

## MAIN GROUP ORGANOMETALLICS

*Dr. S. Draper*

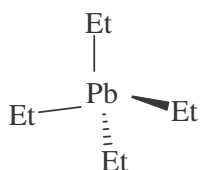
*8 lecture course*

**Introduction to organometallic chemistry – Elschenbroich and Salzer**

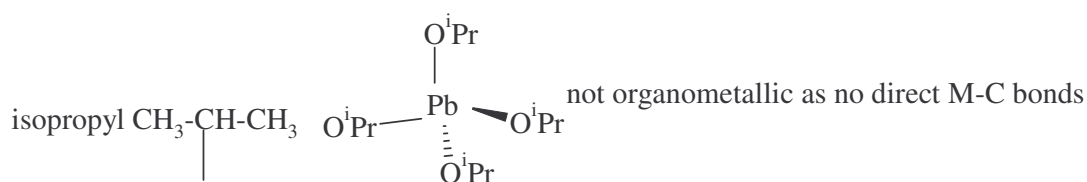
**General Inorganic Chemistry – Housecroft and Sharpe**

**Introduction to OMC Chemistry - P.Powell Chapman & Hall 1988 547,4.488**

Definition direct M-C bonds e.g.



colourless liquid, toxic does not readily burn or hydrolyse



Metals make C bonding unusual, large variety of M-C interactions only recently explored - 1950 onwards.

Main Group Metals – Groups 1, 2, 3, 4 will be considered

Many types of M-C bonds are extremely reactive Li, Al, Be e.g. organolithium, Grignard reagents, LiMe spontaneously inflammable in air,  $(\text{BeMe}_2)_n$  catches fire in dry  $\text{CO}_2$

Uses: catalysts : polymerisation, hydrogenation, hydrosilation

## **General Properties of Organometallic Compounds**

The strength of M-C bonds decreases down a group hence the formation of  $\text{M-R}_n$  compounds becomes more endothermic.

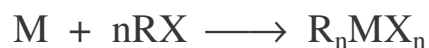
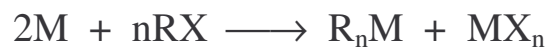
One reason is the increasing disparity in energies of the C and M frontier orbitals.

Main feature to consider is the polarity of the M-C bond i.e. the electronegativity difference.

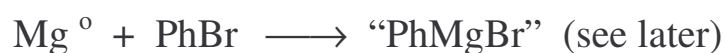
All organometallic compounds are thermodynamically unstable with respect to reaction with  $\text{O}_2$  and  $\text{H}_2\text{O}$  but some are kinetically stable (inert) usually due to a high activation energy.

## Preparation

### 1. Metal + Organic Halide



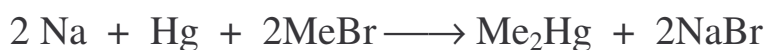
e.g.  $2Li + RCl \longrightarrow RLi + LiCl$  e.g.  $R = {}^tBu$



Driving force is the formation of  $MX_n$ ,  
 $\Delta H_f^\circ(MX_n)$  must compensate for  $\Delta H_f^\circ(R_nM)$  being  $> 0$ .  
Hence for heavy elements Ti, Pb, Bi, Hg, the reaction does not work ( $R_nM \gg 0$ )

To overcome this problem electropositive elements are also incorporated into the reaction:

e.g.



$$\Delta H = 539 \text{ kJmol}^{-1}$$



These are essentially oxidative additions to  $M^0$  i.e. low valent species.

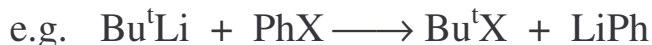




Another problem is the solubility of the LiX e.g. LiI is quite soluble in solvents (most covalent of group 17, small size and high polarising power of Li atoms)

Pure Li gives slow reaction now use Na in Li 0.05 – 0.2%. This gives improved yields depending on R. This exposes the Li surface while the Na decomposes.

## 2. Organometallic + Organic Halide metal - halogen exchange



Reaction requires R' stabilisation of negative charge to be better than R.

Hence good for formation of aryl Li which involves nucleophilic displacement of an  $\text{sp}^2$  C.

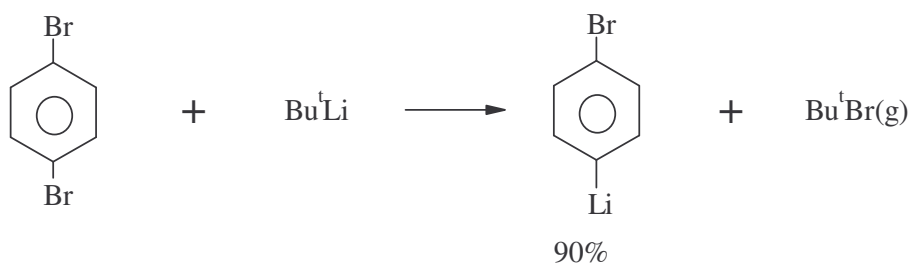
Also reaction is good for X = I , Br occasionally Cl but not F.

A volatile RX should be formed

$\text{Bu}^t\text{Li}$  good starting material as  $\text{Bu}^t\text{I}$  volatile and  $\text{Bu}^t$  is an electronegative group.



