

## **ORGANOMETTALIC COMPOUNDS**

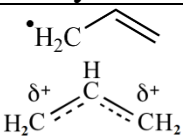
**or**

## **ORAGNO-TRANSITION METAL COMPOUNDS**

The compounds containing at least one covalent bond between a C- atom and a metal [M-C] are known as *organomettalic compounds*. In such case-

*Metal is less electronegative than C-atom.*

**Classification of ligands:** The ligands are classified on the basis of *no. electrons donated by them* in order to form organomettalic compounds. Ligands are generally classified into seven different types-

| System             | No. of electron donated | Name of group | Example  |
|--------------------|-------------------------|---------------|--|
| 1- electron system | 1                       | -yl           | alkyl  |
| 2- electron system | 2                       | alkene        | ethylene   |
| 3- electron system | 3                       | allyl         |  |
| 4- electron system | 4                       | diene         | butadiene  |
| 5- electron system | 5                       | dienyl        | cyclopentadienyl   |
| 6- electron system | 6                       | triene        | benzene  |
| 7- electron system | 7                       | trienyl       | cycloheptatrienyl  |

**Classification of organomettalic compounds:** Organomettalic compounds are classified either any one of the following basis-

1. Based on hapticity
2. Polarity M-C bonds

**1. Classification on the basis of hapticity:** (No .of C-atom attached to metal)

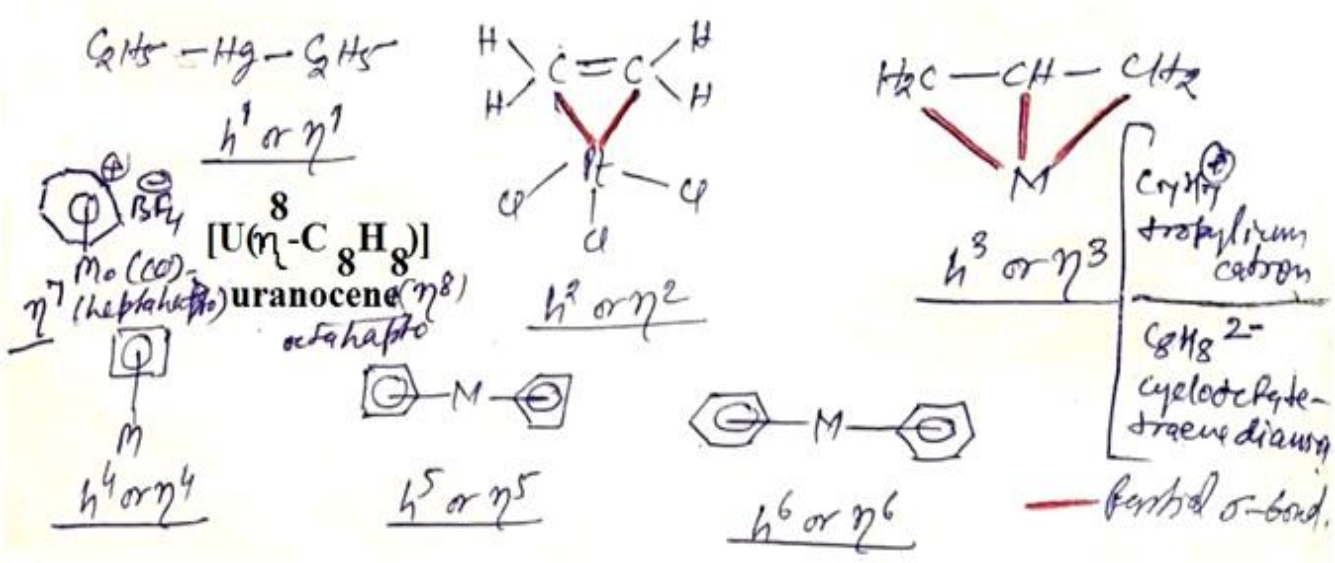
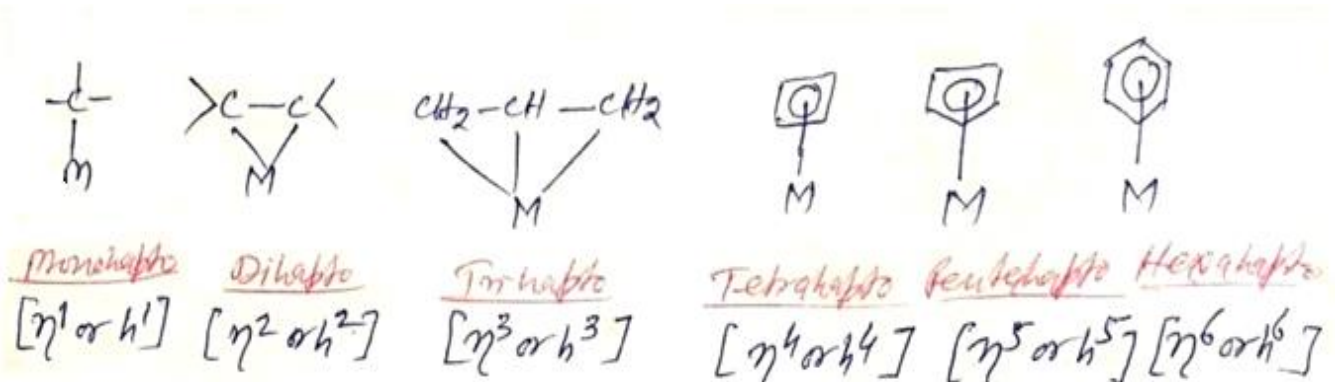
“Number of C-atoms within a bonding distance of M- atom or the no. of C-atoms through which an organic ligand is attached to central M- atom” is known as “**hapticity**” of the ligand.

