Group 2 Organometallics

Group 2 Organometallics

- In many ways the chemistry of group 2 elements (the alkaline earth metals) **mimics that of group 12** elements because both groups have **filled s shells for valence electrons**. Thus, both groups have nominal valency 2 and oxidation state +2.
- All group 2 elements are **electropositive** towards carbon and electronegativity decreases down the group.
- At the same time the atomic radius increases resulting in **increasingly ionic** character, higher coordination numbers, and increased ligand reactivity.
- The group 2 elements are known to form organometallic compounds. Of these, **organomagnesium** compounds, usually in the form of Grignard reagents, are widely used in organic chemistry, while the other organometallic compounds of this group are largely academic.

Organometallics compounds of Beryllium (Organoberyllium)

Synthesis and structure

Transmetallation reaction

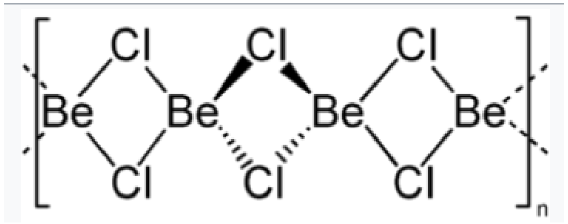
Organoberyllium compounds are best prepared via **transmetallation** reactions either with a Grignard reagent or with other organometallic compounds

$$2\ RMgX + BeCl_2 \rightarrow R_2Be + 2\ MgXCl$$

$$HgMe_2 + Be \rightarrow Me_2Be + Hg$$

- In the gas phase Me_2Be is monomeric with a linear C—Be—C (Be-C = 170 pm), but in the **solid state** it is polymeric and resembles that of $BeCl_2$ with a bonding that is considered electron deficient with 3-center-2-electron bonds.

Beryllium chloride



- With higher alkyls, the amount of polymerisation decreases and the tert-butyl derivative is monomeric and linear in both solid and vapour phases.

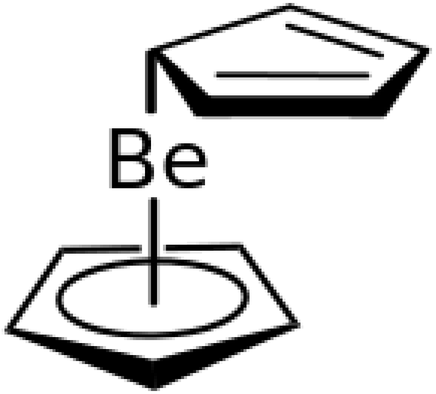
Beryllocene

Metathesis reaction

- The reaction of NaCp with beryllium chloride leads to beryllocene (Cp_2Be)

$$BeCl_2 + 2\ NaCp \longrightarrow Cp_2Be + 2\ NaCl$$

- The solid state structure suggests that the compound has a mixed η^5-C_5H_5 and η^1-C_5H_5 coordination.



Organometallics Compounds of Magnesium

(Organomagnesium)

- Alkyl and aryl magnesium halides (Grignard reagents, **RMgX**) are extremely well-known on account of their uses in synthetic chemistry.
- The general procedure for their preparation was discovered by Victor Grignard in 1900 and involved the direct reaction of magnesium with organohalides.

$$R{-}X + Mg \rightarrow R{-}Mg{-}X \qquad (X = Cl, Br, I)$$

- When the reaction is performed in diethyl ether or THF and in the absence of air and moisture, the compounds are reasonably stable although they need to be used immediately. Grignard reactions often start slowly.

Synthesis and structure

Transmetallation is useful means of preparing pure Grignard reagents

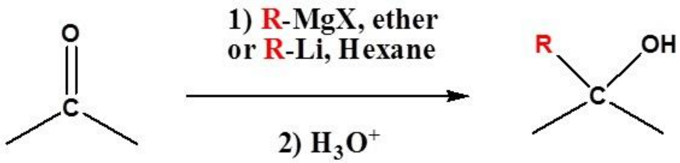
$$Mg + RHgBr \longrightarrow Hg + RMgBr$$

$$Mg + R_2Hg \longrightarrow Hg + R_2Mg$$

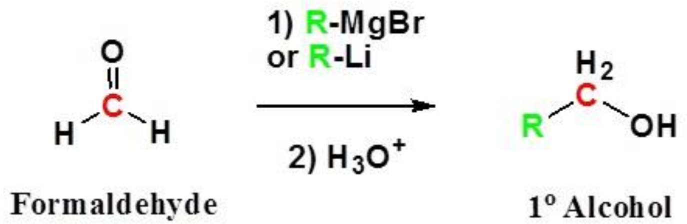
- Two-coordination at Mg in R_2Mg is observed only when the R groups are sufficiently bulky, e.g. $Mg\{C(SiMe_3)_3\}_2$.
- RMgXRMgX are generally solvated and MgMg center is typically tetrahedral (e.g. $EtMgBr.2Et_2O$; $PhMgBr.2Et_2O$)
- Cp_2Mg has a staggered sandwich structure.

