

Advances in the chemistry of Lewis base adducts of alane and gallane

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Abstract

Tertiary amine adducts of alane show a diverse range of structures based on four and five coordinate species, hydride bridging dimeric and polymeric species, and ionic species, whereas those of gallane are usually restricted to four coordinate species. Phosphine adducts of alane are four or five coordinate, and four coordinate for gallane. Stable, volatile adducts of both alane and gallane are available. Mixed donor adducts of alane are accessible, such as those based on *N*-alkylmorpholine, and these have relevance in the binding of $[H_3AlNMe_3]$ to oxidised surfaces. Alane metallates secondary amines, bulky amines excepted which can yield stable amine adducts; secondary amines based on *N,N'*-disubstituted ethylenediamine give a range of products depending on the nature of the alane, the use of $[H_3AlNMe_3]$ is complicated by its tendency to form less reactive $[H_3Al(NMe_3)_2]$. The tricyclohexylphosphine adduct of monochlorogallane is a useful precursor for forming the phosphidogallium species $[H_2Ga(\mu-PCy_2)_3]$ via reaction with $[Li(PCy_2)(THF)_n]$. Reaction of $[H_3AlNMe_3]$ with *p*-Bu¹-calix[4]arene and its dimethyl ether afford respectively a divergent receptor bis-calixarene species and a monocalixarene species with a residual hydride either endo- or exo- to the calixarene cavity. Lewis base adducts of alane and gallane show promise in functional group chemistry with gallane behaving as a milder, more selective reducing agent. Reactions of $(ER)_2$, E=Se or Te, R=alkyl or aryl, with $[H_3MNMe_3]$, M=Al or Ga, afford trimethylamine

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adducts of the tris(selenolato- or tellurolato-)metal(III) species, $[\text{Me}_3\text{NM}(\text{ER})_3]$, and reactions of elemental Se or Te with $[\text{H}_3\text{AlNMe}_3]$ afford the mixed chalcogenide/hydride *trans*- $[\{\text{Me}_3\text{N}(\text{H})\text{Al}(\mu\text{-E})\}_2]$. © 1997 Elsevier Science S.A.

1. Introduction

The chemistry of alane ($=\text{AlH}_3$) and gallane ($=\text{GaH}_3$) has seen major advances in recent years reflecting the potential applications of their Lewis base adducts as volatile precursors in chemical vapour deposition (CVD) technology and other areas of materials science, and applications in synthesis. Both of these areas require a detailed understanding of the structure and properties of such adducts. In earlier articles we traced the developments of the chemistry of Lewis base adducts of alane and gallane to 1993 [1,2]. Herein we focus mainly on the most recent advances which are concerned with an extension of the work on Lewis base adducts, their conversion to aluminium and gallium amides, and group 16 chemistry of alane and gallane. Alane itself is polymeric [3] whereas gallane is dimeric [4] and structurally analogous to diborane. Indeed the chemistry of gallane is more like borane than alane which is related to the periodic anomaly of the group 13 elements, notably the increase in electronegativity of gallium over aluminium (1.8 Ga, 1.5 Al cf. 2.0 B, Allred Rochow), and the associated lower polarization influence of gallium. Differences between the chemistry of alane and gallane also relate to any back-bonding of the d^{10} core of gallium, the frailty of the Ga–H bond relative to the Al–H bond, and the stronger tendency of alane to form hypervalent structures compared with gallium, either via hydride bridges or uptake of more than one Lewis base.

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2. Lewis base adducts: synthesis, structure, stability and theoretical considerations

Lewis base adducts of alane and gallane are accessible by (i) the reaction of an amine hydrochloride or a 1:1 mixture of Lewis base and HCl with LiMH_4 ; (ii) metathetical exchange involving preformed adducts which usually involves treatment of readily available $[\text{H}_3\text{MNMe}_3]$, $\text{M} = \text{Al}$ or Ga , with other Lewis base adducts; and (iii) the treatment of LiGaH_4 with a Lewis base, at least for the synthesis of tertiary phosphine adducts of gallane, the byproduct being LiH [5]. For alane several classes of amine/phosphine species have been authenticated, Fig. 1. There are four coordinate tertiary amine and phosphine adducts, $[\text{H}_3\text{AlL}]$, for example where $\text{L} = \text{quinuclidine}$ [6,7], PR_3 , $\text{R} = \text{Bu}^t$ or Cy , and related bidentate phosphines [8–10]. Related adducts are those which are associated in the solid state via bridging hydrides, $[\{\text{H}_2\text{Al}(\mu\text{-H})_2\text{L}\}_2]$, $\text{L} = \text{NMe}_3$, $\text{NMe}_2(\text{CH}_2\text{Ph})$, 1-methyltetrahydropyridine and

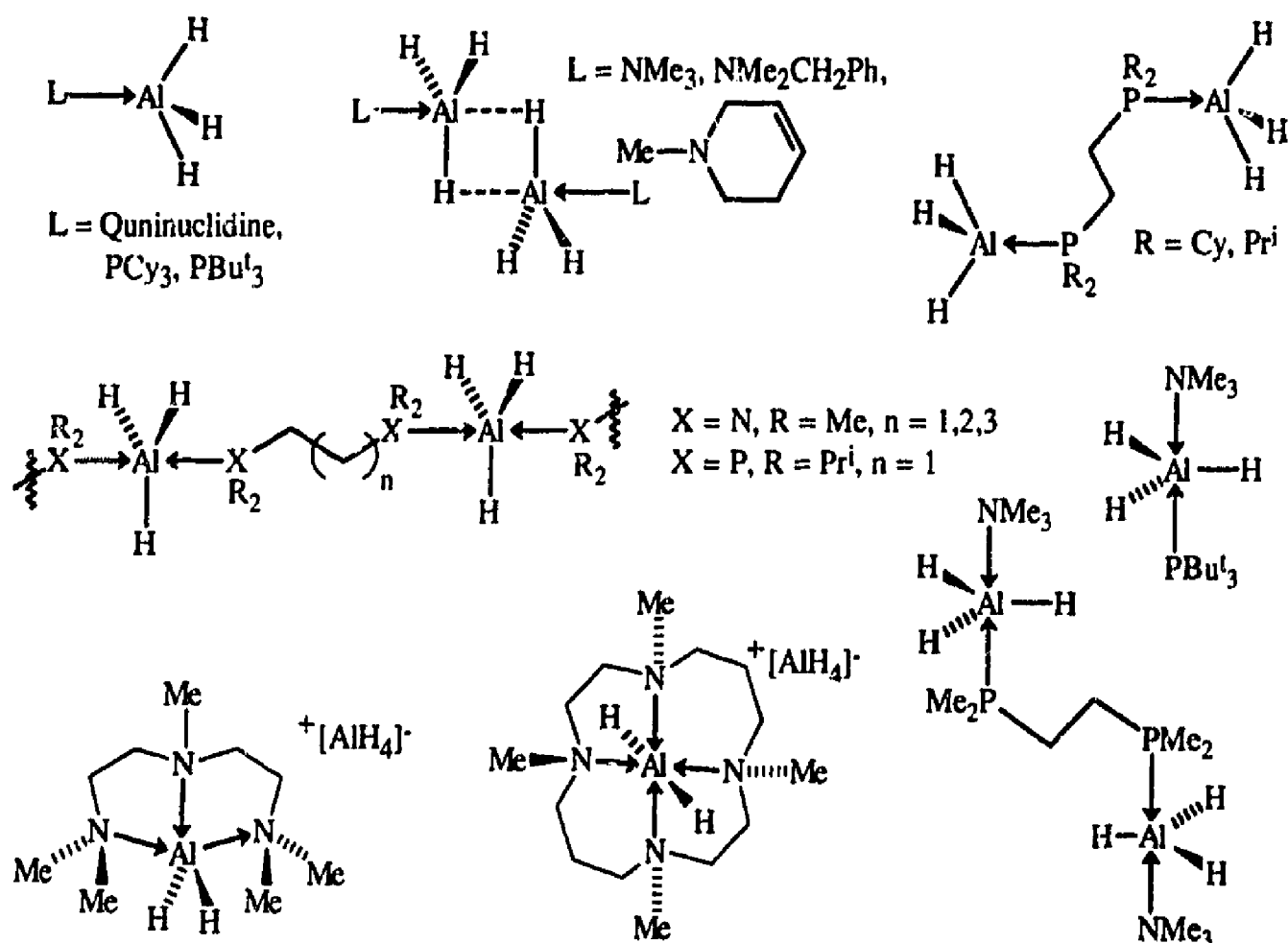


Fig. 1. Structural types for alane derivatives of tertiary amines and phosphines.

$\text{NMe}_2(\text{CH}_2)_3\text{Cl}$. The bridging is unsymmetrical with Al–H contacts at ca. 2.08 and 1.6 Å, the latter being typical of terminally bound H-atoms [10–12]. Then there are five coordinate species bearing two tertiary amine centres in apical positions of a trigonal bipyramidal centre with the three hydride groups in the equatorial plane, e.g. $[\text{H}_3\text{Al}(\text{quinuclidine})_2]$, $[\text{H}_3\text{Al}\{\text{N}(\text{Me})_3\}_2]$ [13], even for potentially bidentate tertiary amines such as *N,N,N',N'*-tetramethylethylenediamine (=TMEDA) [14] and related ligands [15]. Similar five coordinate is found in a unique P-donor analogue based on $\{\text{P}(\text{Pr}^i)_2\text{CH}_2\}_2$ [8]. Finally there are ionic species which have been established for $[\text{H}_2\text{AlL}]^+[\text{AlH}_4]^-$, $\text{L} = \text{N}, \text{N}, \text{N}', \text{N}', \text{N}'', \text{N}''$ -pentamethyldiethylenetriamine (=PMDETA) or *N,N',N'',N''*-tetramethylcyclam (*trans*-isomer) [16].

