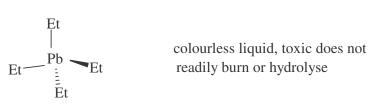
MAIN GROUP ORGANOMETALLICS

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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.



0ⁱPr isopropyl CH₃-CH-CH₃ $O^{i}Pr$ $Pb - O^{i}Pr$ not organometallic as no direct M-C bonds

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, $(BeMe_2)_n$ catches fire in dry CO₂

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. $2Li + RC1 \longrightarrow RLi + LiC1$ e.g. $R = {}^{t}Bu$

Mg $^{\circ}$ + PhBr \longrightarrow "PhMgBr" (see later)

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

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

 $2 \text{ Na} + \text{Hg} + 2\text{MeBr} \longrightarrow \text{Me}_2\text{Hg} + 2\text{NaBr}$

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

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

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

e.g. $Pb^{II}I_2 + MeI \longrightarrow MePb^{1V}I_3$

Organolithium species especially require

(i) work under inert atmosphere (N₂) Ar(ii) dry, degassed solvents/reagents(iii) dry apparatus

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

Reaction requires nucleophilic displacement of sp³ C atom. ΔG very high.

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

Using N₂ in preparation of R-Li gives Li₃N (\Rightarrow purple solution)

Other solvents used cyclohexane, benzene, petrol

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

eg.

BuCl + 2Li
$$\xrightarrow{Et_2O}_{Ar}$$
 LiCl(s) + BuLi
filter evaporate solvent
BuBr + 2Li \longrightarrow LiBr + BuLi
BuBr + BuLi \longrightarrow Bu-Bu + LiBr
octane
Actually a standard method of alkane manufacture.

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 <u>Na</u> 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. $Bu^{t}Li + PhX \longrightarrow Bu^{t}X + LiPh$

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 sp² C.

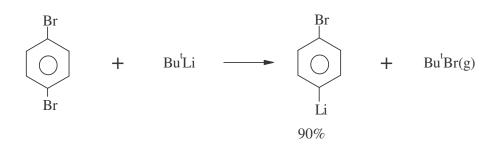
Also reaction is good for X = I, Br occasionally Cl but not F.

A volatile RX should be formed

Bu^tLi good starting material as Bu^tI volatile and Bu^t is an electronegative group.

e.g. $Bu^{t}Li + ArI \longrightarrow ArLi + Bu^{t}I(g)$.

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.

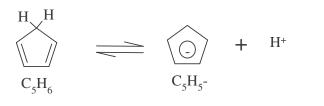
 $\text{SnPh}_4(s) + 4\text{CH}_2 = \text{CHLi}$ $4PhLi + Sn(CH=CH_2)_4$ (readily vinyl v.insoluble in ether available) forces reaction to equilibrium $4Bu^{t}Li + Sn(CH=CH_{2})_{4} \xrightarrow{} pentane$ $4\text{Li}(\text{CH}=\text{CH}_2) + \text{SnBu}_4^{t}$ (incomplete) pyrophoric precipitate $4\text{Li} + \text{Pb}(\text{CH}=\text{CH}_2)_4 \longrightarrow 4\text{Li}(\text{CH}=\text{CH}_2) + \text{Pb}(s)$ Et₂O $Bz_3SnCl + 4MeLi \longrightarrow 3BzLi + Me_4Sn + LiCl$ phenylmethyl useful because BzLi + RX \Box coupling reaction

for isolation : $2Li + HgR_2 \xrightarrow{\text{petrol}} 2LiR + Hg$ benzene

4. Metal - Hydrogen Exchange (metallation)

 $RM + R'H \longrightarrow RH + R'M \qquad M = alkali metal$ e.g. PhNa + PhCH₃ \longrightarrow PhH + PhCH₂Na benzyl sodium

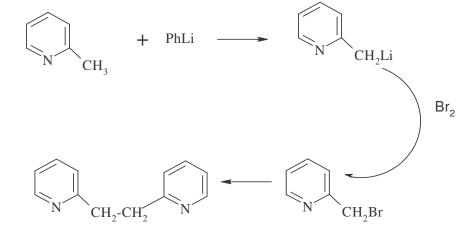
Strong CH acids e.g. acetylene and CpH can react directly with alkali metal. Cp strong acid by organic standards



 $pK_a = 16$ (9 orders of magnitude lower than water) water pH = 7[H⁺] = 10⁻⁷

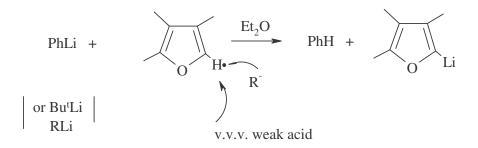
e.g.
$$C_5H_5 + Na \longrightarrow C_5H_5Na + 1/2H_2$$

