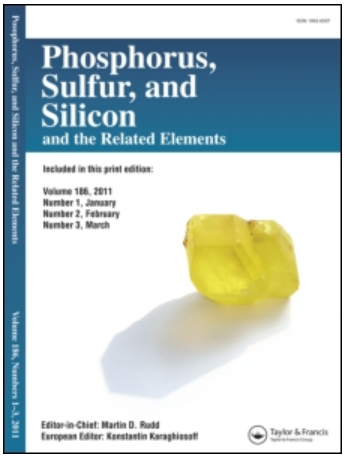

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Alan Cowley's Favorites-Recent Advances in the Chemistry of the Elements of Group 13 and 15

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ALAN COWLEY'S FAVORITES —— RECENT ADVANCES IN THE CHEMISTRY OF THE ELEMENTS OF GROUP 13 AND 15

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ABSTRACT

The access to new III/V compounds is described. The reaction of $AlH_3(NMe_3)_2$ and ammonia yields very pure AlN. The decomposition of $AlH_3(NMe_3)_2$ may be used to generate aluminum wires. The reaction of $C_6F_5NH_2$ and Me_3Ga or Me_3In gives the cubanes $(C_6F_5NGaMe)_4$ and $(C_6F_5NInMe)_4$, respectively. The chemistry of $(Cp^*Al)_4$ is reported. Hetero allylic metal complexes of zinc and cadmium are formed using $(RNHAsNR)_2$ and $Zn(N(SiMe_3)_2)_2$ or $Cd(N(SiMe_3)_2)_2$.

INDRODUCTION

The compounds of the group 13 metals with the elements of group **15** have achieved considerable technological application as III-V semi conductors isoelectronic with Si and Ge. They are used as light emitting diodes and injection lasers, when electrical energy is converted into optical energy. The reverse process of converting optical energy into electrical energy e.g. photoconductivity has also been achieved by III-V semi conductor systems.

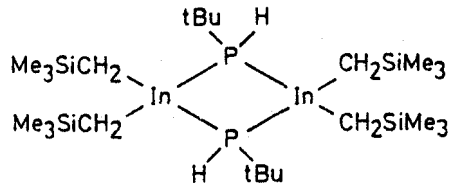
In contrast aluminum nitride has a large band-gap and is valuable as an electrical insulator for microelectronic applications. Furthermore, this compound is receiving increasing attention due to its application in the field of high performance ceramics.

Cowley and Jones have demonstrated in a 1989 review that organometallic compounds are interesting precursors for generating III-V semi conductors.

PREPARATION OF A FOUR-MEMBERED INDIUM-PHOSPHORUS RING

Bradley et al.[2] demonstrated that the pyrolysis of $[Me_2InP\underline{t}Bu_2]_2$ at 480°C resulted only in the formation of pure InP when additional PH_3 was added. Consequently we[3] prepared compounds containing already P-H bonds in the molecule. The reaction of $\underline{t}BuPH_2$ with $(Me_3SiCH_2)_3In$ in the presence of Ag^+ ions leads to $[(Me_3SiCH_2)_2InPH\underline{t}Bu]_2$ **1**.

According to an X-ray analysis, **1** forms a four-membered planar P_2In_2 ring with alternating P-In bonds.



1

Fig. **1** : Molecular structure of compound **1** in the crystal

However the pyrolysis of **1** yields besides InP large amounts of SiC.

THE USE OF $AlH_3 \cdot (NMe_3)_2$ AS A VOLATILE PRECURSOR.

The synthesis of $AlH_3 \cdot (NMe_3)_2$ **2** has been described previously[4,5]. For deposition of elemental aluminum compound **2** was investigated[6]. A palladium acetate solution in chloroform was used for spin-coating an Al_2O_3 substrate sample with an amorphous film of palladium acetate. Using laser direct-write irradiation, Pd is deposited on the substrate. After removing the non-exposed film with chloroform, the Pd prenucleation surface pattern remains. The sample is transferred to a small CVD (chemical vapor deposition) chamber and heated together with compound **2**. Fig. 2 shows the aluminum structure after 1 min exposure to $AlH_3 \cdot (NMe_3)_2$ at 200°C and 2 torr.