The 1:1 alane adduct of 2,2,6,6-tetramethylpiperidine is a remarkable stable secondary amine complex which is monomeric with an eclipsed structure for the arrangement of the hydrides relative to the groups attached to the nitrogen atom. Usually amine adducts of alane have a staggered structure and the eclipsed structure is credence for a $\text{H}^{\delta+} \dots \text{H}^{\delta-}$ interaction involving a hydrogen atom attached to the N-centre and another attached to the Al-centre respectively. The internuclear distance between these hydrogens is 2.31 Å, and represents a transition state for elimination of molecular hydrogen [17]. This adduct is formed by treating the amine with alane in OEt_2 ; the same amine with $[\text{H}_3\text{AlNMe}_3]$ gives the monomeric metallation/elimination product $[\text{H}_2\text{Al}(\text{NMe}_3)\{\text{N}(\text{CMe}_2\text{CH}_2\text{CH}_2)_2\text{CH}_2\}]$. Similarly $\text{HN}(\text{SiMe}_3)_2$ gives a thermally stable adduct of alane or the elimination product $[\text{H}_2\text{Al}(\text{NMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$. The adduct is a distillable liquid at 90 °C, 3 Torr,

decomposing beyond this temperature to polymeric alane and free amine [18]. Clearly the steric hindrance of the secondary amine stabilises the adducts towards molecular hydrogen elimination and amide formation.

Mixed tertiary amine/phosphine and mixed tertiary amine/ether adducts have been characterised as five coordinate species, again with the donor groups in apical positions of trigonal bipyramidal metal centres. These include $[\{\text{H}_3\text{Al}(\text{NMe}_3)(\text{PMe}_2\text{CH}_2)_2\}]$ [6], $[\text{H}_3\text{Al}(\text{NMe}_3)(\text{P}^t\text{Bu}_3)]$ [9] and the polymeric compound $[\text{H}_3\text{Al}\{\text{NMe}(\text{CH}_2\text{CH}_2)_2\text{O}\}]$ (see below). Interestingly the corresponding thiomorpholine adduct is monomeric, presumably with the Lewis base bound only through the N-centre [9]. Calculations at the DZP-ECP level on $[\text{H}_3\text{Al}(\text{NH}_3)_2]$ show that there is an inherent stability of five coordinate species with the three hydride groups in the trigonal plane, in accordance with results for the bis-amine adducts. This is a structural feature of the mixed donor complexes and the bis-tetrahydrofuran adduct [19]. Recent studies have yielded even more complicated structures for mixed donor ligands for *N*-ethylmorpholine (see below) [20].

The addition of P^tBu_3 to $[\text{H}_3\text{AlNMe}_3]$ results in elimination of trimethylamine affording $[\text{H}_3\text{AlP}^t\text{Bu}_3]$ which can also be prepared by the reaction of LiAlH_4 with hydrochloric acid/phosphine [9]. Displacement of NMe_3 in this reaction is surprising considering the relative donor strength of the ligands towards alane, and the thermal stability of the mixed donor complex $[\{\text{H}_3\text{Al}(\text{NMe}_3)(\text{PMe}_2\text{CH}_2)\}_2]$ [6]. Moreover, theory on the $\text{NH}_3/\text{AlH}_3/\text{PMe}_3$ system predicts a stabilisation energy of $9.03 \text{ kcal mol}^{-1}$ for $[\text{H}_3\text{Al}(\text{NH}_3)\text{PMe}_3]$ relative to $[\text{H}_3\text{AlPMe}_3]$ and NH_3 , and $2.72 \text{ kcal mol}^{-1}$ relative to $[\text{H}_3\text{AlNH}_3]$ and PMe_3 , ignoring zero point energy corrections (D95*/D95*) [6]. The dissociation energy of $[\text{H}_3\text{AlNH}_3]$ to AlH_3 and NH_3 is predicted to be 26 kcal mol^{-1} [21].

Bulky trialkyl phosphine adducts of alane are stable up to ca. 160°C where they decompose directly to aluminium metal. Other trialkyl phosphines and arylphosphines are unstable above ca. -20°C decomposing to polymeric alane [8,9]. Theoretical considerations give $[\text{H}_3\text{AlPH}_3]$ stabilised by $13.2 \text{ kcal mol}^{-1}$ relative to AlH_3 and PH_3 whereas dimerisation of H_3AlPH_3 to $[\text{H}_2\text{Al}(\mu\text{-H})]_2$ (en route to polymeric alane) is favoured by $5.84 \text{ kcal mol}^{-1}$ ($6\text{-}31\text{G}^* + \text{DZP}$) [6,8,9]. Bulky phosphines must block the thermodynamically favoured dimerisation process.

The stabilities of some phosphine, and amine adducts of alane are summarised in Table 1, and are of importance in the application of the adducts in CVD [22]. Tertiary amine adducts of alane usually decompose to aluminium, hydrogen and ligand above ca. 100°C . However, the adducts of 1,3,5-trimethylhexahydro-1,3,5-triazine which undergo C–N cleavage above 123°C [15] are an exception. Polydentate tertiary amines further enhance the stability of the adducts, e.g. $[\text{H}_3\text{AlNMe}_3]$ decomposes $>100^\circ\text{C}$ whereas $\text{H}_3\text{Al}(\text{TMEDA})$ decomposes $>170^\circ\text{C}$ and stronger bases do likewise with $[\text{H}_3\text{Al}(\text{quinuclidine})]$ decomposing $>190^\circ\text{C}$ [6].

Structurally authenticated alane derivatives involving Lewis bases donating through an O-centre are $[\text{H}_3\text{Al}(\text{THF})_2]$, $[\{\text{AlH}_2(\mu\text{-H})\text{THF}\}]_2$ [19] which are analogous to amine adducts, the mixed-donor complex $[\text{H}_3\text{Al}(\text{N-methylmorpholine})]_\infty$ [6], and the related alane rich complexes

Table 1

Decomposition temperatures of selected Lewis base adducts of alane and gallane, $H_3ML \rightarrow M + H_2 + L$

$[H_3AlNMe_3]$	> 100 °C	[2]
$[H_3Al(NMe_2CH_2Ph)]$	> 130 °C	[11]
$[H_3Al(Quinuclidine)]$	> 190 °C	[6]
$[H_3Al(TMEDA)]_\infty$	> 170 °C	[11, 15]
$[H_2Al(PMDETA)]^+ [AlH_4]^-$	> 182 °C	[16]
$[H_3AlN\{NH(SiMe_3)_2\}]$	> 100 °C ^a	[18]
$[H_3AlN\{N(H)(CMe_2CH_2)_2CH_2\}_2]$	> 165 °C	[17]
$[H_3AlPCy_3]$	> 163 °C	[8]
$[H_3Al(PR_2CH_2)_2]_2$, R = Pr ⁱ , Cy	> 150, > 165 °C	[8]
$[H_3Al(PPr^i_2CH_2)_2]$	> 150 °C	[8]
$[H_3Al(PPh_2CH_2)_2]$	> 0 °C ^a	[9]
$[(Me_3N)H_3Al(PMe_2CH_2)_2]$	> 50 °C	[6]
$[H_3GaNMe_3]$	> 0 °C	[28]
$[H_3Ga(Quinuclidine)]$	> 100 °C	[26]
$[H_3Ga(NMe_2CH_2)_2]$	> -10 °C	[26, 27]
$[H_3GaPCy_3]$	> 130 °C	[5]
$[H_3GaPBu^i_3]$	> -14 °C	[9]
$[H_3Ga(PMe_2CH_2)_2]$	> 100 °C	[5, 27]
$[H_3Ga(PPh_2CH_2)_2]$	> 0 °C	[9]

^aDecomposition to polymeric AlH_3 and free ligand.

$[(H_3Al)_2L]$ and $[(H_3Al)_{1.5}L]$, $L = N$ -ethylmorpholine [20], Fig. 2. These O-donor complexes give insight into possible decomposition processes of Lewis base adducts of alane, and also gallane, in the presence of air and/or moisture as well as how such complexes bind to oxidised silicon surfaces [23]. Indeed, adsorption studies on the interaction of $[H_3AlNMe_3]$ with hydroxyl free oxidised silicon surfaces under UHV conditions show that the metal centre expands its coordination sphere binding as a five coordinate species, $[H_3AlNMe_3(O=)]$ ($O=$ = surface O-centre), with a higher partial pressure of the alane resulting in formation of hydride bridged species, $[H_2Al(Me_3N)(\mu-H)_2AlH_2(O=)]$ [23]. (Such species have been modelled using ab initio calculations on $[H_3AlNH_3(OH_2)]$ and $[H_2Al(H_3N)(\mu-H)_2AlH_2(OH_2)]$ [23], and related calculations have been reported for $[H_3AlO(R)SiH_3]$, $R = H$ or CH_3 [24].) In contrast, dissociative adsorption prevails for $[H_3GaNMe_3]$ yielding the four coordinate species, $[H_3Ga(O=)]$. This is in accordance with the preference of gallane to maintain four fold coordination, although the primary process may be the formation of five coordinate mixed donor species, $[H_3GaNMe_3(O=)]$ [25].

The synthesis of $[(H_3Al)_2L]$ involves adding N -ethylmorpholine immediately at -78 °C to alane in OEt_2 formed by the addition of H_2SO_4 (98%) to an OEt_2 solution of $LiAlH_4$. For the synthesis of $[(H_3Al)_{1.5}L]$, the appropriate quantity of H_2SO_4 is added to a mixture of the hydrochloride salt of the morpholine and $LiAlH_4$ in Et_2O [20]. Both of these N -ethylmorpholine complexes have polymeric structures arising from spontaneous self assembly into one dimensional or two

