

Organometallic Chemistry

Organometallic chemistry is the study of compounds containing at least one bond between a C atom of an organic compound and a metal (alkali & alkaline earth metals, transition metals, lanthanides and actinides).

An organo metallic compound is defined as one that possess a **metal-carbon** bond. The organic group may be the alkyl radical or a carbon atom in a molecule. But some non-metal atoms less electronegative than carbon form direct bond with carbon. B, As, P and Si elements can form bonds directly with carbon and but these are not organo metallic compounds.

IA	IIA					IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1												
Li 1.0	Be 1.5							B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2							Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Co 1.7	Ni 1.7	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0					Br 2.8
		Rh 2.4	Pd 2.4	Ag 1.8	Cd 1.5		Sn 1.7					I 2.5
					Hg 1.5		Pb 1.6					

In some organic compounds the **metal atoms are linked to oxygen** instead of carbon atom
Example acetates (derivatives of carboxylic acids) alkoxides (derivatives of alcohols)
These are **not organo metallic** compounds. Some compounds in which though **C-M bonds are present** the metal atom is not bonded to an alkyl carbon. **are not included** in organo metallic compounds. For example metal **carbides** (CaC_2) metal **cyanides** (NaCN) metal carbonyls { $\text{Ni}(\text{CO})_4$ }.

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NOMENCLATURE

The name of the **metal atom follows the name of the alkyl** or aryl group.
But the number of alkyl groups of the same kind bonded to the metal atom is indicated by a prefix to the name of the group.

$\text{H}_3\text{C} - \text{Li}$	Methyl Lithium
$\text{H}_3\text{C} - \text{Zn} - \text{CH}_3$	Dimethyl Zinc
$(\text{H}_3\text{C})_4 \text{Pb}$	Tetramethyl lead

The organometallic compounds may contain H-atoms besides the alkyl groups: $(\text{CH}_3)_3\text{SnH}$

The organo metallic compounds are generally divided into two types:

- i) **Symmetrical or normal** : In these compounds, all the alkyl groups are same **Ex: $(\text{C}_2\text{H}_5)_4\text{Pb}$**
- ii) **Mixed types** - This type of compounds have different alkyl groups. Some of these mixed organo metallic compounds may contain other than hydrogen atoms also.

Ex: $(\text{C}_2\text{H}_5)_4\text{Hg}$, $(\text{C}_4\text{H}_9)\text{CH}_3\text{MgBr}$, $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$, $(\text{CH}_3)_3\text{SnH}$

However all the bonds in the compounds need not be metal carbon bonds. Atleast one metal- carbon is sufficient to be called organo metallic compounds.

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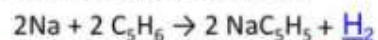
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Ionic organometallic compounds

Highly electropositive metals form ionic organometallic compound by non-directional electrostatic forces. **alkali and alkaline earth** metals

Ex : $(C_6H_5)_3C^- Na^+$; $(C_5H_5)_2Ca^{2+}$, $(C_5H_5)_2Na$

Cyclopentadienyl sodium is prepared by reaction of cyclopentadiene with sodium, in an inert solvent like benzene



The organometallic compounds are classified into **4** types depending upon **nature of bond between metal and carbon**

- ionic organometallic compounds**
- σ -bonded covalent organometallic compounds**
- π -bonded covalent organometallic compounds**
- Alkyl bridged organometallic compounds**

σ -bonded covalent organometallic compounds

Covalent bond is present between the metal atom and the carbon atom of an organic group. This kind of bond is formed by metals with low electropositive nature. A metal atom and a carbon atom share a pair of electrons forming a σ -bond in these compounds.



Trichlorocyclopentadienyl silicon

In many complexes, both σ - and π -bonding exist between the metal atom and carbon.

π -bonded covalent organometallic compounds

Transition metal atoms only generally form π -bonded compounds. **Ferrocene**, an iron compound, was the first compound of this type. Two C_5H_5 rings are enclosing the iron atom. This is a sandwich compound.

In this compound all the Fe-C distances are identical. The ring structure is symmetric about the metal atom. The π -electrons of cyclopentadienyl anion overlap the vacant d-orbitals of the metal and form π -bonds. As a consequence these compounds are known as π -bonded compounds. Ethylene, acetylene, dienes like butadiene, aromatic molecules give these compounds

Bridged Organometallic compounds

Two metal atoms are bridged by alkyl groups. Bridging groups have 2 e 3 c bonds.

Some of the examples for this type of compounds are Dimeric trialkyl aluminium $(AlR_3)_2$ Polymeric dimethyl beryllium $[Be(CH_3)_2]_n$, Polymeric diethyl magnesium $[C_2H_5)_2Mg]_n$

These compounds exist as either dimeric or polymeric substances. The M-C bonds in the bridge groups have identical bond lengths. All bonds can not be considered as 2 electron, 2 centre covalent bonds; bridge bonds are 2e 3c bonds.

