#### *MAIN GROUP ORGANOMETALLICS*

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*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

$$
\begin{array}{c}\nO^i Pr \\
\downarrow \\
\text{isopropyl CH}_3-\text{CH-CH}_3 & O^i Pr\n\end{array}
$$
\n
$$
\begin{array}{c}\nO^i Pr \\
\downarrow \\
O^i Pr\n\end{array}
$$
\n
$$
\begin{array}{c}\nO^i Pr \\
O^i Pr\n\end{array}
$$

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,  $(BeMe<sub>2</sub>)<sub>n</sub>$  catches fire in dry  $CO<sub>2</sub>$ 

Uses: catalysts : polymerisation, hydrogenation, hydrosilation

# **General Properties of Organometallic Compounds**

The strength of M-C bonds decreases down a group hence the formation of  $M-R_n$  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  $O_2$  and  $H_2O$  but some are kinetically stable (inert) usually due to a high activation energy.

### **Preparation**

**1. Metal + Organic Halide**  $2M + nRX \longrightarrow R_nM + MX_n$  $M + nRX \longrightarrow R_nMX_n$ e.g.  $2Li + RCl \longrightarrow RLi + LiCl$  e.g.  $R = {}^{t}Bu$  $Mg^{\circ}$  + PhBr  $\longrightarrow$  "PhMgBr" (see later)

Driving force is the formation of MX,  $\Delta H_f^{\circ}(MX_n)$  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.

 $2$  Na + Hg + 2MeBr  $\longrightarrow$  Me<sub>2</sub>Hg + 2NaBr

 $\Delta$ H=539 kJmol<sup>-1</sup>

 $4 \text{ Na} + 4 \text{ Pb} + 4 \text{ EtCl} \longrightarrow \text{Et}_4\text{ Pb} + 3 \text{ Pb} + 4 \text{ NaCl}$ 

These are essentially oxidative additions to  $M<sup>o</sup>$  i.e. low valent species.

e.g.  $Pb^{II}I_2 + Mel \longrightarrow MePb^{IV}I_3$ 

**Organolithium species** especially require

(i) work under inert atmosphere  $(N_2)$  Ar (ii) dry, degassed solvents/reagents (iii) dry apparatus

$$
2Li + RX \xrightarrow{Et_2O} RLi + LiX
$$

Reaction requires nucleophilic displacement of sp<sup>3</sup> C atom.  $\Delta G$ very high.

Cannot do reaction in the presence of active H such as in  $H_2O$ .

Using N<sub>2</sub> in preparation of R-Li gives Li<sub>3</sub>N ( $\Rightarrow$  purple solution)

Other solvents used cyclohexane, benzene, petrol

 $X = Cl$  preferred to other halides as avoids competing coupling reaction

eg.

$$
BuCl + 2Li
$$
  
\n
$$
Et_{2}O
$$
  
\n
$$
LiCl(s) + BuLi
$$
  
\nfilter evaporate solvent  
\n
$$
BuBr + 2Li
$$
  
\n
$$
BuBr + BuLi
$$
  
\n
$$
BuBr + BuLi
$$
  
\n
$$
BuBr + BuLi
$$
  
\n
$$
BuBu + BuLi
$$
  
\n
$$
BuBu + EuLi
$$
  
\n
$$
vctane
$$
  
\n
$$
Dctane
$$
  
\n
$$
Dctane
$$

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

 $RM + R'X \longrightarrow RX + R'M$   $M = Li$ 

e.g.  $Bu^tLi + PhX \longrightarrow Bu^tX + Liph$ 

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  $sp<sup>2</sup>$  C.

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

A volatile RX should be formed

Bu<sup>t</sup>Li good starting material as Bu<sup>t</sup>I volatile and Bu<sup>t</sup> is an electronegative group.

e.g. Bu<sup>t</sup>Li + ArI  $\longrightarrow$  ArLi + Bu<sup>t</sup>I(g).

*p*-dibromobenzene does not react with Li (metal) but does react with Bu t 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**

 $RM + R'M' \longrightarrow RM' + R'M$ .

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

Requires the careful control of reaction conditions.

 $4Bu^tLi + Sn(CH=CH_2)_4 \longrightarrow 4Li(CH=CH_2) + ShBu^t$  $4PhLi + Sn(CH=CH<sub>2</sub>)<sub>4</sub>$   $\longrightarrow$   $SnPh<sub>4</sub>(s) + 4CH<sub>2</sub>=CHLi$  $+$  Sn(CH=CH<sub>2</sub>)<sub>4</sub>  $+$  4Li(CH=CH<sub>2</sub>) + SnBu<sup>1</sup><sub>4</sub>  $4Li + Pb(CH=CH<sub>2</sub>)<sub>4</sub>$   $\longrightarrow$   $4Li(CH=CH<sub>2</sub>) + Pb(s)$  $Et<sub>2</sub>O$  $\text{Bz}_3\text{SnCl} + 4\text{Meli} \longrightarrow 3\text{BzLi} + \text{Me}_4\text{Sn} + \text{LiCl}$ vinyl vinsoluble in ether forces reaction to equilibrium pentane \ (incomplete pyrophoric precipitate (incomplete) phenylmethyl (readily available)

useful because BzLi + RX  $\implies$  coupling reaction

for isolation : 2Li + HgR<sub>2</sub> 
$$
\xrightarrow{\text{petrol}}
$$
 2LiR + Hg  
benzene