*p*-dibromobenzene does not react with Li (metal) but does react with Bu<sup>t</sup>Li



Competing reactions are coupling  $\longrightarrow$  R-R'

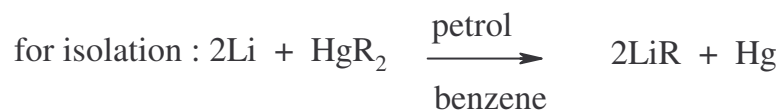
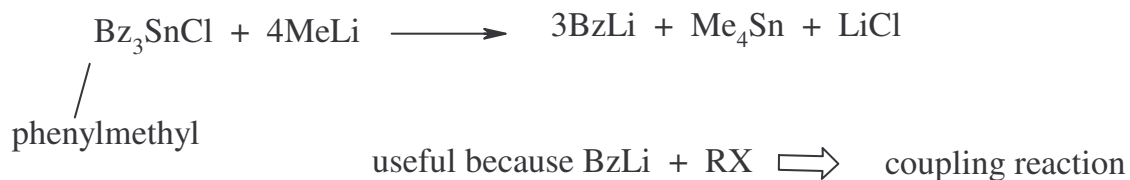
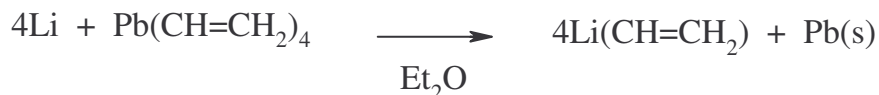
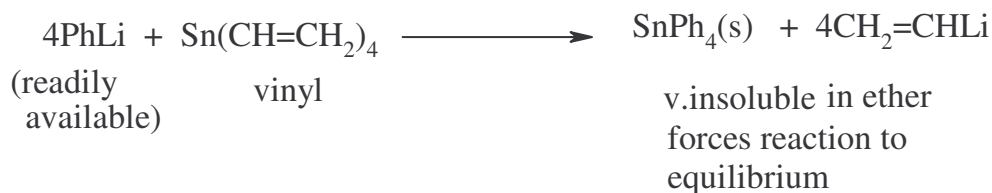
Reactions are often fast and but some kinetic control at low temp. is possible.

### 3. Metal -metal exchange

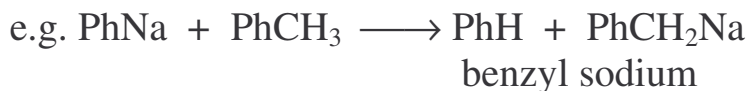


A convenient but difficult preparation for unsaturated derivatives e.g. vinyls and allyls.

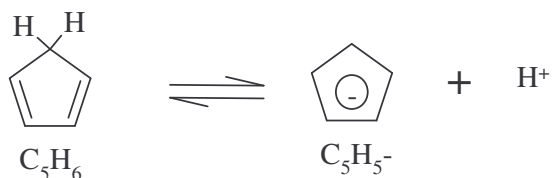
Requires the careful control of reaction conditions.



#### 4. Metal - Hydrogen Exchange (metallation)



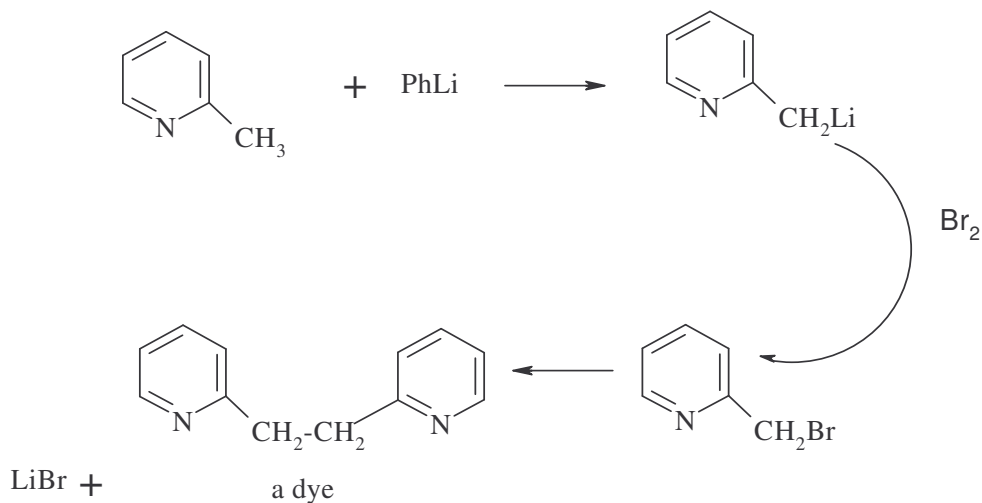
Strong CH acids e.g. acetylene and CpH can react directly with alkali metal. Cp strong acid by organic standards



