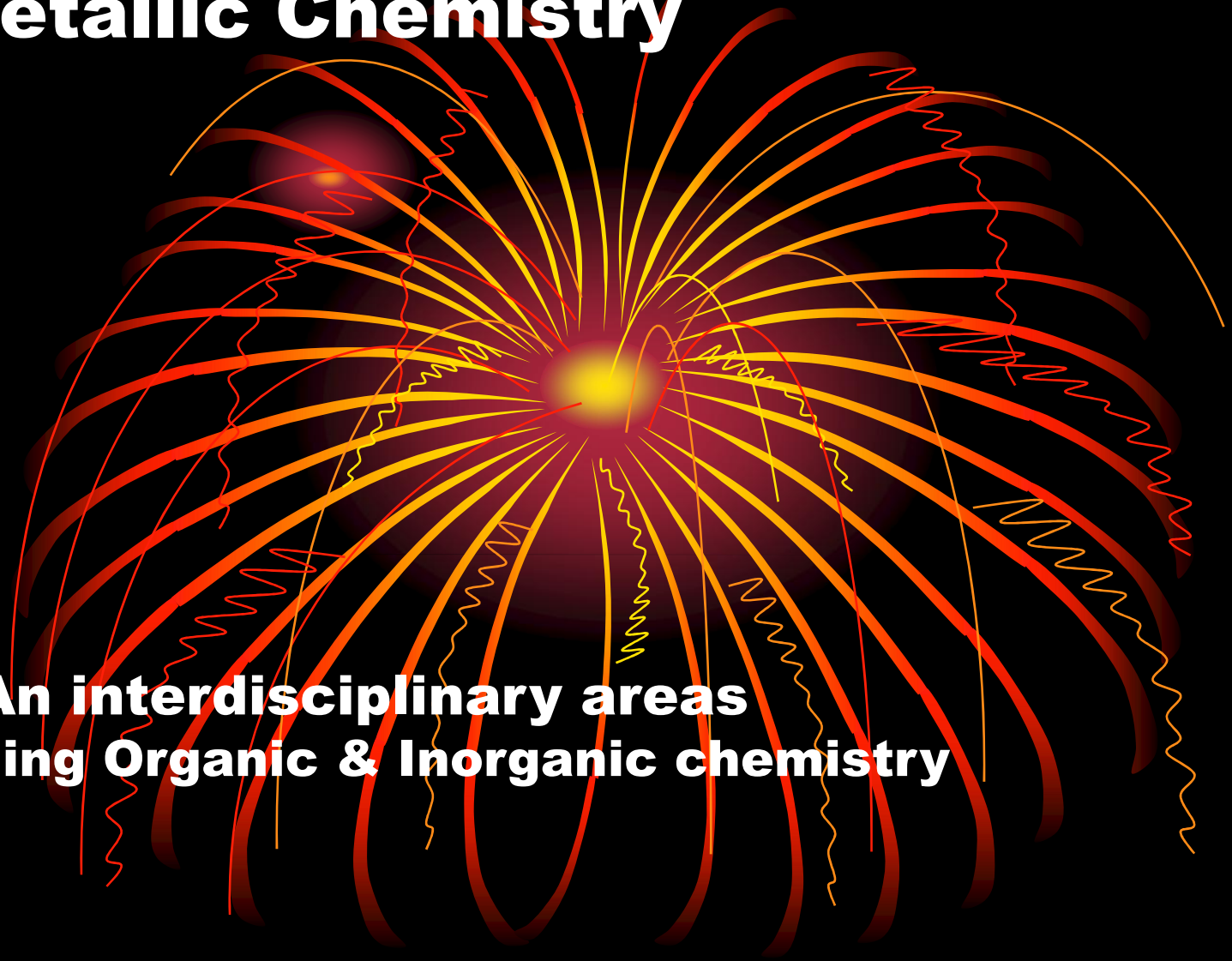
Organometallic Chemistry



An interdisciplinary areas
Including Organic & Inorganic chemistry

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Organometallic Chemistry

CHEMISTRY OF M-C LINKAGES

It bridge Inorganic and Organic chemistry

half the research work is on organometallic compounds.

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OMC play a vital role in the economy

10 of the world's top 30 chemicals are produced using OMC Catalyst

Organometallic Chemistry

Definition of organometallics

The compounds containing at least one M-C bond between metal and cabon of organic molecule, ion and radical is called Organometallic compounds (OMC)

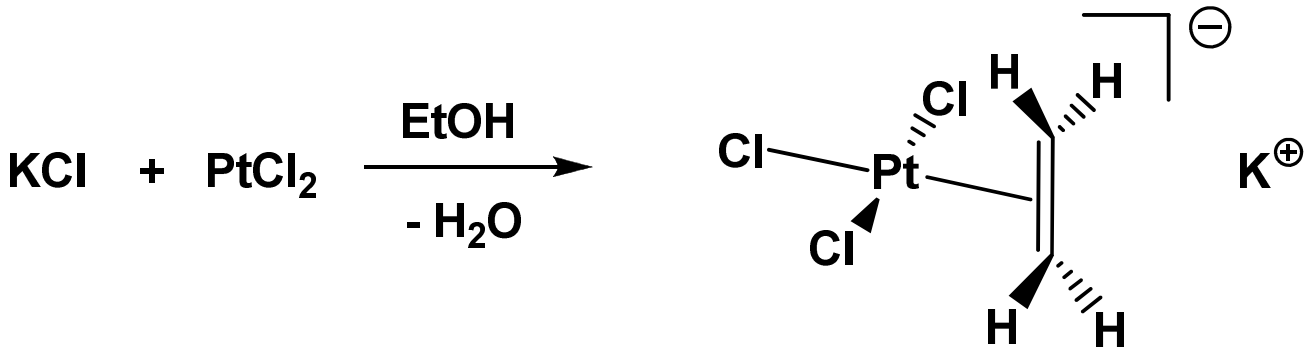
M-C **e.g** **$Na-CH_3$**

C must be carbon from organic group

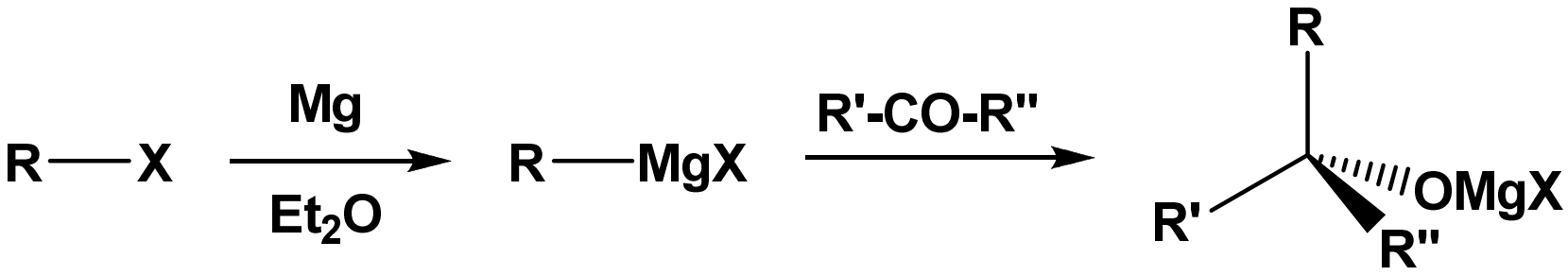
'Classically, compounds having bonds between one or more metal atoms and one or more carbon atoms from organic group are termed as organometallic compounds'

History: First organometallic compounds

- 1827 Zeise's salt (platinum - olefin complex)



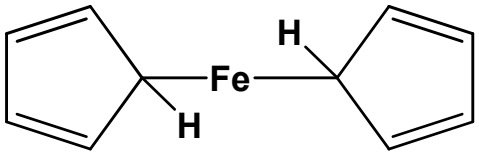
- 1912 Nobel prize Victor Grignard and Paul Sabatier



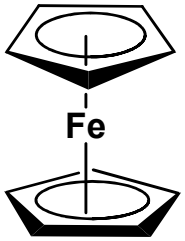
Discovery of ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$

1973: Nobel prize: Geoffrey Wilkinson and Ernst Otto Fischer on sandwich compounds

– Though Keally, Pauson, and Miller report the synthesis, the Nobel prize was given to Wilkinson and Woodward (for reporting the correct structure)



Pauson, 1951



correct structure
Woodward and Wilkinson, 1952

The organometallics (OMC'S) are similar to

1.Metal carbonyls e.g. $Ni(CO)_4$, 2.Cyanos e.g. NaCN.

However, They are NOT considered as omc's because; the carbon bonded to metal is not the part of a typical organic substrate.

The M-C bonds are weaker than M-N, M-O & M-X

C in OMC is negatively polarized [nucleophile] while,

(in OC [e.g. C-N, C-O] C is positively polarized [electrophile]

The bond weakness is the basis for use of OMC's in the syntheses.