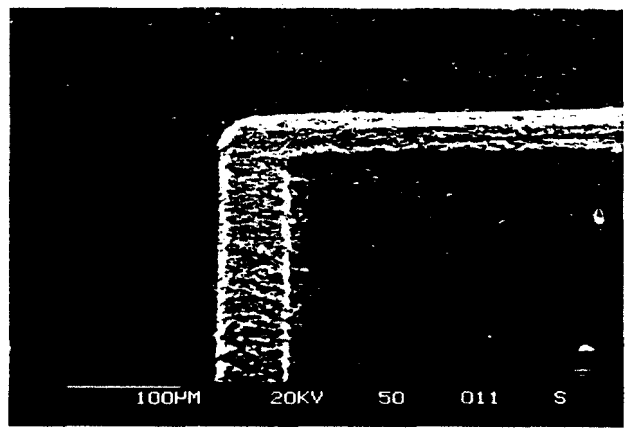


Fig. 2. Aluminum structure (50μm white, 7 μm high) generated by CVD

The reaction of water- and oxygen-free ammonia with $AlH_3 \cdot (NMe_3)_2$ gives a white, air-sensitive solid, which is heated in the presense of ammonia to 1100°C yielding high purity aluminum nitride. The yield of aluminum nitride is almost quantitative[7].

Due to the high solubility of $AlH_3 \cdot (NMe_3)_2$ in organic solvents it can be used also in solution to produce the polymeric precursor. Although exact information about the structure of the polymeric precursor cannot be given, we suggest, however, that the solid is a polymer of composition $[Al(NH_2)NH]_n$.

Another route to AlN is the reaction of Mes_3Al (Mes = 1,3,5-$Me_3C_6H_2$) with ammonia. The first step of the reaction is the formation of the 1:1 adduct of $Mes_3Al \cdot NH_3$. At elevated temperatures (66°C) the adduct eliminates MesH to yield the four-membered ring compound

$(Mes_2AlNH_2)_2$ **3**. This was isolated and characterized by an X-ray structural analysis. The molecular structure of **3** is shown in Fig. 3.

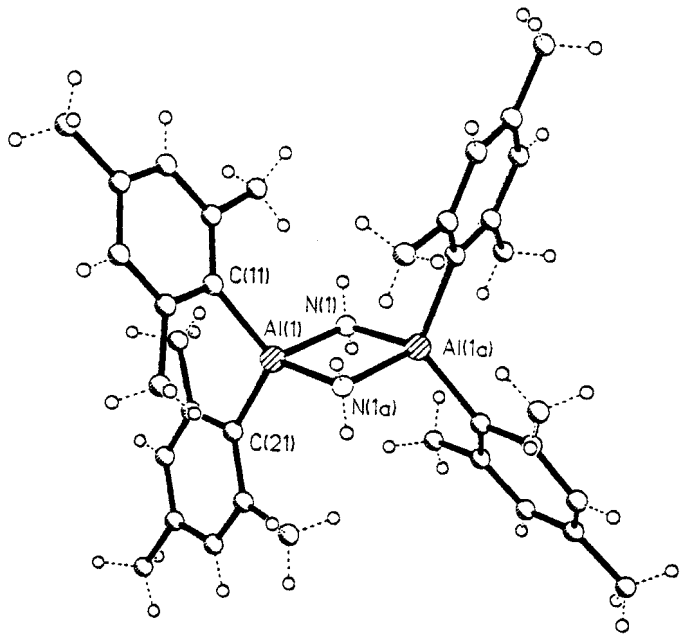


Fig. 3: Molecular structure of $(Mes_2AlNH_2)_2$ **3**

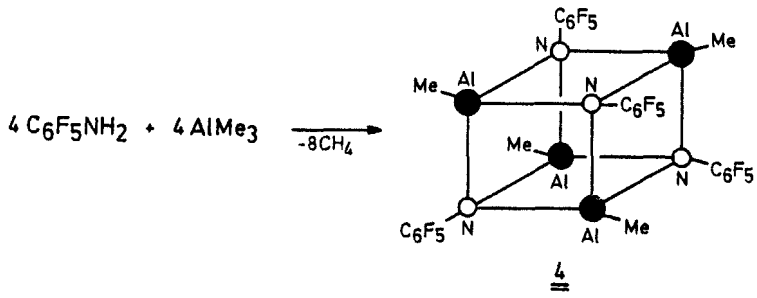
The structure exhibits a four-membered planar Al_2N_2 ring. Compound **3** is converted at 600°C to AlN under elimination of MesH.