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Organometallic compounds of the Group 1 elements:

These react violently with water, are pyrophoric, and therefore prepared in organic solvents like tetrahydrofuran (THF). Ionic organometallic compounds of the Group 1 metals are formed with H⁺-donating organic compounds: sodium metal in THF reacts with cyclopentadiene to yield the cyclopentadienide anion, which is an important intermediate in the synthesis of d-block organometallic compounds.



Sodium and potassium alkyls are solids, insoluble in organic solvents and have high melting points. Their method of synthesis is by a transmetallation reaction, involving the breaking of a metal-carbon bond and formation of a metal-carbon bond to a different metal.

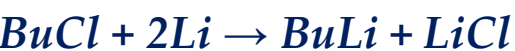


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In Group 1 organometallic compounds, organolithiums are most important. They are either liquids or low melting solids, most thermally stable in the entire group, and are soluble in organic and nonpolar solvents such as THF. They can be synthesized either from reaction of an alkyl halide and lithium metal or by reacting butyllithium, $\text{Li}(\text{C}_4\text{H}_9)$, (abbreviated to BuLi) with an organic compound.



*One of the characteristics of many main-group organometallic compounds is the presence of bridging alkyl groups. In presence of ether as the solvent, methyl lithium exists as $\text{Li}_4(\text{CH}_3)_4$ with a tetrahedron of Li atoms and bridging CH_3 groups. In hydrocarbon solvents, $\text{Li}_6(\text{CH}_3)_6$ is formed; its structure is derived from an octahedral arrangement of Li atoms. Other alkyllithiums also form similar structures except but if the alkyl groups are bulky, as in *t*-butyl, $-\text{C}(\text{CH}_3)_3$, to form tetramers. Alkyllithiums are mostly electron-deficient compounds.*

Organolithium compounds have widespread applications in organic synthesis, the most important reactions being those in which they act as nucleophiles attacking groups like carbonyl group.

Organolithium compounds are also used to convert p-block halides to other organoelement compounds: Boron trichloride reacts with butyllithium in THF to give an organoboron compound:



Butyllithium is used as a stereospecific initiator in solution polymerization to form various polymers and elastomer.

Other organolithium compounds have applications in the synthesis of a range of pharmaceuticals, antihistamines, antidepressants, analgesics, anticoagulants and also to prepare vitamins A and D. Alkylolithiums can be used in the synthesis of other d-metal organometallic compounds.



Group II organometallic compounds

Group II organometallic compounds are unstable in water and ignite spontaneously on exposure to air.

Methylberyllium can be prepared by transmetallation from methylmercury in a hydrocarbon solvent:



Alkyl- and arylmagnesium halides also known as Grignard reagents provide R-, alkyl groups. They are prepared from magnesium metal and an organohalide. To activate Mg, a trace of iodine is added. The reaction takes place in ether or THF.



Grignard reagents are also used to prepare organometallic compounds of other metals. In Grignard reagents, the metal atom has a coordination number of 2 only in solution for a bulky alkyl group. Else, it is solvated with the Mg atom surrounded by a tetrahedral arrangement of solvent molecules. The **Schlenk equilibria** is a complex equilibria in solution showing existence of several species, (R_2Mg , RMgX , and MgX_2), depending on temperature, concentration, and solvent factors. Organomagnesiatioin is a unique reaction involving addition of an unsaturated compound to the Grignard reagent, in an organic solvent



Another application of Grignard reagents is Wurtz coupling forming a carbon-carbon



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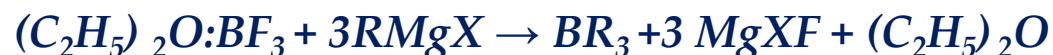
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Group 13 organometallic compounds:

Organoboron compounds: Organoboranes BR_3 are synthesized by hydroboration of an alkene with diborane, B_2H_6

$$B_2H_6 + 6CH_2=CH_2 \rightarrow 2B(CH_2CH_3)_3$$

or from a Grignard reagent $RMgX$



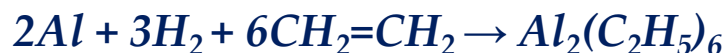
The sodium salt of tetraphenylborate ion, $[B(C_6H_5)_4]$, more commonly written BPh_4^- is used as a precipitating agent and can be used in gravimetric analysis.

Organoaluminium compounds:

Alkylaluminium compounds can be prepared on a small scale by transmetallation of a mercury compound:



The alkylaluminium compounds exist as dimers where Al-C-Al bonds are longer than terminal C-Al bonds, as in diborane. Higher alkylaluminium compounds are formed by reaction of metal, alkene, and H_2 gas at elevated temperatures (60-110°C) and pressures (10-20 Mpa).



Triethylaluminium finds application as the Ziegler-Natta polymerization catalyst.