The organomettalic compounds are classified on the basis of no. of C-atom attached with metal. eg. M-CH<sub>3</sub> this type of compounds are called as monohapto compounds and designated as  $\eta^1$  or h<sup>1</sup>. Similarly, if two C-atoms are attached with metal, they are known as dihapto compounds and designated as  $\eta^2$  or h<sup>2</sup>. eg. ethylene compounds.

If three C-atoms are attached with metal, they are known as trihapto compounds and designated as  $\eta^3$  or  $h^3$ . If four C-atoms are attached with metal, they are known as tetrahapto compounds and designated as  $\eta^4$  or  $h^4$ .

In cyclopentadienyl system, since 5 C-atoms are attached with metal, they are known as pentahapto compounds and designated as  $\eta^5$  or  $h^5$ . [similarly hexahapto-  $\eta^6$  or  $h^6$ ; heptahapto-  $\eta^7$  or  $h^7$ ; octahapto-  $\eta^8$  or  $h^8$ ].


What is difference between hapticity and denticity?



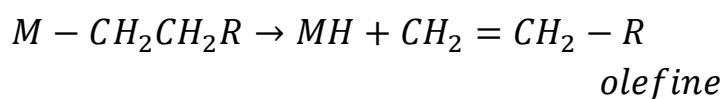
## 2. Classification on the basis of polarity of M-C bonds:

The following five M-C bond types are found in organometallic compounds-

- a. ionic bonds
- b.  $\sigma$ -covalent bonds (bicentric bielectronic bonds)
- c. electron deficient bonds
- d. both  $\sigma$ - and  $\pi$ -bonds
- e. delocalized bond in polynuclear system

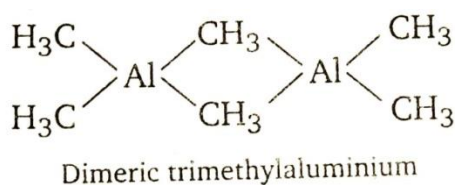
**a. Ionic compounds:** The organometallic compounds of high electropositive metals (alkali & alkaline earth & even lanthanides & actinides with *electronegativity value approximately less than 1*) are predominantly ionic in nature with exception of Li, Be & Mg. The metal is present in the cationic forms i.e.  $M^{n+}$  & the organic groups in carbanion forms, the negative charge of the carbanions can either be localized at a particular C-atom (as a ethyl sodium  $CH_3CH_2^-Na^+$ ) or can be delocalized over several C-atoms (as in sodium cyclopentadienyl   $Na^+$ ). These type of compounds are generally colourless, extremely reactive (towards water protic reagents etc), non-volatile solvents & soluble in hydrocarbon solvent on heating. They are generally decomposed without melting.