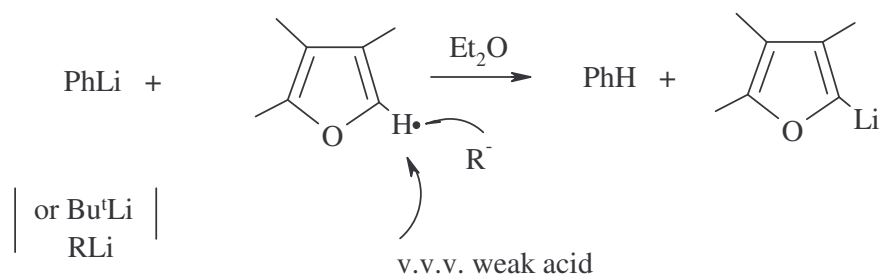
$\text{pK}_a = 16$  (9 orders of magnitude lower than water)  
water  $\text{pH} = 7$   $[\text{H}^+] = 10^{-7}$



Others require reaction of mildly acidic H with organometallic reagent

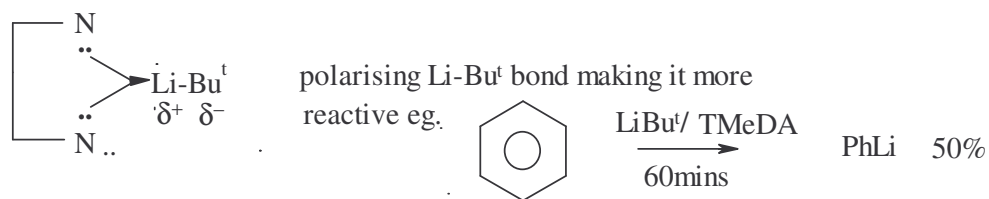






Believed mechanism involves nucleophilic attack of carbanion  $\text{R}^-$  at most acidic H.

Most reactive, i.e. best source of highly reactive carbanion is TMEDA complex



(see section on structure and bonding later for a more detailed explanation of increased reactivity)

## 5. Metal + Organometallic



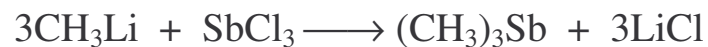
where M = Li - Cs, Be - Ba, Al, Ga, Sn, Pb, Bi, Se, Zn, Cd.

(RM') should be weakly exothermic or endothermic.

Reaction occurs due to difference in  $\Delta (\Delta G_f^\circ)$  RM and RM'.

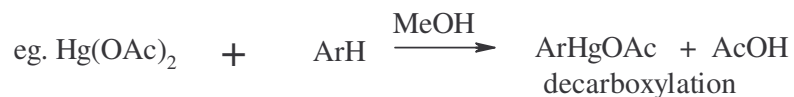
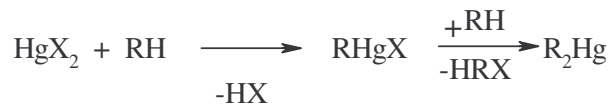
## 6. Organometallic + Metal Halide

Important method of making organometallics out of less electropositive metals i.e. requires M to be more electropositive than M'.

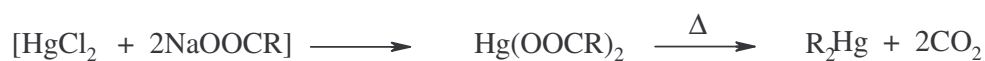


## Less versatile synthesis routes

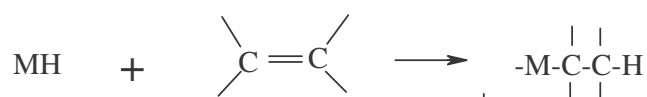
### Mercury Salts and Organic Compounds



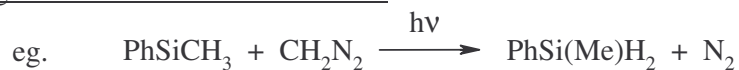
### Pyrolysis of Carboxylates



### Metal Hydrides + Unsaturated Species



### Organometallic + Carbene Source



insertion of  $\text{CR}_2$  into M-H or M-X bond is favoured over M-C bond.

## Structure and Bonding in Organolithiums.

Organolithium species tend to oligomerise in solution and in the solid state. Methyl lithium is actually cubic body-centered  $(\text{LiCH}_3)_4$  units. The lattice is built up of distorted cubes with alternate occupation of the corners by C and Li.

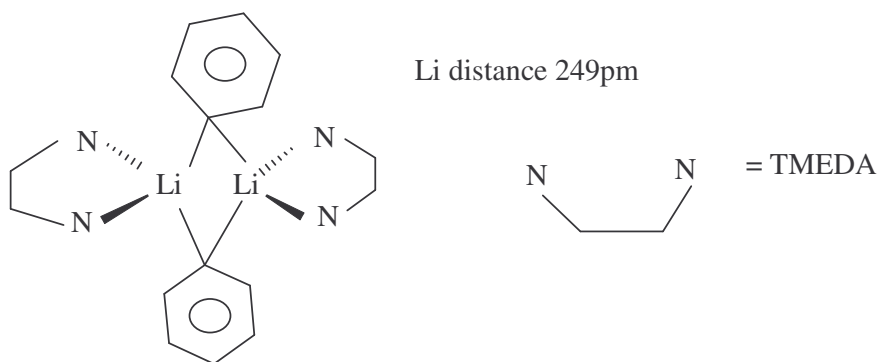
See diagram

\* The methyl groups of one  $(\text{LiCH}_3)_4$  unit interact with the Li atoms of a neighbouring  $\text{Li}_4$  tetrahedron. Reason for formation of heterocubane structure is that in a monomer  $\text{LiR}$  unit too few valence  $e^-$  are available to fill the valence orbitals of Li  $\Rightarrow$  multicentre bonding.