$$(Mes_2AlNH_2)_2 \xrightarrow[-\ 4MesH]{600°C} 2AlN$$

3

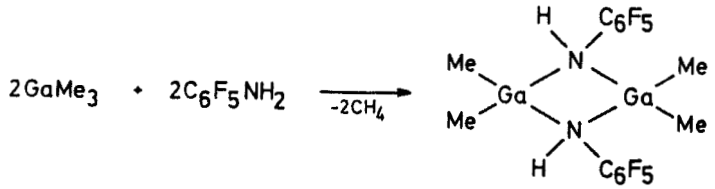
PREPARATION OF AMINOMETALLANES AND CUBANES OF ALUMINUM, GALLIUM AND INDIUM

The first aluminum-nitrogen compound with cubane structure of composition $(PhNAlPh)_4$ was prepared in 1962 and structurally characterized ten years later[9]. In the meantime several more compounds of this type have been described[10,11]. Starting materials for the synthesis of aluminum-nitrogen compounds are trimethyl-aluminum and primary amines. The reaction of $C_6F_5NH_2$ and $AlMe_3$ results in the formation of the cubane **4**.



On the basis of an X-ray structural analysis we observed an Al-N bond lenghts of compound **4** in the range of 190.5 to 196.7 pm.

Power et al.[11] have transferred these reactions to the corresponding Ga-N compounds and have thus observed that under C-H activation an intramolecular elimination of hydrocarbons takes place. In order to prevent C-H activation we have treated $GaMe_3$ and $InMe_3$ each with pentafluoroaniline.



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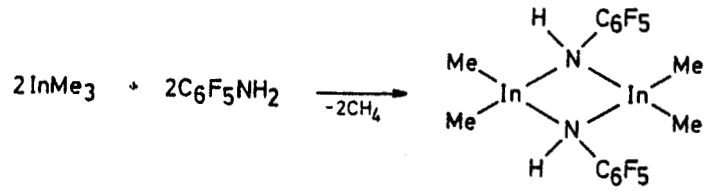
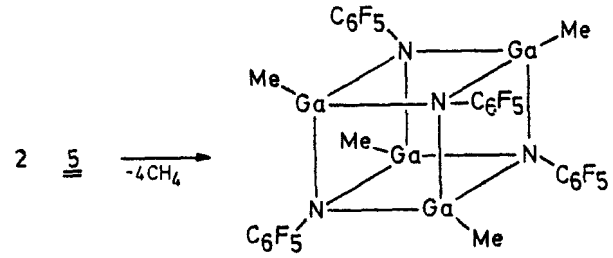


6

The aminogallane **5** and the aminoindane **6** have been obtained in high yield. The X-ray crystal structures of **5** and **6** have been investigated, both have a planar four-membered ring containing alternating metal-nitrogen bonds. The mass spectra of **5** and **6** showed that also in the gas phase the molecular ions are observed.

Compounds **5** and **6** are converted to the corresponding cubanes **7** and **8** by heating the aminometallanes without solvent and subsequent recrystallization of the products from n-hexane.



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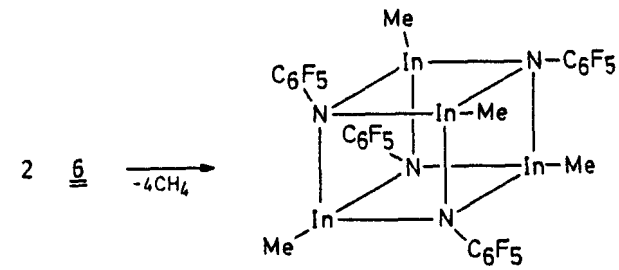


8

Compound **7** belongs to the rare class of iminogallanes $(RNGaR')_n$ and compound **8** is the first structurally characterized iminoindane $(RNInR')_n$.

The structure of **7** consists of fourfold coordinated Ga and N atoms, which together form a regular cube. However, the angles deviate significantly from the 90° angle of a perfect cube (angles at Ga and N lie between 85.9(2) and 94.0(2)°), in contrast to $(MeAlNC_6F_5)_4$, for which angles of almost 90°C are observed. The Ga-N bond lengths lie between 197.2 and 203.9 pm. The mean Ga ....Ga distance in **7** is 290 pm and the N .... N distance 276 pm.