Group 14 organometallic compounds:

Tin and lead form tetravalent organo compounds. Organotin compounds are used as fungicides, pesticides and antifouling agent, and in stabilization of PVC plastics. Alkyltin compounds are synthesized by metathesis and by using a Grignard reagent:



Tetraethyl lead, an antiknock agent in petrol, and other alkyllead compounds, R_4Pb , can be synthesized using a Grignard reagent or an organolithium compound:



These monomeric molecules exhibit tetrahedral geometry around Pb atom. Halide derivatives involve bridging halide atoms forming chains. Monomers are favoured by more bulky organic substituents: $\text{Pb}(\text{CH}_3)_3\text{Cl}$ has bridging Cl atoms forming a chain structure but mesityl derivative $\text{Pb}(\text{Me}_3\text{C}_6\text{H}_2)_3\text{Cl}$ is a monomer.

Bonding of d-block organometallic compounds is by σ , π and δ bonds. (18 valence e-s)

Six σ bonding interactions are possible in an octahedral complex in presence of π -acceptor ligands.

With strong-field ligands, a 16-electron configuration is the most energetically favourable configuration for a square-planar complex having only eight bonding molecular orbitals. Ligands donate electrons in pairs, thus some ligands are neutral and others are treated as charged.

The oxidation number of the metal atom is the difference of total charge of the complex and the charges on any ligands.

The difference of group number and oxidation number of the metal gives the number of electrons provided by the metal.

The total electron count is the sum of the number of electrons on the metal atom and the number of electrons provided by ligands.

Ligands in d-block organometallic compounds are CO, phosphines, hydrides, alkyl, alkenyl, alkynyl, aryl groups, diene and polyene (butadiene, cyclobutadiene, cyclooctatriene, allyl, cyclopentadiene, cycloheptatriene, carbenes, noble gases, dinitrogen or nitrogen monoxide (NO)).

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Nomenclature of organometallic compounds is similar to that of coordination compounds, but certain ligands having multiple bonding modes, involve hapticity.

Hapticity is the number of ligand atoms that are considered formally to be bonded to the metal atom. The hapticity is denoted η^n , where n is the number of atoms.

Some ligands (e.g. H) can bond to more than one metal atom in the same complex, and are then referred to as bridging ligands.

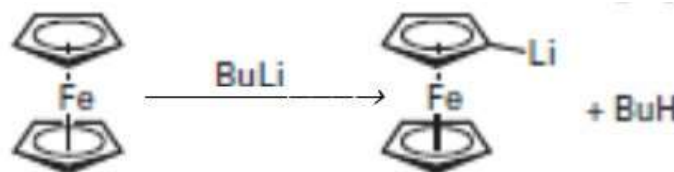
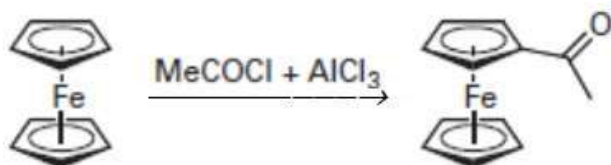
μ_2 -CO is a carbonyl group that bridges two metal atoms and a μ_3 -CO bridges three. There is an increasing occupation of the π^ orbital as the CO molecule bonds to more metal atoms and more electron density from the metals enters the CO π^* orbitals.*

Compounds of d-block elements: d-block carbonyls: Metallocenes: $(Cp)_2Fe$

Many Cp complexes have two ring systems, with the metal sandwiched between the two rings, and called 'sandwich compounds'. The starting material for these compounds is sodium cyclopentadienide, NaCp, used to prepare ferrocene, $Fe(C_5H_5)_2$.



Deprotonation of cyclopentadiene gives a convenient precursor to many metal cyclopentadienyl compounds; bound cyclopentadienyl rings behave as aromatic compounds and will undergo Friedel-Crafts electrophilic reactions.



Ferrocene and its derivatives are widely used as anti-knock agents in petrol as they are considerably less toxic than tetraethyl lead. Ferrocene is also added to diesel fuel to reduce the production of soot during combustion. Ferrocene is also used in handheld glucose sensors for diabetics. In these sensors the redox couple of the tri-substituted ferrocene derivative is used to determine the level of glucose in a blood sample. Ferrocene compounds have also been developed as electron transfer catalysts.

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Metal-metal bonding and metal clusters: A cluster includes all compounds with metal-metal bonds that form triangular or larger cyclic structures.

E- count: The 18-electron rule is suitable for identifying the correct number of electrons for clusters with fewer than six metal atoms; the Wade-Mingos-Lauher rules identify a correlation between the valence electron count and the structures of larger organometallic complexes. The bonding electrons we are dealing with are referred to as the cluster valence electrons (CVEs).