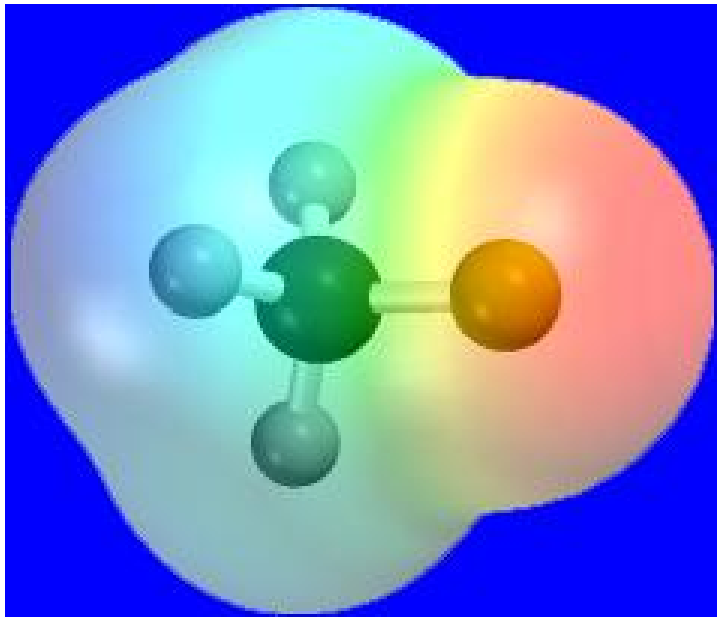
OMC Reactivity depends on electro+vity of M, therefore for compounds of the same group elements, the reactivity steadily decrease as we move down in the group.

Electronegativities

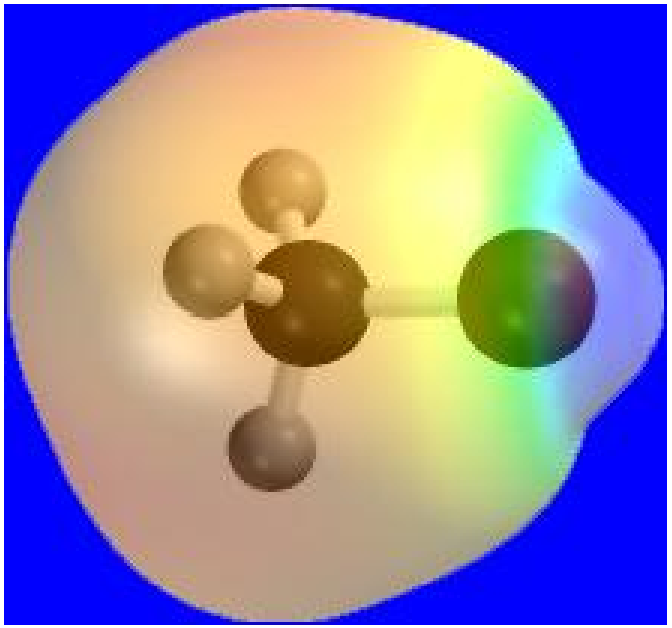
F	4.0
O	3.5
N	3.0
C	2.5
H	2.1

H	2.1
Cu	1.9
Zn	1.6
Al	1.5
Mg	1.2
Li	1.0
Na	0.9
K	0.8

Polarities of Bonds



CH_3F



CH_3Li

SYSTEM OF NOMENCLATURE

Three general types of nomenclature.

1. Binary Type Nomenclature:

Used to name salt like ionic species.
OMC of ionic character are considered as derivatives of inorganic salts.
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e.g. $CH_3Mg^+Br^-$: methylmagnesium (II) bromide.

$C_6H_5Hg^+OOCCH_3^-$: phenylmercury(II) acetate.

$(CH_3)_3Sn^+Br^-$: trimethyltin (IV) bromide.

The usual rules for naming the substituents are used
e.g.$(C_6H_2Cl_3)_2Hg$: bis(trichlorophenyl) mercury.

2. Substitutive Nomenclature:

OMC of the main-group elements are similarities to organic compounds.
Therefore, organic nomenclature rules can be used.
They are named by first naming the organic group with proper ending followed by name of metal.
The *s* and *p*-Block organometallics are named either as
i) derivatives of hydride or
ii) ii) substituents in organic compounds.

i) As Derivatives of Hydride:

The first system is based on the concept of a parent hydride
e.g. SiH_4 = silane, AsH_3 = arsane etc.

The OMC are considered as the derivatives of parent hydrides formed by replacement of H. (used for naming *p*-block element compounds)

$B(CH_3)_3$ –Trimethylborane, $Si(CH_3)_4$ –Tetramethylsilane,

$As(C_2H_5)_3$ –triethylarsane, $B(C_6H_{11})_2H$ -dicyclohexylborane.

ii) As Substituents in Organic Compounds:

The name of OMC is derived from organic group attached via a carbon. Bonds are highly covalent

The ending –e of the parent organic species is changed to –yl followed by the name of metal without any gap.

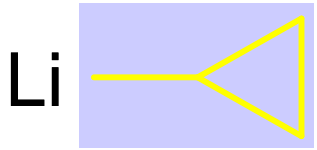
For normal chain, the locant '1' is omitted, for branched chain; the locant number including '1' must be cited.
For example:

CH_3- CH_2- CH_2- CH_2- CH_2- Na : Pentanylsodium.

***This method is used to name covt OMC having saturated, acyclic and monocyclic hydrocarbon substituent groups.**

e.g. BuLi : Butyllithium,
CH_3Na : Methylsodium,
CH_3 –CH_2Li : Ethyllithium,
CH_2=$CHCH_2Na$: 2-Propenylsodium,
CH_2=CHNa : Ethylenesodium,

Naming:examples



Cyclopropyllithium

$H_2C{=}CHNa$

Vinylsodium

$CH_3CH_2MgCH_2CH_3$

Diethylmagnesium

CH_3MgI

Methylmagnesium iodide

3. Co-ordination Nomenclature (For OMC of *d*- and *f*-block elements)

OMC are thought to be produced by addition reactions therefore, It name is built according to co-ordination chemistry rules.

The OMC containing an organic ligand are named by replacing final –e of parent compounds by –ide.

E.g. CH_3 – methanide,
C_5H_5– cyclopentadienide.

Names of Neutral and cationic names are not modified.

η, μ, k Notations:

To designate the points of attachment of ligands to metal(s), the η, κ, and μ-notations are used.

1. η (eta) notation

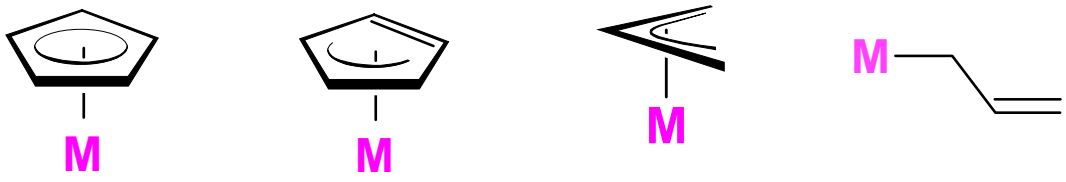
The numbers of C-M bonds are specified by prefix η(*eta*), called *hapticity.

If the ligand bonds through one atom, it is called *monohapto.* Some ligands, e.g. benzene, may bond to M through 1, 2 or 3 π bonds. So, we can describe benzene as *bi-, tetra- or hexa-hapto* and use the notation *η2, η4* and *η6,*

$(C_6H_6)_2Cr$: bis(η6-benzene)chromium.

For example

η^x



η^5-Cp	η^3-Cp	η^3-allyl	η^1-allyl

2. The μ (*mu*) Notation:

***Organic species that bridge two M are indicated by prefix μ (*mu*),which appears before ligand and separated by a hyphen.**

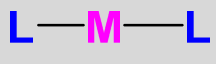
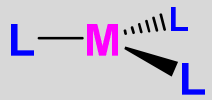
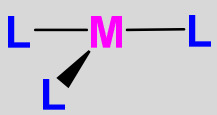
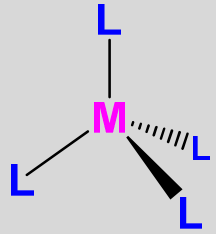
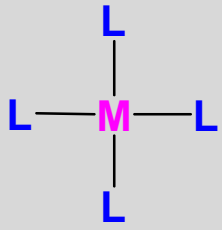
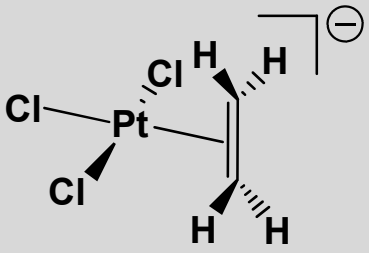
If bridging ligand is complex, it is enclosed in bracket. For example: (μ -ethane-1,1-diyl)bis(pentacarbonylrhenium)

3. The k (kappa) Notation:

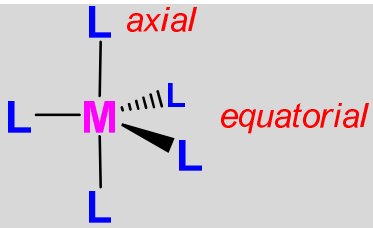
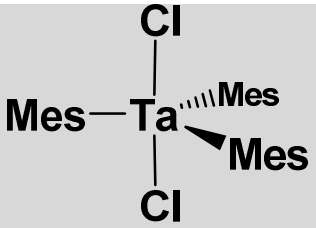
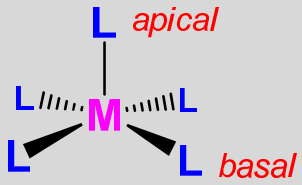
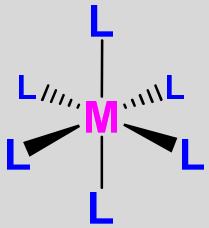
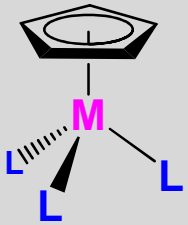
***The points of attachment (ligation) of a polyatomic ligand to M are indicated by the italic element symbol preceded by k (kappa)**