The crystal structure of **8** showed a slightly distorted cube of alternating indium and nitrogen atoms. The mean In-N-In angle is 95.5(4)° and the mean N-In-N angle 84.3(4)°. In **8** the angles between the In and N atoms deviate even more from those of an ideal cube than in compound **7**. Thus, the heavier the participating metal atom is the greater the deviations. This tendency is certainly to be attributed to the differences in size of the metals and also to the fact that the degree of hybridization decreases with increasing atomic mass. The In-N distances in **8** are between 216.7 and 222.7 pm and are thus significantly longer than those for the homologous aluminum and gallium compounds. The mean In .... In distance is 326 and the mean N ....N distance 296 pm. In the mass spectra of **7** and **8** the signals for the molecular ions appear with high relative intensities. This indicates that compound **7** and **8** are also stable in the gas phase.

MONOMERIC SUPERMESITYLGALLIUM- AND SUPERMESITYLINDIUM DIHALIDES

The supermesitylgallium- and supermesitylindium dihalides of composition sMesGaCl$_2$ (**9**) (sMes = C$_6$H$_2$(tBu)$_3$), sMesGaBr$_2$ (**10**), sMesInCl$_2$ (**11**) and sMesInBr$_2$ (**12**) were prepared from sMesLi and the corresponding halides[13,14].

$$MX_3 + sMesLi \xrightarrow[-\ LiX]{} sMesMX_2$$

M = Ga, In

X = Cl, Br

The bromides **10** and **12** were obtained in good yields in comparison to the chlorides **9** and **11**. The crystal structures of **9** - **12** consist of

monomeric molecules. The geometry around the metal atoms in all structures is trigonally planar. The presence of the sMes substituents stabilizes **9** - **12** as monomeric molecules. By contrast $MesGaCl_2$[15] is polymeric and $(Mes_2InCl)_2$[16] is a dimer. It is quite obvious that the ortho tBu groups of the sMes ligand protect the metal atom better than the o-methyl groups of the Mes ligand.

PREPARATION AND REACTIONS OF ALUMINUM(I) COMPOUNDS

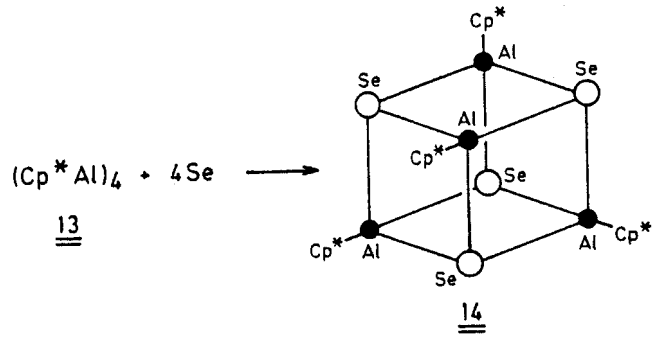
$(Cp^*Al)_4$ (**13**) (Cp^* = C_5Me_5) was originally prepared by Schnöckel et al.[17] by reaction of AlCl with Cp_2^*Mg. An alternative route to compound **13** was developed in our laboratory[18]. The reduction of Cp^*AlCl_2 with potassium gives $(Cp^*Al)_4$ in a 20 percent yield.

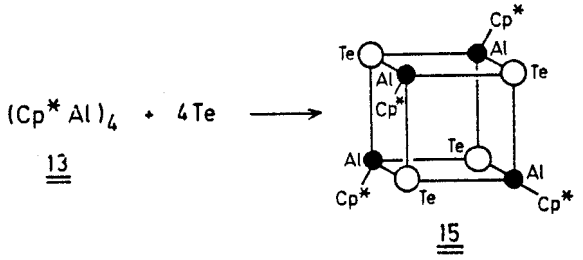
$$4\ Cp^*AlCl_2 + 8\ K \longrightarrow (Cp^*Al)_4 + 8\ KCl$$