### Bonding

The axial Li ( $sp^3$ ) orbital interacts with the methyl groups of neighbouring  $(\text{LiCH}_3)_4$  units. These intermolecular forces result in the low volatility and insolubility of  $(\text{LiCH}_3)_4$  in non-solvating media.

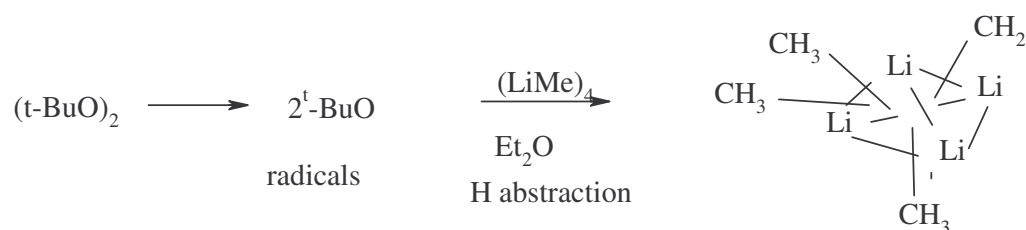
The structure of  $t$  butyl lithium is similar but the intermolecular forces are weaker and hence  $t\text{BuLi}$  is soluble in hydrocarbons and sublimates at  $70^\circ\text{C}/1\text{ mbar}$ . Coordinating solvents will tend to give monomeric or dimeric species as the coordination sites on Li are occupied.



Two techniques have been used to confirm the existence of tetrameric species in solution;

data : ESR and  $^6\text{Li}$  and  $^7\text{Li}$  NMR.

ESR looks at the transition of unpaired  $e^-$ .



$^7\text{Li}$  NMR better sensitivity

$^6\text{Li}$  NMR better resolution.



confirmed inter and intra Me exchange

indication of Li-C polarity more covalent lower magnetic field values and solvent shifts

Coupling to  $^{13}\text{C}$  enriched species confirmed tetrameric structure of  $^t\text{BuLi}$ .

$$\text{Multiplicity} = 2nI + 1$$

In ESR spectrum

interaction of C radical with  $\text{H}_2$

$$\Rightarrow \text{triplet} = 2 \times 2 \times 1/2 + 1 = 3$$

interaction of C radical with  $3\text{Li}$  ( $I = 3/2$ )

$$\Rightarrow \text{decet} = 2 \times 3 \times 3/2 + 1 = 10$$

$\Rightarrow$  spectrum is triplet of decets.

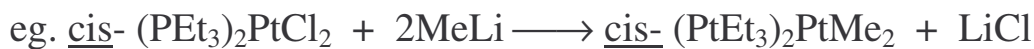
## Reactivity of Organolithium Compounds

General Li-R bond is polar covalent rather than ionic (cf. Na. K). Polarity is due to small size of lithium metal cation.  $\text{Li}^+$  acts like a hard acid polarising the  $e^-$  cloud of e.g.  $\text{CH}_3^-$  (a soft base). Due to its polar/covalent character LiR are less reactive than NaR and in many ways more useful, selective

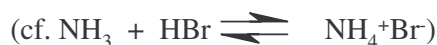
## Reactions of Organolithium Compounds

See diagram

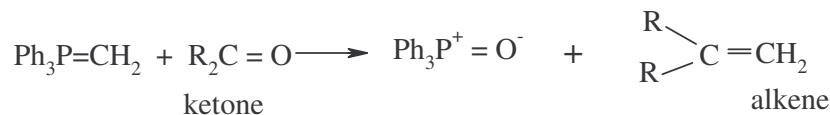
\* Also true of transition metal species



## Wittig Reagents

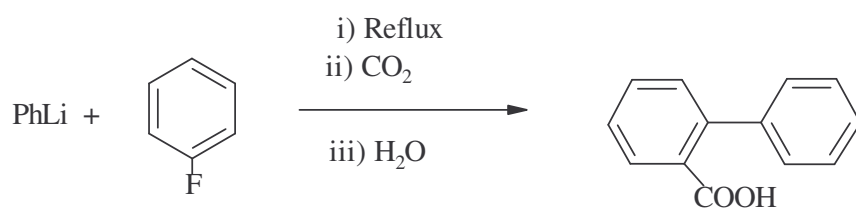


R = Ph, Bu<sup>t</sup> triphenylphosphine methyllide  
(Wittig reagent)