***Metal-Metal bonding may be indicated in names by italicized atomic symbols of the appropriate metal atoms, separated by a long dash and enclosed in parentheses.**

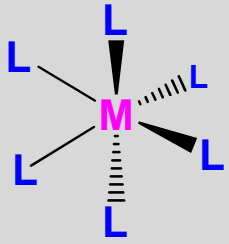
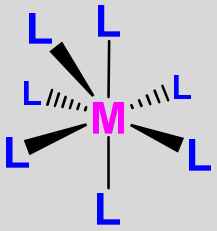
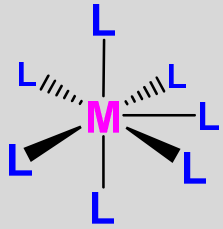
Coordination geometries

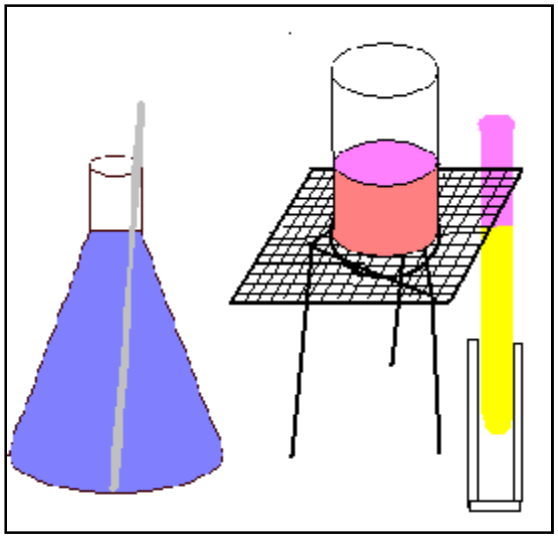
CN	Geometry	Example
2 linear		$[NC–Ag–CN]^-$
3, trigonal		$Pt(PPh_3)_3$
3, T shape		$[Rh(PPh_3)_3]^+$
4, tetrahedron		$Ti(CH_2Ph)_4$
4, square planar		

Coordination geometries

CN	Geometry	Example
5, trigonal bipyramid		
5, square pyramid		$[Co(CNPh)_5]^{2+}$
6, octahedron		$W(CO)_6$
6, pseudo-octahedron		$FeCp_2$

Coordination geometries

CN	Geometry	Example
6, antiprism		WMe_6
7, capped octahedron		$[ReH(PR_3)_3(MeCN)_3]^+$
7, pentagonal biprism		$[IrH_5(PPh_3)_2]$



Preparation of OMC's

GENERAL:

OMCs are similar to H- compounds (similar elect-ve of M-C, C-H & M-H)

***The species that lose H form ionic compounds with alkali metals.**

OMC's are used in organic synthesis.
They are superior to Grignard reagents (e.g. in alkene polymerization).

***They are liquids or low melting solids, thermally stable than other OMC of the same group. Soluble in organic and non-polar solvents. All OMC's of alkali metals are unstable.**

***In alkaline earth metals, the reactivity and electropositivity ↑ in the group. Therefore, the OMC of Be and Mg are covalent, while Ca, Sr and Ba form only few ionic compds that are unstable and of little utility.**

***OMC's of group 13 elements exist as electron deficient species having +3 OS (e.g.Al3+), with 3c-2e bonding.**
Organoaluminium compounds are used for alkene polymerization, catalysts& chemical intermediates.
Trialkylaluminum is a diamer but often written as the monomer, AlR_3.

A) Organolithium Compouds

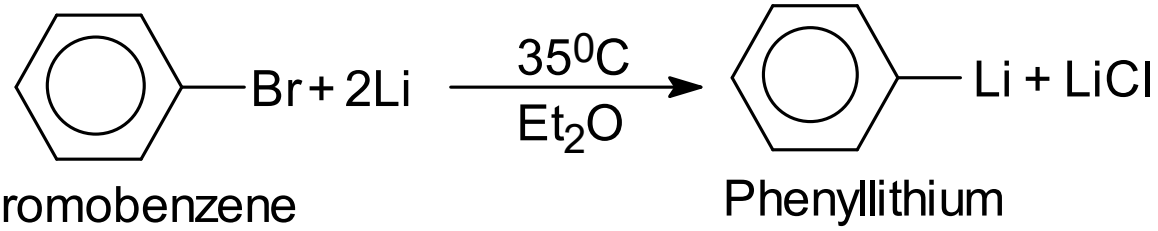
i) Reaction of Alkyl or Aryl Halide with Li Metal:

Alkyl/Aryl halides react with lithium in inert solvent such as ether, benzene, petroleum ether, cyclohexane etc.

The moisture and air must be excluded as they react with reactant and products.

1. $4R{-}X + 8Li \xrightarrow{\text{ether}} 4R{-}Li + 4\,LiX$

2.



Bromobenzene → Phenyllithium

Examples

3. $4CH_3Cl + 8Li \xrightarrow{\text{solvent}} (CH_3Li)_4 \text{ OR } (CH_3)_4Li_4 + 4LiCl$

4. $C_2H_5Cl + 2Li \longrightarrow C_2H_5Li + 2LiCl$

5. $C_6H_5Br + 2Li \longrightarrow C_6H_5Li + 2LiCl$

6. $\underset{\text{Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} + 2Li \xrightarrow[Et_2O]{-10^0C} \underset{\text{Butyllithium}}{CH_3CH_2CH_2CH_2Li} + LiCl$

Features:

***The organolithiums react slowly with ether, therefore, the synthesis is usually carried out in inert atmosphere of nitrogen or argon at low temperature.**

***The use of cyclohexane as solvent, alkyl or aryl chlorides over bromides and iodides minimizes the possibility of side reactions**

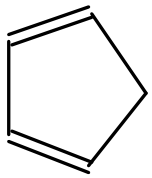
***The yield and reactivity is improved by adding 0.5-1% Na.**

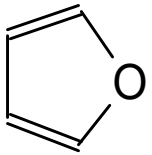
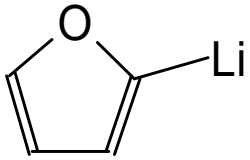
ii) Metal Hydrogen Exchange (Metallation):

Alkyl and aryl lithium can be synthesized by reacting the Organic compounds with alkyl/ n-butyl lithium, ($(C_4H_9)Li$ called nBuLi).
The reaction, in general, can be written as;

1. $RH + R'Li \rightleftharpoons RLi + R'H$

2. $C_2H_6 + (C_4H_9)Li \rightleftharpoons C_2H_5Li + C_4H_{10}$
   Ethane ButylLithium Ethyllithium Butane

3.  $+ CH_3Li \longrightarrow C_5H_5Li + CH_4$

4.  $+ PhLi \longrightarrow$  $+ C_6H_6$

The reactions gives small aggregates having multi-center bonding;

e.g. $(CH_3)_4Li_4$ or $(C_2H_5)_6Li_6$

which contain bridging alkyl groups

*When ethers are solvent, methyl lithium exists as $(CH_3)_4Li_4$.

*while in hydrocarbon solvents (e.g THF), it exist as $(CH_3)_6Li_6$.

*LiCl destroys $(CH_3)_4Li_4$, so, LiCl is added in reaction.

iii) M-X Exchange (Metathesis/ Double Displacement):

Double displacement reaction betn OMC (MR') & organohalide, (RX) involves M-X exchange therefore, it is called *metal-halogen exchange* or *metathesis*.

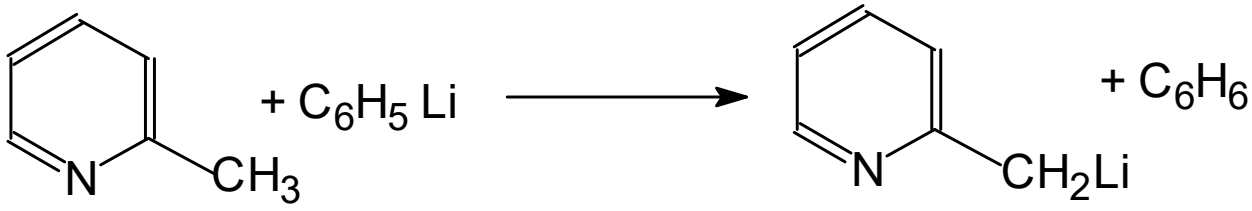
A large number of OMC are prepared in this way.
The common reagents used are;
alkyllithium,
alkylmagnesium and
alkylaluminium.