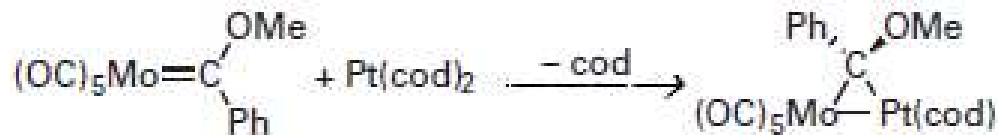
Synthesis of clusters

1. Thermal expulsion of CO from a metal carbonyl:



2. Condensation of a carbonyl anion and a neutral organometallic complex $[\text{Ni}_5(\text{CO})_{12}]^{-2} + [\text{Ni}_5(\text{CO})_4] \rightarrow [\text{Ni}_6(\text{CO})_{12}]^{-2} + 4\text{CO}$

3. Condensation of an organometallic complex with an unsaturated organometallic compound.



(cod: 1,5-cyclooctadiene)

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Organometallic cluster compounds are rare for the early d metals and unknown for the f metals, but a large number of metal carbonyl clusters exist for the elements of Groups 6 to 10. The bonding in the smaller clusters can be readily explained in terms of local M-M and M-L electron pair bonding and the 18-electron rule. E.g. $\text{Mn}_2(\text{CO})_{10}$ and $\text{Os}_3(\text{CO})_{12}$.

In $\text{Mn}_2(\text{CO})_{10}$ each Mn atom is considered to have 17 electrons (seven from Mn and 10 from the five CO ligands) before we take into account the Mn-Mn bond. This Mn-Mn bond consists of two electrons shared between the two metal atoms, and hence raises the electron count of each by 1, resulting in two 18-electron metal atoms, but with a total electron count of only 34, not 36.

In $\text{Os}_3(\text{CO})_{12}$, each $\text{Os}(\text{CO})_4$ fragment has 16 electrons before metal-metal bonding is taken into consideration and each metal shares two further electrons with adjacent metals, so increasing the number of electrons around each metal to 18, but with a total of only 48 and not 54 electrons. The bonding electrons we are dealing with are referred to as the cluster valence electrons (CVEs), and it quickly becomes apparent that a cluster of x metal atoms with y metal-metal bonds needs $18x - 2y$ electrons. Octahedral M₆ and larger clusters do not conform to this pattern, and the polyhedral skeletal electron pair rules, known as Wade's rules, have been refined by Mingos and Lauher to apply to metal clusters. These Wade-Mingos-Lauher rules are summarized in Table [PTO]; they apply most reliably to metal clusters in Groups 6 to 9.