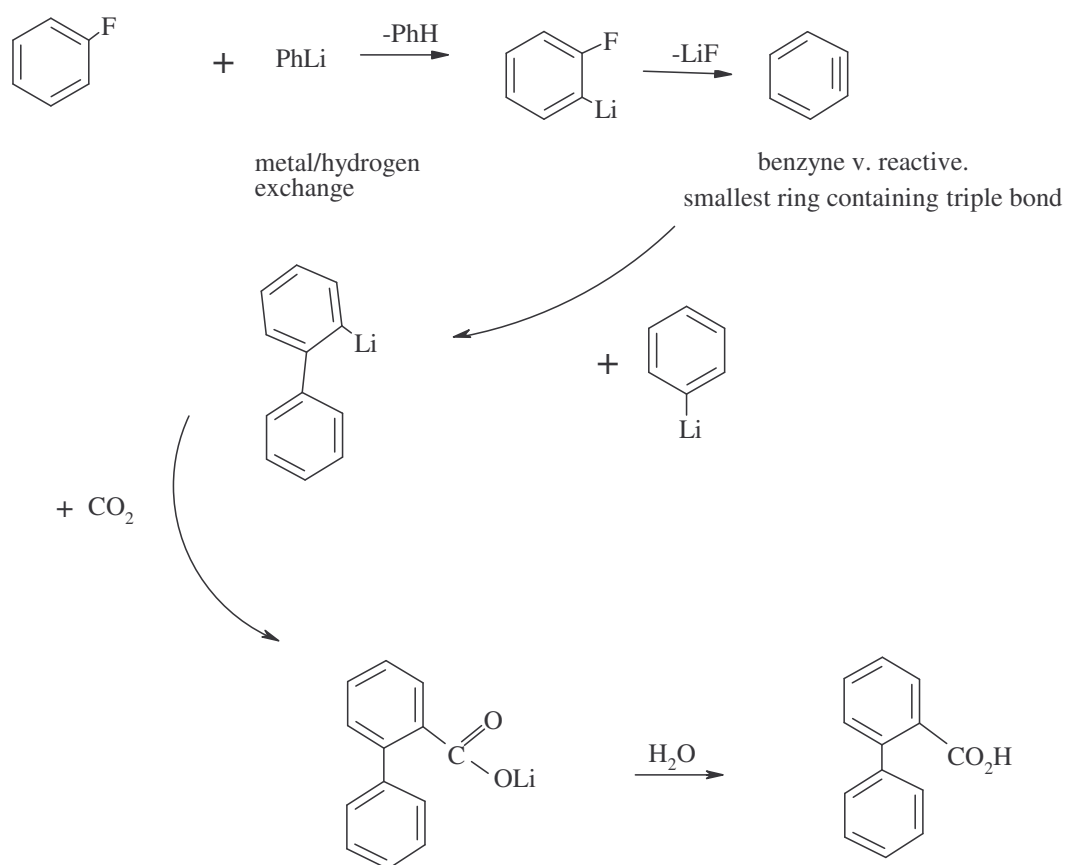
ketone  $\rightarrow$  branched alkene  
aldehyde  $\rightarrow$  straight chain alkene