**b.  $\sigma$ -covalent compounds:** These type of compounds are typical for all p- block non-transition elements but are also encounters in transition metal derivatives. These are classical covalent bonds formed by pairing of two electrons of opposite spin. These types of compounds are found by most elements with values of *electronegativity higher than 1*. Thus the bonds Sn-C, Pb-C, As-C, etc. are  $\sigma$ -covalent bonds with some polar character  $M^{\delta+}-C^{\delta-}$  depending upon the electronegativity difference between the element & carbon. It is important to note that the presence of electron attracting substituent in the organic group (such as substitution H by F) increases the stability of M-C bonds. Thus the  $M-CF_3$  &  $M-C_6F_6$  compounds are more stable than their non-fluorinated analogue. Transition metal  $\sigma$ - bonded derivatives are found to be unstable & there is a tendency of organic group to be eliminated as an olefin ( $\beta$ -elimination).

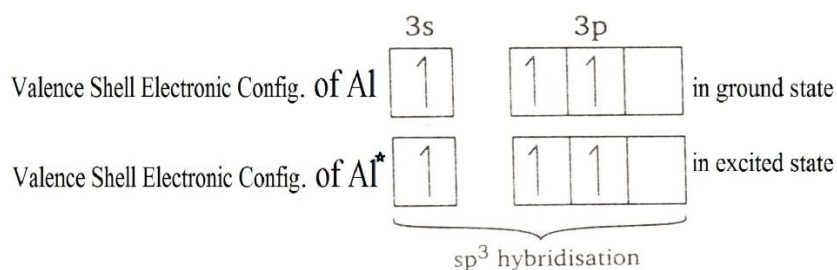


**c. Electron deficient compounds:** (Li, Be, B, Mg, Al)  
(Three centered bonds / Banana Bonds)

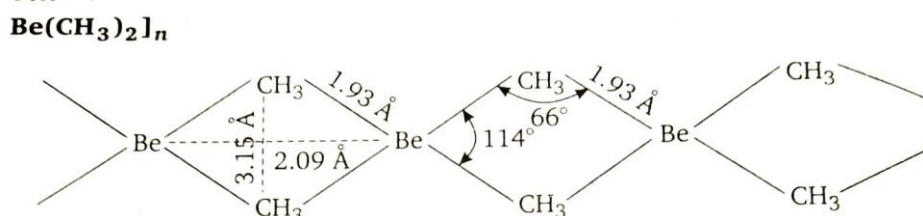
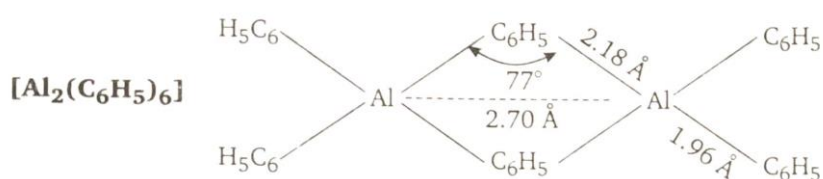
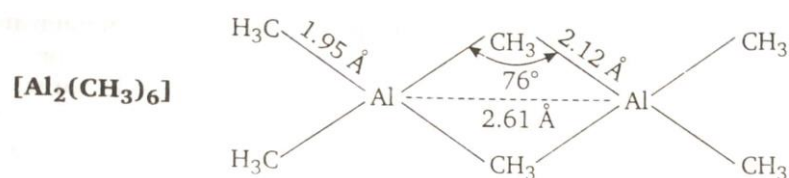
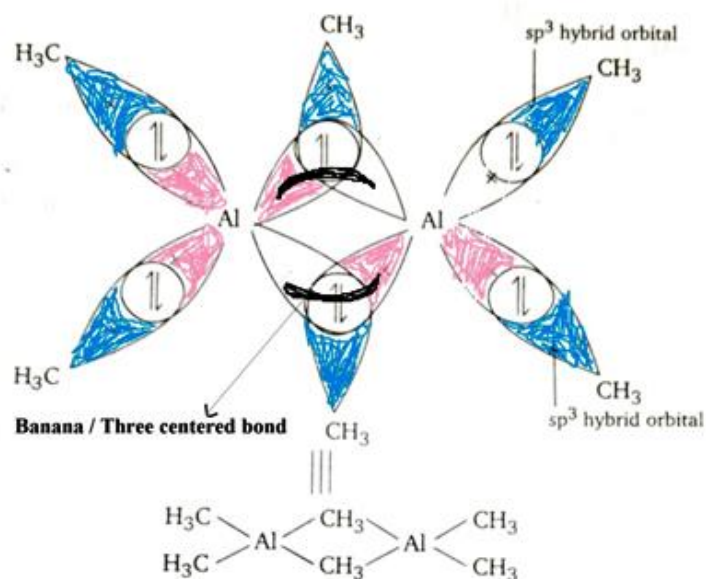
The organometallic compounds formed by Li, Be, B, Mg & Al are electron deficient in nature and bonding may be explained on the basis of *three centered bonds or banana bonds*. Such bonds are weaker than normal covalent bonds and generally form when valence electrons available for bond formation are few to fill all bonding orbitals with electron pairs. This may be explained by taking methyl derivative of Al as an example. The structure of this compound is shown below-