Butyllithium is most suitable for preparing lithium derivatives of comparatively acidic hydrocarbons.
This type of reaction can be represented as;

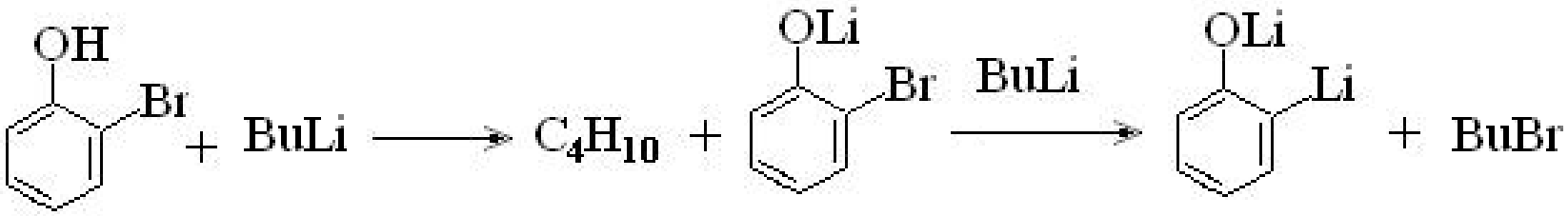
RX + MR' → RM + R'X

examples

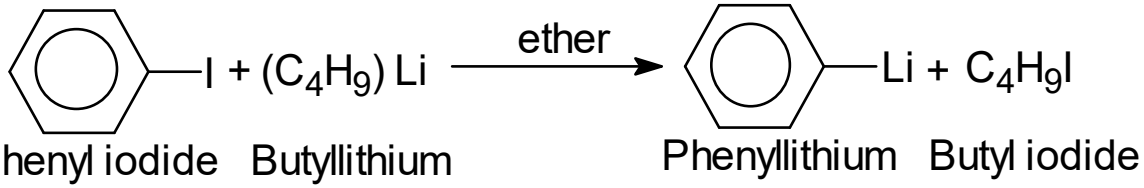
1.



2.



3.



iv) Transmetallation:

One OMC react with other, the exchange of organic part takes place between them, such reaction is called transmetallation reaction.

These reactions are most convenient to prepare vinyl, allyl and unsaturated derivatives.

$$PhLi + (CH_2{=}CH)_4Sn_4 \rightarrow CH_2{=}CHLi + Ph_4Sn$$

Lithium alkyls can also be prepared by metal displacement reaction. Usually organomercury compounds are used when the isolation of the product is required.

For example:

$$R_2/Ar_2Hg + 2Li \rightarrow 2R/ArLi + Hg$$

$$(CH_3)_2Hg + 2Li \rightarrow 2CH_3Li + Hg$$

Organolithium compounds are mainly used in homogeneous catalysis, for example, in stereospecific polymerization of alkene

B) ORGANOBERYLLIUM

i) Metathesis:

Beryllium halide reacts with an OMC of a different metal (e.g.lithium,sodium etc.).

$BeCl_2 + 2\ CH_3Li \xrightarrow{ether} Be(CH_3)_2 + 2LiCl$ (Dimethylberyllium)

$BeCl_2 + 2\ MgCH_3Cl \xrightarrow{ether} (CH_3)_2Be + 2\ MgCl_2$

$BeCl_2 + 2\ C_6H_5Li \xrightarrow{ether} Be(C_6H_5)_2 + 2LiCl$ (Diphenylberyllium)

$3(C_2H_5)_2Be + 2(C_6H_5)3B \rightarrow 2(C_2H_5)_3B + 3(C_6H_5)_2Be$

Diphenylberyllium

$BeCl_2$ reacts with $Na[C_5H_5]_2$ to give Bis(cyclopentadienyl)Be (double displacement). The anion is transferred to less electropositive Be(II).

$BeCl_2 + 2\ Na\ [C_5H_5] \rightarrow [C_5H_5]_2Be + 2NaCl$

Beryllium is less electro+ (or more electro-) than Li, Na, Mg, so it forms OMC while more electropositive metal forms halide.

However, the product is always associated with ether molecules which can not be separated easily.

ii) Transmetallation from Mercury Alkyl:

This method is used to get ether free product.

Pure Be is heated with mercury alkyl or aryl.

$$Be + (CH3)_2Hg \xrightarrow{110^0C} (CH_3)_2Be + Hg$$

$$Be + (C_6H_5)_2Hg \xrightarrow{110^0C} (C_6H_5)_2Be + Hg$$

The product is collected by vaccum distillation.

OMC's of Be are toxic, have no commercial applications.

They are used in laboratory as synthetic intermediates.

C) Organoalluminium

i)Transmetallation:

Alkyl aluminium compounds are prepared in laboratory by transmetallation of a mercury compound. For example,

$$3\ R_2Hg + 2Al \xrightarrow{90^0C} 2\ R_3Al + 3Hg$$ **[R is alkyl or aryl group]**

ii) Reaction of alkyl halide with Al metal:

The reaction of Al &chloromethane gives Dimethylaluminium, $(CH_3)_4Al_2Cl_2$. This is then reduced with sodium to give $(CH_3)_6Al_2$.

$$2Al + 3CH_3Cl \xrightarrow[AlCl_3]{\text{Trace of } I_2} (CH_3)_3Al_2Cl_3$$

$(CH_3)_3Al_2Cl_3$ disproportionate to $(CH_3)_4Al_2Cl_2$ and $(CH_3)_2Al_2Cl_4$.

NaCl is added to remove $(CH_3)_2Al_2Cl_4$ as soluble $Na[CH_3AlCl_3]$ then $(CH_3)_4Al_2Cl_2$ is separated by distillation. It is then reacted with Na

$$3(CH_3)_4Al_2Cl_2 + 6\,Na \longrightarrow 2(CH_3)_6Al_2 + 2Al + 6NaCl$$

The commercial synthesis of triethylaluminium is carried using Al & alkene and H_2gas at 110^0C temp. under pressure (hydroalumination)
This route is relatively cost effective.

$$Al + 3/2H_2 + 3\,C_2H_4 \longrightarrow (C_2H_5)_3Al$$

iii) From Alkyl Aluminium Hydride:

Aluminium hydride reacts with olefins to give aluminium alkyls

$$AlH_3 + 3\ CH_2{=}CH_2 \rightarrow (CH_2CH_3)_3Al$$

The reaction is specific to Al hydrides.

Aluminium hydrides are made by reaction of Al, H_2 and aluminium alkyls.

Organoaluminium compounds are used as Zeigler Natta catalyst for alkene polymerisation & in aluminium alkoxides & amides making.

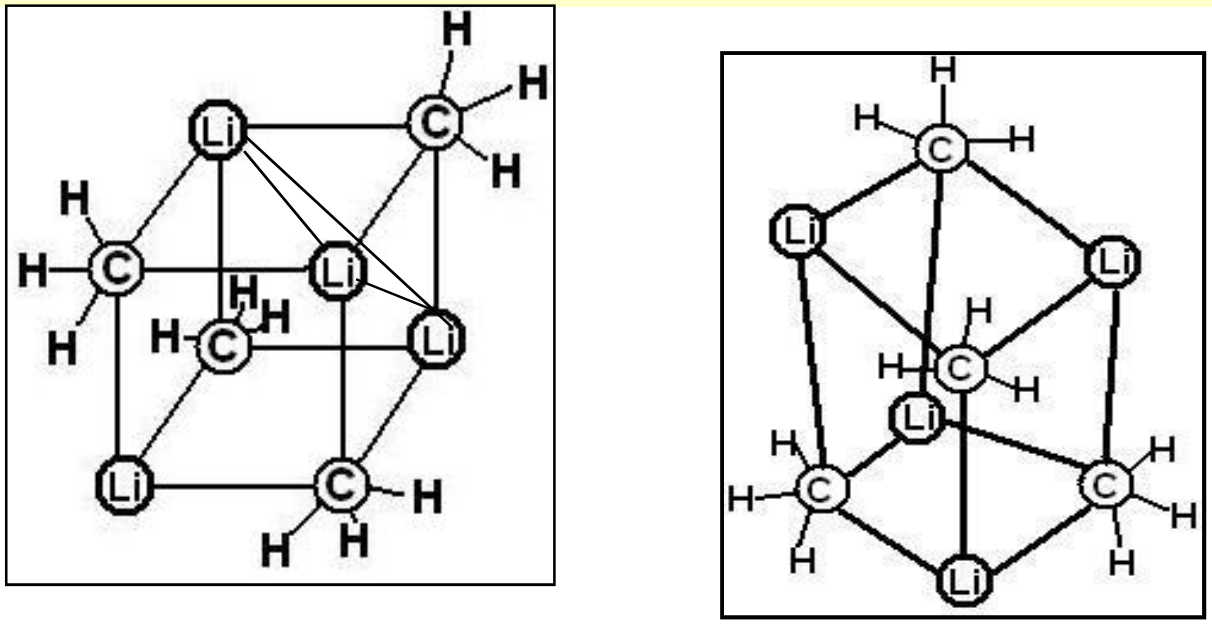
STRUCTURAL STUDY OF ALKYL LITHIUM:

1. They are crystalline & polymers (in liq &sol state)
2. They are Covalent
3. OMC of Li are tetramer & hexamer.
4. The alkyl compounds are electron deficient.
5. The synthesis always gives some quantity of aggregates having multi-centre bonding & bridging alkyl groups e.g. $(CH_3)_4Li_4$ & $(C_2H_5)_6Li_6$.
6. The tendency of 'aggregation' decreases with increasing bulkiness of organic groups.
7. The monomeric do not satisfy octate rule, therefore, they form aggregates where e- are delocalized in multi-centered bonds.