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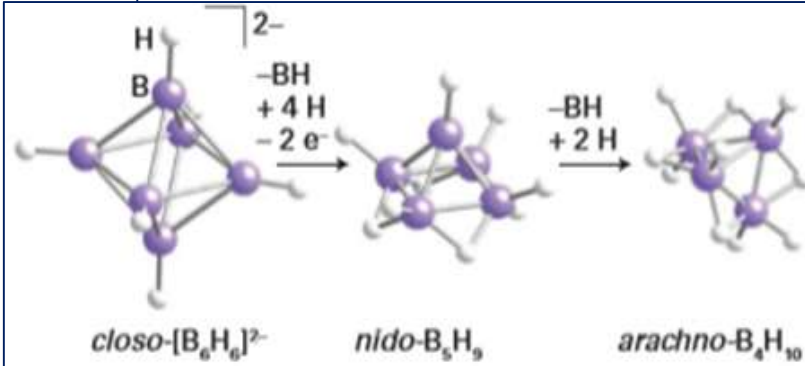
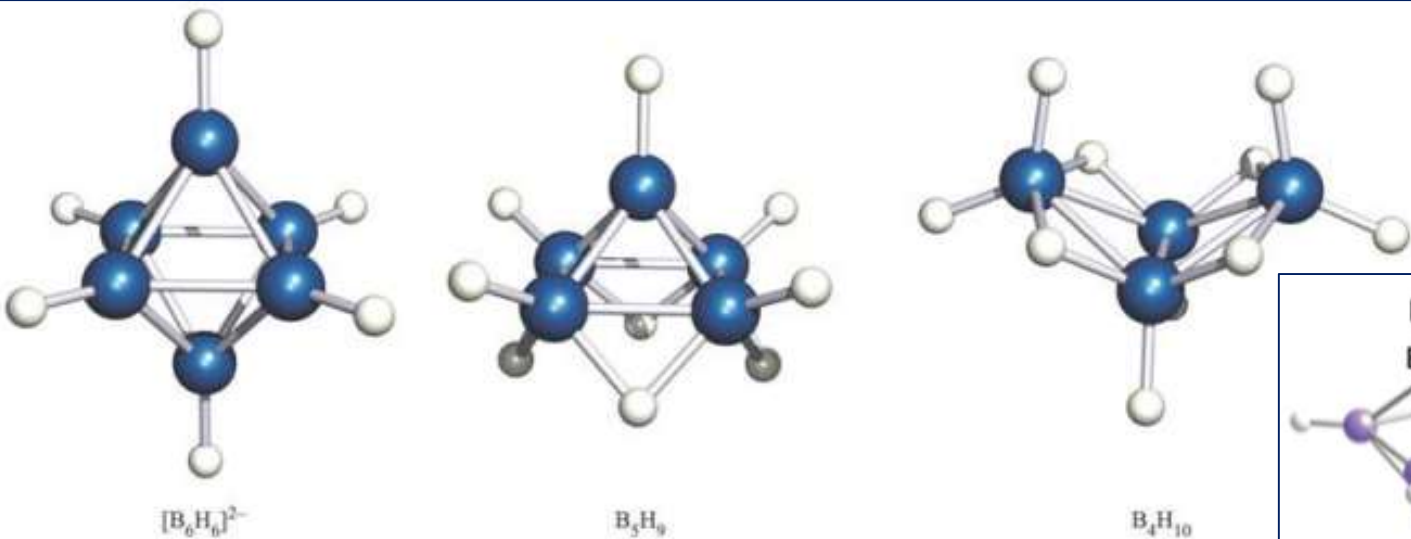
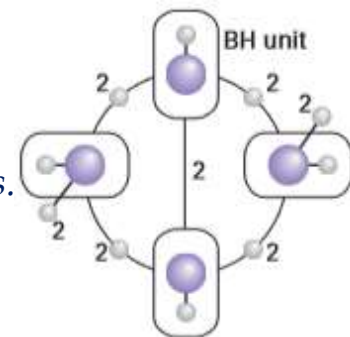
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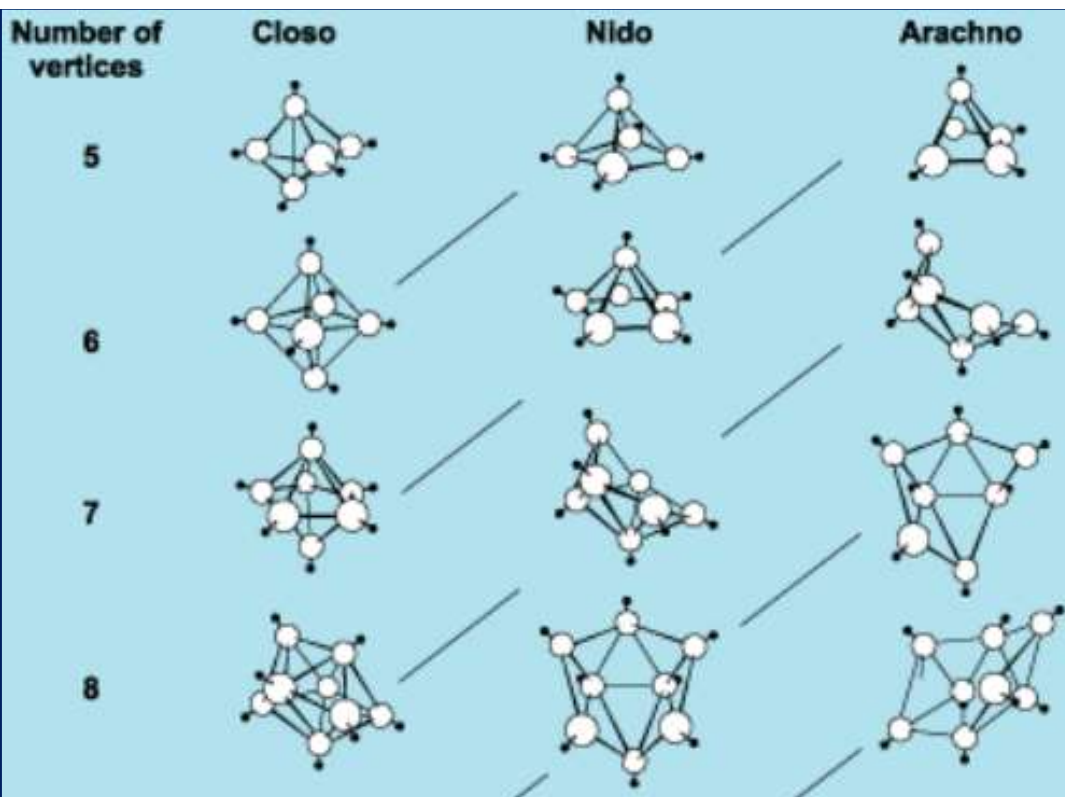
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According to Wade's rules species of formula $[B_nH_n]^{2-}$ and $n + 1$ pairs of skeletal electrons have a closo structure, with a B atom at each corner of a closed deltahedron and no B-H-B bonds. This series of anions is known for $n = 5$ to 12.

Boron clusters of formula B_nH_{n+4} and $n + 2$ pairs of skeletal electrons have the nido structure. They can be regarded as derived from a closo-borane that has lost one vertex but have B-H-B bonds as well as B-B bonds.

E.g. B_5H_9 . Clusters of formula B_nH_{n+6} and $n+3$ skeletal electron pairs have an arachno structure.