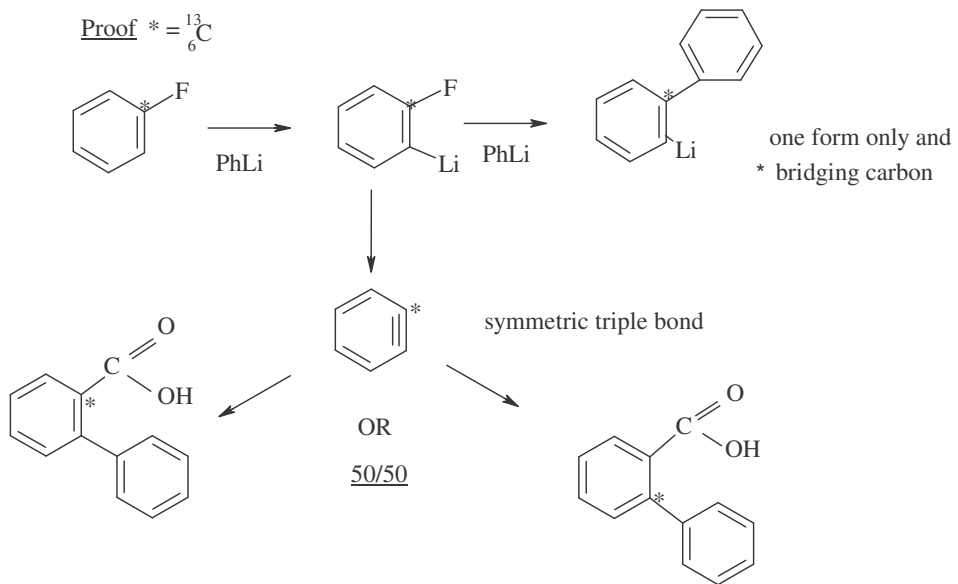
## Reaction of LiR with Organofluorines



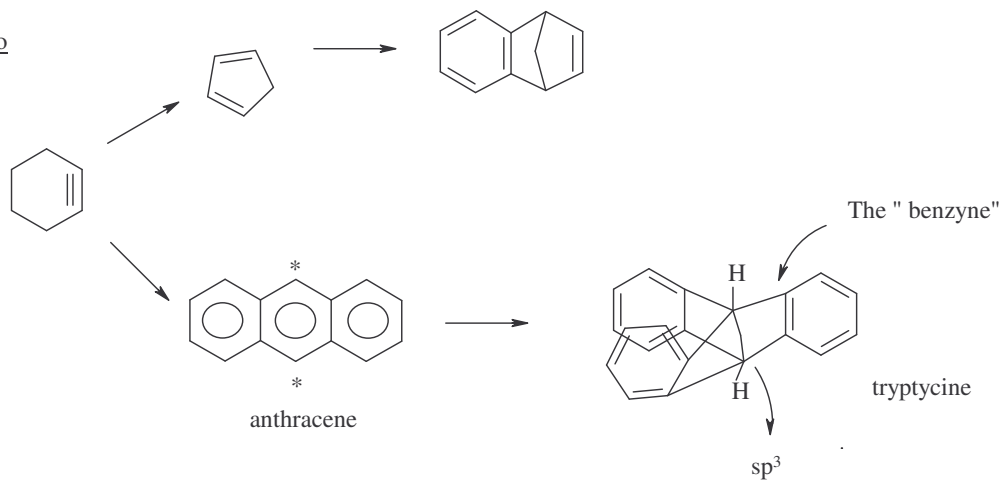
fluorobenzene, ortho H are a little acidic.

Mechanism

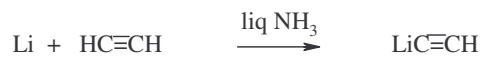




Also



### Acetylides



extreme reaction under hexane reflux



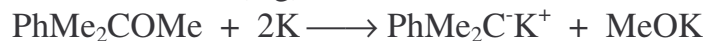
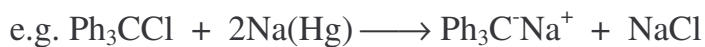
ie.  $\text{Li}_4\text{C}_3$



spontaneous  
name.







bright red – used to remove oxygen from

inert gases

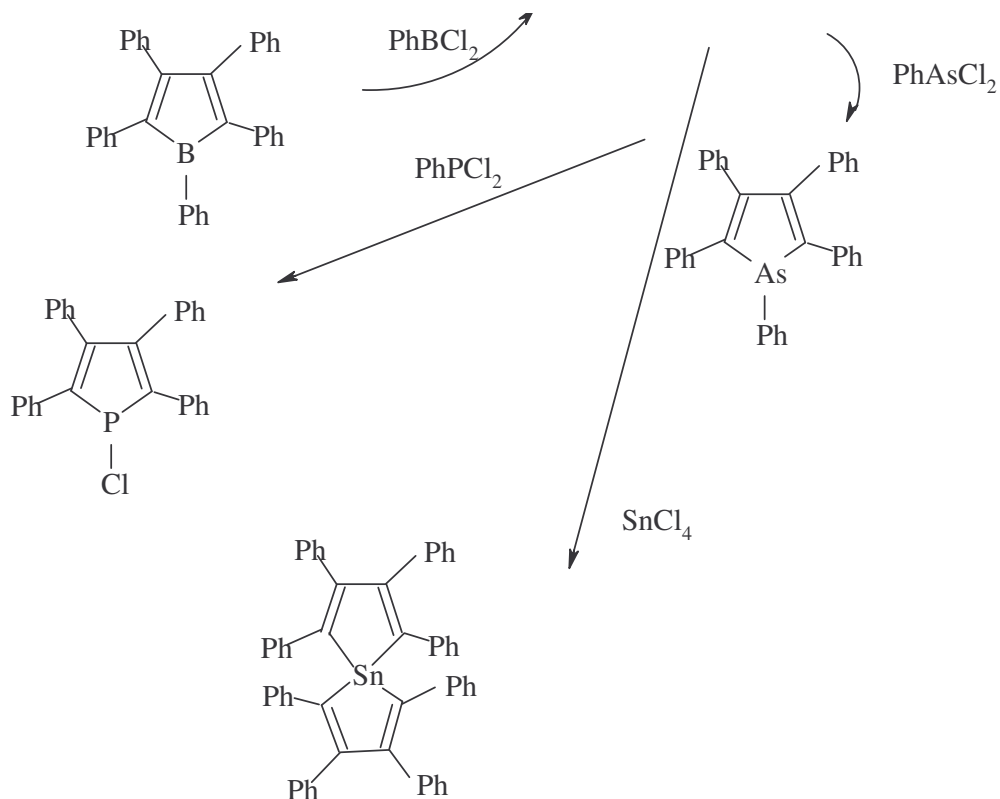
### Addition Compounds



Reaction result of electron transfer from metal to give radical ions.

Stability of radical depends on homo/lumo gap.

Some of the resulting radical dimerisations are useful in synthesis:



## Group II Organometallic Species

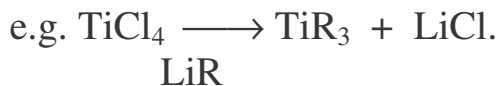
Grignard Reagents:  $\text{Mg} + \text{RX} \xrightarrow[\text{or THF}]{\text{Et}_2\text{O}}$   $\text{EtMgX}$  exothermic  
but  $\text{Et}_2\text{O}$  substituted is less reactive



equilibrium. R = alkyl, aryl.