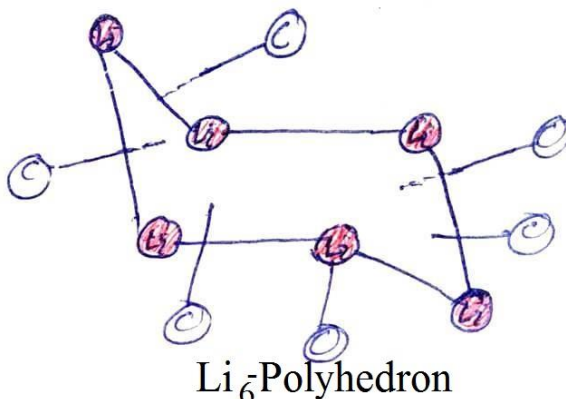
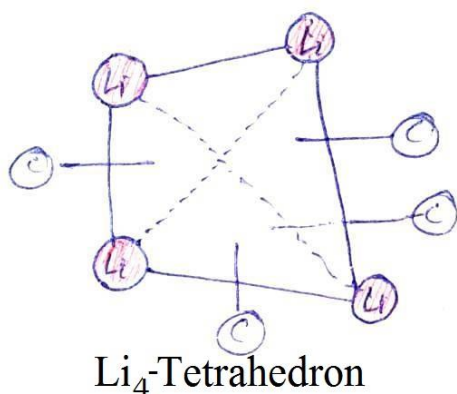
There are four terminal –CH<sub>3</sub> groups which are attached to Al with the help of normal covalent bonds. There are two bridging –CH<sub>3</sub> groups attached to both Al. The bonding of involves three centered bond.



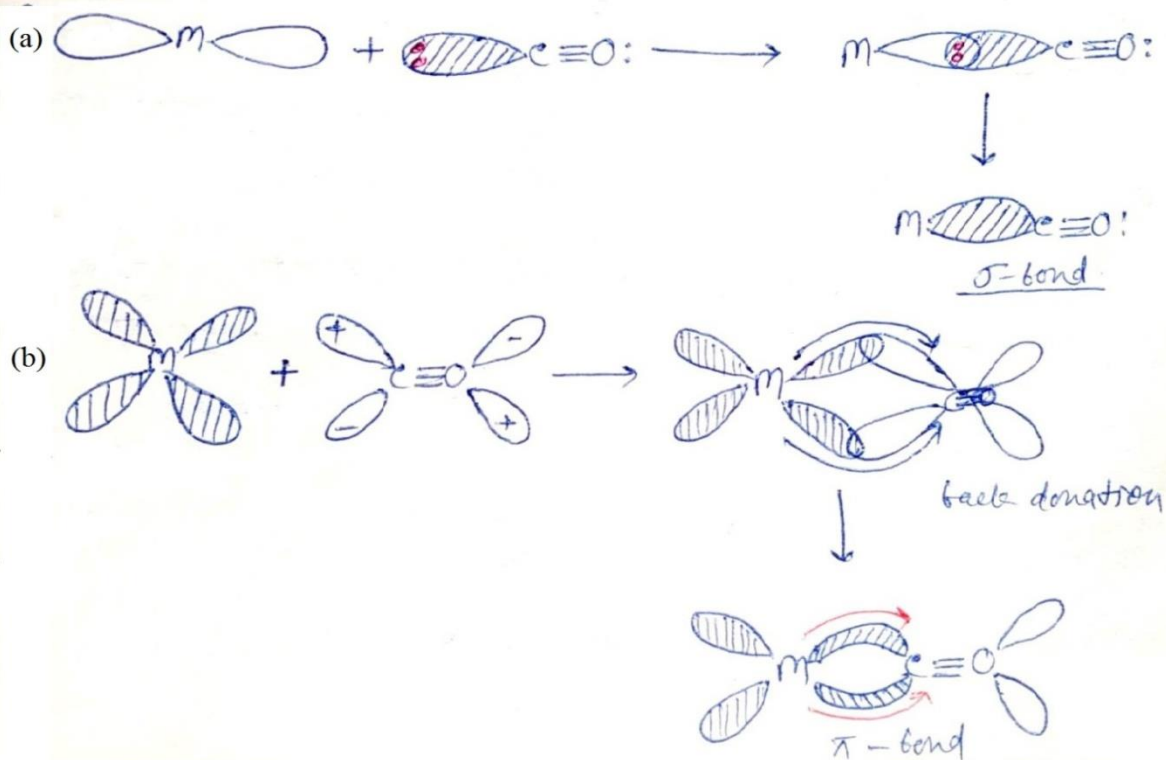
The outermost electronic configuration of Al is ns<sup>2</sup> np<sup>1</sup>. During formation of compounds Al shows sp<sup>3</sup> hybridization. Each Al has four sp<sup>3</sup> hybrid orbitals; out of four hybrid orbitals to overlapped with orbitals of terminal –CH<sub>3</sub> groups forming normal covalent bonds. In addition one hybrid orbital of one Al containing one electron overlaps with orbital of –CH<sub>3</sub> groups containing one electron and one of the sp<sup>3</sup> hybrid hybrid orbital of another Al which is vacant to form three-centered bond. In this compound, two such three centered bonds are present. The formation of bonds is shown as below-