8. XRD study indicates presence of 4 Li at the corners of a tetrahedron (td).

Each of CH_3 lies above middle of each td face & forms a triple bridge to the 3 Li atoms which make up the face of Td

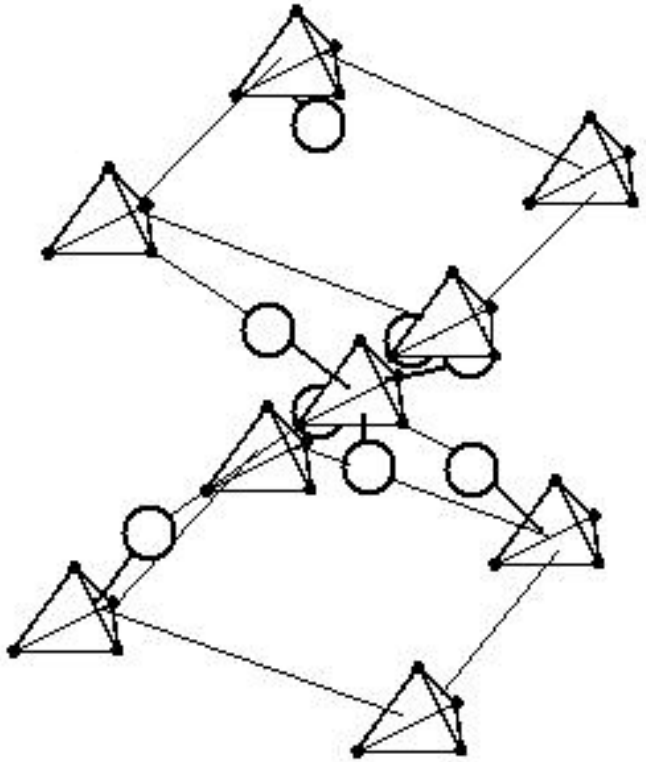
(distorted cube)

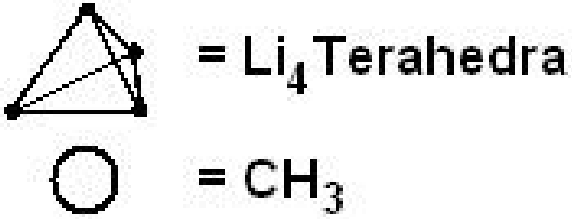


Unit cell showing distorted cubic structure of $Li_4(CH_3)_4$ unit.

9. Each C in $(CH_3)_4Li_4$ unit is bonded with adjacent Li_4 tetrahedra providing a sort of linking throughout the solid lattice.

Thus, a number of $(CH_3)_4Li_4$ units are interconnected along cube diagonals via $-CH_3$ bridging groups as show below;





10. In $(CH_3)_4Li_4$, each Li has 3 adjacent C atoms & each C atom has 3 Li and 3 H atoms as nearest neighbours.

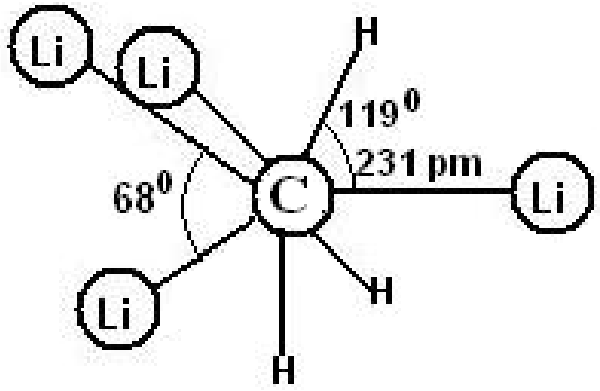
Li- C length within tetrahedron is 231 pm.

The Li- C in adjescent tetrahedron is, however, little higher (236 pm).

It has 12 Li-C links with only 8 e^- to hold them indicating that compound is electron deficient.

C has CN = 7 (it is bonded to 3 H, 3 Li in one tetrahedron and 1 Li in the adjacent tetrahedron).

Li also has CN = 7 (since it is bonded to 3 Li atoms, 3 methyl C in a tetrahedron and 1 Li in another tetrahedron).

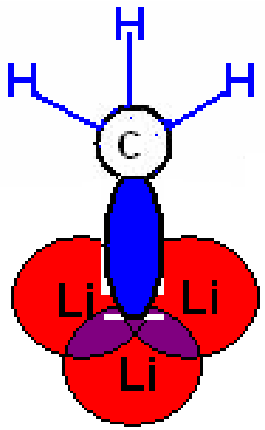


9. **The CN = 7 cannot be explained as the C atom has only one *s* and three *p* orbitals available for bonding.**

It can be explained on the basis of formation of *four centered-two electron (4c-2e) bonds*.

The bond is formed by overlap of sp^3 HO of C and *s* type AO of each of the 3 Li atoms. The bond has two electrons and is localized over four centers (Li_3C).

This 4c-2e bond is present over each face of Li_4 tetrahedra.



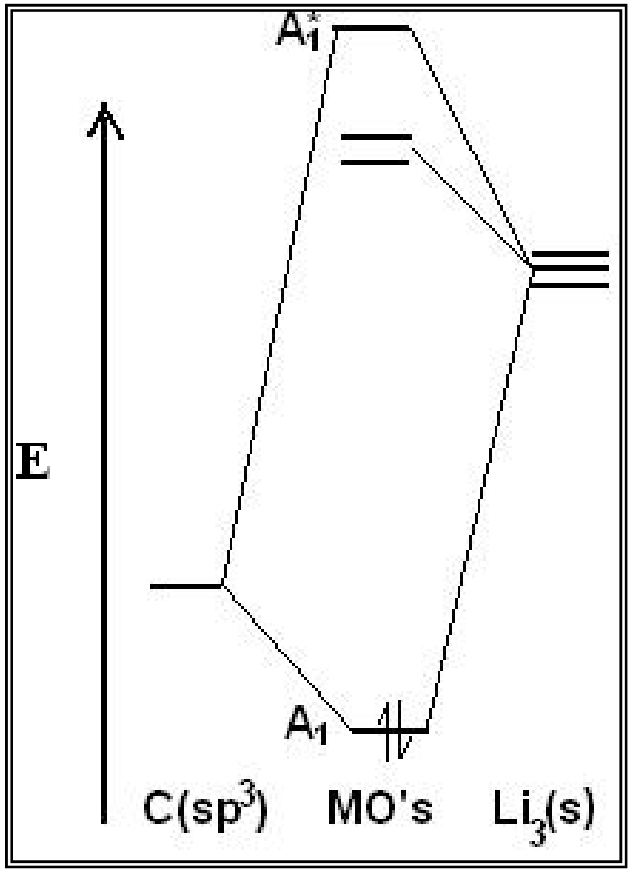
Localized 4 centered MOs pointing towards centre of Li_3C

11. **According to MOT, 4c-2e bonding is explained by formation of a set of semilocalized MO's**

Totally symmetric combinations of one sp^3 HO of C and three *s* type AO from 3 Li gives four MOs.

Out of 4 MOs one is bonding, two are nonbonding and one is antibonding.

The lowest energy MO (bonding) occupies two electrons (one from C & one from Li) while other MOs are empty.



2. STRUCTURAL STUDY OF ALKYL

BERYLLIUM:

Be(4): $1S^2,2S^2,2P^0$(GS), $1S^2,2S^1,2P^1$(ES),

So it has two electron for bonding.

C has only one electron in SP^3 HO.

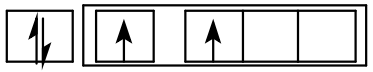
So to bind two CH_3 and one Be we need four electons. Therefore,

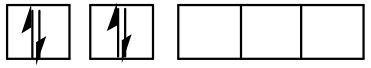
Alkylberyllium compounds are electron deficient.

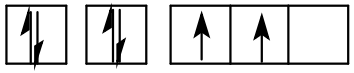
2. Methylberyllium, is a monomer in vapour phase. In solid state, it exists as polymer.
3. Bulkier alkyl groups attached to Be atom show lower degree of polymerisation.
4. XRD studies indicated polymeric structure with tetrahedral Be co-ordinated by methyl groups.
5. The structure of $(CH_3)_2Be$ is analogous to $BeCl_2$.
6. The bonding in $Be(CH_3)_2$ is 3c-2e bonds (Analogous compound BeCl2 has 2c-2e bonding)

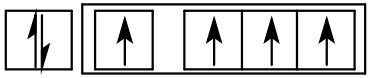
7. The 3c-2e bonding:

In $Be(CH_3)_2$, both, Be and C are sp^3 hybridized.

