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.

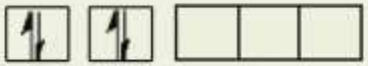
2. Methylberyllium, is a monomer in vapour phase. In solid state, it exists as polymer.
3. Bulkier alkyl groups attached to Be atom show lower degree of polymerisation.
4. XRD studies indicated polymeric structure with tetrahedral Be co-ordinated by methyl groups.
5. The structure of $(CH_3)_2Be$ is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

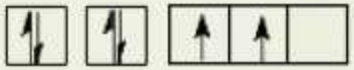
Be(4) : $1s^2$, $2s^2$(G.S)

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)

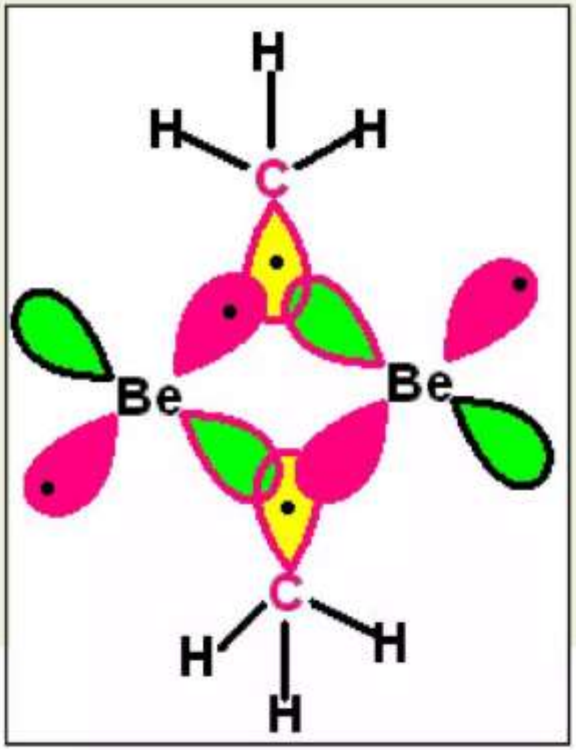
[*sp*^{3} hybridization]

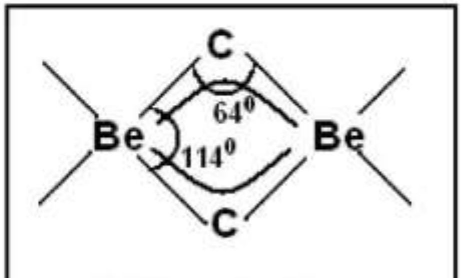
In Be, one *s* orbital (with one electron) and three *p* orbitals (with one electron) hybridize to produce 4*sp*^{3} HO's containing two electrons.

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.

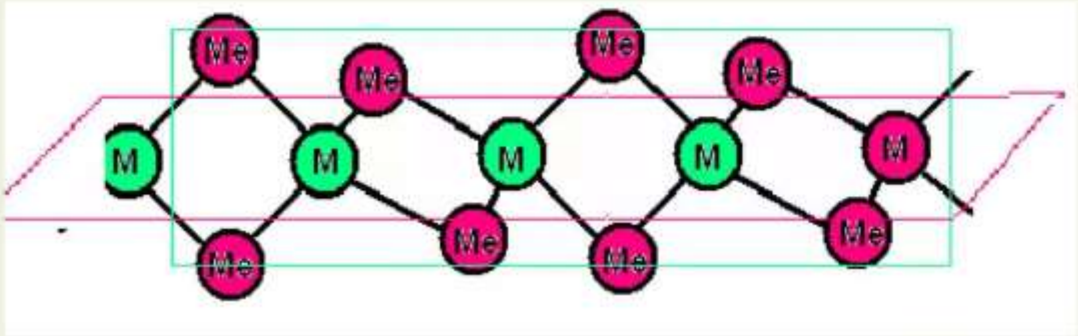
- It has 2 bridging CH_3 groups linking 2 adjacent Be atoms by 3c-2e bonds.
- The overlap of 1sp^3 HO(empty) of first Be, 1sp^3 HO of C (from CH_3) containing 1 electron and sp^3 HO of another Be containing 1 electron give 3c-2e bonding.
- Similarly, other 3c-2e bond is formed. The overlap of 1*sp*3 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.





C-C length 315 pm
Be-Be length 209 pm

- 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.



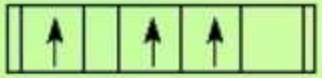
Polymeric structure of M(Me)2, M = Be, Mg.

STRUCTURAL STUDY OF ALKYL ALUMIN

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,

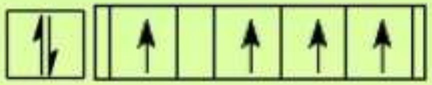
4. 3C bonding involves sp^3 hybrid orbital from two Al atoms and bridging alkyl carbon atoms.

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



sp^3 hybridization.