In a *closo* polyhedral borane structure:

The number of pairs of framework bonding electrons is determined by subtracting one B-H bonding pair per boron.

The $n+1$ remaining framework electron pairs may be used in boron-boron bonding or in bonds between boron and other hydrogen atoms.



Number of valence electrons = $6(3) + 6(1) + 2 = 26$ or 13 pairs of electrons.

Six pairs of electrons are involved in bonding to terminal hydrogens (one per boron).

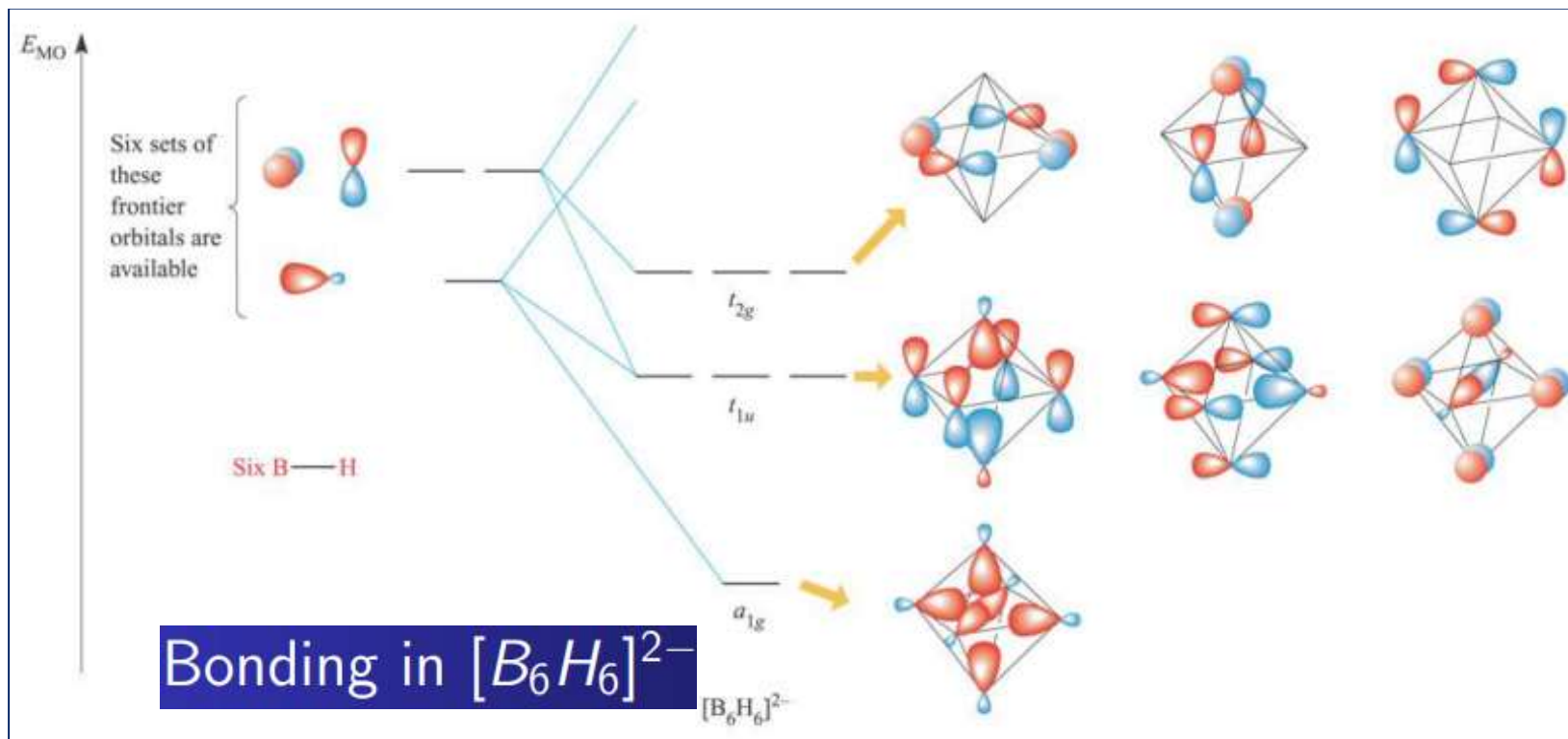
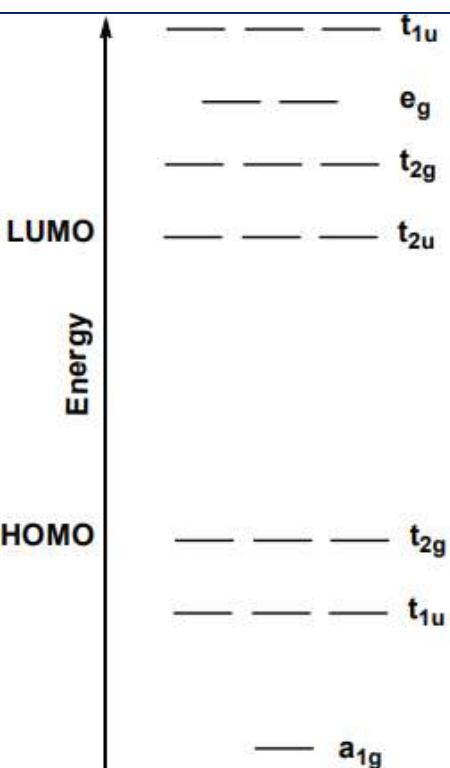
Therefore seven ($n + 1$) pairs of electrons are involved in framework bonding, where n = number of boron atoms in cluster.