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

 $RM + R'H \longrightarrow RH + R'M$   $M = alkali metal$ e.g. PhNa + PhCH<sub>3</sub>  $\longrightarrow$  PhH + PhCH<sub>2</sub>Na benzyl sodium

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



e.g. 
$$
C_5H_5 + Na \longrightarrow C_5H_5Na + 1/2H_2
$$

Others require reaction of mildly acidic H with organometallic reagent









Believed mechanism involves nucleophilic attack of carbanion 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**

 $M + RM' \longrightarrow RM + M'$ 

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'.

 $RM + M'X \longrightarrow RM' + MX$ 

 $3CH_3Li + SbCl_3 \longrightarrow (CH_3)_3Sb + 3LiCl$ 

# **Less versatile synthesis routes**

# Mercury Salts and Organic Compounds

$$
HgX_2 + RH \longrightarrow RHgX \xrightarrow{-HK} R_2Hg
$$
  
eg. Hg(OAc)<sub>2</sub> + ArH  $\xrightarrow{MeOH}$  ArHgOAc + AcOH  
decarboxylation

Pyrolysis of Carboxylates

$$
[HgCl_2 + 2NaOOCR] \longrightarrow Hg(OOCR)_2 \xrightarrow{\Delta} R_2Hg + 2CO_2
$$

Met al Hydrides + Unsaturated Species

$$
MH + \bigg\downarrow C = C \longrightarrow -M-C-C-H
$$
\n
$$
eg. Et2AIH + C2H4 \longrightarrow Et3Al \nhydroelimination
$$

PhSiCH<sup>3</sup> + CH2N<sup>2</sup> PhSi(Me)H<sup>2</sup> + N<sup>2</sup> Organometallic + Carbene Source eg. hν

 $Ph_3GeH + PhHgCBr_3 \longrightarrow Ph_3GeCBr_2H + PhHgBr$ 

insertion of  $CR_2$  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. Methyllithium is actually cubic body-centered  $(LiCH<sub>3</sub>)<sub>4</sub>$  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  $(LicH_3)_4$  unit interact with the Li atoms of a neighbouring  $Li<sub>4</sub>$  tetrahedron. Reason for formation of heterocubane structure is that in a monomer LiR unit too few valence e are available to fill the valence orbitals of Li  $\Rightarrow$ multicentre bonding.

## **Bonding**

The axial Li  $(sp<sup>3</sup>)$  orbital interacts with the methyl groups of neighbouring  $(LicH<sub>3</sub>)<sub>4</sub>$  units . These intermolecular forces result in the low volatility and insolubility of  $(LicH_3)_4$  in nonsolvating media.

The structure of <sup>t</sup> butyl lithium is similar but the intermolecular forces are weaker and hence <sup>t</sup>BuLi is soluble in hydrocarbons and sublimes at 70° C/1 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  ${}^{6}$ Li and  ${}^{7}$ li NMR.

ESR looks at the transition of unpaired e .



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

Coupling to<sup>13</sup>C enriched species confirmed tetrameric structure of 'BuLi.

Multiplicity =  $2nI + 1$ 

In ESR spectrum

interaction of C radical with  $H_2$ <sup>.</sup>  $\Rightarrow$  triplet = 2 x 2 x 1/2 +1 = 3

interaction of C radical with  $3Li (I = 3/2)$  $\Rightarrow$  decet = 2 x 3 x 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. Li<sup>+</sup> acts like a hard acid polarising the  $e^-$  cloud of e.g.  $CH_3^-$  (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

eg. cis-  $(PEt_3)_2$ PtCl<sub>2</sub> + 2MeLi  $\longrightarrow$  cis-  $(PtEt_3)_2$ PtMe<sub>2</sub> + LiCl

# **Wittig Reagents**

 $Ph_3P + MeBr \longrightarrow Ph_3PCH_3^+Br$  phosphonium salt

(cf. NH<sub>3</sub> + HBr 
$$
\longrightarrow
$$
 NH<sub>4</sub><sup>+</sup>Br)

 $Ph_3PCH_3^+Br^- + LiR \longrightarrow Ph_3P=CH_2 + LiBr + RH$ 

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

 $R$ <sup>C</sup> = CH<sub>2</sub> R  $Ph_3P=CH_2 + R_2C = O \longrightarrow Ph_3P^+ = O^$ ketone alkene

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

## **Reaction of LiR with Organofluorines**



fluorobenzene, ortho H are a little acidic.

Mechanism





name.