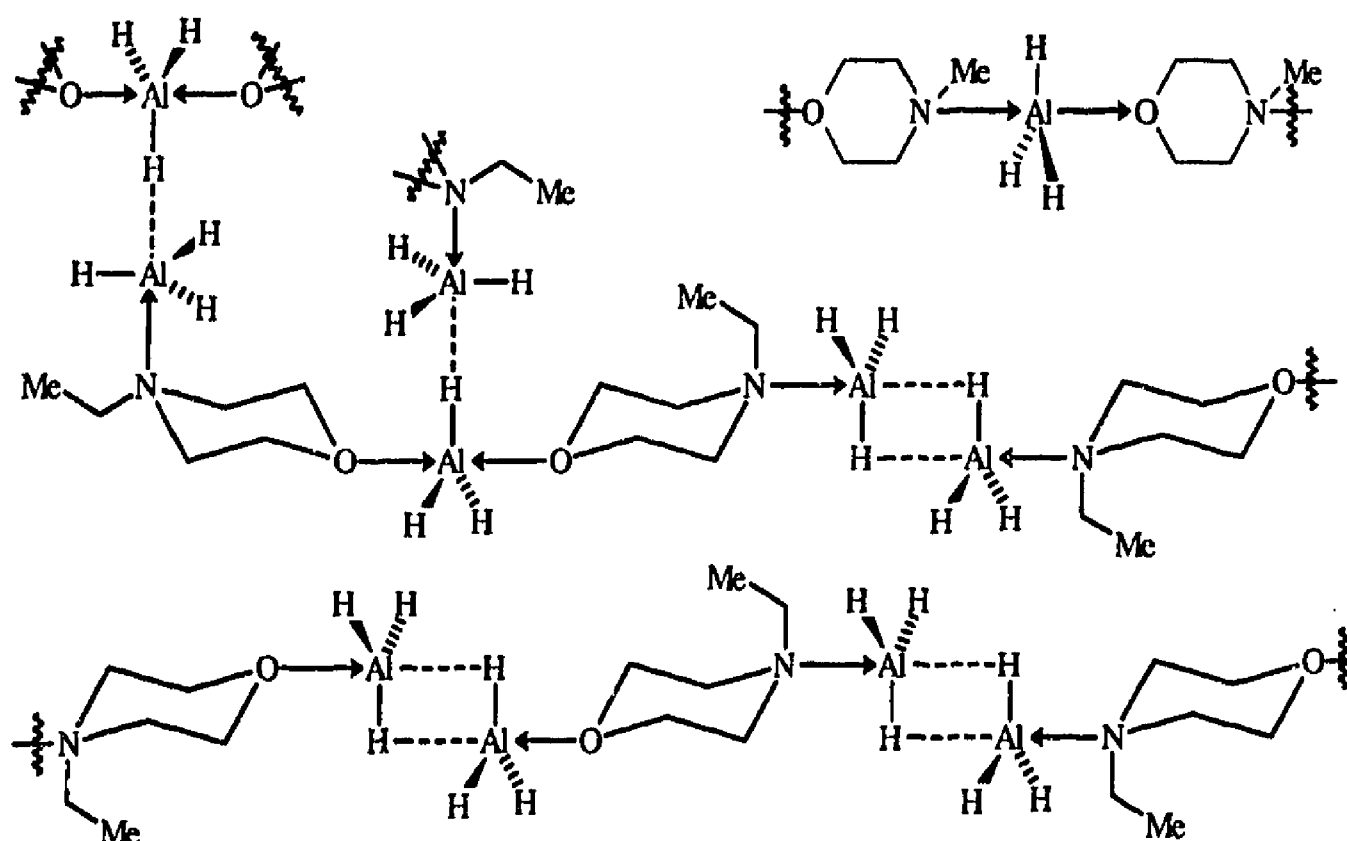


Fig. 2. Polymeric structures based on alkylmorpholine and alane.

dimensional arrays with head-to-head hydride bridging and/or two O-donating groups to the same metal centre, Fig. 2. Compound $[(\text{H}_3\text{Al})_2\text{L}]$ forms a polymeric chain due to the linking of discrete N and O bound AlH_3 units which are linked via hydride bridging. While this is also an aspect of $[(\text{H}_3\text{Al})_{1.5}\text{L}]$ there are however, several other important additional features which give rise to a two-dimensional net-like structure. The repeating asymmetric unit in $[(\text{H}_3\text{Al})_{1.5}\text{L}]$ consists of 4 L and 2×3 different AlH_3 centres giving in total 3 different Al environments. One Al centre behaves in a similar fashion to that as seen in $[(\text{H}_3\text{Al})_2\text{L}]$. However the other two Al centres which are both 5 coordinate help form the two-dimensional structure through the formation of single weak $\text{Al}\cdots\text{H}$ interactions. This is a new structural type for alane with both structures taken together summarising the structural variety found for all other characterised neutral Lewis base adducts of alane. The polymer which is formed from the 1:1 reaction of LiAlH_4 with the hydrochloride salt of *N*-methylmorpholine (L') (see above) gives a simpler asymmetric unit in compliance with the stoichiometry of the reaction; the repeating unit $(\text{H}_3\text{AlL}')$ has each metal centre five-coordinate, bound by both O- and N-centres from different morpholine moieties. The structure is devoid of intermolecular hydride bridging, Fig. 2 [26]. The only other type of Lewis base adduct of alane involves a C-centred carbene [26].

Tertiary amine adducts of gallane have played a pivotal role in the development of the chemistry of gallane. The trimethylamine adduct, $[\text{H}_3\text{GaNMe}_3]$, decomposes above ca. 0°C , and attempts to form adducts with polydentate tertiary amines via ligand displacement involving H_3GaNMe_3 results in rapid decomposition to metal, hydrogen and amine. For example with TMEDA decomposition occurs $> -10^\circ\text{C}$, and for (–)-Sparteine and PMDETA $> -20^\circ\text{C}$ [27]. In contrast, for alane these adducts are more stable than the trimethylamine adduct [9,15]. TMEDA and

TMPDA (= *N,N'*-tetramethylpropylenediamine) and H_3GaNMe_3 initially afford $[\text{H}_3\text{Ga}(\text{TMEDA or TMPDA})]$ [27,28] which decompose in vacuo to give the gallane rich species $[(\text{H}_3\text{Ga})_2(\text{TMEDA or TMPDA})]$. $[\text{H}_3\text{Ga}(\text{TMPDA})]$ has been structurally characterised at -100°C [28] revealing a polymeric structure with trigonal bipyramidal metal centres with the N-donors in apical positions, similar to the isostructural alane analogue [15]. The gallane rich species $[(\text{H}_3\text{Ga})_2(\text{TMEDA})]$ has four coordinate metal centres associated with each N-centre of the amine, Fig. 3 [27,29]. Quinuclidine forms a volatile, remarkably stable adduct $[\text{H}_3\text{Ga}(\text{quinuclidine})]$ which decomposes $>100^\circ\text{C}$, reflecting the higher basicity of the amine relative to NMe_3 [27]. *N*-methylmorpholine and *N*-methylthiomorpholine yield unstable adducts, decomposing above -20°C [7].

For gallane, four-coordination is more stable than five or any bridging hydride species, and the only precedence for either of these species for monodentate amines is $[\text{H}_3\text{Ga}(\text{NMe}_3)_2]$ which decomposes above -23°C to the amine and $[\text{H}_3\text{GaNMe}_3]$ [30]. Oxidised silica surface bound $[\text{H}_3\text{Ga}(\text{O}=\)]$ may form via a five coordinate intermediate $[\text{H}_3\text{GaNMe}_3(\text{O}=\)]$ [25]. Ab initio calculations (D95*+DZP) on the model species for this, $[\text{H}_3\text{GaNH}_3(\text{OH}_2)]$, shows it to be energetically favoured relative to $[\text{H}_3\text{GaNH}_3]$ and H_2O by only $0.67\text{ kcal mol}^{-1}$, and $[\text{H}_3\text{Ga}(\text{OH}_2)]$ and NH_3 by 7.8 kcal mol^{-1} [25].

All structurally characterised Lewis base adducts of gallane are presented in Fig. 3. Like the phosphine adducts of alane, aryl substituted phosphines result in lower decomposition temperatures. For gallane, decomposition is exclusively to gallium, hydrogen and free ligand, Table 1. Low stability here is consistent with the lower base strengths of aryl-substituted phosphines. However, unlike aluminium the use of bulky trialkylphosphine to stabilise phosphine adducts is not essential, but steric hindrance does result in less air sensitive material, with the tricyclohexylphosphine adduct being stable in air [5]. A substantial survey of the potential energy surface of $[\text{H}_3\text{GaPH}_3]$ using the ECP-DZ basis set gives the monomer as the minimum [5,9], as for $[\text{H}_3\text{GaNH}_3]$ [26]. Ab initio molecular orbital calculations have also been reported for $[\text{H}_3\text{GaAsH}_3]$ demonstrating that it should be a stable molecule [31].

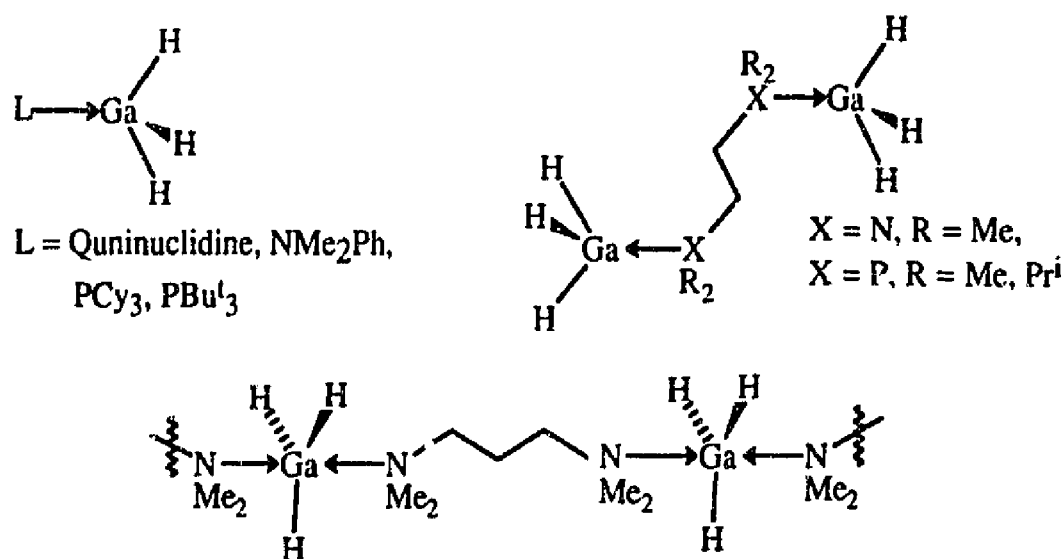


Fig. 3. Structural types for gallane derivatives of tertiary amines and phosphines amines.