Others require reaction of mildly acidic H with organometallic reagent



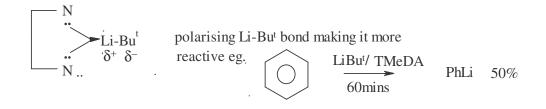
LiBr 🕂





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 Δ (Δ G f^{o}) 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

$$HgX_{2} + RH \longrightarrow RHgX \xrightarrow{+RH} R_{2}Hg$$

-HX
eg. Hg(OAc)₂ + 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 +
$$C = C$$
 \longrightarrow $-M - C - C - H$
eg. Et₂AlH + C₂H₄ \longrightarrow Et₃Al hydroelimination

$$\frac{\text{Organometallic} + \text{Carbene Source}}{\text{eg.}} \text{PhSiCH}_3 + \text{CH}_2\text{N}_2 \xrightarrow{\text{hv}} \text{PhSi(Me)H}_2 + \text{N}_2$$

 $Ph_3GeH + PhHgCBr_3 \longrightarrow Ph_3GeCBr_2H + PhHgBr$

insertion of $\mathrm{CR}_2~$ 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 <u>cubic</u> body-<u>centered</u> (LiCH₃)₄ units. The lattice is built up of distorted cubes with alternate occupation of the corners by C and Li.

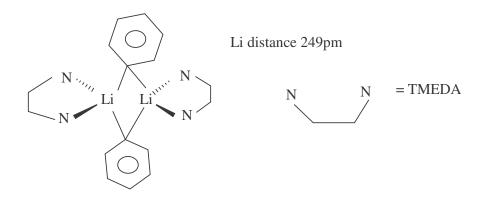
See diagram

* The methyl groups of one $(LiCH_3)_4$ unit interact with the Li atoms of a neighbouring Li₄ tetrahedron. Reason for formation of <u>heterocubane</u> 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^3) orbital interacts with the methyl groups of neighbouring $(LiCH_3)_4$ units. These int<u>er</u>molecular forces result in the low volatility and insolubility of $(LiCH_3)_4$ in non-solvating media.

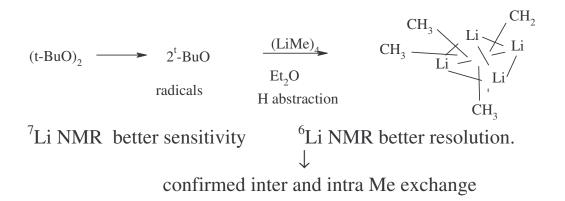
The structure of ^t butyl lithium is similar but the intermolecular forces are weaker and hence ^tBuLi is soluble in hydrocarbons and sublimes at 70° C/1 mbar. Coordinating solvents will tend to give monomeric or dimeric species as the coordination sites on Li are occupied.



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

data : ESR and ⁶Li and ⁷li NMR.

ESR looks at the transition of unpaired e^{-1} .



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

Coupling to¹³C enriched species confirmed tetrameric structure of ^tBuLi.

Multiplicity = 2nI + 1

In ESR spectrum

interaction of C radical with $H_2^ \Rightarrow$ 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^+ 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. \underline{cis} - (PEt₃)₂PtCl₂ + 2MeLi $\longrightarrow \underline{cis}$ - (PtEt₃)₂PtMe₂ + LiCl

Wittig Reagents

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

(cf.
$$NH_3 + HBr \longrightarrow NH_4^+Br$$
)

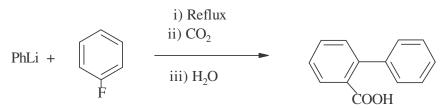
 $Ph_3PCH_3^+Br^- + LiR \longrightarrow Ph_3P=CH_2 + LiBr + RH$

R= Ph, Bu^t triphenylphosphine methylide (Wittig reagent)

 $Ph_{3}P=CH_{2} + R_{2}C = O \longrightarrow Ph_{3}P^{+} = O^{-} + R \xrightarrow{R} C = CH_{2}$ ketone alkene