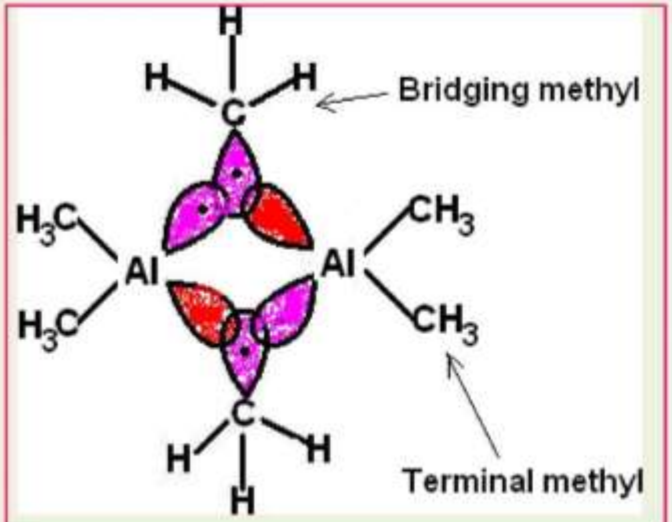
C(6) : $1s^2, 2s^1, 2p^3$. (E.S)



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.



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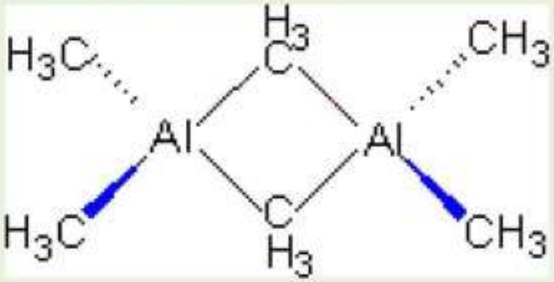
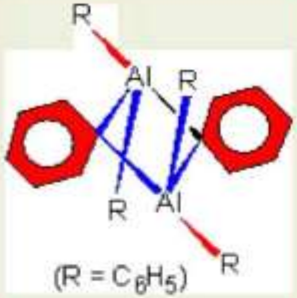




Though R is bulkier, still the compound exists as dimer

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).

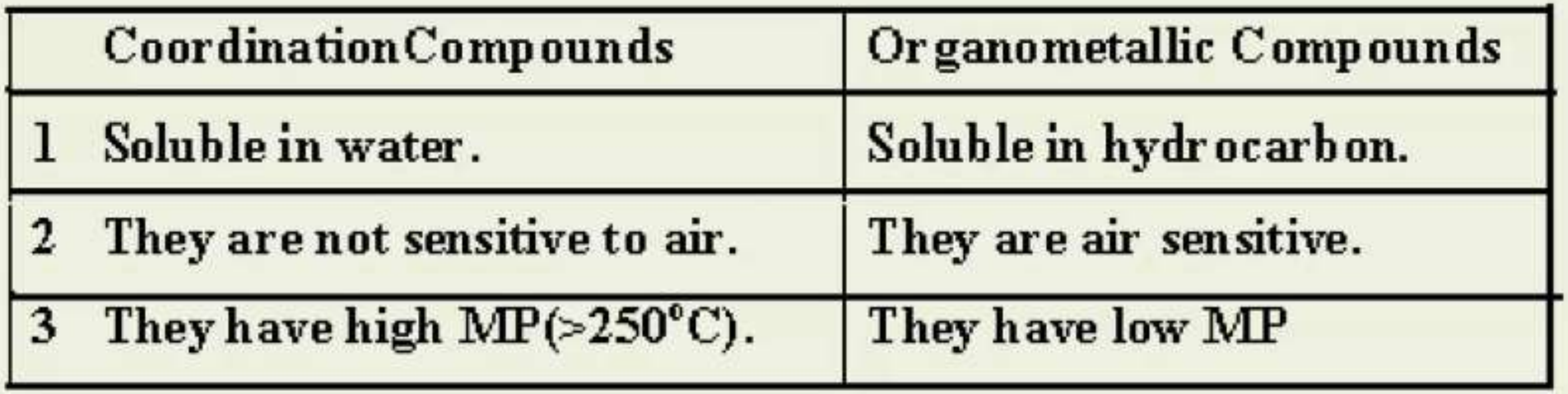
When x is 1,2,3 etc. then they are called mononuclear, binuclear or trinuclear carbonyls respectively.

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.

Difference Between



	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^{0}C.
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^{0}C.
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.

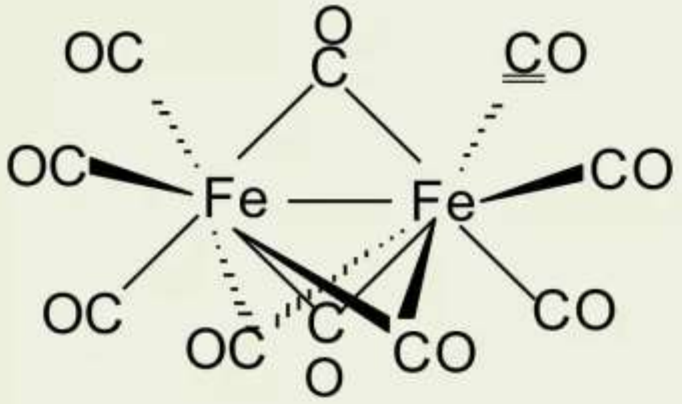
In such compounds, the factors such as CFSE, nature M-C of bonding affects the stability of the compound.