Heterobimetallic complexes of alane and gallane have been prepared. Reaction of the quinuclidine adduct of alane with zirconocene dihydride affords the doubly bridging species, $[(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})(\mu\text{-H})_2\text{AlH}_2(\text{quinuclidine})]$, Fig. 4 [32]. Reaction of 2 equivalents of LiGaH_4 or one equivalent of NaGaH_4 with $[\text{ZnCl}_2(\text{PMDETA} \text{ or } \text{TMEDA})]$ afford the complexes $[(\text{PMDETA})\text{ClZn}(\mu\text{-H})\text{GaH}_3]$ and $[(\text{TMEDA})\text{ClZn}(\mu\text{-H})_2\text{GaH}_2]$, Fig. 5. The corresponding borane complex has also been prepared for the TMEDA case (using NaBH_4), and has been structurally authenticated along with the gallane product containing PMDETA [33]. The bridging hydride in $[(\text{PMDETA})\text{ClZn}(\mu\text{-H})\text{GaH}_3]$ is almost linear (173° , Zn, Ga–H $2.01(5)$ and $1.42(5)$ Å) with the hydride in an apical position of a distorted trigonal

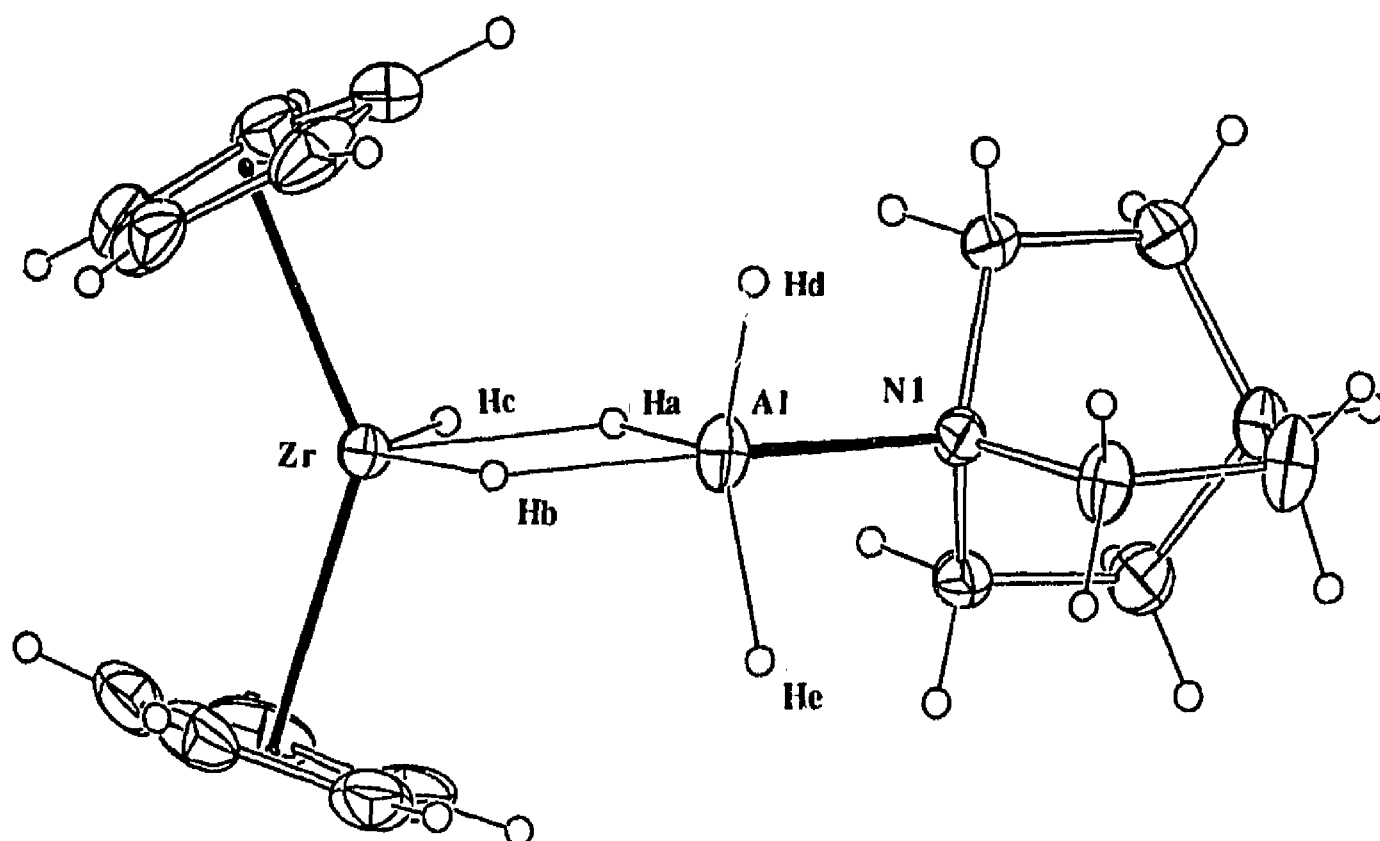


Fig. 4. Molecular structure of $[(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})(\mu\text{-H})_2\text{AlH}_2(\text{quinuclidine})]$. Selected geometries (Å and $^\circ$): Zr–Ha,b,c 1.91(2), 1.83(2), 1.79(2); Al–Ha,b,d,e 1.72(3), 1.79(2), 1.58(3), 1.47(3); Al–N1 2.066(2); Ha–Zr–Hb,c 66(1), 63(1); Hb–Zr–Hc 129(1); Zr–Ha–Al 111(1); Zr–Hb–Al 112(1); N1–Al–Ha,b,d,e 87.8(7), 158.1(7), 94.2(9), 96.6(9); Ha–Al–Hb,d,e 71(1), 212(1), 117(1); Hb–Al–Hd,e 93(1), 97(1); Hd–Al–He 121.2(2).

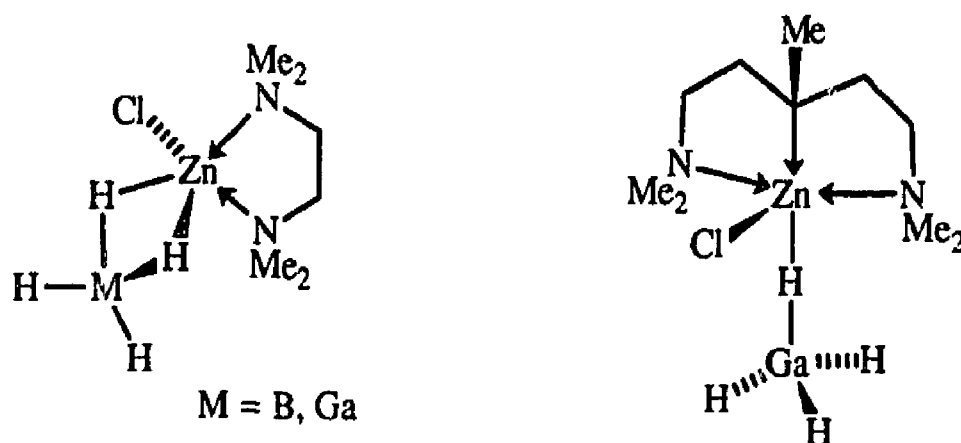


Fig. 5. Mixed Zn/Ga hydrides, and a related borahydride species [33].

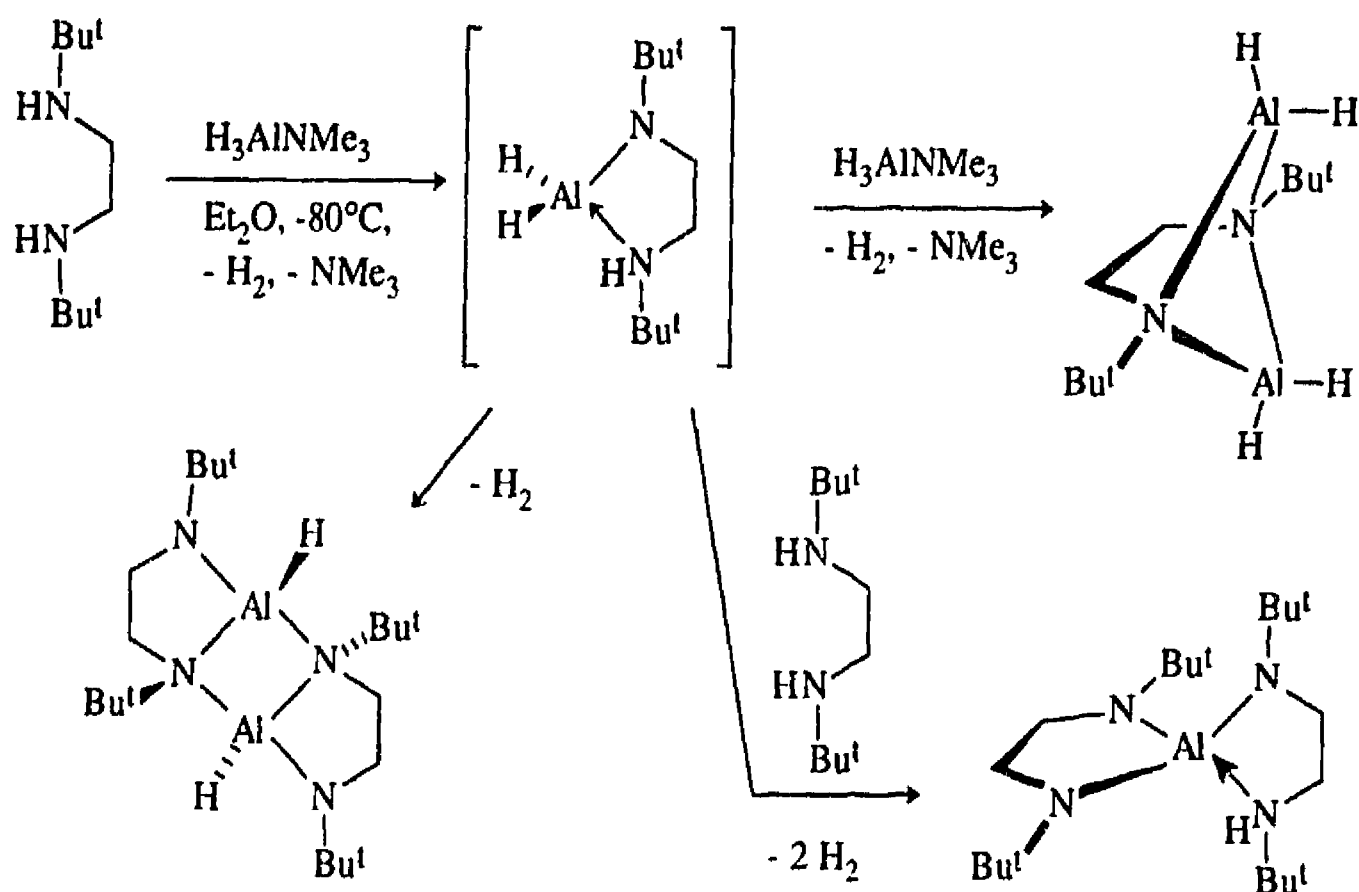
bipyramidal zinc centre, the other apical position is occupied by the unique N-centre. In [(TMEDA)ClZn(μ -H)₂GaH₂] the less sterically demanding amine donor interaction results in two bridging hydrides linking the tetrahedral gallium centre to zinc (inferred by both spectroscopy and the crystal structure of the borane analogue). These bimetallic Zn/Ga compounds decompose to grey materials at room temperature over several hours for the PMDETA species, and within an hour for that containing TMEDA. Bimetallic compounds [(CO)_nMGaH₂(NMe₃)], M = Co, *n* = 4 and M = Mn, *n* = 5, have direct gallium to transition metal bonding [34].

