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*.

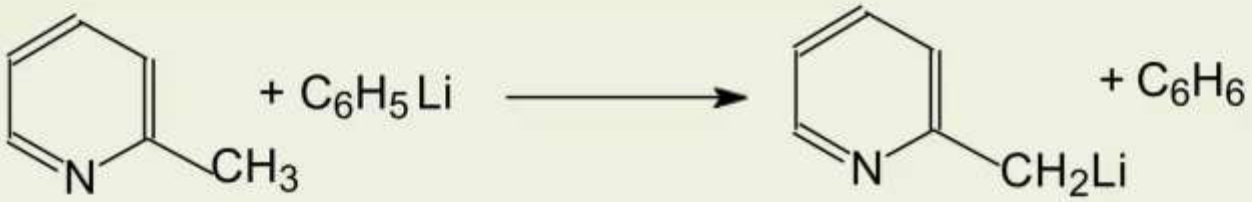
A large number of OMC are prepared in this way.
The common reagents used are;
alkyllithium,
alkylmagnesium and
alkylaluminium.

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

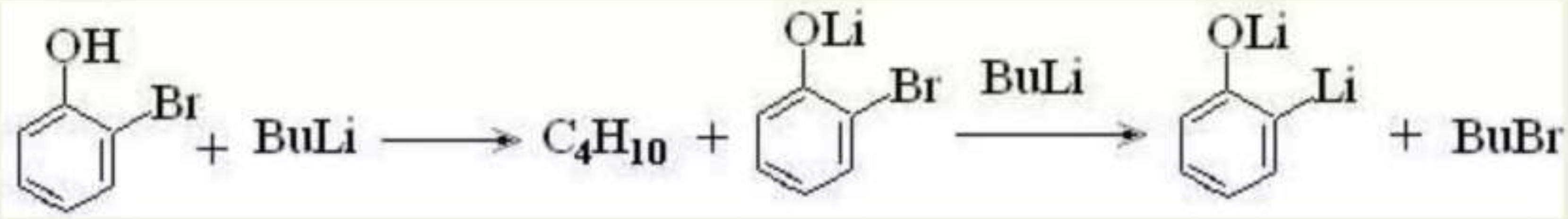
$$RX + MR' \rightarrow RM + R'X$$

Examples

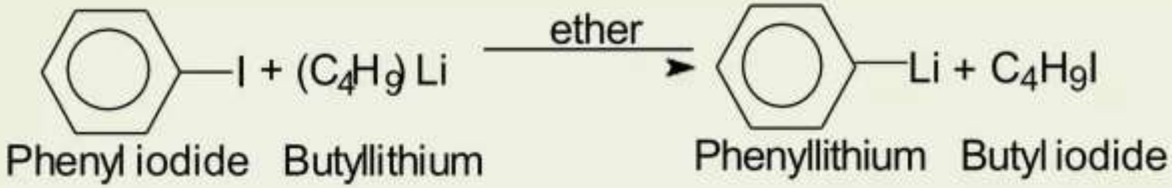
1.



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.).

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

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

$BeCl_2 + 2\,C_6H_5Li \xrightarrow{\text{ether}} Be(C_6H_5)_2 + 2LiCl$ **(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.

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

$$\mathrm{Be + (C_6H_5)_2Hg \rightarrow (C_6H_5)_2Be + Hg}$$

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.

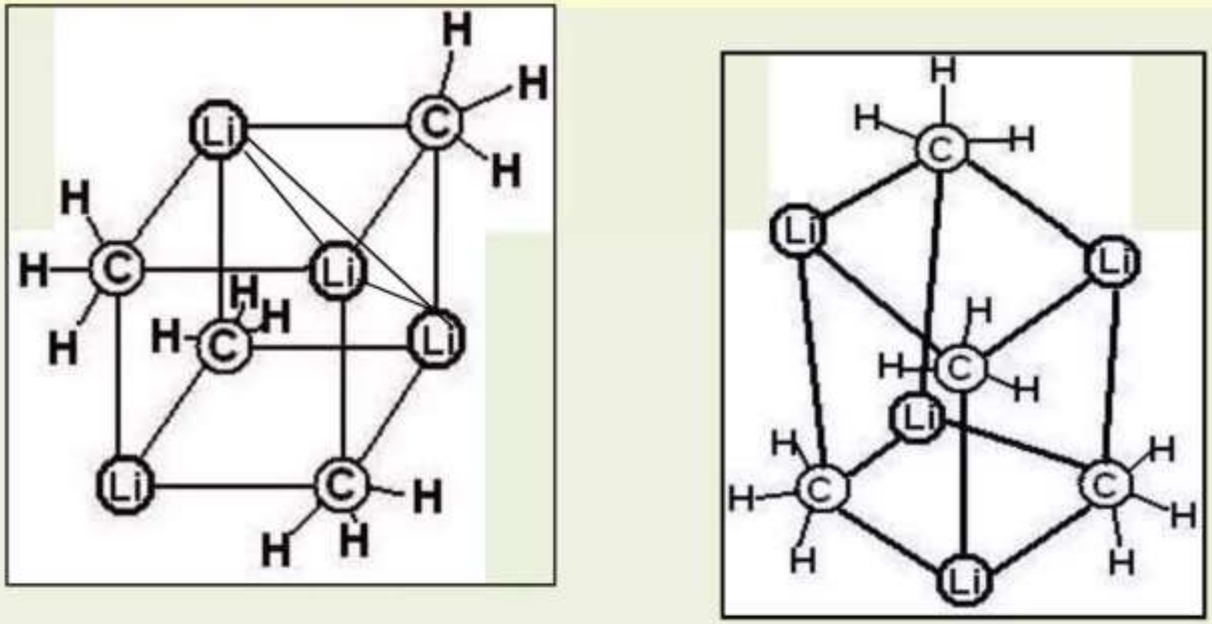
STRUCTURAL STUDY OF ALKYL LITHIUM:

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

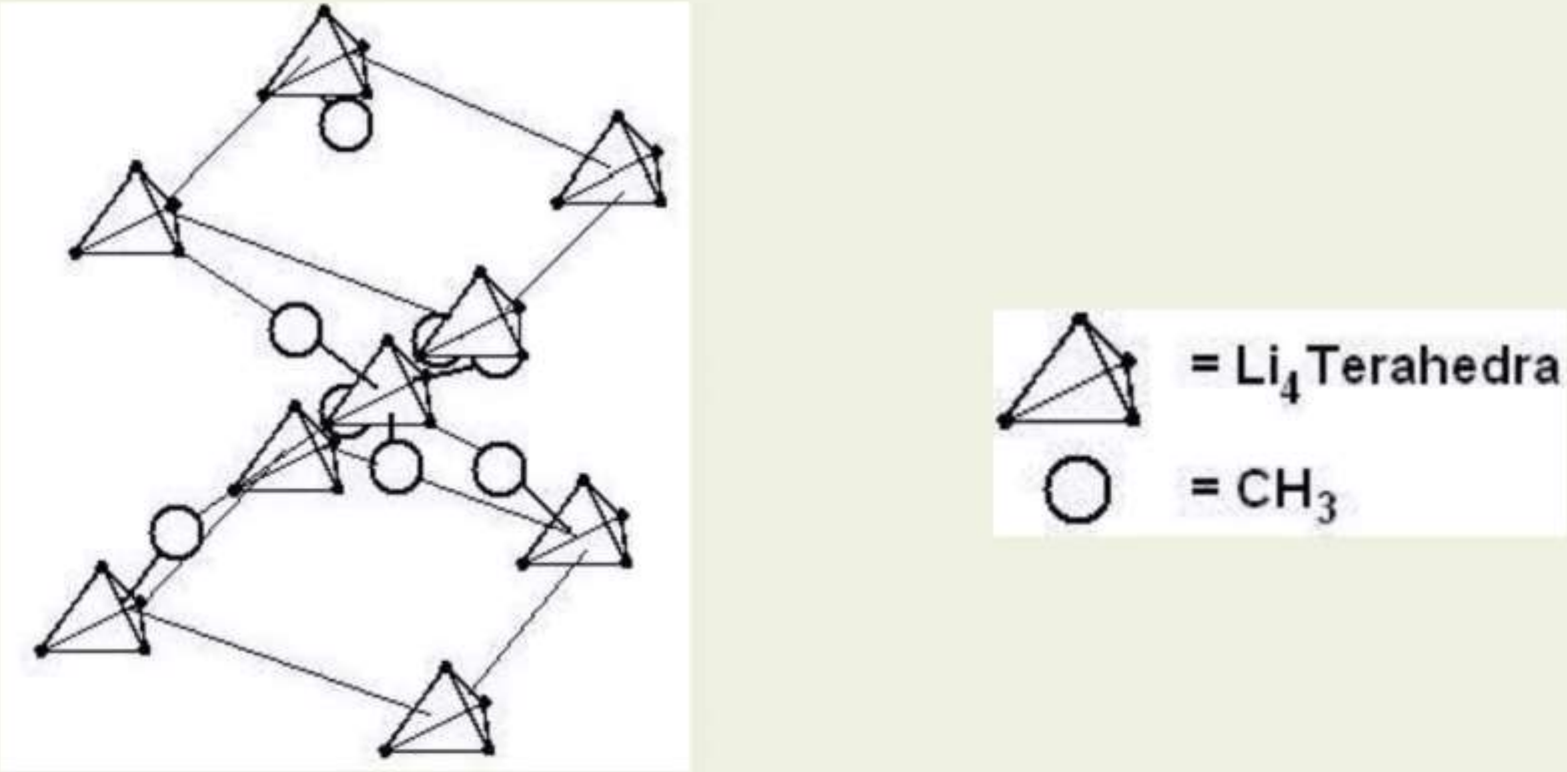
(distorted cube)



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.

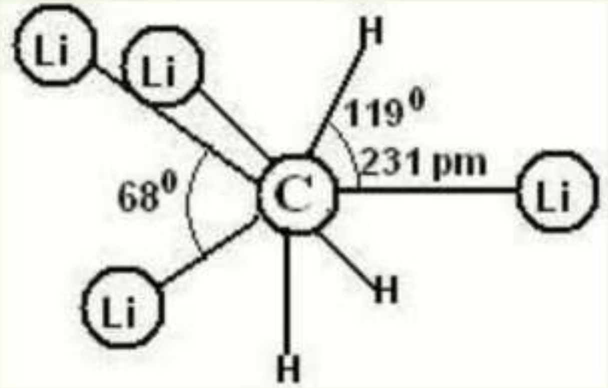
Li- C length within tetrahedron is 231 pm.

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).

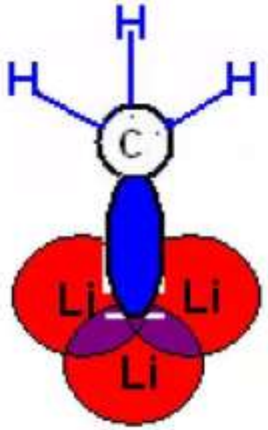


9. The CN = 7 cannot be explained as the C atom has only one *s* and three *p* orbitals available for bonding.

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.