Learning Objectives

In this lecture you will learn the following

- Preparation and reactivity of organoboron and organo aluminium compounds.
- Influence of Lewis acidity on structural features

Organoboron Compounds

BMe₃ 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 BX₃ and organometallic compounds of metals with low electronegativity, such as RMgX or AlR₃.

\[
\ce{BF3 + 3CH3MgBr -> B(CH3)3 + 3MgBrF (solvent: used: dibutyl ether)}
\]

Why dibutyl ether as a solvent: Has much lower vapor pressure than BMe₃ 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 BMe₃ and OBu₂ (Me₃B:OBu₂).

Although, trialkyl- and triarylboron compounds are mild Lewis acids, strong carbanion reagents lead to anions of the type [BR₄]⁻.

Example, Na[BPh]₄: The bulky anion hydrolyses very slowly in neutral or basic water and is useful for the preparation of large positive cations.

\[
\ce{Na[BPh]4 + K+ -> K[BPh]4}
\]

K[BPh]₄ is insoluble, used for the gravimetric estimation (determination) of potassium, an example of the low solubility of large-cation and large-anion salts in water.

Organohaloboron compounds are more reactive than simple trialkylboron compounds.

Preparation:

\[
\ce{2 BCl3 + 6AlR3 -> 3R2BCl + 6AlR2Cl (metathesis)}
\]

\[
\ce{2 BCl3 + BMe3 -> [diborane] 3BMeCl2 (redistribution: reaction)}
\]

Reactions: (Protolysis reactions with ROH, R₂NH and other reagents)
\[ \text{BMeCl}_2 + 2\text{HNR}_2 \rightarrow \text{BMe}_2(\text{NR}_2) + [\text{R}_2\text{NH}_2]\text{Cl} \]

\[ \text{BMe}_2\text{Cl} + \text{Li(C}_4\text{H}_9) \rightarrow \text{BMe}_2(\text{C}_4\text{H}_9) + \text{LiCl} \]

### Organoaluminium compounds

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 $\sim 75^\circ$.

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.

\[ \text{Al}_2(\text{CH}_3)_6 \rightleftharpoons 2\text{Al(CH}_3)_3 \] $K = 1.52 \times 10^{-8}$

\[ \text{Al}_2(\text{C}_4\text{H}_9)_6 \rightleftharpoons 2\text{Al(C}_4\text{H}_9)_3 \] $K = 2.3 \times 10^{-4}$

Perpendicular orientation of pheynl groups in $\text{Al}_2\text{Ph}_6$

Triphenylaluminium exists as a dimer with bridging $\eta^1$-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 $\pi$-orbitals to the Al atoms.

Tendency for bridging: $X > \text{Ph} > \text{alkyl}$

**3c,2e bonds formed by a symmetric combination of Al and C orbitals**
An additional interaction between the πτ orbital on C and an antisymmetric combination of Al orbitals.

**Synthesis**

Very useful as alkene polymerization catalysts and chemical intermediates. Expensive carbanion reagents for the replacement of halogens organic groups by metathesis.

Laboratory scale preparations involves: \[\ce{2Al + 3Hg(CH3)2 -> Al2(CH3)6 + 3Hg}\]

Commercial method: \[\ce{2Al + CH3Cl -> Al2Cl2(CH3)4}\]

\[\ce{Al2Cl2(CH3)4 + 6Na -> Al2(CH3)6 + 2Al + 6NaCl}\]

Commercial method for ethylaluminium and higher homologs: \[\ce{2Al + 3H2 + 6RHC=CH2 ->[60-110°C][110-200atm] 2Al2(CH2CH2R)6}\]

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 reaction.
Reactions:

Alkylaluminum compounds are mild Lewis acids 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(C4H9)3

Tendency towards bridging structure is: PR2 > X > H > Ph > R.

Problems:

1. Propose a structure for Al2(Me)4Cl2.

Solution:
Similar to diborane:

2. For these compounds (H3Si)2O and (CH3CH2)2O, which do you expect to have the lower force constant, Si-O-Si bending or C-O-C bending?

Solution:
Lower force constant for Si-O-Si bending.

3. Explain how the difference in reactivity between Al-C and Si-C bonds with O-H groups leads to the choice of different
strategies for the synthesis of aluminum and silicon alkoxides.

**Solution:**

\[
\ce{Al2Me6 + 6MeOH \rightarrow 2Al(OMe)3 + 6CH4}
\]

For reaction of \( \text{Al}_2\text{Me}_6 \) with alcohols, see the text book by Shriver and Atkins. Tetramethylsilane does not react with methyl alcohol. Therefore, the appropriate reagent is tetrachlorosilane and the reaction is:

\[
\ce{SiCl3 + 4MeOH \rightarrow Si(OMe)4 + 4HCl}
\]

4. Compare formulas of the most stable hydrogen compounds of germanium and arsenic with those of their methyl compounds. Can the differences be explained in terms of the relative electronegativities of C and H?

**Solution:**

\( \text{GeH}_4, \text{GeR}_4; \text{AsH}_3, \text{AsR}_3 \)

The stability of hydrides and alkyls are very similar for each element. This may due to similar H and C electronegativity.

5. To buy from a chemical company, the price of trimethylaluminum is higher than that of triethylaluminum. Is it due to the methods of synthesis? Rationalize the price difference.

**Solution:**

Triethylaluminum can be made in larger quantities by direct reaction of aluminum, hydrogen gas and ethane gas which is a cheaper method.

\[
\ce{2Al + 3H2 + 6RHC=CH2 ->[60-110^\circ C][110-200atm] 2Al2(CH2CH2R)6}\]

Preparation of trimethylaluminum involves a more expensive route such as MeCl and aluminum to form \( \text{Al}_2\text{Me}_4\text{Cl}_2 \) followed by treatment with sodium metal. The sodium metal and MeCl are not cheap as compared to ethane and hydrogen gases.

\[
\ce{2Al + CH3Cl -> Al2Cl2(CH3)4}\]

\[
\ce{Al2Cl2(CH3)4 + 6Na -> Al2(CH3)6 + 2Al + 6NaCl}\]