3. Aluminium and gallium amides and lithium aluminium amides derived from metallations of *N,N'*-disubstituted ethylenediamines

In recent publications we have reported our observations with the metallation and hydrometallation of various secondary amines and imines by some aluminium and gallium hydride sources, as an extension of our research on the reactivity of group 13 metal hydrides [1,2]. We have focused attention on substituted ethylenediamines bearing *N-t*-butyl [35,36] and *N*-trimethylsilyl substituents [36], 1,4-di-*t*-butyl-1,4-diazabutadiene [38–42], and related 1,4-diazabut-1-enes [41], as well as bulky monofunctional secondary amines [17,18]. In this section of the review we report on the reactions of various aluminium hydride sources ([H₃AlNMe₃], AlH₃ in OEt₂, LiAlH₄ and [H₂(Cl)AlNMe₃]) with *N,N'*-di-*t*-butylethylenediamine, *N,N'*-bis(trimethylsilyl)ethylenediamine and various substituted analogues of the former amine for the purpose of examining the effect of the steric demand of the ligand on the product distributions of these reactions and its effect on the stability of the complexes formed. Many of these reactions have been investigated in depth under a variety of conditions and as a result we have established mechanistic information on the generation of the various products and through the structural characterisation of the products we have inferred reasons for the stability/instability of the products and some unstable reactive intermediates.

N,N'-Di-*t*-butylethylenediamine is readily metallated by [H₃AlNMe₃] affording three aluminium amide species, [*trans*-{ μ -N(Bu^t)CH₂CH₂NBu^t}AlH₂]₂, [(CH₂- μ -NBu^t)₂(AlH₂)₂] and [{HN(Bu^t)CH₂CH₂NBu^t}Al{N(Bu^t)CH₂}]₂ depending on the stoichiometry of the reaction, as outlined in Scheme 1.

The metallation of *N,N'*-di-*t*-butylethylenediamine proceeds via the formation of an unstable secondary amine stabilised amido-aluminium dihydride [{HN(Bu^t)CH₂CH₂NBu^t}AlH₂]. Although the amido-aluminium dihydride species could not be isolated, the preparation of three crystallographically authenticated stable analogues has been achieved by the replacement of a hydride with a chloride substituent on the aluminium centre or by the addition of alkyl substituents on the five membered chelate ring of the ligand, Scheme 2. Using [H₂(Cl)AlNMe₃] as the metallating agent, the chlorohydrido-species [{HN(Bu^t)CH₂CH₂NBu^t}AlHCl] can be isolated. The C-alkylated analogues derived from *N,N'*-di-*t*-butyl-2-*t*-butylethylenediamine and *rac-N,N'*-di-*t*-butyl-2,3-dimethylethylenediamine gain their stability due to the increased steric demand of the ligands. The crystal structure of



Scheme 1.

$[\text{rac}\{-\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$, Fig. 6, shows the eclipsed geometry of the acidic amine proton and one of the aluminium hydrides. The stability of $[\text{rac}\{-\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$ towards the elimination of hydrogen relative to the unsubstituted analogue $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2]$ (187°C vs $<25^\circ\text{C}$) is remarkable given the remoteness and limited extent of the protection afforded by the 2,3-dimethyl substituents. The results of the X-ray crystal structure determinations of the foregoing three species provide a means of substantiating the structure of the unstable intermediate dihydride species $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2]$ in the metallation reaction of *N,N'*-di-*t*-butylethylenediamine with $[\text{H}_3\text{AlNMe}_3]$.

The complexes $[\text{rac}\{-\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$ and $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{C}(\text{Bu}^t)\text{HNBu}^t\}\text{AlH}_2]$ are obtained from the reactions of *rac-N,N'*-di-*t*-butyl-2,3-dimethylethylenediamine and *N,N'*-di-*t*-butyl-2-*t*-butylethylenediamine with $[\text{H}_3\text{AlNMe}_3]$ or AlH_3 in a 1:1 stoichiometric ratio or with either a two fold excess or deficiency of the hydride source. This indicates the stability of $[\text{rac}\{-\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$ and $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{C}(\text{Bu}^t)\text{HNBu}^t\}\text{AlH}_2]$ with respect to loss of hydrogen to form a diamido-alane complex and also stability with respect to reactions of $[\text{rac}\{-\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$ and $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{C}(\text{Bu}^t)\text{HNBu}^t\}\text{AlH}_2]$ with both *rac-N,N'*-di-*t*-butyl-2,3-dimethylethylenediamine and *N,N'*-di-*t*-butyl-2-*t*-butylethylenediamine, and $[\text{H}_3\text{AlNMe}_3]$ or AlH_3 to forming analogues of the dialuminium amide and aluminium triamide found for the case of the reactions involving *N,N'*-di-*t*-butylethylenediamine. In addition, isolated samples of $[\text{rac}\{-\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$ and $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{C}(\text{Bu}^t)\text{HNBu}^t\}\text{AlH}_2]$

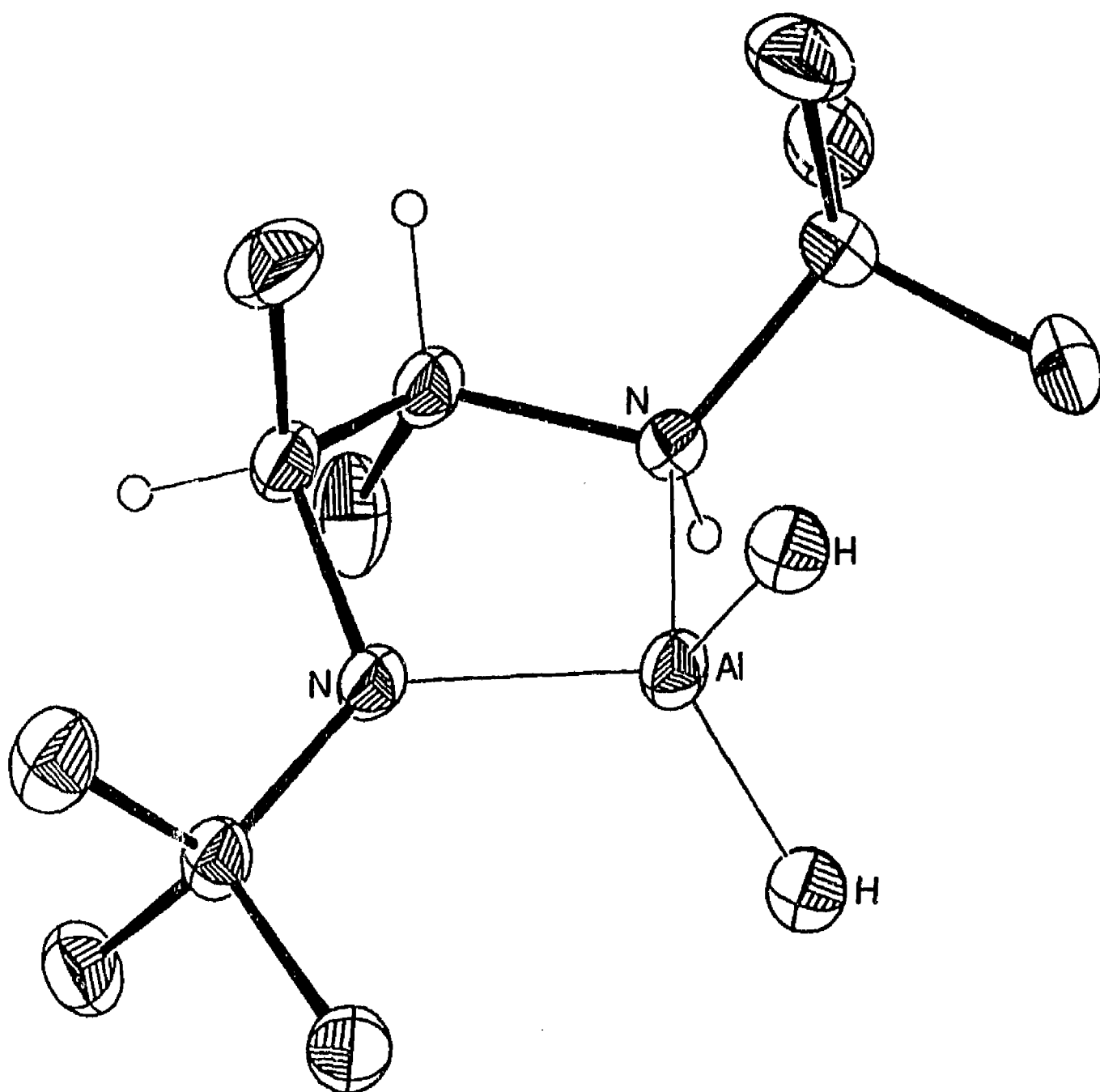
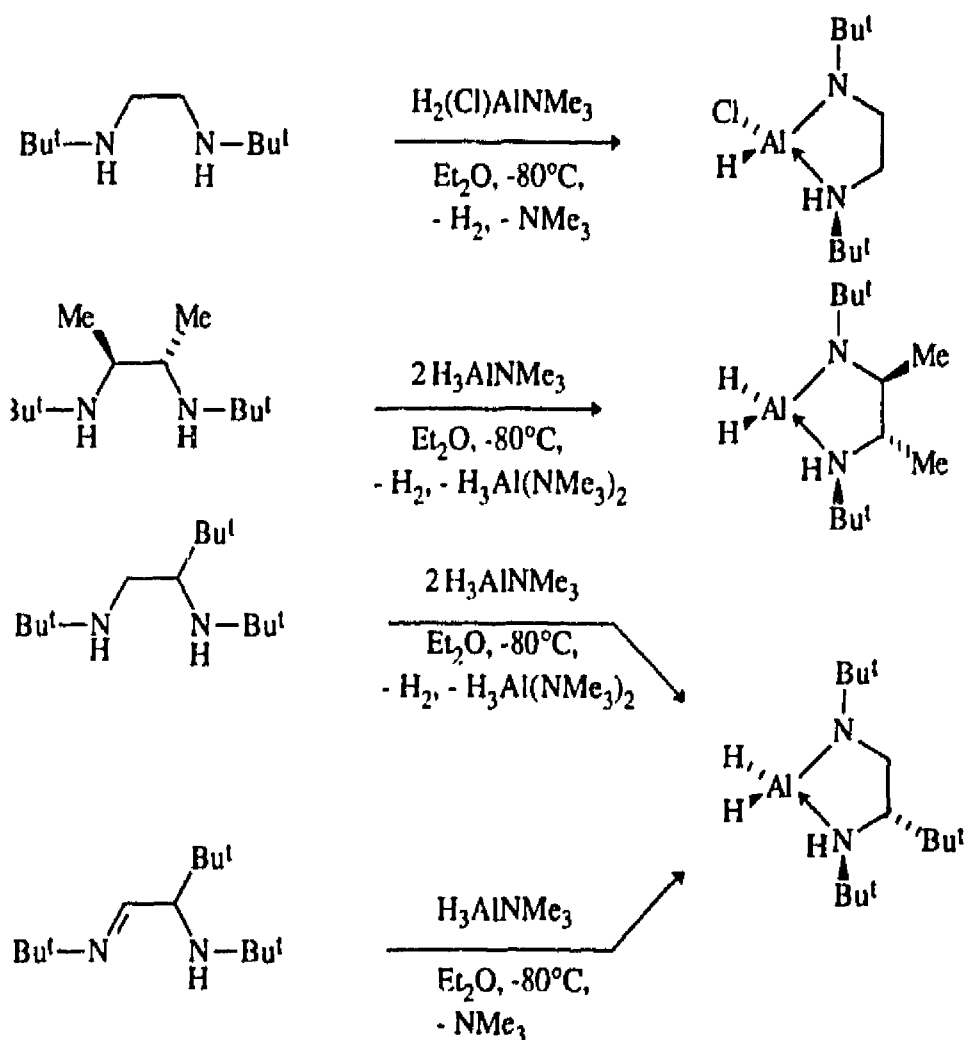