Be(4) : $1s^2$, $2s^2$(G.S) 

Be(4) : $1s^2$, $2s^1$,$2p^1$ (E.S)  [sp^3 hybridization]

C(6) :$1s^2$, $2s^2$,$2p^2$.(G.S) 

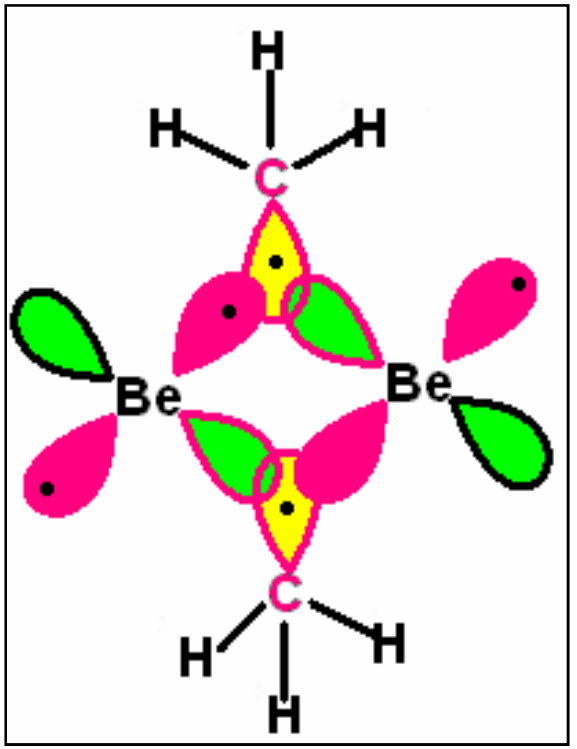
C(6):$1s^2$, $2s^1$,$2p^3$.(E.S)  [sp^3 hybridization]

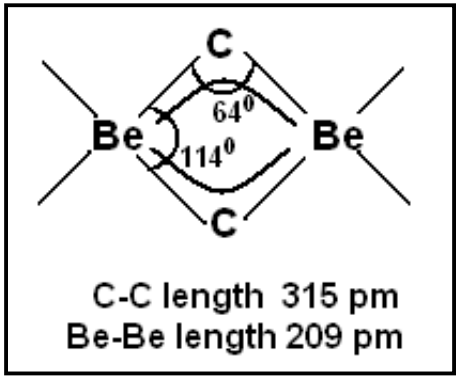
In Be, one *s* orbital (with one electron) and three *p* orbitals (with one electron) hybridize to produce 4sp^3 HO's containing two electrons.

In this way only two HOs contain unpaired electrons, while other two HOs are empty.

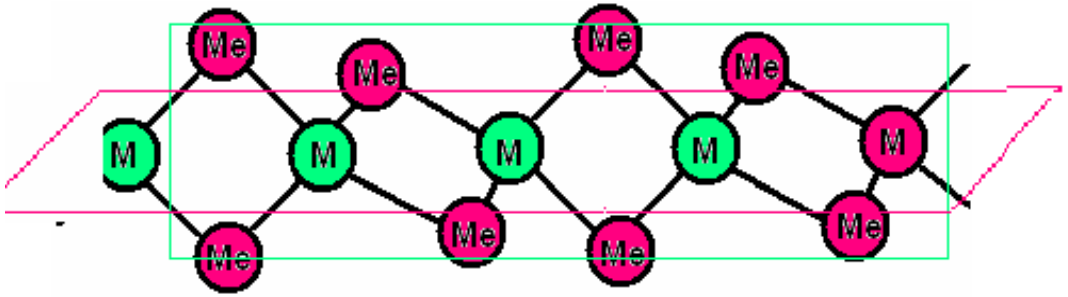
The 'C' HOWEVER forms 4 HOs containing four unpaired electrons.

- It has 2 bridging CH_3 groups linking 2 adjacent Be atoms by 3c-2e bonds.
- The overlap of 1*sp*^{3} HO(empty) of first Be, 1*sp*^{3} HO of C (from CH_3) containing 1 electron and sp^3 HO of another Be containing 1 electron give 3c-2e bonding.
- Similarly, other 3c-2e bond is formed. The overlap of 1*sp*3 HO of first Be containing 1 electron, 1*sp*3 HO of C from other methyl group containing 1 electron and an empty *sp*3 HO of other Be.
- The bonding pair of electron is delocalized over three centers. Each C atom in Me_2Be shows a CN = 5.





- **Simple methyl beryllium is polymeric However, higher alkyls are progressively less polymerized.**
- **E.g, diethyl and isopropyl beryllium are dimeric, while t- butyl beryllium is monomeric.**



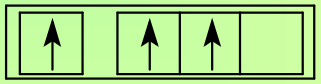
Polymeric structure of M(Me)2, M = Be, Mg.

STRUCTURAL STUDY OF ALKYL ALUMINIUM

1. Tri alkyls & aryls of Al are dimers (in solid & vapour phase) with terminal and bridging methyl/ aryl groups.
2. $(Me_3Al)_2$ is a solid (mp 15^0C) with methyl bridging involving 3c bonding (similar to $AlCl_3$,with methyl groups replacing Cl atoms).
3. In $AlCl_3$, the bridging Al–Cl–Al bonds are normal 2c-2e bonds While in alkylaluminium compounds, the Al–C–Al bonds are 3c- 2e bonds & are longer than the terminal Al-C bonds,

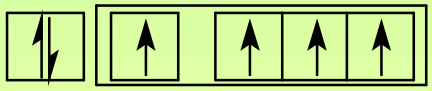
4. 3C bonding involves sp^3 hybrid orbital from two Al atoms and bridging alkyl carbon atoms.

Al(13) : $1s^2$, $2s^2$, $2p^6$,$3s^1$,$3p^2$ (E.S)



sp^3 hybridization.

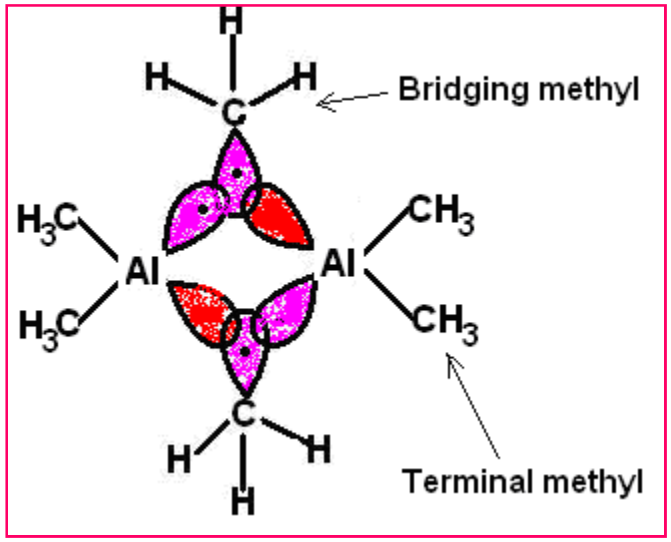
C(6) : $1s^2$, $2s^1$,$2p^3$. (E.S)



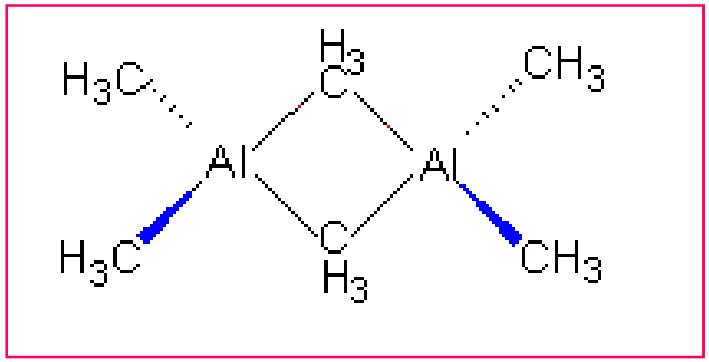
sp^3 hybridization.

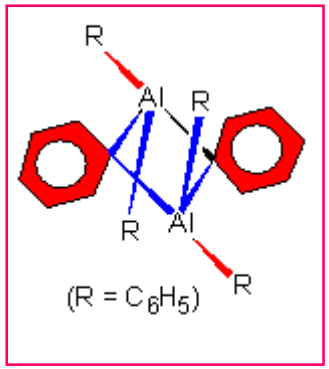
The hybridization on both Al and C is sp^3. Out of 4 HOs on Al, one is empty. This empty HO of one Al, half filled HO of other Al and half filled HO of one methyl C overlap to produce one bridge bond involving 3c-2e.

Similarly, second bridge is produced by overlap of one half filled HO of first Al, empty HO of other Al and half filled HO of second methyl C.



<= Dimer =>





Though R is bulkier, still the compound exists as dimer

5. **Triphenyl aluminium exists as a dimer with bridging phenyl groups This structure has less steric hindrance. The 3c-2e bonding is strengthened due to participation of phenyl pi orbital.**
6. **Steric factors also have a powerful effect on the structures of aluminium alkyls. For example, triphenyl aluminium is a dimer but the mesityl, (2,4,6-(CH3)3C6H2)3Al compound is a monomer.**

7.NMR study of Me_6Al_2

At 25^0C shows 1 resonance peak.

However, when spectrum is taken at -75^0C, it shows 2 resonance peaks.

The two lines corresponding to presence of 2 types of H envt. One due to bridging and other due to terminal Me groups.

This means at RT, two types of alkyl groups (bridging and terminal) are interchanged rapidly giving only one peak.

This kind of rapid exchange of alkyl groups provides a facile mechanism for alkyl exchange reactions.

MONONUCLEAR CARBONYL

Definition:

Compounds of Transition metals with carbon monoxide are termed as metal carbonyls or simply carbonyls.

The general formula is $M_x(CO)_y$. M transition element.

The metal atom act as *Lewis acid* while CO act as *Lewis base* (ligand).