**d. Delocalized bonds in polynuclear system:** The bonds between the Li-Li tetrahedron or Li<sub>6</sub> polyhedron in some polymeric (LiR)<sub>n</sub> where (n=4 or 6) involve delocalized Li-Li bonds; the organic groups (R) are attached simultaneously to several Li-atoms. In this case isolated *Li-C bonds are not found*. The formation of this type of bond can be explained on the basis of molecular orbital theory. A similar situation occurs in clusters present in metal carbonyls and carboranes. The structures are shown below-



**f. Compound involving both  $\sigma$ - and  $\pi$ -bonds:** Bonding between transition metal atoms and unsaturated organic molecules are found by electron donation in two opposite directions i.e. from ligand to metal [ $L \rightarrow M$ ] (direct donation,  $\sigma$ -bond) and from metal to ligand [ $M \rightarrow L$ ] (back donation,  $\pi$ -bonding) to participate. In  $M \rightarrow L$  bonds, the metal should have a partially occupied d-orbital and the unsaturated organic molecules must have vacant antibonding molecular orbitals. The simplest example is the bond formation between CO and metal in metal carbonyls. The formation of  $\sigma$ - and  $\pi$ -bonds in metal carbonyls is shown below-



The CO molecule has a lone pair of electron in a molecular orbital delocalized at carbon which can be transferred into a vacant orbital of metal forming a  $\sigma$ -bond. The CO molecule has vacant antibonding molecular orbital which can accept electron from occupied orbital of metal to form a  $\pi$ -bond.

## Nomenclature or I.U.P.A.C. Name of O.T.M. Compounds:

(O.T.M. = Organotransition metal)

(a) Simple O.T.M. Compounds: Like monohapto ( $\eta^1$ )

name of organic group + metal name

| Compound   | Name               |
|--|--------------------|
| $\text{H}_3\text{C}-\text{Be}-\text{CH}_3$   | Dimethylberyllium  |
| $\text{H}_5\text{C}_6-\text{Hg}-\text{C}_6\text{H}_5$                                | Diphenylmercury    |
| $\text{CH}_3-\text{Li}-\text{CH}_3$  | Methyl lithium     |
| $\text{H}_3\text{C}-\text{Zn}-\text{C}_2\text{H}_5$                                  | Ethylmethylzinc    |
| $\text{H}_3\text{C}-\text{Cd}-\text{CH}_3$   | Dimethylcadmium    |
| $\text{W}(\text{CH}_3)_6$  | Hexamethyltungsten |
| $(\text{CH}_3)_4\text{Pb}$   | Tetramethyllead    |
| $(\text{CH}_3\text{CH}_2)_4\text{Pb}$  | Tetraethyllead     |
| $\text{H}_3\text{C}-\text{Al}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ | Trimethylaluminium |