Fig. 6. Molecular structure of $[\text{rac-}\{\text{HN}(\text{Bu}^t)\text{C}(\text{Me})\text{HC}(\text{Me})\text{HNBu}^t\}\text{AlH}_2]$. For clarity methyl hydrogen atoms are omitted.

$\text{HNBu}^t\}\text{AlH}_2]$ show no trace of decomposition via metallation of the remaining acidic amine proton even under reflux in benzene.

The amido-aluminium dihydride $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2]$ is only stable at low temperature and in the absence of either of the starting materials eliminates molecular hydrogen on warming to room temperature to give the dimeric diamido-aluminium hydride $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}]_2]$. The reaction of *N,N'*-di-*t*-butylethylenediamine with two equivalents of $[\text{H}_3\text{AlNMe}_3]$ in diethyl ether at -80°C yields the bridging dialuminium diamide $[(\text{CH}_2\text{-}\mu\text{-NBu}^t)_2(\text{AlH}_2)_2]$. Increasing the stoichiometric ratio of *N,N'*-di-*t*-butylethylenediamine to two equivalents leads to the formation of the aluminium triamide $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{Al}\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$.

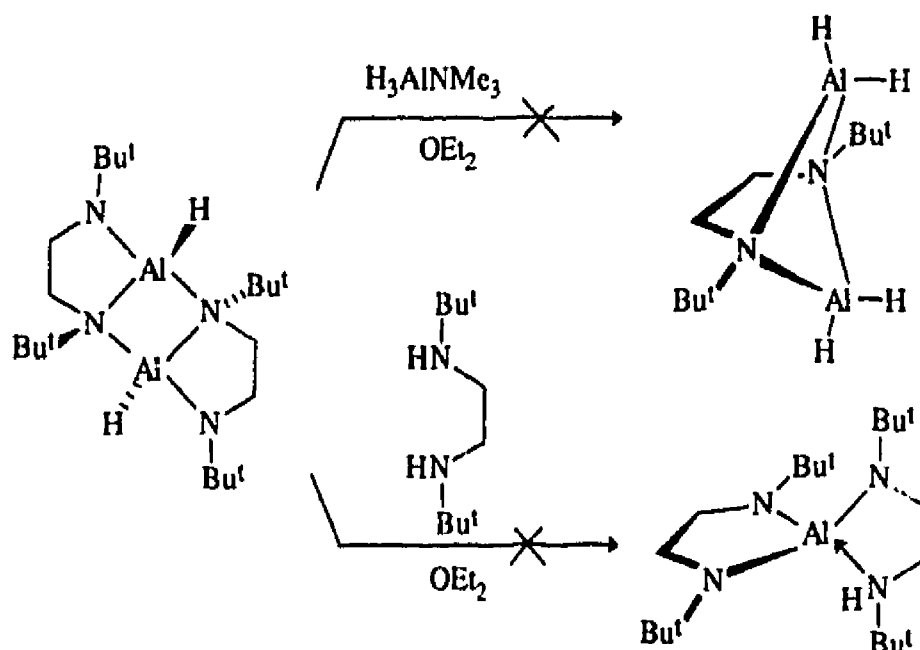
The dimeric diamido-aluminium hydride $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}]_2]$ is stable toward reaction with either *N,N'*-di-*t*-butylethylenediamine or $[\text{H}_3\text{AlNMe}_3]$ in OEt_2 at 25°C , Scheme 3. This lack of reaction of



Scheme 2.

$[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ further implicates the unstable amido-aluminium dihydride $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2]$ as an intermediate in the formation of the dialuminium amide $[(\text{CH}_2\text{-}\mu\text{-NBu}^t)_2(\text{AlH}_2)_2]$ and the aluminium triamide $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{Al}\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$. Furthermore, the alkyl substituted analogues of the amido-aluminium dihydride $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2]$ can be converted to the aluminium rich complexes in the presence of $[\text{H}_3\text{AlNMe}_3]$.

Hydrogen elimination from the intermediate dihydride $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2]$ followed by association of the resulting monomers results in the formation of the aluminium diamide $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ with bridging amido-groups. The X-ray crystal structure determination of $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ shows a dimeric species with C_i symmetry. The complex possesses a planar four-membered Al_2N_2 ring in which both aluminium centres are tetrahedrally coordinated. The bidentate dimetallated ethylenediamide ligands are positioned in a *trans*-arrangement with respect to the planar Al_2N_2 core. The diamido-gallium hydride obtained from the hydrogallation of 1,4-di-*i*-propyl-1,4-diazabutadiene with $[\text{H}_3\text{GaNMe}_3]$, $[\text{trans-}\{\mu\text{-N}(\text{Pr}^i)\text{CH}_2\text{CH}_2\text{NPr}^i\}\text{GaH}\}_2]$, has a similar structure to $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ [41]. The metallation of the less hindered *N,N'*-diethylethylenediamine by $[\text{H}_3\text{AlNMe}_3]$ gives the trialuminium species [44] $[(\text{CH}_2\text{NEt})_2\}_2\text{Al}_3\text{H}_5]$ which has a similar structure to a gallium diamide $[(\text{CH}_2\text{NMe})_2\}_2\text{Ga}_3\text{H}_5]$, also prepared by metallation of the ethylenediamine by $[\text{H}_3\text{GaNMe}_3]$ [41].



Scheme 3.

The reaction of *N,N'*-di-*t*-butylethylenediamine with two equivalents of $[\text{H}_3\text{AlNMe}_3]$ yields the dialuminium amide $[(\text{CH}_2\text{-}\mu\text{-NBu}^t)_2(\text{AlH}_2)_2]$. The formation of $[(\text{CH}_2\text{-}\mu\text{-NBu}^t)_2(\text{AlH}_2)_2]$ most likely proceeds via the intermediate amido-aluminium dihydride $\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}_2$ which then binds $[\text{H}_3\text{AlNMe}_3]$ or AlH_3 at the amido-centre prior to the metallation of the secondary amine. The diminished steric hindrance of *N,N'*-di-*t*-butylethylenediamine relative to the C-alkylated amines *N,N'*-di-*t*-butyl-2-*t*-butylethylenediamine and *rac-N,N'*-di-*t*-butyl-2,3-dimethylethylenediamine facilitates the second metallation by $[\text{H}_3\text{AlNMe}_3]$ to give dialuminium amides. In the cases of these alkyl substituted amido-aluminium dihydride complexes their reactivity is reduced and the additional equivalent of $[\text{H}_3\text{AlNMe}_3]$ is converted to $[\text{H}_3\text{Al}(\text{NMe}_3)_2]$ which is slow to react with the ethylenediamines whereas in the reactions involving AlH_3 this is not the case [36]. The importance of this finding is that a two-fold equivalent of the hydride source can be necessary for the complete, facile conversion of bulky substrates in their reactions with aluminium hydrides under mild conditions, i.e. “six active hydride equivalents”. The gallium analogue of the dialuminium amide, $[(\text{CH}_2\text{-}\mu\text{-Nt-Bu})_2(\text{GaH}_2)_2]$, has been prepared by the hydrometallation pathway involving *N,N'*-1,4-di-*t*-butyl-1,4-diazabutadiene and $[\text{H}_3\text{GaNMe}_3]$ [39]. The X-ray crystal structure determination of $[(\text{CH}_2\text{-}\mu\text{-NBu}^t)_2(\text{AlH}_2)_2]$, Fig. 7, shows that the geometry constraints of the AlH_2 units in both bridging positions forces the four membered Al_2N_2 ring to be butterfly shaped, folded along the N–N vector.

The formation of the aluminium triamide $\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{Al}\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2$ results from the reaction of two equivalents of *N,N'*-di-*t*-butylethylenediamine with $[\text{H}_3\text{AlNMe}_3]$ in diethyl ether at -80°C . The X-ray crystal structure determination of $\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{Al}\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2$ revealed a monomeric species possessing a central four-coordinate aluminium centre devoid of hydrides. The aluminium centre is coordinated by two bidentate ligands with one of the ligands having both of the acidic protons removed and the other ligand having one remaining amine proton.