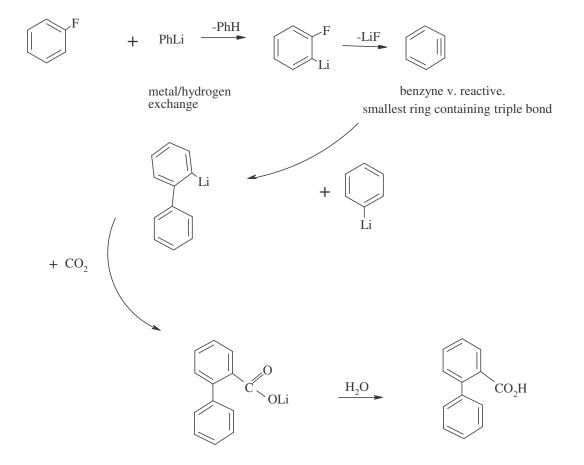
ketone \rightarrow branched alkene aldehyde \rightarrow straight chain alkene

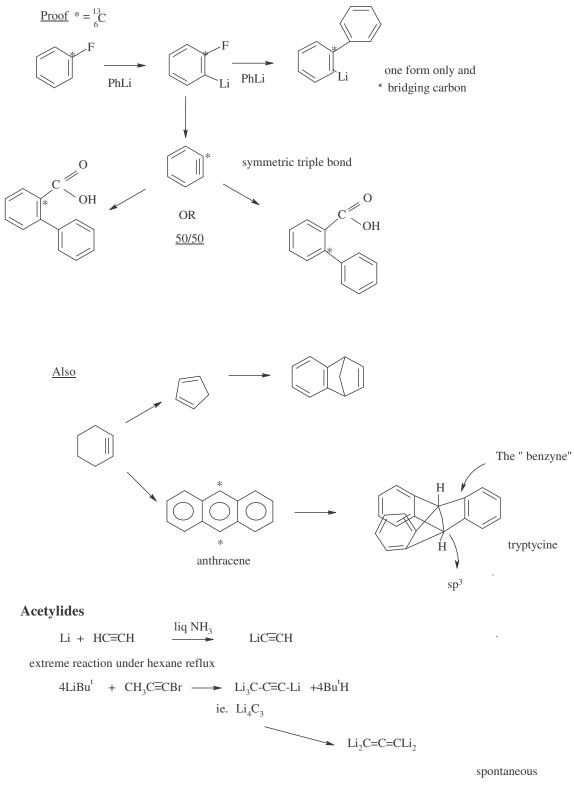
Reaction of LiR with Organofluorines



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

 $\begin{array}{ccc} R_2Hg \ + \ excess \ Na & \longrightarrow & 2 \ RNa_{(s)} \ + \ Na(Hg) \\ & \ light \ petroleum & amalgam \end{array}$

Not prepared from organochlorides due to coupling

 $\begin{array}{rccc} RX \ + \ 2Na \longrightarrow & RNa \ + \ NaX \\ & \left| \longrightarrow R_2 \ + \ NaX \\ & RX \end{array} \right.$

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° C so no excess of RX builds up.

Reactivity due to pronounced carbanionic character . e.g.

$$\begin{array}{cccc} CH_{3}CH_{2}\text{-}O\text{-}CH_{2}CH_{3} + KC_{4}H_{9} \longrightarrow C_{4}H_{10} + K^{+}[CH\text{-}O\text{-}C_{2}H_{5}] & & | \\ & & | \\ & & \text{diethyl ether} & & CH_{3} \\ & & \text{ether cleavage} & \downarrow \\ & & KOC_{2}H_{5} + H_{2}C = CH_{2} \end{array}$$

Stability

MeNa decomposes > 200° C in a complex reaction giving mainly 6MeNa \longrightarrow 6CH₄ + Na₂C + 6Na

EtNa decomposes 90-100°C via β elimination. C₂H₅Na \longrightarrow NaH + C₂H₄

Aromatic Compounds

Stability of RNa increases if the respective carbanion is stabilised by resonance.
e.g. C₅H₅Na or Ph₃CK
Substitution Compounds : brightly coloured, wide variety of reactivity.

e.g.
$$Ph_3CCl + 2Na(Hg) \longrightarrow Ph_3C^*Na^+ + NaCl$$

 $PhMe_2COMe + 2K \longrightarrow PhMe_2C^*K^+ + MeOK$
bright red – used to remove oxygen from

