GENERAL:

OMCs are similar to H- compounds (similar elect-ve of M-C, C-H & M-H)

*The species that lose H form ionic compounds with alkali metals.

OMC's are used in organic synthesis.

They are superior to Grignard reagents (e.g. in alkene polymerization).

*They are liquids or low melting solids, thermally stable than other OMC of the same group. Soluble in organic and non-polar solvents. All OMC's of alkali metals are unstable.

*In alkaline earth metals, the reactivity and electropositivity ↑ in the group. Therefore, the OMC of Be and Mg are covalent, while Ca, Sr and Ba form only few ionic compds that are unstable and of little utility.

*OMC's of group 13 elements exist as electron deficient species having +3 OS (e.g.Al3+), with 3c-2e bonding.

Organoaluminium compounds are used for alkene polymerization, catalysts& chemical intermediates.

Trialkylaluminum is a diamer but often written as the monomer, AIR₃.

A) Organolithium Compouds

i) Reaction of Alkyl or Aryl Halide with Li Metal:

Alkyl/Aryl halides react with lithium in inert solvent such as ether, benzene, petroleum ether, cyclohexane etc.

The moisture and air must be excluded as they react with reactant and products.

2. Bromobenzene
$$35^{\circ}C$$
 Et₂O Phenyllithium

Examples

$$^{4.}$$
C₂H₅Cl+2Li → C₂H₅Li +2LiCl

^{5.}
$$C_6H_5Br+2Li$$
 \rightarrow $C_6H_5Li+2LiCI$

Features:

*The organolithiums react slowly with ether, therefore, the synthesis is usually carried out in <u>inert atmosphere of</u> <u>nitrogen or argon at low temperature</u>.

*The use of cyclohexane as solvent, alkyl or aryl chlorides over bromides and iodides minimizes the possibility of side reactions

*The yield and reactivity is improved by adding 0.5-1% Na.

ii) Metal Hydrogen Exchange (Metallation):

Alkyl and aryl lithium can be synthesized by reacting the Organic compounds with alkyl/ n-butyl lithium, ((C₄H₉)Li called nBuLi). The reaction, in general, can be written as;

4.
$$\bigcirc O + PhLi \longrightarrow \bigcirc \bigcirc Li + C_6H_6$$

The reactions gives small aggregates having multicenter bonding;

e.g. (CH₃)₄Li₄ or (C₂H₅)₆Li₆

which contain bridging alkyl groups

*When ethers are solvent, methyl lithium exists as (CH₃)₄Li₄.

*while in hydrocarbon solvents (e.g THF), it exist as (CH₃)₆Li₆.

*LiCl destroys (CH₃)₄Li₄, 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

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:

$$(CH_3)_2Hg + 2Li \rightarrow 2CH_3Li + Hg$$

Organolithium compounds are mainly used in homogeneous catalysis, for example, in stereospecific polymerization of alkene

i) Metathesis:

Bervilium halide reactor that had a different the saly LL U M

(e.a.lithium.sodium etc.).

ether

Be(CH₃)₂ + 2LiCl (Dimethylberyllium) BeCl₂ + 2 CH₃Li \rightarrow

ether

BeCl₂ + 2 MgCH₃Cl \rightarrow $(CH_3)_2Be + 2 MgCl_2$

ether

BeCl₂+ 2 C₆H₅Li → $Be(C_6H_5)_2 + 2LiCI$ (Diphenylberyllium)

 $3(C_2H_5)_2Be + 2(C_6H_5)3B \rightarrow$ $2(C_2H_5)_3B + 3(C_6H_5)_2Be$

Diphenylberyllium

BeCl₂ reacts with Na[C₅H₅]₂ to give Bis(cyclopentadienyl)Be (double displacement). The anion is transferred to less electropositive Be(II).

[C₅H₅]₂Be + 2NaCl $BeCl_2 + 2 Na [C_5H_5] \rightarrow$

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.