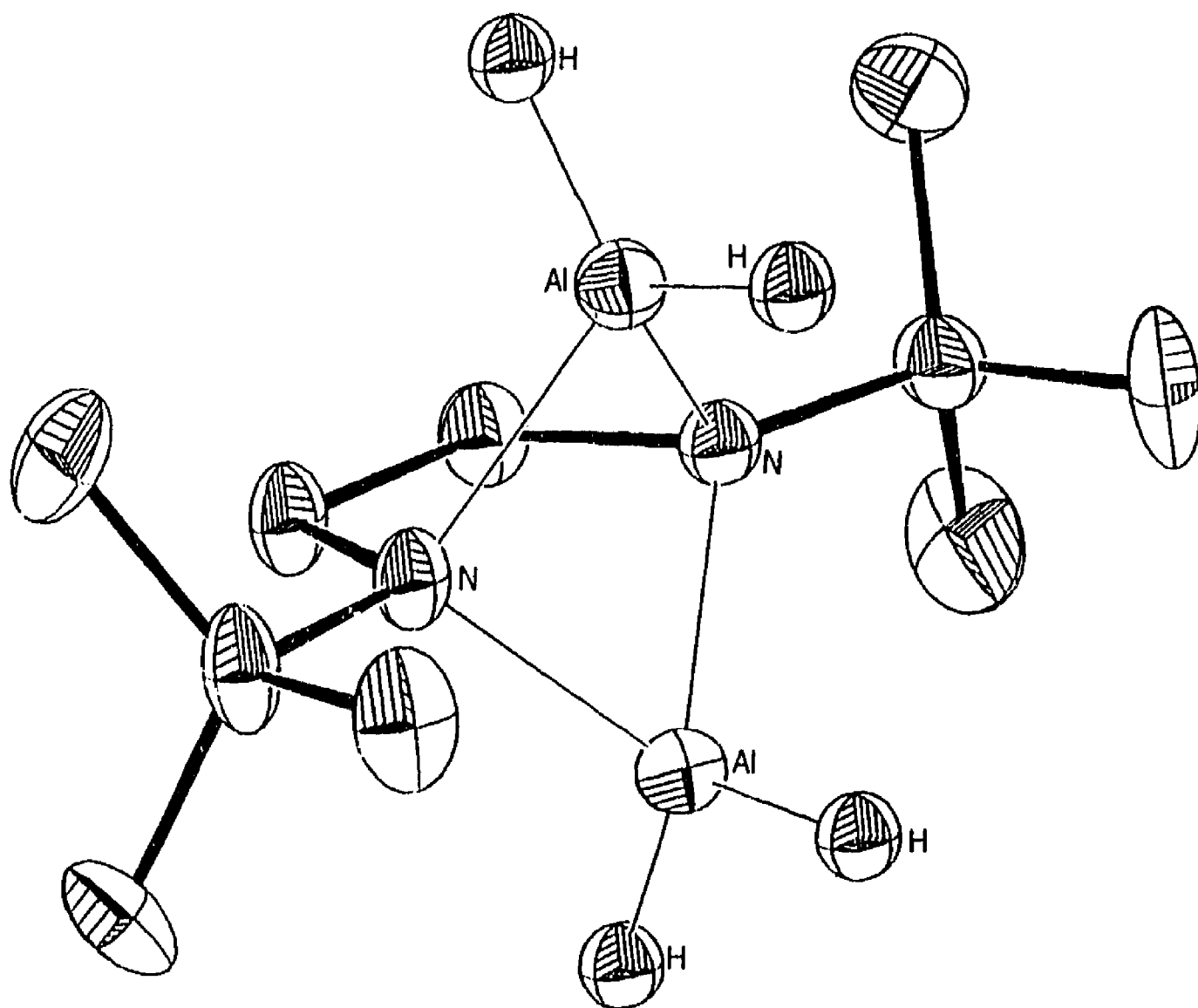


Fig. 7. Molecular structure of $[(\text{CH}_2-\mu\text{-NBu}')_2(\text{AlH}_2)_2]$. For clarity methyl and methylene hydrogen atoms are omitted.

The reaction of *N,N'*-bis(trimethylsilyl)ethylenediamine with $[\text{H}_3\text{AlNMe}_3]$ gives products based on metallation (H_2 elimination), $[\text{trans-}\{\mu\text{-N}(\text{SiMe}_3)\text{-CH}_2\text{CH}_2\text{NSiMe}_3\}\text{AlH}\}_2]$ and $[\{\text{HN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NSiMe}_3\}\text{Al}\{\text{N}(\text{SiMe}_3)\text{CH}_2\}_2]$, which are analogous to the *t*-butyl complexes $[\text{trans-}\{\mu\text{-N}(\text{Bu}')\text{-CH}_2\text{CH}_2\text{NBu}'\}\text{AlH}\}_2]$ and $[\{\text{HN}(\text{Bu}')\text{CH}_2\text{CH}_2\text{NBu}'\}\text{Al}\{\text{N}(\text{Bu}')\text{CH}_2\}_2]$, Fig. 8. Further, products derived from N–Si bond cleavage and metallation, $[\{\text{CH}_2\text{N}(\text{SiMe}_3)\}_2\text{AlH}\}_2\{\text{HAlN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NAlH}_2\}]$ and $[\text{H}_2\text{Al}\{\text{CH}_2\text{N}(\text{SiMe}_3)\}_2\text{Al-N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NAl}(\text{H})_2\text{NMe}_3]$ were isolated. Differences in the chemistry of this system also extend to the inability to form the dialuminium amide analogue, $[(\text{CH}_2-\mu\text{-NSiMe}_3)_2(\text{AlH}_2)_2]$, presumably arising from the decreased stability of the intermediate $[\{\text{HN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NSiMe}_3\}\text{AlH}_2]$ so that it eliminates hydrogen to yield the dimeric aluminium diamide rather than react with additional $[\text{H}_3\text{AlNMe}_3]$. Attempts to prepare a stable mono-chloride substituted analogue of $[\text{Me}_3\text{SiN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\text{AlH}_2]$ by the reaction of *N,N'*-bis(trimethylsilyl)ethylenediamine with $[\text{H}_2\text{Al}(\text{Cl})\text{NMe}_3]$ yields the redistributed dichloride species $[\text{Me}_3\text{SiN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\text{AlCl}_2]$ and $[\{\text{HN}(\text{SiMe}_3)\text{-CH}_2\text{CH}_2\text{NSiMe}_3\}\text{Al}\{\text{N}(\text{SiMe}_3)\text{CH}_2\}_2]$, Scheme 4. Presumably the monochloride $[\text{Me}_3\text{SiN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\text{AlHCl}]$ exchanges to yield a mixture of

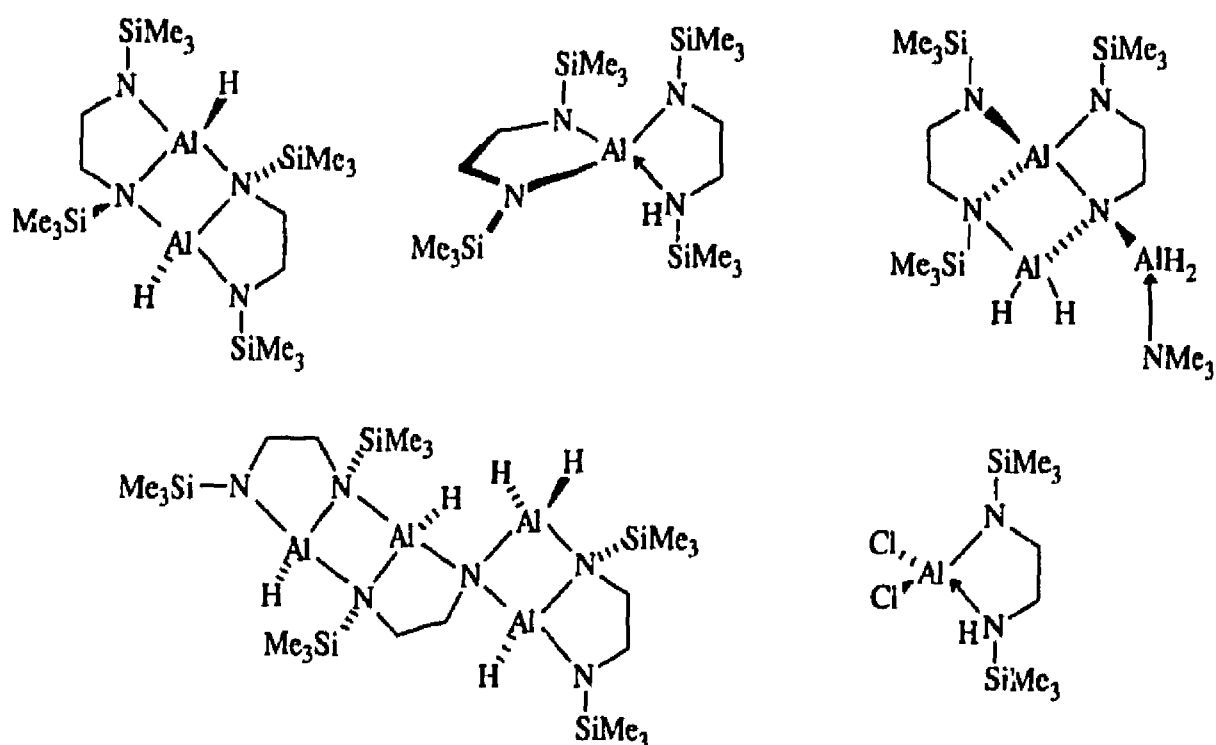
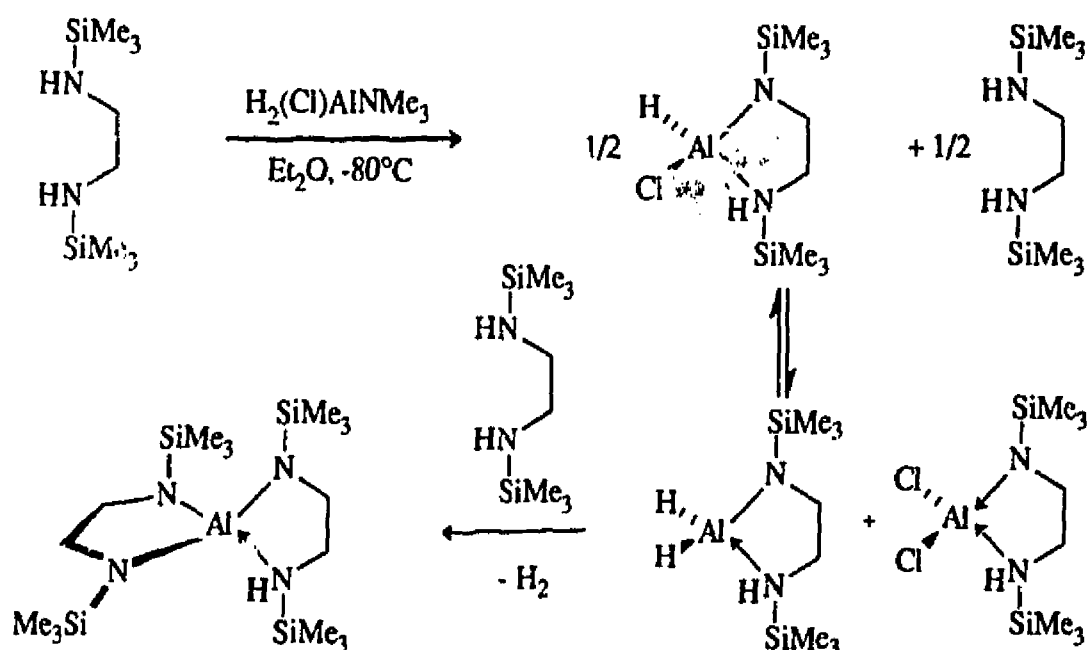


Fig. 8. Structures of complexes derived from the reaction of $[\text{H}_3\text{AlNMe}_3]$ or $[\text{H}_2(\text{Cl})\text{AlNMe}_3]$ with *N,N'*-bis(trimethylsilyl)ethylenediamine.