Reactions of Grignard Reagents

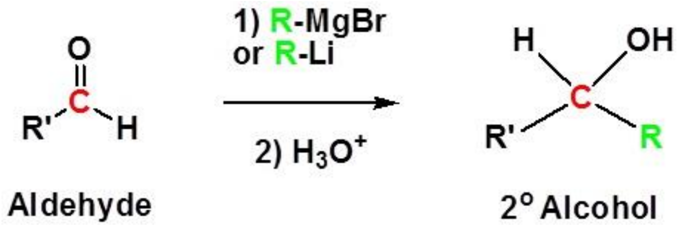
Because organometallic reagents react as their corresponding carbanion, they are excellent nucleophiles. The basic reaction involves the nucleophilic attack of the carbanionic carbon in the organometallic reagent with the electrophilic carbon in the carbonyl to form alcohols.



Both Grignard and Organolithium Reagents will perform these reactions.
Addition to formaldehyde gives 1° alcohols

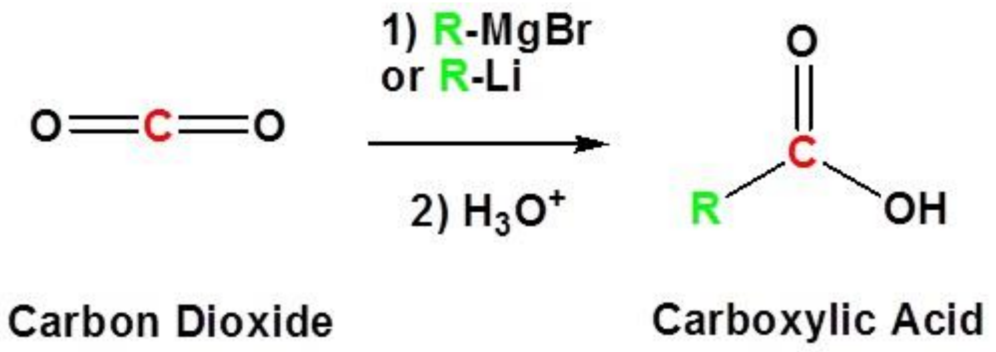


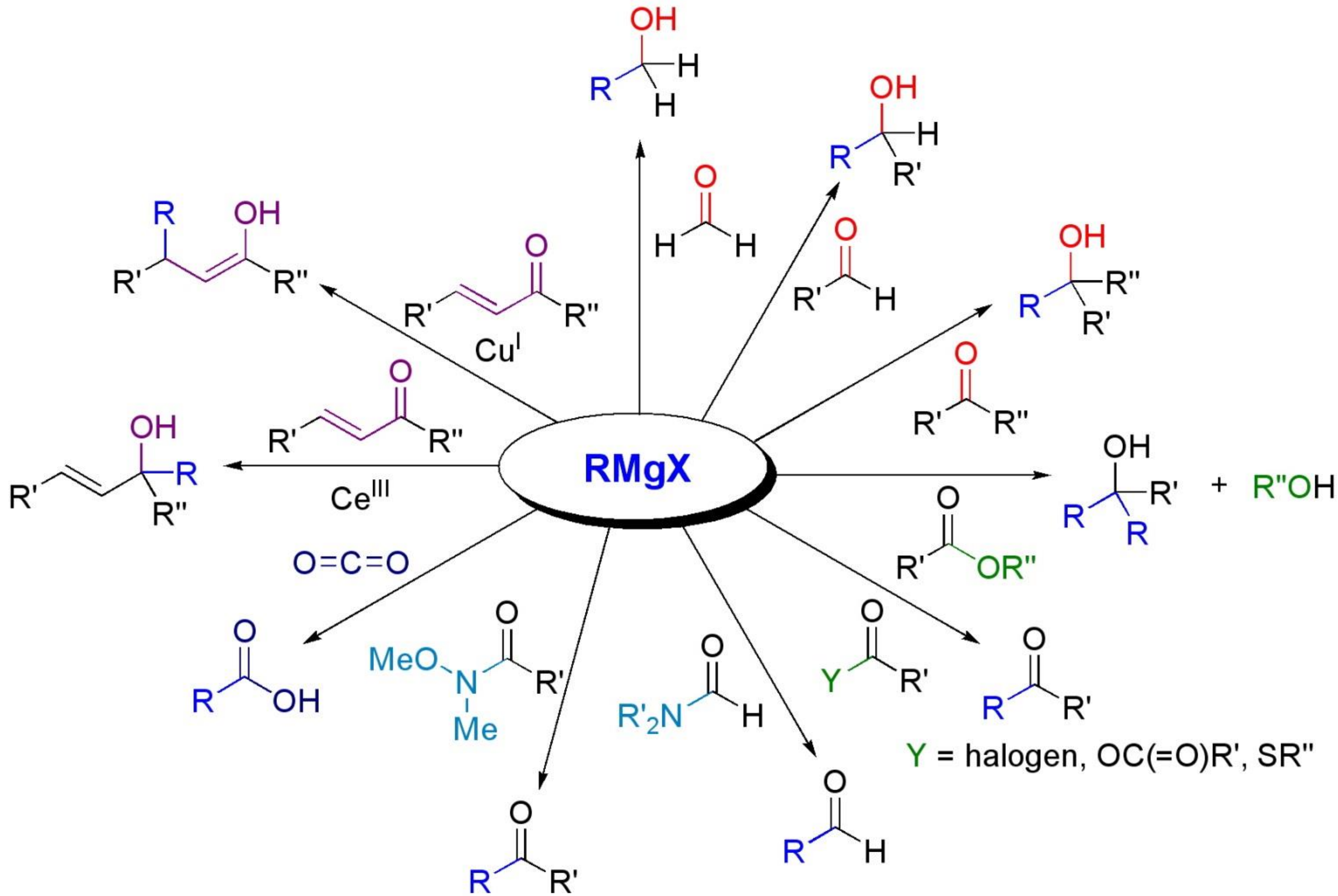
Addition to aldehydes gives 2° alcohols



Addition to ketones gives 3° alcohols

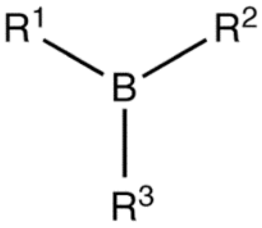
Addition to carbon dioxide (CO_2) forms a carboxylic acid




RMgX
Cu^{I}
Ce^{III}
O=C=O
Y = halogen, OC(=O)R', SR''

P-block organometallic compounds

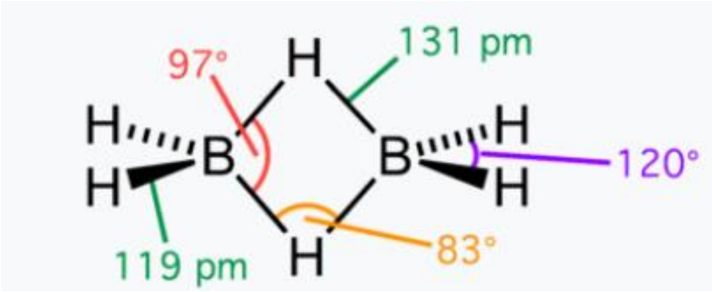
Organoboron Compounds



• Organoborane or organoboron compounds are chemical compounds of boron and carbon that are organic derivatives of BH_3, for example **trialkyl boranes**.

• The C-B bond has **low polarity** (the difference in electronegativity 2.55 for carbon and 2.04 for boron), and therefore alkyl boron compounds are in general stable even though easily oxidized by O_2 forming oxides and other products.

- In part because its lower electronegativity, boron often forms electron-deficient compounds, such as the triorganoboranes.
- Vinyl groups and aryl groups donate electrons and make boron less electrophilic and the C-B bond gains some double bond character. (Vinyl: -CH=CH2)
- Like the parent borane, diborane, organoboranes are classified in organic chemistry as strong electrophiles because boron is unable to gain a full octet of electrons. Unlike diborane however, most organoboranes do not form dimers.