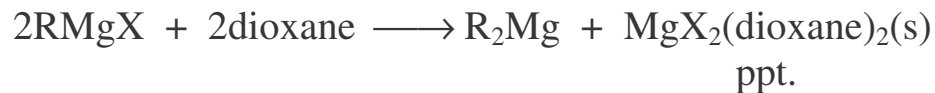
Reducing and organylating ability of lithium and magnesium reagents:

Although  $\text{LiR} > \text{RMgX} > \text{MgR}_2$  at organylating, LiR is also a reducing agent

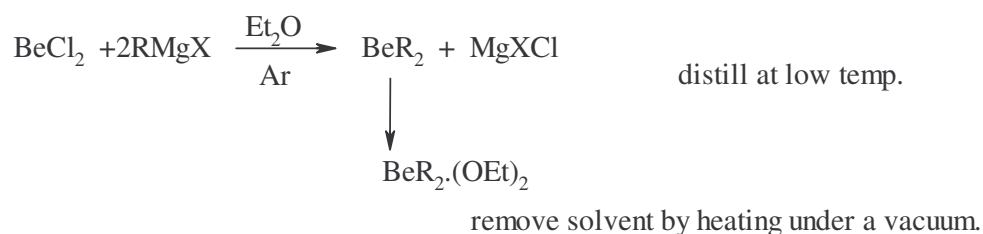


Actually better to use  $\text{MgR}_2$

Improved organylation of  $\text{MgR}_2$  can be obtained using dioxane as solvent which complexes to halide to give an insoluble salt.



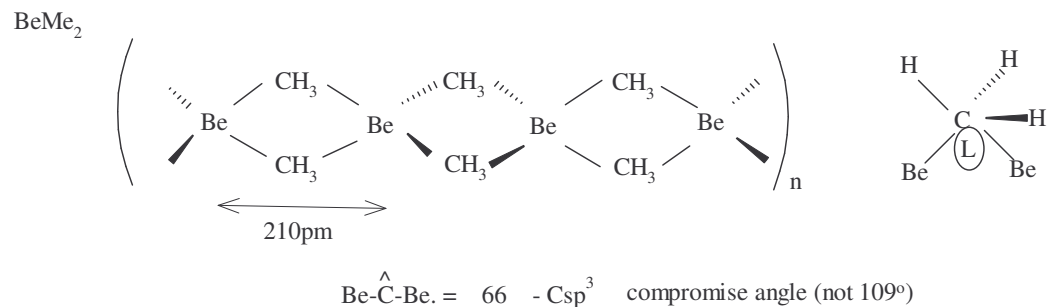
## Synthesis of "BeR<sub>2</sub>"



(Vapour phase - monomer, dimer, trimer, - monomer linear sp hybridised.)

In solid phase - IR  $\nu(\text{CH})$  low 2912, 2885. i.e. bonds long - electron withdrawing due to Be-CH<sub>3</sub> bridges.

### Structure of solid



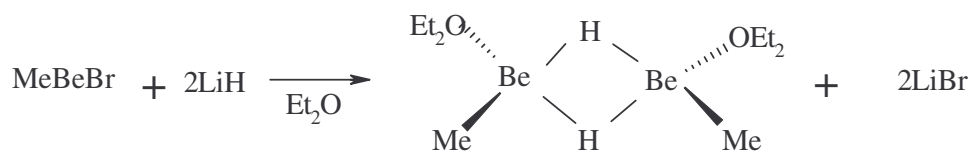
Both Be and C effectively sp<sup>3</sup>.

Remember that e<sup>-</sup> deficient compounds were seen for Li, Be, B. When four coordinate there are not enough valence e<sup>-</sup> for 2C - 2e<sup>-</sup> bonds.

Here see 3 centre -2 electron bonds (cf. B<sub>2</sub>H<sub>6</sub> and Al<sub>2</sub>Me<sub>6</sub> with 3 electrons on B and Al. These can form dimers).

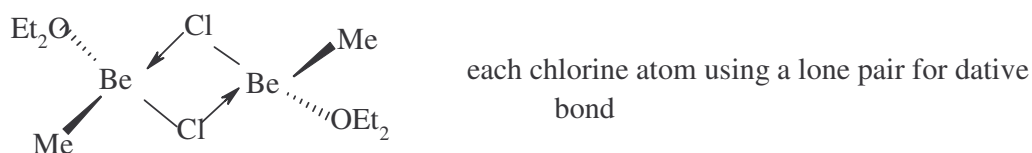
Species extremely reactive – hydrolyse, explosive in presence of any active H

NB Organoberyllium hydride prepared

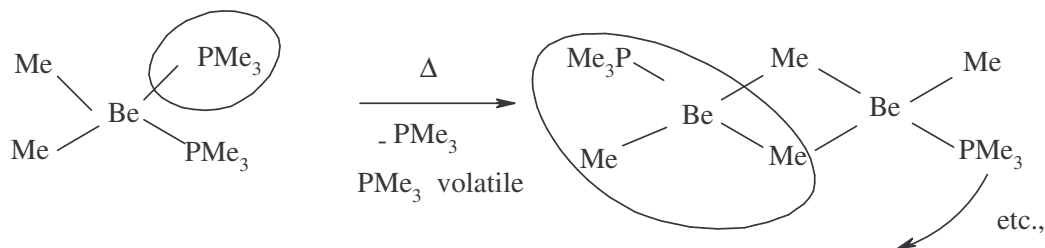
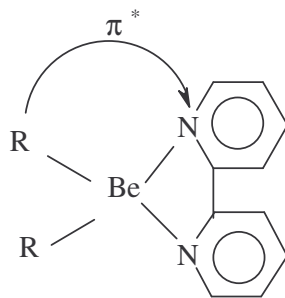


