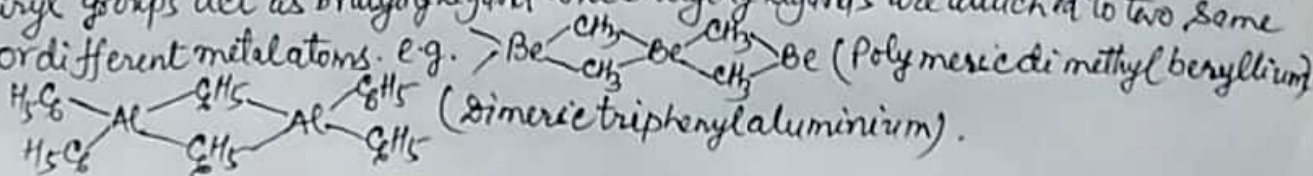
e.g.  $\text{CH}_3\text{K}$  (Methyl potassium),  $\text{C}_5\text{H}_5\text{Na}$  (Sodium cyclopentadienide),  $\text{R-Mg}^+\text{X}^-$  (alkyl magnesium halide),  $\text{R}_2\text{Zn}^{2+}\text{R}^{2-}$  (Dialkyl zinc),  $\text{R-C}\equiv\text{C-Na}^+$  (Sodium alkynide) etc.

(ii) Covalent Organometallics: The organometallic compounds which contain M-C covalent bond, may be localised or delocalised are called covalent organometallics. These may be of two types: (a)  $\sigma$ -bonded covalent organometallics: These are formed by Gr. 12, 13, 14 & 15 metals, and metal atom bonded to C-atom by  $\sigma$ -covalent bond (M-C).

e.g.  $\text{B}(\text{CH}_3)_3$  (trimethyl boron),  $\text{Si}(\text{CH}_3)_4$  (tetramethyl silicon),  $\text{Pb}(\text{C}_2\text{H}_5)_4$  (tetraethyl lead) etc.

(b)  $\pi$ -bonded organometallics: These are formed by the transition metals with unsaturated organic groups/molecules or  $\pi$  bonded ligands like alkenes (olefins), alkynes, cyclopentadiene, allenes. In these compounds, overlapping of the filled  $\pi$ -m.o of the ligand with the vacant orbital of the metal takes place, giving M- $\pi$ -C bond. e.g.  $(\eta^5\text{C}_5\text{H}_5)_2\text{Fe}$  (Ferrocene),  $\text{V}[\text{PtCl}_3(\text{H}_2\text{C}=\text{CH}_2)]$  (Zeisel's salt),  $\text{Cr}(\text{C}_6\text{H}_6)_2$  or  $\text{Cr}(\eta^5\text{-C}_6\text{H}_5)_2$  (dibenzene chromium) etc.

(c) Electron deficient Organometallics: In these organometallic compounds, alkyl or aryl groups act as bridging ligand. The bridging ligands are attached to two same or different metal atoms. e.g.





2. On the basis of hapticity (i.e. no. of bonded C-atoms): Hapticity is the number of C-atoms of an organic group/molecule which are directly bonded to the metal atom. It is denoted by symbol ' $\eta$ ' and no. of C-atoms using suitable numeral superscript. On hapticity, organometallic compds can be classified as monohapto ( $\eta^1$ ), dihapto ( $\eta^2$ ), trihapto ( $\eta^3$ ), tetrahapto ( $\eta^4$ ) ... octahapto ( $\eta^8$ ). e.g.  $[(\eta^6-C_6H_6)M(CO)_3]$  ( $M=Cr, Mo, W$ ),  $[(\eta^5-C_5H_5)_2Fe]$  (ferrocene),  $[(\eta^8-C_8H_8)_2U]$  (uranocene),  $K[PtCl_3(\eta^5-C_5H_5)]$  (Zeise salt) etc.

3. On the basis of composition: On the basis of composition, organometallic compounds are of two types: (i) simple organometallic compds (ii) mixed organometallic compounds.

(i) Simple organometallic compds: In these compounds, only hydrogen/alkyl gr. is bonded to the metal atom. e.g.  $(CH_3)_3SnH$  (trimethyltin),  $CH_3ZnCH_2CH_3$  (ethylmethylzinc) etc.

These are further divided into two types: (a) Symmetrical organometallic/organometallic compds: In these compds, only one type of alkyl gr. is present. e.g.  $(CH_3)_4Pb$ .

(b) Unsymmetrical organometallic compds: In these compds, more than one type of alkyl grs. are present. e.g.  $H_3C-Zn-CH_2CH_3$  (ethylmethylzinc).

(ii) Mixed organometallic compds: In these compounds, groups other than alkyl grs/H-atoms are also directly bonded to the metal atom. e.g.  $[(CH_3)_2SnCl_2]$  (dichlorodimethyltin),  $C_2H_5MgI$  (ethylmagnesium iodide),  $[(\eta^6-C_6H_6)Cr(CO)_3]$  etc.

→ Nomenclature of Organometallic Compds: IUPAC introduced some rules for uniformity in the nomenclature of organometallic compounds. The nomenclature rules for organometallic compounds are similar to coordination compounds.

On the basis of the nature of cation & anions of the compds, these are classified as:

(a) Cationic compounds, such as  $Na^+(\bar{C}\equiv CR)$ ,  $Mg^{2+}(C_5H_5)_2$  etc.

(b) Anionic compounds, such as  $K^+[PtCl_3(C_5H_5)]^-$  etc.

(c) Neutral compounds, such as  $(CH_3)_4Si$ ,  $[Cr(\eta^6-C_6H_6)_2]$  etc.