- BMe_3 is colorless, gaseous (b.p. -22 °C), and is monomeric. It is pyrophoric but not rapidly hydrolyzed by water. Alkylboranes can be synthesized by metathesis between BX_3 and organometallic compounds of metals with low electronegativity, such as RMgX or AlR_3.

$$BF_3 + 3\,CH_3MgBr \longrightarrow B(CH_3)_3 + 3\,MgBrF \quad \text{(solvent used: dibutyl ether)}$$

- Why dibutyl ether as a solvent: Has much lower vapor pressure than BMe_3 and as a result the separation by trap-to-trap distillation on a vacuum line is easy.

- Also, there is a very weak association between BMe_3 and OBu_2 ($Me_3B{:}OBu_2$).

- Although, trialkyl- and triarylboron compounds are mild Lewis acids, strong carbanion reagents lead to anions of the type $[BR_4]^-$.

$$BR_3 + R^- \rightarrow [BR_4]^-$$

Organohaloboron compounds

OrganoHaloBoron compounds are more reactive than simple trialkylboron compounds.

Preparation

$$2\,BCl_3 + 6\,AlR_3 \longrightarrow 3\,R_2BCl + 6\,AlR_2Cl \text{ (metathesis)}$$

$$2\,BCl_3 + BMe_3 \xrightarrow[\text{(diborane)}]{} 3\,BMeCl_2 \text{ (redistribution reaction)}$$

Reactions:

(Protolysis reactions with ROH (alcohol), R_2NH (amine) and other reagents)

$$3\,BMeCl_2 + 2\,HNR_2 \longrightarrow BMe_2(NR_2) + [R_2NH_2]Cl$$

$$BMe_2Cl + Li(C_4H_9) \longrightarrow BMe_2(C_4H_9) + LiCl$$

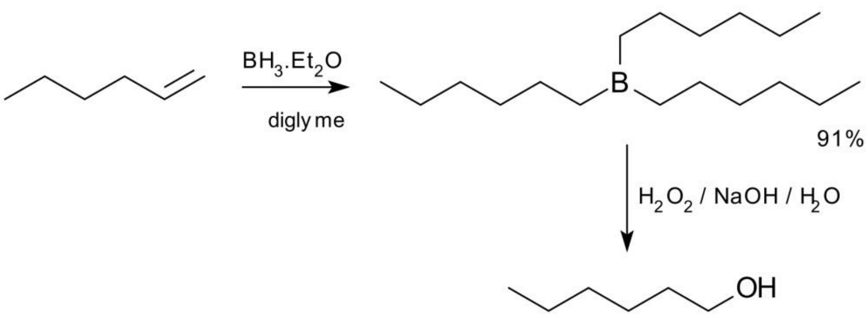
The 1st reaction: a boron compound with two methyl groups and one amine group attached to the boron and ammonium chloride salt formed by **protonating** the amine and combining it with a chloride ion.
The 2nd reaction is a **substitution** reaction where the chloride in BMe_2Cl is replaced by a C_4H_9 group (forming a butyl group), resulting in the formation of $BMe_2(C_4H_9)$ and LiCl.