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^-
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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.

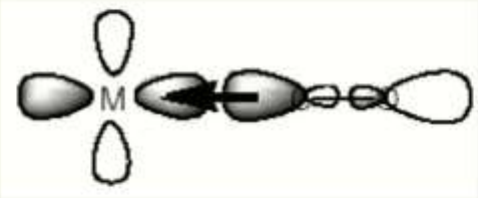
4. Many carbonyl compounds have metal in a zero oxidation state. The very low oxidation states are not found with sigma-bonding ligands such as H_2O & NH_3.

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’

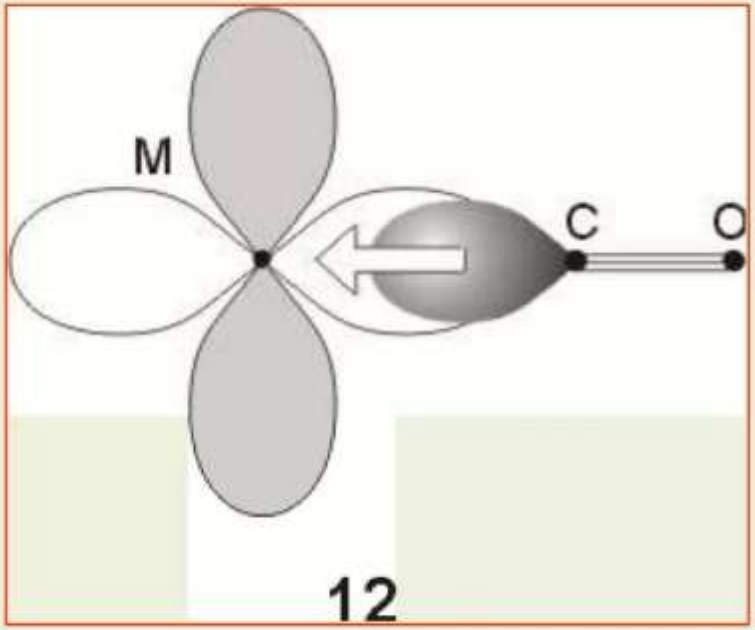
A filled *d* orbital on the metal overlap with the pi LUMO of the carbon monoxide. These two orbitals have the correct symmetry for overlap. This removes the electron density from the metal center, back onto the carbonyl ligand to some extent (M→Cp). This additional bond is a $d\pi$–$p\pi$ bond.

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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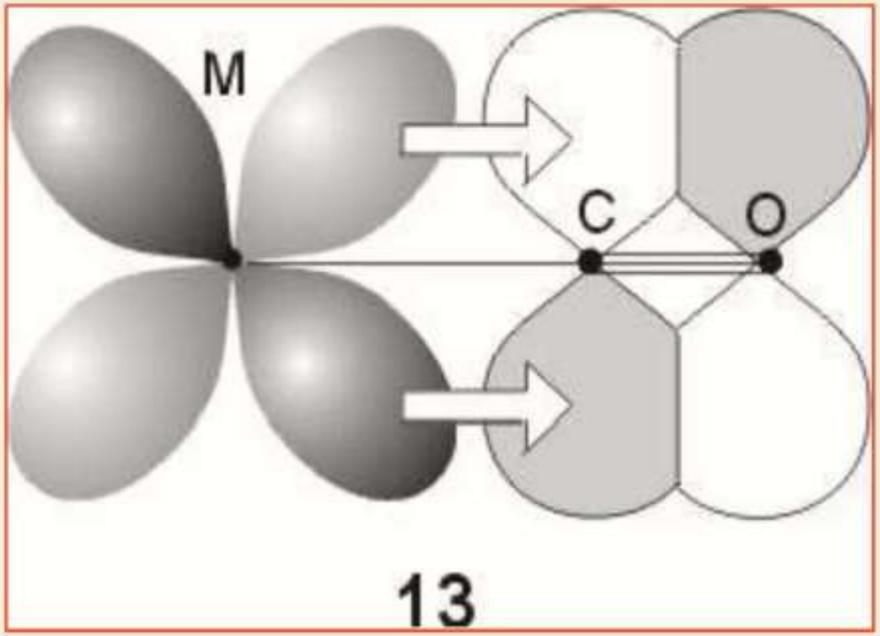

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e.g. Ni$(CO)_4$], [Fe$(CO)_5$], [Cr$(CO)_6$], [$Mn_2(CO)_{10}$], [$Co_2(CO)_8$], Na_2[Fe$(CO)_4$], Na[Mn$(CO)_5$]