Type	Formula	Skeletal Electron Pairs
<i>Closo</i>	$[B_nH_n]^{2-}$	$n + 1$
<i>Nido</i>	B_nH_{n+4}	$n + 2$
<i>Arachno</i>	B_nH_{n+6}	$n + 3$
<i>Hypho</i>	B_nH_{n+8}	$n + 4$
<i>Klado</i>	B_nH_{n+10}	$n + 5$

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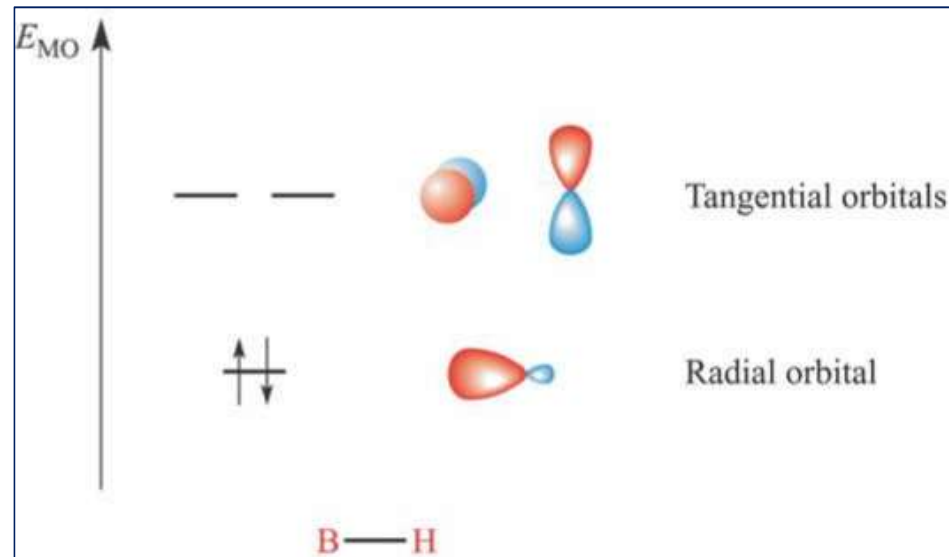


When the six B-H units come together, a total of 18 (6×3) atomic orbitals combine to form 18 molecular orbitals.

There are seven orbitals with net bonding character delocalized over the skeleton.

All of the bonding orbitals are filled ($n + 1$ framework bonding pairs), so seven pairs of electrons are used to hold the cluster together. The bonding cannot be interpreted using a localized electron model.

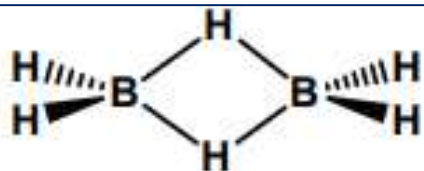
There is a considerable energy gap between the bonding MOs and the remaining largely antibonding MOs, contributing to the stability of the cluster.



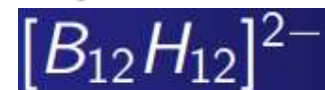
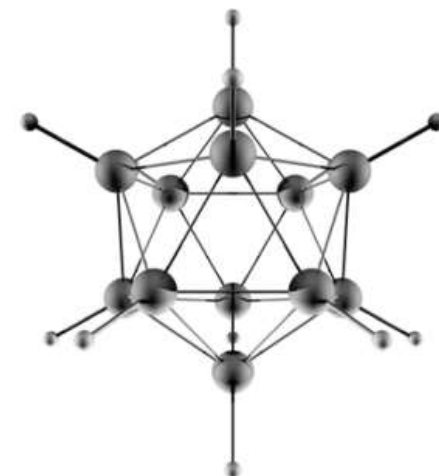
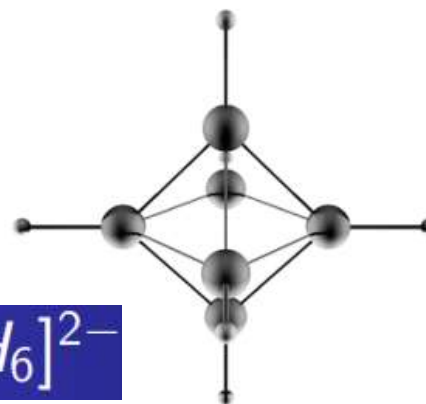
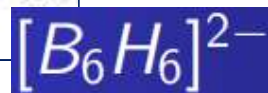
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This is an electron-deficient compound held together by two 3c-2e bonds.