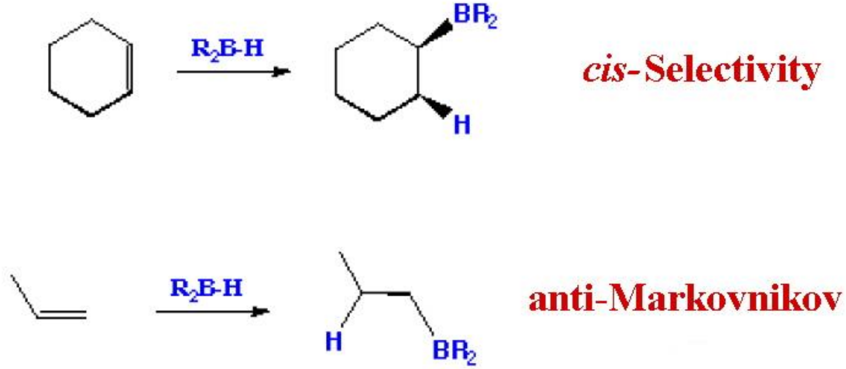
Hydroboration

- The hydroboration-oxidation reaction is a two-step organic chemical reaction that converts an alkene into a neutral alcohol by the net addition of water across the double bond.

- The hydrogen and hydroxyl group are added in **a syn addition leading to cis stereochemistry**. Hydroboration-oxidation is an anti-Markovnikov reaction, with the hydroxyl group attaching to the less-substituted carbon.

- The reaction was first reported by Herbert C. Brown in the late 1950s and he received the Nobel Prize in Chemistry in 1979. Shown below is the original reaction described in 1957 where hex-1-ene is converted to hexanol.



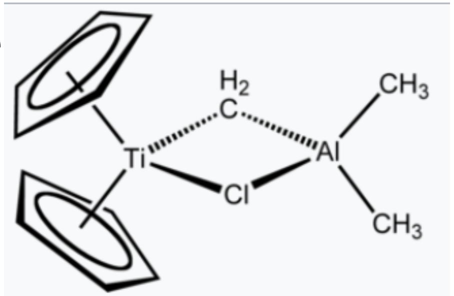


Organoaluminium compounds

- Organoaluminium chemistry is the study of compounds containing bonds between carbon and aluminium bond.

- It is one of the major themes within organometallic chemistry. Illustrative organoaluminium compounds are the dimer, trimethylaluminium, the monomer triisobutylaluminium, and the titanium-aluminium compound called Tebbe's reagent. $C_{13}H_{18}AlClTi$

Tebbe's reagent

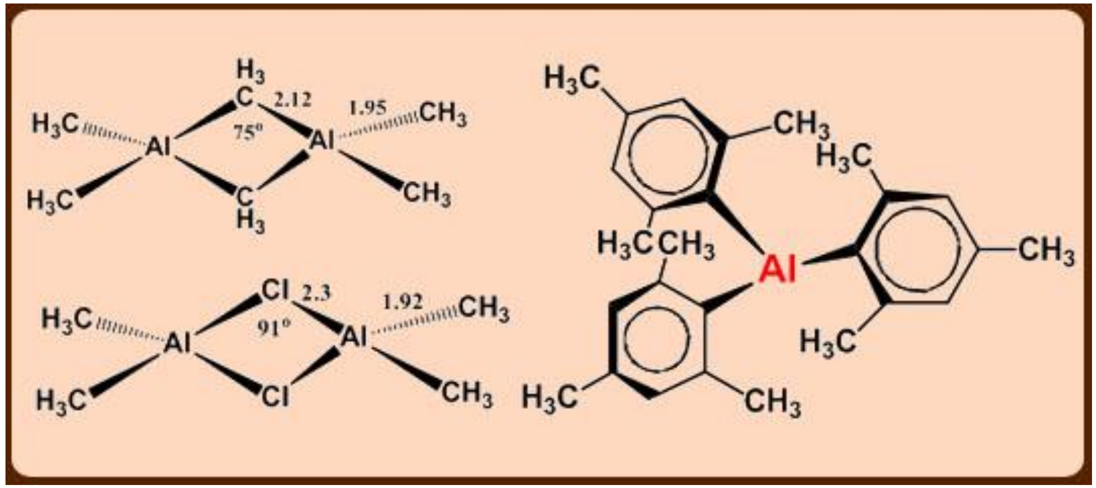


- The behavior of organoaluminium compounds can be understood in terms of the polarity of the C−Al bond and the high Lewis acidity of the three-coordinated species.

- Industrially, these compounds are mainly used for the production of polyolefins. (**Polyethylene (PE)**: Made from ethylene (CH_2=CH_2) or CH_2=$CHCH_3$)

- With less bulky alkyl groups, dimerization occurs and one of the distinguishing features of alkyl bridge is the small Al-C-Al angle, which is ~ 75°.