When x is 1,2,3 etc. then they are called mononuclear, binuclear or trinuclear carbonyls respectively.

The elements from groups 8,9 and 10 form many carbonyls. In carbonyl metal is,

The important features are;

1) CO is not a strong ligand still it forms a strong bond with M.
2) M are always in lower OS, (zero & low positive or negative OS.
3) Almost all carbonyls obey 18 valence electron rule.
4) All carbonyl compounds are volatile and toxic. The toxicity is dueto strong, irreversible bonding with Hb in blood.
5) The transition metal organometallic compounds are very similar to many of the co-ordination compounds in physical and chemical properties.
6) In fact, the properties of organometallics are much more 'organic' in nature.

CC Vs OMC

	Coordination Compounds	Organometallic Compounds
1	Soluble in water.	Soluble in hydrocarbon.
2	They are not sensitive to air.	They are air sensitive.
3	They have high MP(>250°C).	They have low MP

Name	Structure	Properties
Hexacarbonyl vanadium(0)	Octahedral (d^2sp^3)	It is a greeny black, paramagnetic, volatile, solid, soluble in organic solvents, Solution is yellow-orange. It is a 17-electron species. Decomposes at 70^0C.
Hexacarbonyl chromium/ molybdenum (0) tungsten(0)	Octahedral (d^2sp^3)	All are white, crystalline, stable, 18- electron species, volatile, soluble in organic solvents, sublime under vacuum.
Pentacarbonyl manganese(0)	Trigonal bi pyramidal (dsp^3)	17-electron species, readily dimerises to 18-electron $Mn_2(CO)_{10}$ species, which is yellow, crystalline. The Mn-Mn bond is long , weak ,can be broken easily.
Pentacarbonyl iron(0)	Trigonal bi pyramidal (dsp^3)	Diamagnetic, yellow, toxic volatile liquid, soluble in organic solvents, B.P. 103^0C.
Pentacarbonyl ruthenium(0) Pentacarbonyl osmium(0)	TBP(dsp^3)	Colorless liquids, form cluster compounds.
Tetracarbonyl cobalt(0)	Tetrahedral (sp^3)	It is a 17- electron species, dimerises to orange $Co_2(CO)_8$ which is low-melting solid, exists in two isomeric forms. Forms black solid cluster compounds, $Co_4(CO)_{12}$ & $Co_6(CO)_{16}$
Tetracarbonyl nickel(0)	Tetrahedral (sp^3)	Very toxic, colourless, inflammable liquid

The 18 electron rule (EAN)

It states that 'thermodynamically stable organo-metallics has the sum of the metal *d* electrons plus the electrons donated by the ligands is equal to 18'.

The central metal ion can accommodate electrons in *d*, *s*, and *p* orbitals, giving a max. of 18.

In this way, the metal attains electron configuration of the next higher noble gas.

The 18-electron rule is also known as the 'noble-gas rule' or the 'effective atomic number (EAN) rule'.

Complexes with 18e counts are referred as ***saturated***, because they have no empty low-lying orbitals to which another incoming ligand can bind. Complexes with counts lower than 18e are called ***unsaturated*** and can electronically bind additional ligands.

The 18-e Rules:

Counting of electrons:

The rule is used to predict the existence & number of metal-metal bonds. Most stable OMC obey the rule.

CO supplies 2 electrons to metal.

The intramolecular partitioning of electrons has to ensure that the total complex charge remains unchanged.

A metal-metal bond, if present, contributes one electron to the count on each metal. Metal-metal double or triple bonds supply 2 & 3 electrons, respectively, to each metal.

The electron pair of a bridging ligand such as CO donates one electron to each of the bridged metals

However other stable compounds with electron other than 18 do exist.

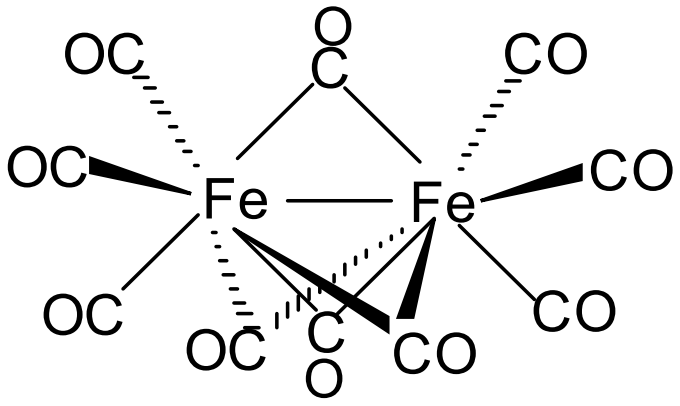
In such compounds, the factors such as CFSE, nature M-C of bonding affects the stability of the compound.

Some of the organometallic compounds of *d* block (Groups 9& 10) obey 16-e- rule.

$V(CO)_6$ have 17 e-, therefore called 17e- species. It readily completes 18-e- configuration by accepting an electron from reducing agent or by dimerising with another molecule.

For example, $Mn(CO)_5$ has 17-electrons. Two molecules 'share' their odd electron, in order to form a Mn-Mn bond. Consequently each Mn becomes an 18- e-species.

A simple example



3 CO -- 6 e^-
3 μ CO -- 3 e^-
Fe -- 8 e^-
Fe-Fe -- 1 e^-
18 e^-

Tetracarbonyl nickel(0), $Ni(CO)_4$.
[28(Ni) + 2 X 4 (CO) = 36 (Kr)]

Pentacarbonyl iron(0), $Fe(CO)_5$.
[26(Fe) + 2 X 5(CO) = 36 (Kr)]

Bonding in Metal Carbonyls

1. Spectroscopic study indicated that CO, is present as a part of the molecule.

2. Simple carbonyl contains terminal CO groups which bonds through C and not O. However, polynuclear carbonyls may contain bridging CO.

3. In carbonyls, the sigma bonding is reinforced by additional pi bonding which stabilizes
   i) complexes & ii) very low oxidation states of metal.

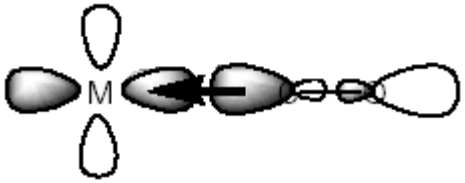
4. Many carbonyl compounds have metal in a zero oxidation state. The very low oxidation states are not found with sigma-bonding ligands such as H_2O & NH_3.

5. In CO, the highest energy occupied molecular orbital (HOMO) is a sigma 2*p* orbital & lowest energy unoccupied molecular orbitals (LUMOs) are the pi 2*p* antibonding orbitals.

Bonding in Metal Carbonyls

6. 6 CO ligands are simultaneously donating electrons to a Metal via the overlap of the HOMO of CO with an empty *d or hybrid* orbital of the M.

   This leads to formation of σ bond between M and CO i.e. (M←CO).



7. However by this, electron density on the metal ion becomes very high. To stabilize low oxidation states excess electron density is to be removed, this is done by another type simultaneous bonding with CO. This simultaneous bonding called ‘back bonding’

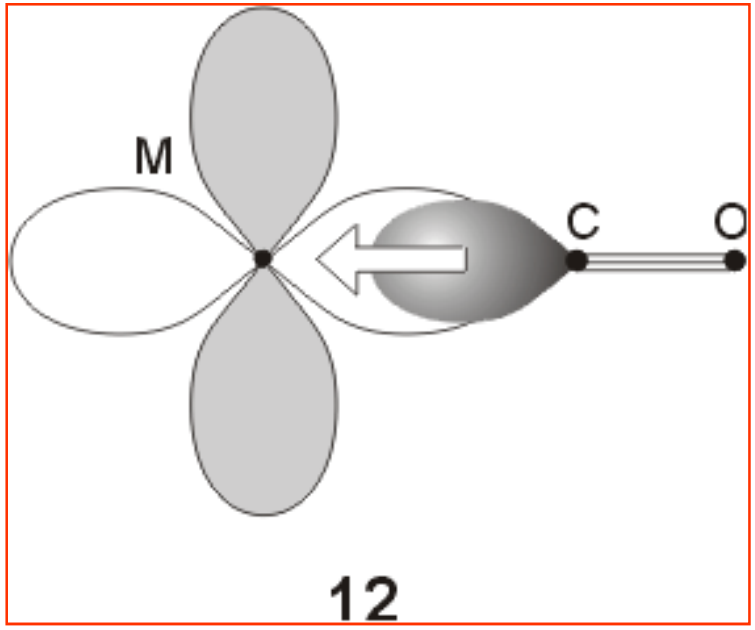
A filled d orbital on the metal overlap with the pi LUMO of the carbon monoxide. These two orbitals have the correct symmetry for overlap.This removes the electron density from the metal center, back onto the carbonyl ligand to some extent (M→Cp). This additional bond is a $d\pi$–pπ bond.

So, the carbon monoxide is said to be a sigma-donor and pi-acceptor and the metal is a sigma-acceptor and pi-donor.

Thus the electrons flows from carbon monoxide to metal through the σ bonding and a flow through the π bonding in the reverse direction. This interaction is known as *back bonding* or *synergistic bonding*.

This *synergistic effect* leads to a strong, short, almost double, covalent bond between metal and carbon atoms.