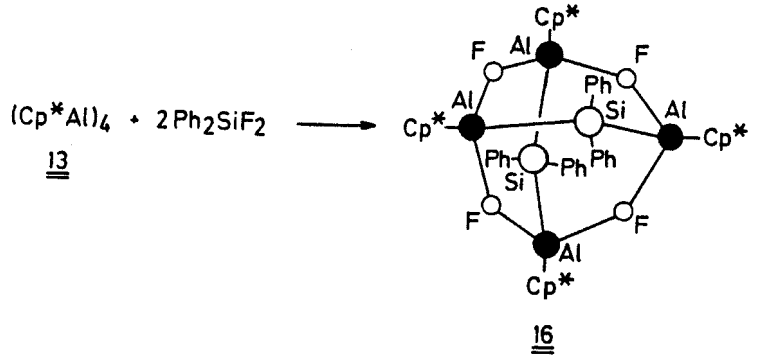
13

Compound **13** has a tetrahedral structure giving in the ^{1}H-nmr as well as in the ^{27}Al-nmr spectra each a singlet (δ_H = 1.89 ppm, δ_{Al} = -78.3 ppm). The formation of the monomer Cp^*Al in solution at elevated temperatures was not observed[18].

Compound **13** reacts with selenium, tellurium and Ph_2SiF_2 yielding compounds **14-16**.







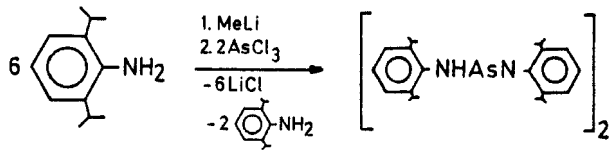
Compounds **14-16** have been characterized by X-ray structural analysis. **14** and **15** are forming a regular cube with Al-Se bond lengths in the range of 246.2 - 249.7 pm and Al-Te of 268.8 - 275.0 pm, respectively. The angles at Al, Se and Te deviate only slightly from an ideal 90° angle of a

cube (mean Se-Al-Se 94.61°, Te-Al-Te 95.06°, Al-Se-Al 85.19°, Al-Te-Al 84.68°).The Cp^* groups in **14** and **15** are bonded to aluminum in a η^5 arrangement.

Particularly interesting is the reaction of **13** and Ph_2SiF_2 giving the oxidized product **16**. The X-ray analysis of **16** demonstrated that rare Si-Al bonds have been formed. The fluorine atoms function as bridges between the aluminum atoms. This reaction clearly shows the broad preparative potential of compound **13**.

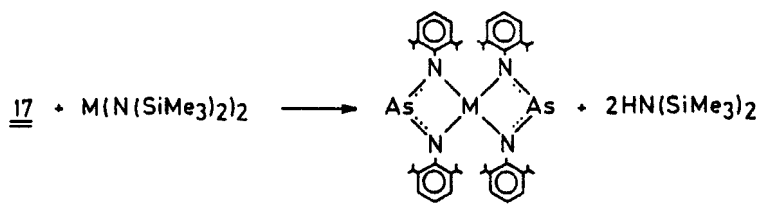
HETERO ALLYLIC METAL COMPLEXES OF ARSENIC AND NITROGEN

Lappert et al.[19] reported on the preparation of monomeric RNHAsNR compounds using bulky substituents R. However, the reaction of 2,6-diisopropylaniline under the same conditions gave only the dimer **17**[20].



17

The proton in **17** is acidic enough to react with $Zn(N(SiMe_3)_2)_2$ and $Cd(N(SiMe_3)_2)_2$ yielding compounds **18** and **19**.



18 : M = Zn
19 : M = Cd

For compounds **18** and **19** isotypical structures have been found. The molecules of both compounds are arranged in such a way that they are forming chainlike arrangements. The As .... As contacts however are too weak assuming As .... As bonding interactions (As-As, **18** : 387.4 pm; **19** : 382.5 pm). The molecules each form two four-membered rings connected by the Zn and Cd atoms, respectively, in a spirocyclic manner. The As-N bonds in **18** and **19** are rather short and may be compared (**18** : As-N 174.4(2) and 174.2(2) pm; **19** : As-N 169.5(3) and 173.9(4) pm) with values calculated by Pauling[21] for the As-N double bond of 173 pm.

This synthesis gives surprisingly very stable compounds containing arsenic of low coordination numbers.

Obviously this route is an extension to compounds having low coordinated elements without using bulky substituents.

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