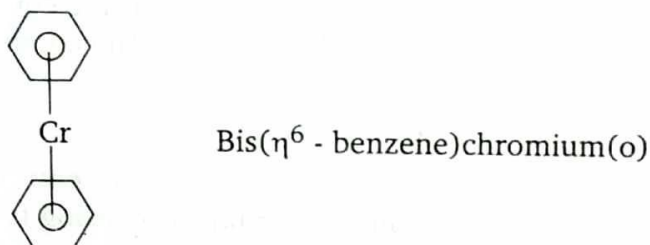
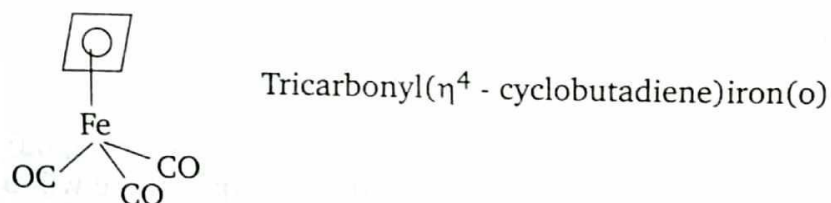
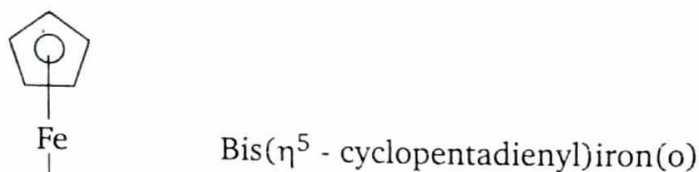
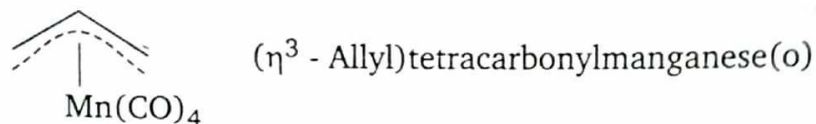
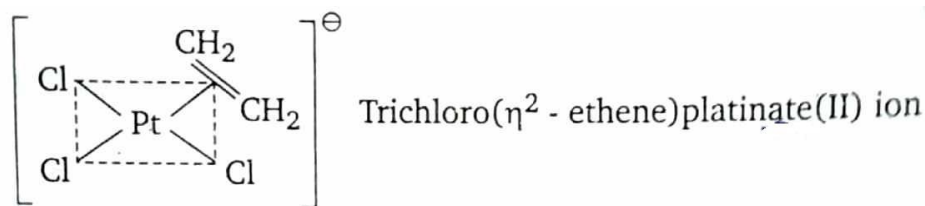
(b) Binary O.T.M. Compounds of p-block element: The name of *binary compounds of hydrogen with p-block elements* generally end with the suffix 'ane'.

|                |         |                |           |
|----------------|---------|----------------|-----------|
| $\text{CH}_4$  | Methane | $\text{GeH}_4$ | Germane   |
| $\text{SiH}_4$ | Silane  | $\text{SnH}_4$ | Stannane  |
| $\text{AsH}_3$ | Arsane  | $\text{PH}_3$  | Phosphane |
| $\text{SbH}_3$ | Stibane | $\text{BH}_3$  | Borane    |

The names of O.T.M. compounds of p-block elements or derivatives of these hydrides may be written as-

|  |                        |
|--|------------------------|
| $\text{B}(\text{CH}_2\text{CH}_3)_3$                       | Triethylborane         |
| $\text{Sb}(\text{C}_2\text{H}_5)_3$                        | Trivinylstibane        |
| $\text{PH}_2\text{CH}_3$                                   | Methylphosphane        |
| $\text{Si}(\text{CH}_3)_4$                                 | Tetraethylsilane       |
| $\text{CH}_3\text{SnH}_2\text{Cl}$                         | Chloro(methyl)stannane |
| $(\text{H}_3\text{C})_3\text{Si}-\text{Si}(\text{CH}_3)_3$ | Hexamethyldisilane     |
| $\text{As}(\text{CH}_3)_3$                                 | Trimethylarsane        |
| $\text{B}(\text{C}_6\text{H}_{11})_2\text{H}$              | Dicyclohexylborane     |
| $\text{Si}(\text{CH}_3)_3\text{Cl}$                        | Chlorotrimethylsilane  |
| $\text{Se}(\text{C}_6\text{H}_5)_2$                        | Diphenylselane         |

(c) The hapticity of the polyhapto ligands is represented by 'η' with appropriate numerical superscript.



(d) Name of organometallic compounds with bridging ligands may be written as follows-