Borane Cluster Structures

Deltahedral Cages With Five to Twelve Vertices



$n = 5$
Trigonal
bipyramid



$n = 6$
Octahedron



$n = 7$
Pentagonal
bipyramid



$n = 8$
Dodecahedron



$n = 9$
Tricapped
trigonal prism



$n = 10$
Bicapped
square-antiprism



$n = 11$
Octadecahedron






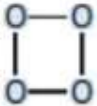



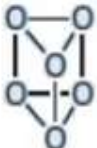


$n = 12$
Icosahedron

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Number of metal atoms	Structure of metal framework	CVE count	Example
1	Single atom 	18	Ni(CO)_4
2	Linear 	34	$\text{Mn}_2(\text{CO})_{10}$
3	Closed triangle 	48	$[\text{Co}_3(\text{CH})(\text{CO})_9]$
4	Tetrahedron 	60	$\text{Co}_4(\text{CO})_{12}$
	Butterfly 	62	$[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$
	Square 	64	$\text{Os}_4(\text{CO})_{16}$
5	Trigonal bipyramid 	72	$\text{Os}_5(\text{CO})_{16}$
	Square pyramid 	74	$\text{Fe}_5\text{C(CO)}_{16}$
6	Octahedron 	86	$\text{Ru}_6\text{C(CO)}_{27}$
	Trigonal prism 	90	$[\text{Rh}_6\text{C(CO)}_{15}]^{2-}$

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Carbonyl complexes and the 18-electron rule

To obey the 18-electron rule, many carbonyl complexes are anions or cations, as in:

$[\text{V}(\text{CO})_6]^-$	$[\text{Mn}(\text{CO})_6]^+$	$[\text{Fe}(\text{CO})_4]^{2-}$
$\text{V}(0) = d^5$	$\text{Mn}(0) = d^7$	$\text{Fe}(0) = d^8$
$6 \text{ CO} = 12e$	$6 \text{ CO} = 12e$	$4 \text{ CO} = 8e$
$1^- = +1e$	$1^+ = -1e$	$2^- = 2e$
<hr/>	<hr/>	<hr/>
$= 18e$	$= 18e$	$= 18e$
Formal oxidation state = V(-I)	Formal oxidation state = Mn(I)	Formal oxidation state = Fe(-II)

[NOTE: In applying the 18-electron rule, metal ions are always considered to be **zero-valent, not the formal oxidn. state]**

The rule states that the sum of the d-electrons possessed by the metal plus those donated by the ligands must total eighteen : (2 per $\text{C}\equiv\text{O}$)

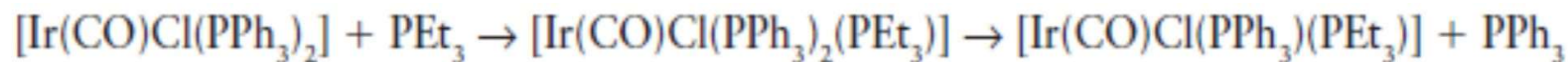
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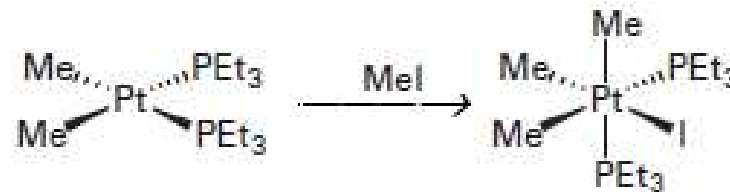
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Reactions of d-metal organometallic compounds:

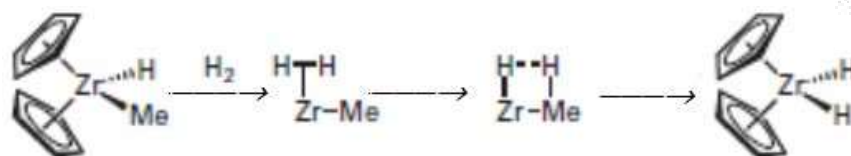
1. Ligand substitution



2. Oxidative addition and reductive elimination



3. σ -Bond metathesis



transition state

4. 1,1-Migratory insertion reactions



5. 1,2-Insertions and β -hydride elimination



6. α,γ,δ -Hydride eliminations and cyclometallations



Course Code: SC202

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The reaction of chloroform (CHCl_3) with $[\text{Co}_2(\text{CO})_8]$ yields a compound of formula $[\text{Co}_3(\text{CH})(\text{CO})_9]$. Both NMR and IR data indicate the presence of only terminal CO ligands and the presence of a CH group. Propose a structure consistent with the spectra and the correlation of CVE with structure.