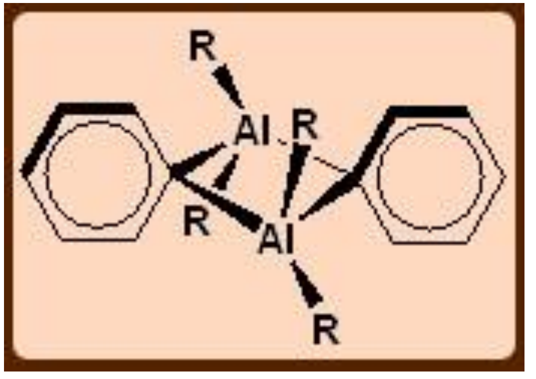
The 3c,2e bonds are very weak and tend to dissociate in the pure liquid which increases with increase in the bulkiness of the alkyl group.



$$Al_2(CH_3)_6 \rightleftharpoons 2\ Al(CH_3)_3 \quad K = 1.52 \times 10^{-8}$$
$$Al_2(C_4H_9)_6 \rightleftharpoons 2\ Al(C_4H_9)_3 \quad K = 2.3 \times 10^{-4}$$

- Dimerization: Trimethylaluminum and triisobutylaluminum tend to dimerize, forming structures with two aluminum atoms connected by bridging alkyl groups.
- Al-C-Al angle: The Al-C-Al angle in these dimeric structures is approximately 75 degrees.

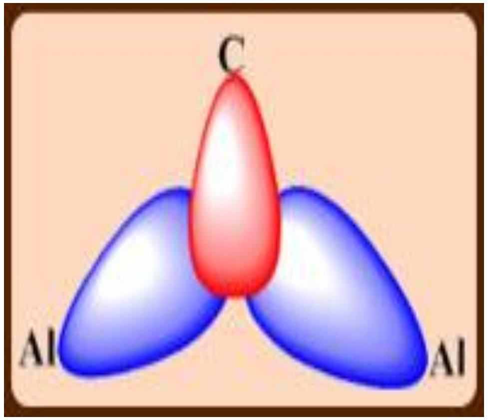
Perpendicular orientation of pheynl groups in Al_2Ph_6 Triphenylaluminium exists as a dimer with bridging η^1-phenyl groups lying in a plane perpendicular to the line joining the two Al atoms.

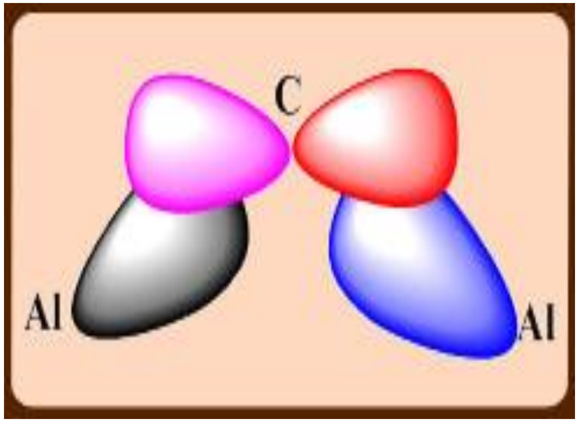


This structure is favored partly on steric grounds and partly by supplementation of the Al-C-Al bond by electron donation from the phenyl π-orbitals to the Al atoms.

Tendency for bridging: X > Ph > alkyl

3c,2e bonds formed by a symmetric combination of Al and C orbitals





An additional interaction between the pπ orbital on C and an antisymmetric combination of Al orbitals.

Synthesis of Organoaluminium compounds

Laboratory scale preparations involves:

$$2\ Al + 3Hg(CH_3)_2 \longrightarrow Al_2(CH_3)_6 + 3\ Hg$$

Commercial method:

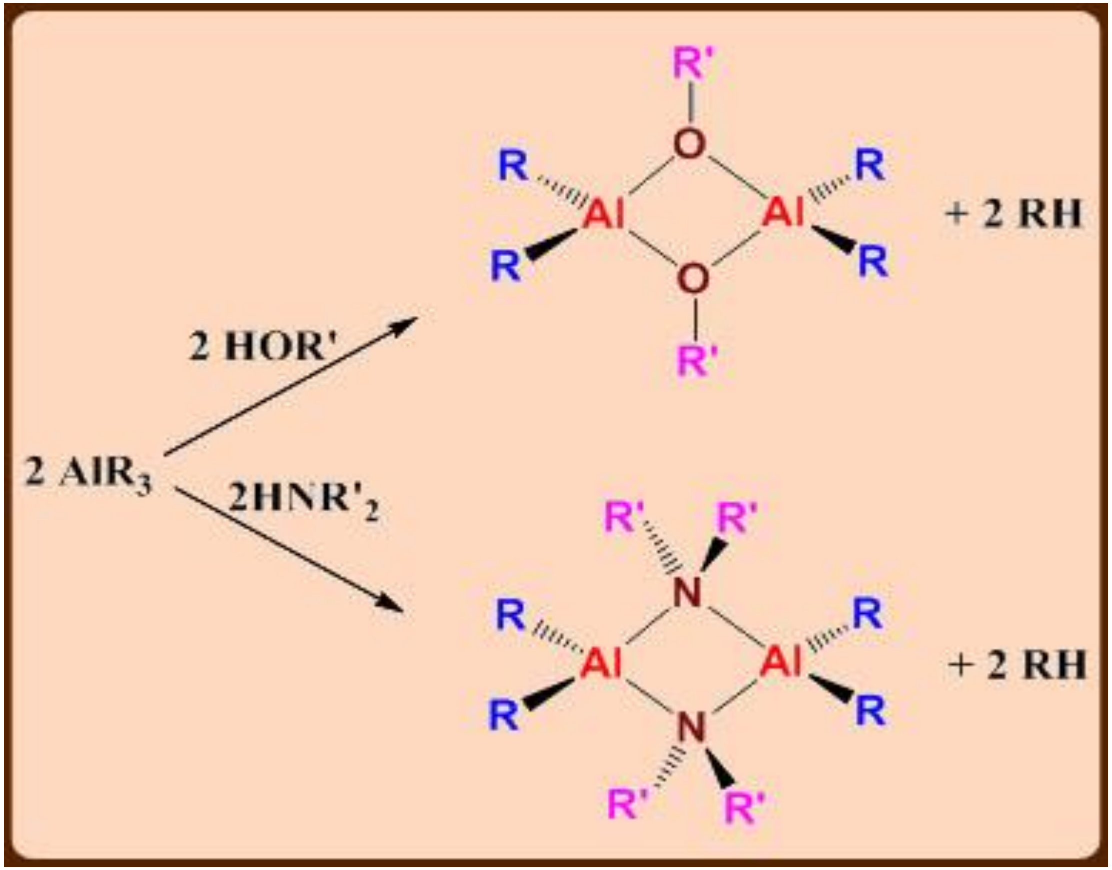
$$2\ Al + CH_3Cl \longrightarrow Al_2Cl_2(CH_3)_4$$

$$Al_2Cl_2(CH_3)_4 + 6\ Na \longrightarrow Al_2(CH_3)_6 + 2\ Al + 6\ NaCl$$

Commercial method for ethylaluminium and higher homologs:

$$2\ Al + 3\ H_2 + 6\ RHC{=}CH_2 \xrightarrow[110\text{ - }200\ \text{atm}]{60\text{ - }110\ ^0C} 2\ Al_2(CH_2CH_2R)_6$$

The reaction probably proceeds by the formation of a surface Al—H species that adds across the double bond of the alkene in a hydrometallation (Al-H) reaction.


2 HOR'
2 AlR3
2HNR'2
+ 2 RH
+ 2 RH
Al
O
N
R
R'

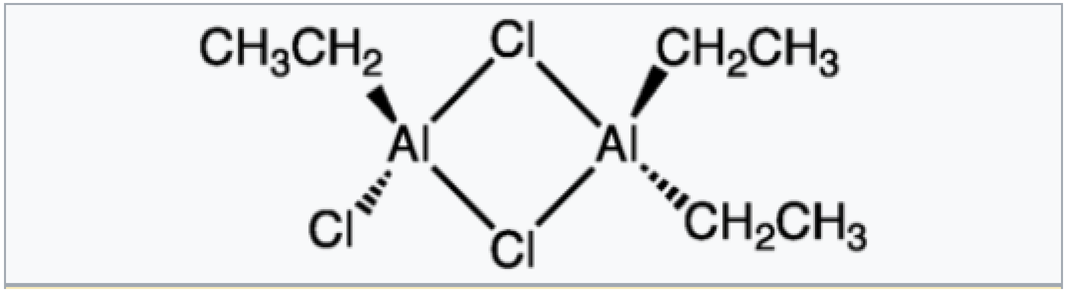
Properties And Reactions Of Organoaluminum Compounds

- Alkylaluminum compounds are mild Lewis acids (accpet pair of e-) and form complexes with ethers, amines and anions. When heated, often **β-hydrogen elimination** is responsible for the decomposition of ethyl and higher alkylaluminium compounds. E.g. $Al(^{i}C_4H_9)_3$
- Tendency towards bridging structure is: $\mathbf{PR_2^- > X^- > H^- > Ph^- > R^-}$
- In hydrocarbon solution and in the solid state there is a tendency for R_3Al to **dimerize**; this is very dependent on the size of the R group, e.g. a **dimer** for Me but **monomer** for tert-butyl.
- $Me(t\text{-}Bu)_5Al_2$ is found to be a dimer as well with the methyl group and 1 of the t-Bu groups in the bridging positions.
- The bridging ability is found to be Me > Et > t-Bu and clearly the case above is not what would be predicted on purely statistical terms since there are 5 times as many t-Bu groups as Me groups and there are twice as many terminal positions as bridging positions so the methyl group might have been expected to fill a terminal position.