For naming of the organometallic compds, the following rules should be followed:

1. Cation is named first and then the anionic part as in naming a simple salt ( $M^+X^-$ )

2. Naming of ligands: In all types of organometallic compds, ligands are named first and the metal is named after.

(i) If there are two or more different kind of ligands, they are written in the alphabetical order irrespective of the charge on them.

(ii) Anionic ligands are named by replacing 'e' of 'ide', 'ate' or 'ate' of anion name by 'o'.

e.g.  $N_3^-$  (azido),  $NO_3^-$  (nitrate),  $NO_2^-$  (nitrite). Exceptions:  $F^-$  (fluoro),  $Cl^-$  (chloro),  $CN^-$  (cyano).

(iii) Neutral ligands are named as such. Some common neutral ligands give special names. viz.,  $H_2O$  (aquo),  $NH_3$  (ammine),  $CO$  (carbonyl),  $NO$  (nitrosyl) etc.

$-CH_3$  (methyl),  $-C_3H_7$  (propyl),  $-C_2H_5$  (ethyl),  $-C_4H_9$  (butyl),  $CH_2=CH-$  (vinyl or ethenyl),

$CH_2=CH-CH_2-$  (allyl),  $HC\equiv C-$  (ethynyl),  $CH_3-C\equiv C-$  (propynyl) etc.

(iv) Cationic ligands are named by using 'ium' suffix. e.g.  $H_2N^+NH_2$  (hydrazinium),

$C_7H_7^+$  (tropyllium),  $NO^+$  (nitrosylium) etc.



(3)

3. Indication of No. of ligands: The number of simple ligand is indicated by using prefixes di (for 2), tri (for 3), tetra (for 4), penta (for 5) etc. In case of polydentate ligands, prefixes bis (for 2), tris (for 3), tetrakis (for 4), pentakis (for 5), hexakis (for 6) etc. are used.

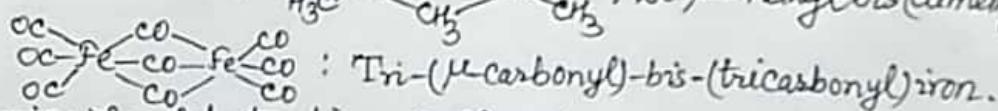
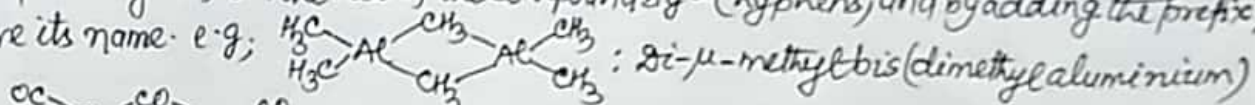
e.g.,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  - Bis( $\eta^5$ -cyclopentadienyl) iron(0).

4. Indication of hapticity: The hapticity of an organic ligand is denoted by the symbol  $\eta$  with appropriate numerical superscript to indicate the no. of C-atom attached with metal.

e.g.,  $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$  - Potassium trichloro( $\eta^2$ -ethene)platinate(II),

$[\text{C}_5\text{H}_5)_2\text{Fe}]$  - Bis( $\eta^5$ -cyclopentadienyl) iron(0),  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$  - Bis( $\eta^6$ -benzene)chromium(0)

5. Naming of bridging ligands: The bridging group/ligand is indicated in the formula by separating it from the rest of the compound by - (hyphens) and by adding the prefix ' $\mu$ ' before its name. e.g.,



6. Naming of metal atom/ion: Different rules are followed for naming different type of compounds (mononuclear).

(i) Anionic Complexes: In anionic complexes, metal ion is named by using suffix 'ate' to its name, and oxidation no. of the metal by roman numeral (I, II, ...) in the small bracket at the end of the complex. In some cases, the name of metal is derived from the Latin name as follows:

For example: Pb (Plumbate), Ag (argentate), Fe (ferrate), Au (aurate), Cu (cuprate), Sn (stannate) etc.

e.g.,  $\text{K}_3[\text{Fe}(\text{CN})_5\text{CO}]^{3-}$ : Potassium carbonylpentacyanoferrate(II)

$\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$ : Potassium trichloro( $\eta^2$ -ethene)platinate(II)

(ii) Cationic & Neutral Complexes: In cationic and neutral complexes, metal atom/ion is named in usual way followed by its oxidation no./state in small bracket.

e.g.,  $[\text{Fe}(\eta^4\text{-C}_4\text{H}_6)_2]$ : Bis( $\eta^4$ -cyclobutadienyl) iron(0),

$[\text{Co}(\text{CO})_3(\eta^7\text{-C}_7\text{H}_7)]^+$ : Tricarbonylcycloheptatrienylcobalt(III)

$[\text{PtCl}_2(\text{NH}_3)(\eta^2\text{-C}_2\text{H}_4)]^0$ : Ammine dichloro(ethene)platinum(II)

The name of organometallic compounds of p-block elements (13 to 16) may given as derivatives of their respective hydrides:

e.g.,  $[\text{B}(\text{C}_2\text{H}_5)_3]$ : Triethylborane;  $[\text{Sb}(\text{H}_2\text{C}=\text{CH})_2]$ : Divinylstibine;

$[\text{Si}(\text{CH}_3)_4]$ : Tetramethylsilane;  $[\text{Ge}(\text{CH}_3)\text{Cl}_3]$ : Methyltrichlorogermore.

$[\text{Sn}(\text{CH}_3)_2\text{HCl}]$ : Chloro(methyl)stannane;  $[\text{As}(\text{CH}_3)_3]$ : Trimethylarsine.

Exercise: Give the IUPAC names of following organometallic compounds:

(1)  $\text{K}[\text{B}(\text{C}_6\text{H}_5)_4]$  (2)  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$  (3)  $[\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_8)]$

(4)  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  (5)  $[\text{Mn}(\text{CO})_5\text{CH}_3]$