Synergic Bonding: Back bonding



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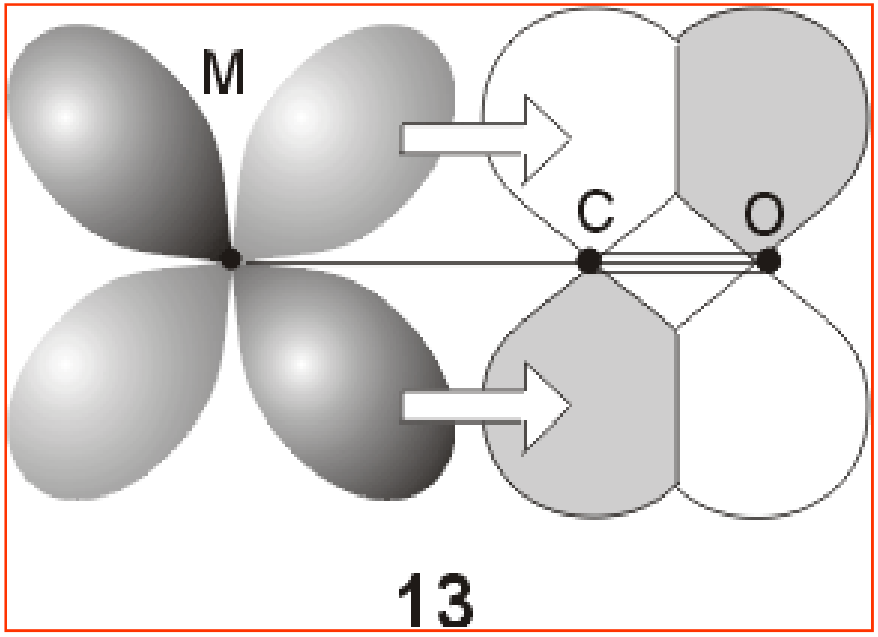
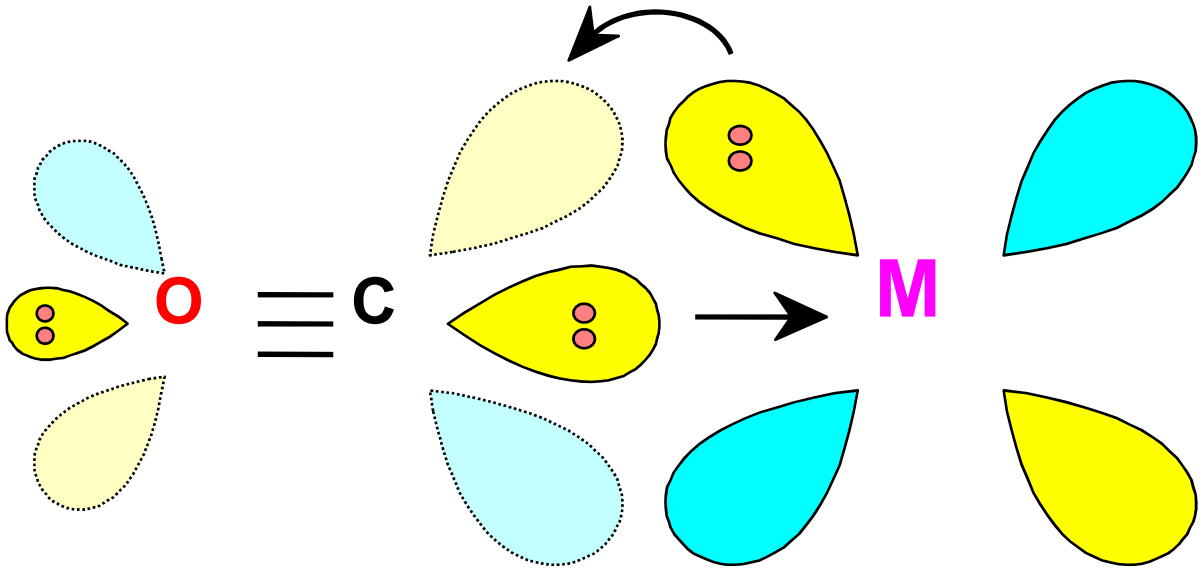
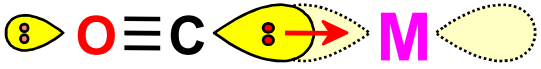


13

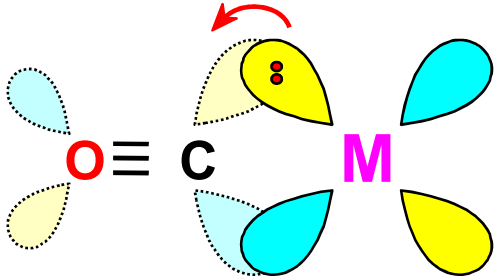
e.g. $Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Co_2(CO)_8]$, $Na_2[Fe(CO)_4]$, $Na[Mn(CO)_5]$



σ orbital serves as a very weak donor to a metal atom



CO-M sigma bond



M to CO pi back bonding

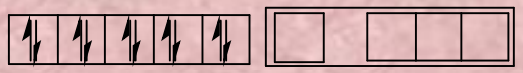
Structure of some Metal-Carbonyls

- **Electron diffraction studies indicated that in;**
- **$Ni(CO)_4$ is tetrahedral (sp^3 hybridn.)**
- **$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ are octahedral (d^2sp^3)**
- **$Fe(CO)_5$ has trigonal bipyramidal (dsp^3)**
- **CO ligand in each case force two s electrons to pair up in *d* orbitals.**

a). **For $Ni(CO)_4$:**

Ni(28) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$ (G.S)

Ni(28) : $3d^{10}, 4s^0$ (E.S)

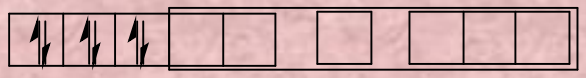


sp^3 hybridization (Tetrahedral)

b) For $Mo(CO)_6$:

Mo(42): $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^4, 5s^2$ (G.S)

Mo(42) : $4d^6, 5s^0$ (E.S)

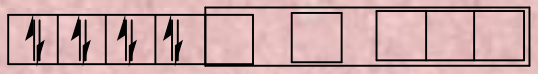


d^2sp^3 hybridization (octahedral)

c)For $Fe(CO)_5$:

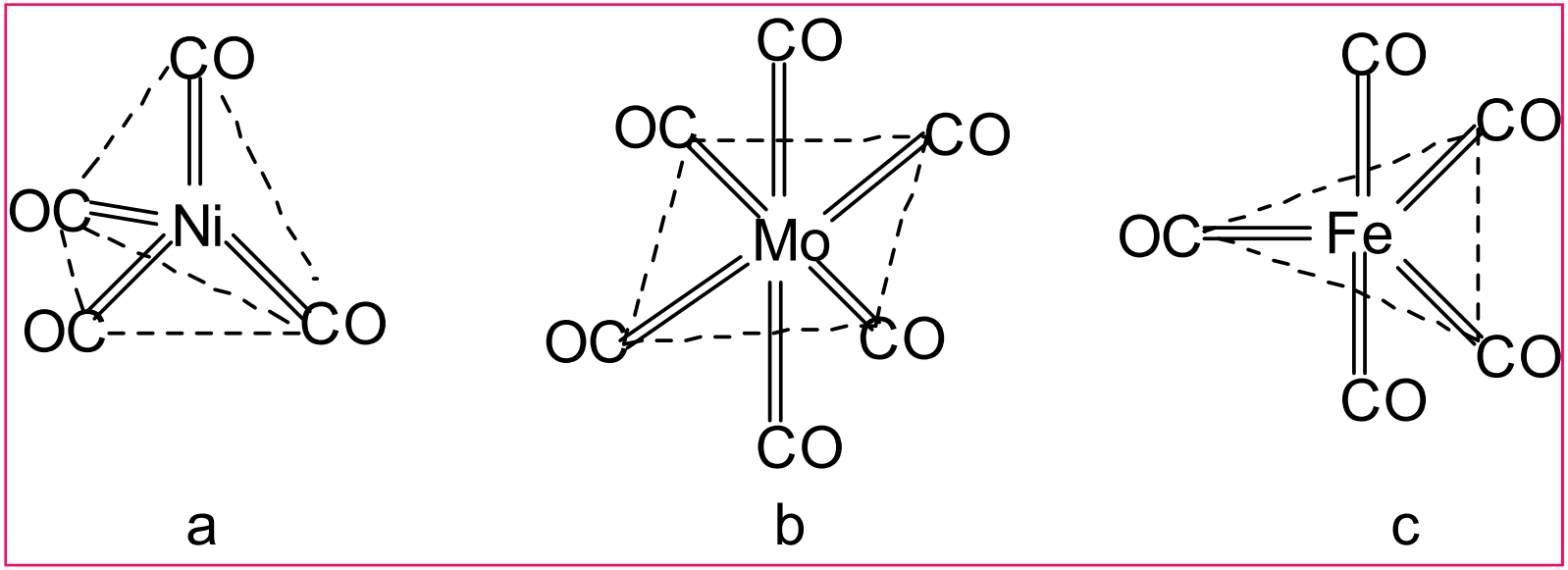
Fe(26): $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$ (G.S)

Fe(26) : $3d^8, 4s^0$ (E.S)



dsp^3 hybridization (tbp)

Structure



THANKS