inert gases

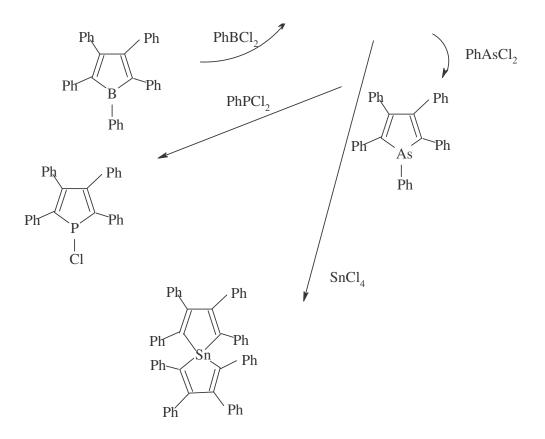
Addition Compounds

 $\begin{array}{rcl} 2Ph_2C=CH_2 &+ 2 \text{ Na} \longrightarrow 2 \text{ Ph}_2C^--CH_2 & \text{Na}^+ \\ & \longrightarrow Ph_2C^--CH_2-CH_2-C^--Ph_2 & (\text{Na}^+)_2 \end{array}$ 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:

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

LiPhC=PhCCPh=CPhLi

 \rightarrow



Group II Organometallic Species

Grignard Reagents: Mg + RX $\xrightarrow{Et_2O}$ EtMgX exothermic or THF but Et₂O substituted is <u>less</u> reactive

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

Reducing and organylating ability of lithium and magnesium reagents:

Although $\underline{LiR} > RMgX > MgR_2$ at organylating, LiR is also a reducing agent

e.g. $TiCl_4 \longrightarrow TiR_3 + LiCl.$ LiR

Actually better to use MgR₂

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.

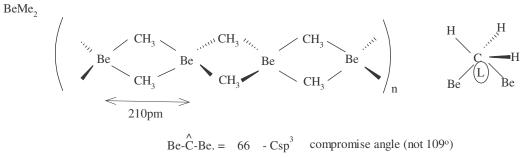
Synthesis of "BeR₂ "

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-CH₃ bridges.

Structure of solid



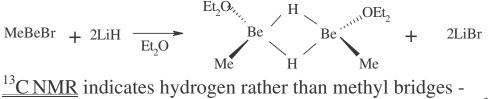
Both Be and C effectively sp³.

Remember that e⁻ deficient compounds were seen for Li, Be, B. When four coordinate there are not enough valence e⁻ for 2C - 2e⁻ 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).

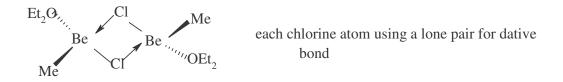
Species extremely reactive – hydrolyse, explosive in presence of any active H

NB Organoberyllium hydride prepared



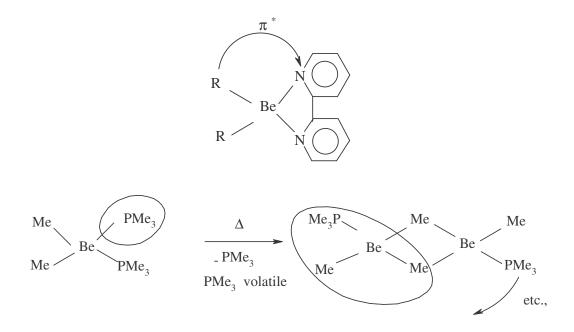
thought to be due to better s orbital overlap of H with Be sp^3 orbitals - 1s orbital. spherical symmetry.

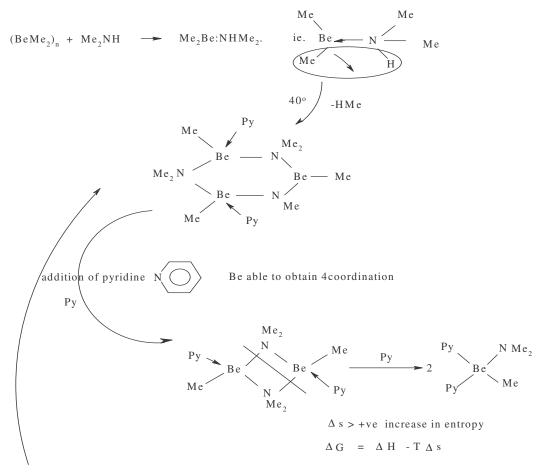
Chlorine bridges are better again – they can provide 3 electrons per atom



Reactions of $(BeMe_2)_n$ with electron donor species eg Me₃N, PMe₃, causes formation of complexes and a breakdown of polymeric structure eg. R₂Be bipy - these compounds deep-red with λ max and E decreasing as the e⁻ attracting power of R decreases. eg R = Ph, Me, Et, Br.

transition observing R to π^* of bipy.





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



Factors to consider

Ring strain favours trimers.

Bulk of NR₂ 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 NEt₂ trimer when BeR=Me as Be <u>R</u> increases \Rightarrow dimers