#### **Heavier Group I Organometallics**

Limited use: ionic character of M-C increases down group. Generally very reactive even slowly metallate hydrocarbons (in which they are insoluble).

#### **Preparation**

 $R_2Hg + \text{excess Na} \longrightarrow 2 \text{ RNA}_{(s)} + \text{Na}(Hg)$ light petroleum amalgam

Not prepared from organochlorides due to coupling

 $RX + 2Na \longrightarrow RNa + NaX$  $\downarrow \longrightarrow R_2 + NaX$ RX

If  $R =$  phenyl and use a fine dispersion of Na, NaPh can be prepared by this route. Require slow addition of PhCl at  $30-32^{\circ}$  C so no excess of RX builds up.

Reactivity due to pronounced carbanionic character . e.g.

$$
CH_3CH_2-O-CH_2CH_3 + KC_4H_9 \longrightarrow C_4H_{10} + K^+[CH-O-C_2H_5]
$$
  
diethyl ether  
ether cleavage  

$$
KOC_2H_5 + H_2C = CH_2
$$

#### **Stability**

MeNa decomposes  $> 200^{\circ}$ C in a complex reaction giving mainly  $6$ MeNa  $\longrightarrow$  6CH<sub>4</sub> + Na<sub>2</sub>C + 6Na

EtNa decomposes 90-100°C via β elimination.  $C_2H_5Na \longrightarrow NaH + C_2H_4$ 

#### **Aromatic Compounds**

Stability of RNa increases if the respective carbanion is stabilised by resonance. e.g.  $C_5H_5Na$  or  $Ph_3CK$ **Substitution Compounds** : brightly coloured, wide variety of reactivity.

e.g. Ph<sub>3</sub>CCl + 
$$
2Na(Hg) \longrightarrow Ph_3CNa^+
$$
 + NaCl  
PhMe<sub>2</sub>COMe +  $2K \longrightarrow PhMe_2C'K^+$  + MeOK  
bright red – used to remove oxygen from  
inert

inert gases

#### **Addition Compounds**

 $2Ph_2C=CH_2 + 2 Na \longrightarrow 2 Ph_2C$ <sup>-</sup>-CH<sub>2</sub> Na<sup>+</sup>  $\longrightarrow$  Ph<sub>2</sub>C<sup>-</sup>-CH<sub>2</sub>-CH<sub>2</sub>-C<sup>-</sup>-Ph<sub>2</sub> (Na<sup>+</sup>)<sub>2</sub> 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:

 $2PhC\equiv CPh + 2Li$  –  ${}^+$ PhC ${}^-=$ CPh $\longrightarrow$ 

LiPhC=PhCCPh=CPhLi



### **Group II Organometallic Species**

Grignard Reagents:  $Mg + RX \frac{Et_2O}{\sqrt{2}}$  EtMgX exothermic or THF but  $Et_2O$  substituted is <u>less</u> reactive

 $2RMgX \implies MgR_2 + MgX_2$ equilibrium.  $R = alkyl$ , aryl.

Reducing and organylating ability of lithium and magnesium reagents:

Although  $LiR > RMgX > MgR<sub>2</sub>$  at organylating, LiR is also a reducing agent

e.g. TiCl<sub>4</sub>  $\longrightarrow$  TiR<sub>3</sub> + LiCl. LiR

Actually better to use MgR<sup>2</sup>

Improved organylation of  $MgR_2$  can b obtained using dioxin as solvent which complexes to halide to give an insoluble salt.

 $2RMgX + 2dioxane \longrightarrow R_2Mg + MgX_2(dioxane)_2(s)$ ppt.

# **Synthesis of "BeR<sup>2</sup> "**

BeCl<sub>2</sub> +2RMgX 
$$
\xrightarrow{\text{Et}_2\text{O}}
$$
 BeR<sub>2</sub> + MgXCl  
distill at low temp.  
BeR<sub>2</sub>(OEt)<sub>2</sub>

remove solvent by heating under a vacuum.

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

In solid phase - IR  $v(CH)$  low 2912, 2885. i.e. bonds long electron withdrawing due to  $Be-CH_3$  bridges.

### **Structure of solid**



Both Be and C effectively  $sp^3$ .

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

Here see 3 centre -2 electron bonds (cf.  $B_2H_6$  and  $Al_2Me_6$  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



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  $(BeMe<sub>2</sub>)<sub>n</sub>$  with electron donor species eg Me<sub>3</sub>N, PMe<sub>3</sub>, causes formation of complexes and a breakdown of polymeric structure eg.  $R_2Be$  bipy - these compounds deep-red with λmax and E decreasing as the e attracting power of R decreases. eg  $R = Ph$ , Me, Et, Br.

transition observing R to  $\pi^*$  of bipy.





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



Factors to consider

Ring strain favours trimers.

Bulk of NR<sup>2</sup> 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  $NEt_2$  trimer when BeR=Me as Be R increases  $\Rightarrow$  dimers