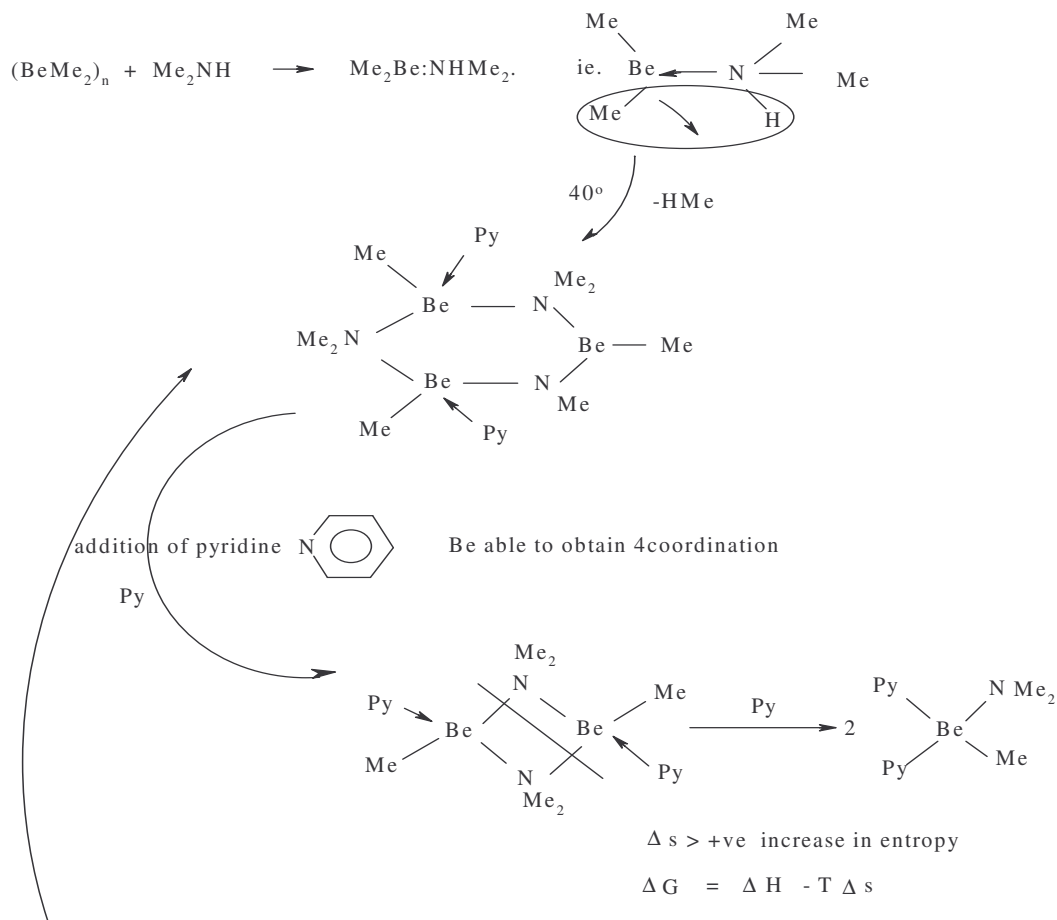
$^{13}\text{C NMR}$  indicates hydrogen rather than methyl bridges - thought to be due to better s orbital overlap of H with Be  $sp^3$  orbitals - 1s orbital. spherical symmetry.

Chlorine bridges are better again – they can provide 3 electrons per atom

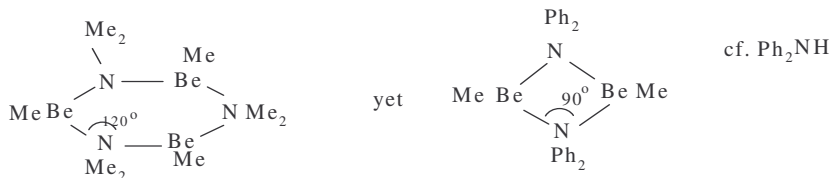


Reactions of  $(\text{BeMe}_2)_n$  with electron donor species eg  $\text{Me}_3\text{N}$ ,  $\text{PMe}_3$ , causes formation of complexes and a breakdown of polymeric structure eg.  $\text{R}_2\text{Be}$  bipy - these compounds deep-red with  $\lambda_{\text{max}}$  and  $E$  decreasing as the  $e^-$  attracting power of R decreases. eg R = Ph, Me, Et, Br. transition observing R to  $\pi^*$  of bipy.





Formation of trimeric or dimeric species depends on steric size of R groups.



Factors to consider

Ring strain favours trimers.

Bulk of  $\text{NR}_2$  substituents. More bulky favours dimer ( looking at external ring angle:

4-membered ring ie dimer has external  $> 360 - 90^\circ = 270^\circ$

entropy favours dimer.

weighing up these factors  $\text{NET}_2$  trimer when  $\text{BeR}=\text{Me}$  as  $\text{Be R}$  increases  $\Rightarrow$  dimers