- Many organoaluminium compounds are commercially available at quite reasonable prices so that is rarely necessary to have to prepare them in the laboratory.
- Reaction of Al turnings with organic halides leads to the alkylaluminium sesqui-halides. The reaction is very exothermic. The sesqui-halides do not have sharp melting or boiling points because they are in fact equilibrium mixtures:

$R_3Al_2X_3$ sesqui-halides equilibria

Ethylaluminium sesquichloride



- It took almost 100 years before K. Ziegler discovered the synthetic and catalytic potential of organoaluminum compounds.
- From an industrial viewpoint, the organic compounds of aluminium are probably the most important organometallic compounds.
- The reasons for this include:

  a) inexpensive synthesis from olefin + H_2 + Al (pressure).

  b) R_3Al can dimerise olefins

  c) higher alcohols (→ detergents) are made from $R_3Al + CH_2{=}CH_2$.

  d) In combination with Ti and Zr compounds, R_3Al can polymerise ethylene to give polyethylene

  e) Reactions with R_3Al proceed in hydrocarbons or even without solvent (unlike RMgX !).

  f) Useful commercially for polymer synthesis catalysts

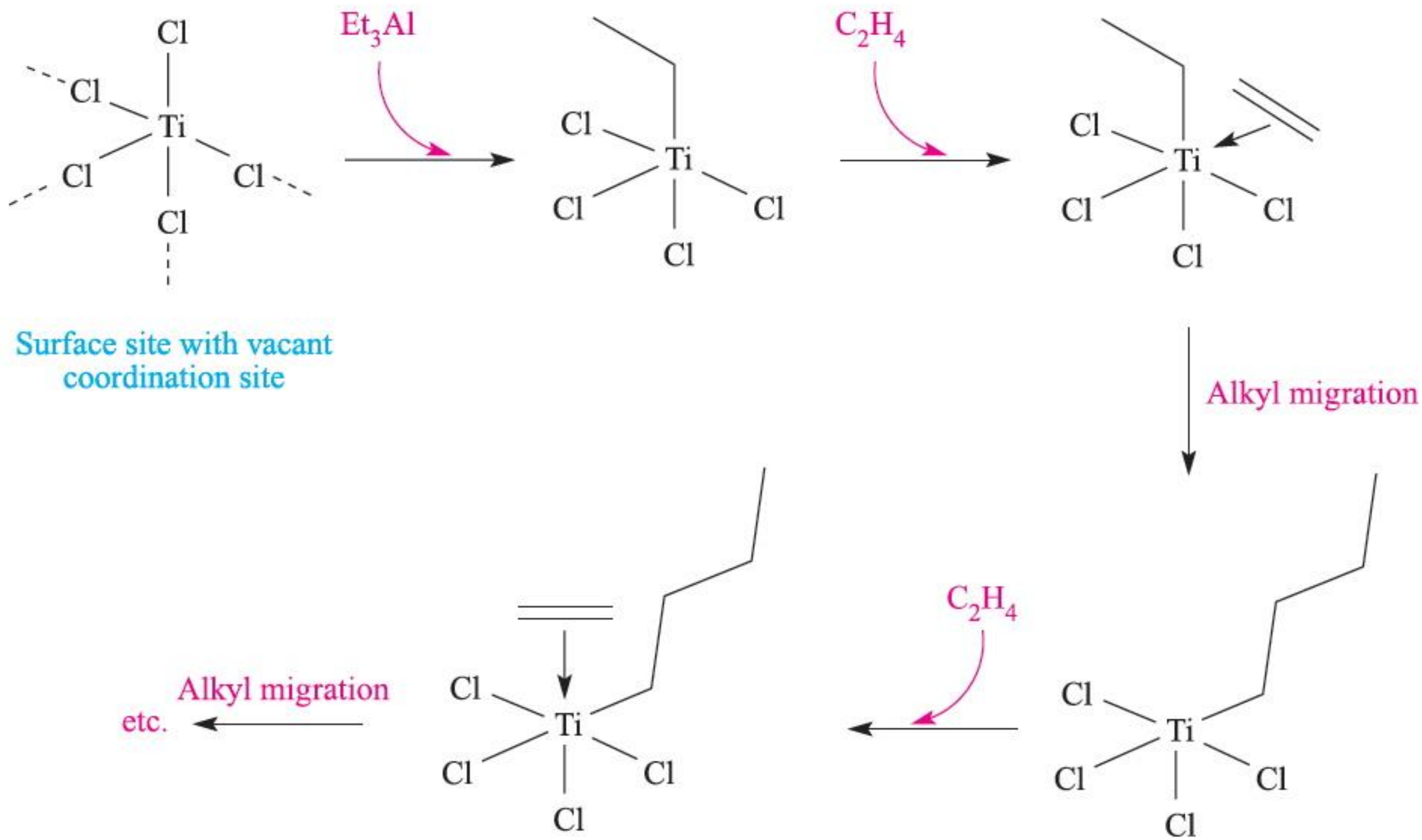
- Karl Ziegler, who pioneered basic research in the field of organoaluminium compounds, developed a strikingly simple yet versatile process for the synthesis of organoaluminium compounds from inexpensive starting materials.
- The Ziegler Direct Process allows the synthesis of triethylaluminium from aluminum metal, hydrogen and ethylene. The process involves the following:

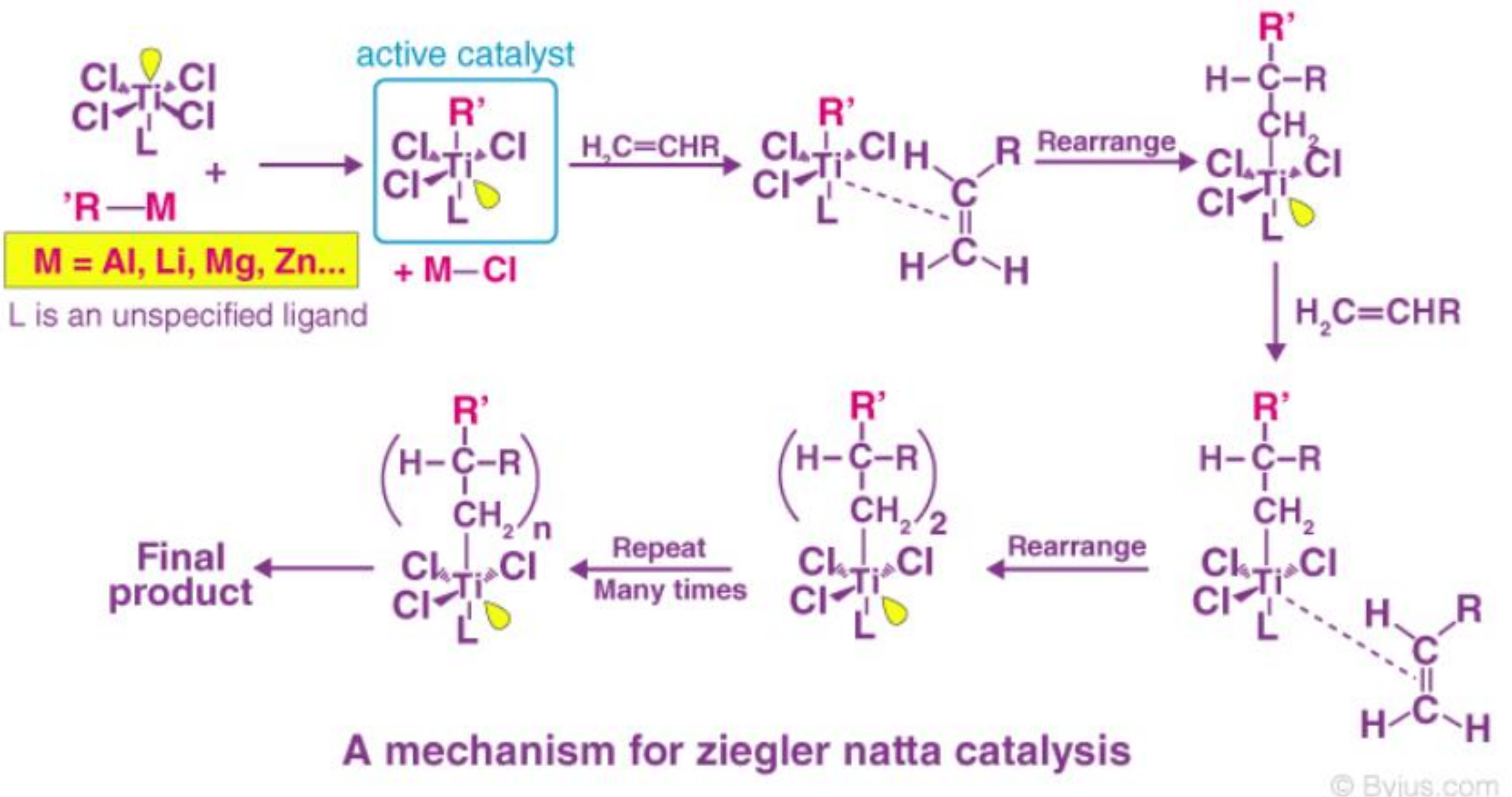
$$2Al + 3H_2 + 6RHC{=}CH_2 \rightarrow Al_2(CH_2CH_2R)_6$$

{R=H for $(Et_3Al)_2$}

- The Ziegler-Natta polymerization catalysts were originally formed from **Et_3Al** with **$TiCl_4$** and a schematic representation of the reactions at the heterogeneous surface is given below:

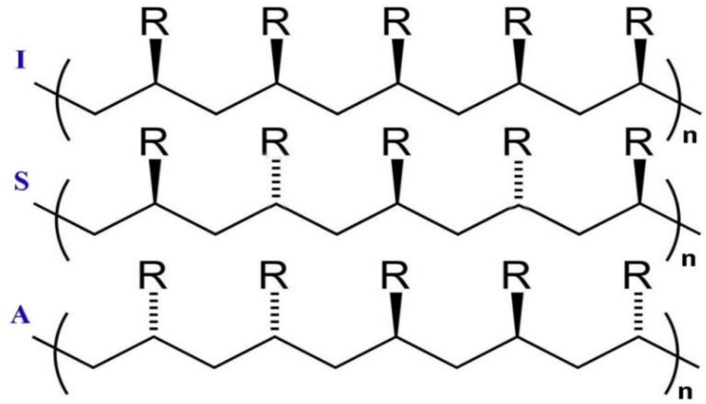
Ziegler Natta polymerisation





A mechanism for ziegler natta catalysis

- Polymerization of ethene to high-molecular mass polyethylene occurred at relatively low pressures and the polymers were **stereoregular**.
- What this means is that **isotactic polymers** are formed where the R groups are all located on the same side of the carbon backbone.
- The resulting product gives a crystalline material since packing is more regular.
- The other varieties of linear polymer are called syndiotactic and atactic and in the first the R groups are on alternate sides of the carbon backbone and in the latter they are randomly distributed



Isotactic, syndiotactic and atactic linear polymer chains