TDC Part I
Paper I, Group B
Inorganic Chemistry

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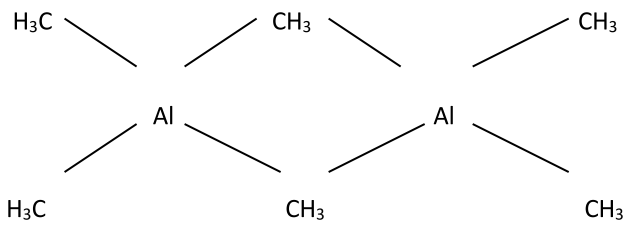
TOPIC: - p-block group 13
Organometallic compounds
Complex formation

Organometallic compounds

Tri-alkyl and tri-aryl derivatives of boron, aluminium, gallium and indium are known. The tri-alkyl derivatives of aluminium are important and are obtained by treating aluminium chloride with the appropriate Grignard reagent.

$$AlCl_3 + 3RMgI \longrightarrow ALR_3$$

These are electron deficient compounds and exists as bridged dimers



The terminal Al-C bond lengths are shorter than the bridge Al – C bond lengths. The bridge bonds are three – centre – two – electron bonds.

Aluminium tri-ethyl is referred to as Ziegler catalyst and is used to carry out polymerization of ethene to give polythene Polymerization is quicker if $TiCl_4$ (Natta Catalyst) is used along with Ziegler catalyst and the reaction does not require high pressure. Vast quantities of polythene (over 15 million tons annually) are made by Ziegler- Natta catalysis. Long chain alcohols can be obtained from ethane and aluminium tri-alkyl. These are converted to sulphonates and used in biodegradable detergents. Aluminium alkyls catalyze the dimerization of propene to isoprene. These reactions are of considerable commercial importance. Ziegler and Natta received the Nobel Prize in Chemistry in 1963.

Complex formation

The Group 13 elements form complexes more readily than the s-block elements. Because of lack of d orbitals, boron exhibits a coordination number of 4 and forms tetrahedral complexes like $NaBH_4$, HBF_4, $BF_3.NH_3$ etc. The lower members form octahedral complexes also e.g. $[AlCl_6]^{2-}$ $[GaCl_6]^{2-}$ etc.

Apart from complexes, aluminium forms double sulphates (alums) of the general formula $M_2SO_4.Al_2(SO_4).24H_2O$ where M is a monovalent metal or ammonium eg. $K_2SO_4.Al_2(SO_4).24H_2O$ is potash alum. Aluminium can be replaced by cations of comparable size and charges like iron, chromium etc.

Anomalous behaviour of Boron

The chemistry of boron closely resembles that of silicon (diagonal relationship). In fact the similarity between boron and silicon is more than that of boron and the lower members of Group 13. This is exemplified by the fact that boron is a non-metal while Al, Ga, In and Tl are metals. Since boron is a non-metal its oxide B_2O_3 (like SiO_2) is acidic, whilst Al_2O_3 and Ga_2O_3 are amphoteric and In_2O_3 basic. Boron like silicon forms hydrides which are volatile liquids; in contrast $(AlH_3)_n$ is a polymeric solid. The halides of B and Si undergo ready hydrolysis while aluminium halides undergo partial hydrolysis. The oxoanions of boron and silicon – borates and silicates polymerize by sharing oxygen atoms to give chains and rings. No such compounds of aluminium are known.