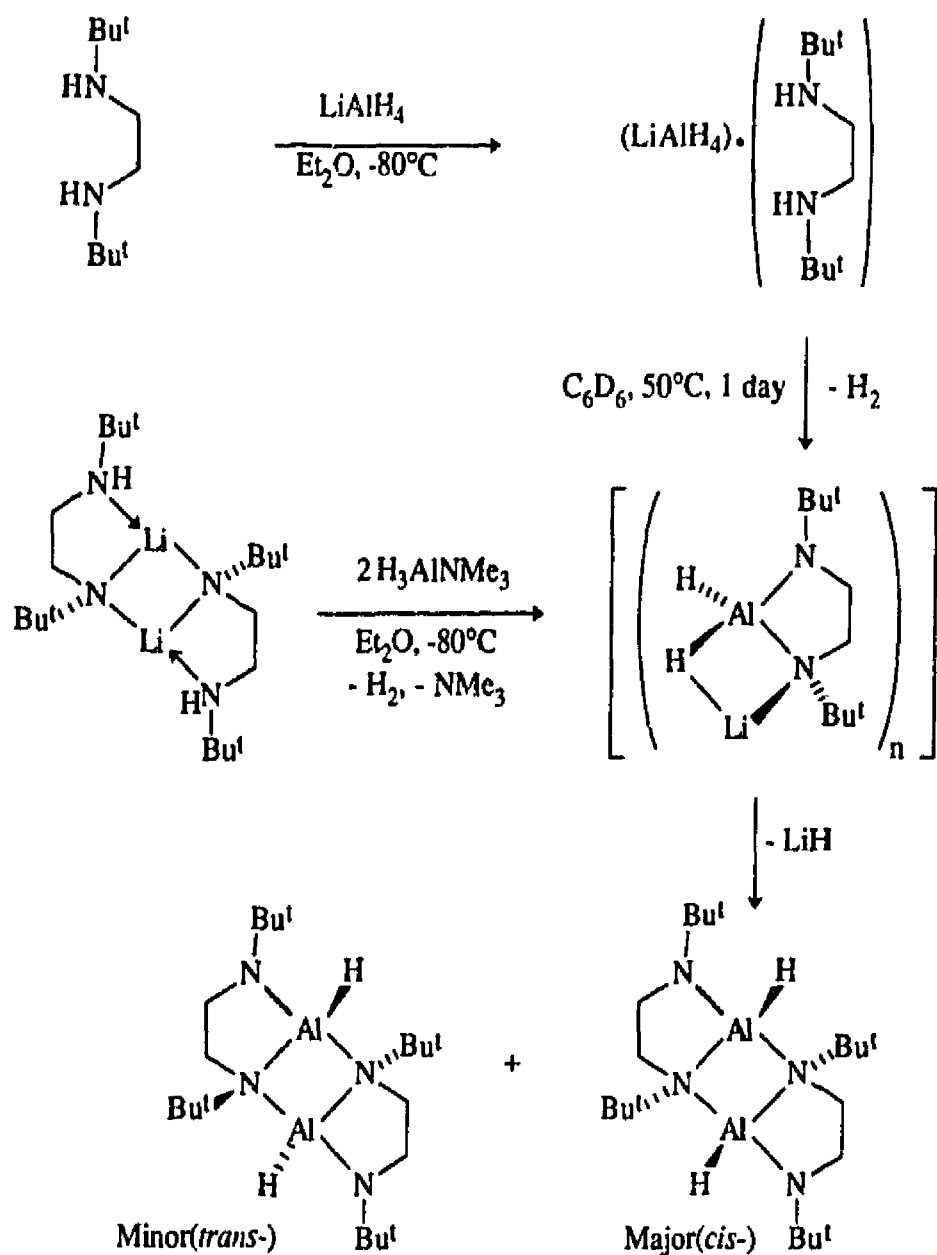
$[\text{HN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\text{AlCl}_2]$ and the dihydride species, the dihydride then reacting with additional *N,N'*-bis(trimethylsilyl)ethylenediamine to yield $[\{\text{HN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NSiMe}_3\}\text{Al}\{\text{N}(\text{SiMe}_3)\text{CH}_2\}_2]$; so driving the equilibrium further in favour of the dichloride species.



Scheme 4.

The dimeric diamido-aluminium hydrides [*trans*-{ μ -N(Bu^t)-CH₂CH₂NBu^t]AlH}₂] and [*cis*-{ μ -N(Bu^t)CH₂CH₂NBu^t]AlH}₂] are prepared via an alternative metallation reaction of the lithium amide [*cis*-{Li[μ -N(Bu^t)CH₂CH₂N(H)Bu^t]}₂] [45] with [H₃AlNMe₃], Scheme 5. The aluminium diamides are obtained as a ca. 9:1 ratio of *cis*:- *trans*-isomers. In contrast,

$[trans-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ is obtained as the sole isomer according to the reaction in Scheme 1.



Scheme 5.

The X-ray crystal structure determination of $[cis-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ shows a dimeric species with pseudo C_2 symmetry. The complex possesses a planar four-membered Al_2N_2 ring in which both aluminium centres are tetrahedrally coordinated. The bidentate dimetallated ethylenediamide ligands are positioned in a *cis*-arrangement with respect to the planar Al_2N_2 core.

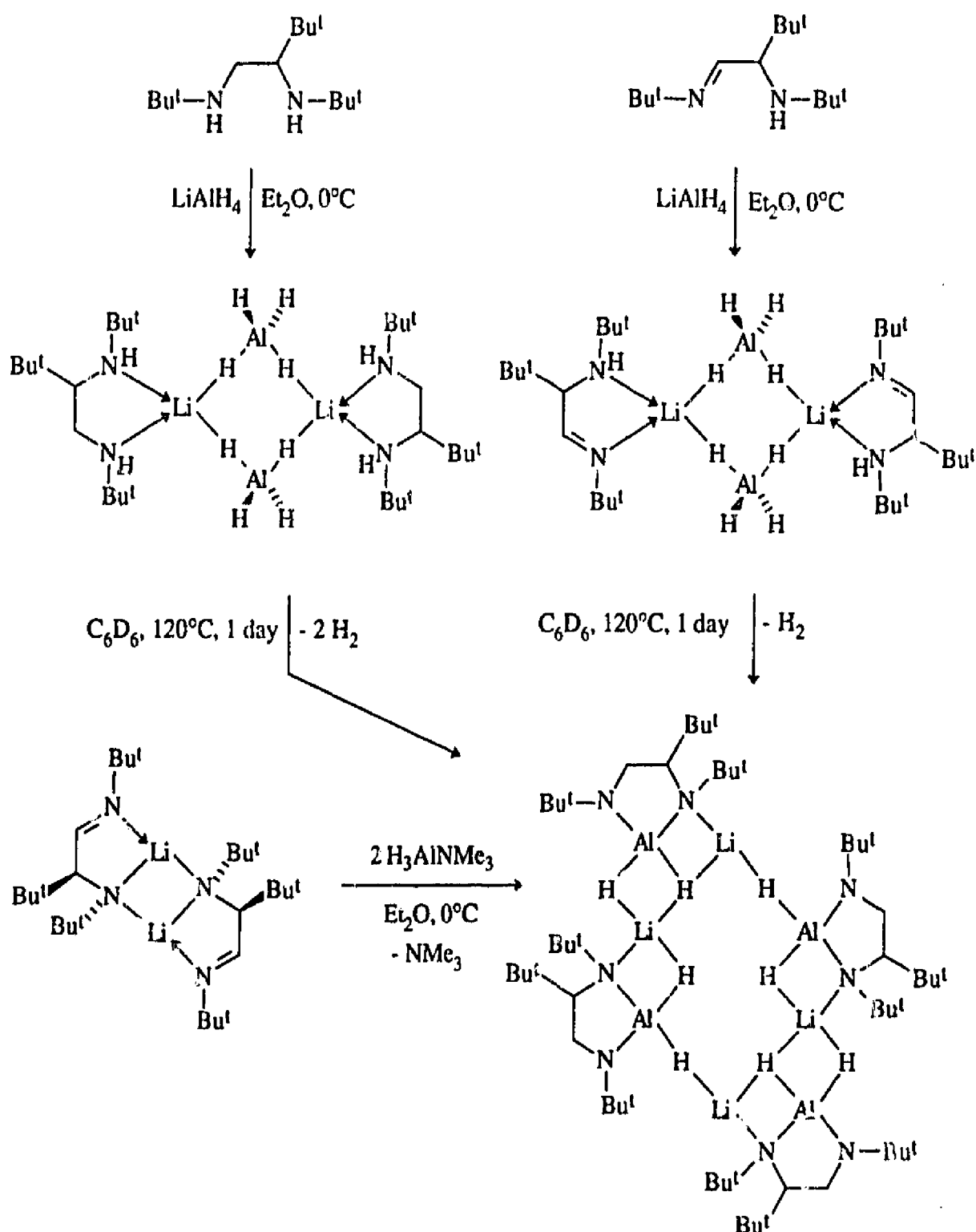
The two dimeric aluminium diamide isomers $[trans-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ and $[cis-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ are not interconvertible in Et_2O at room temperature over several weeks. Treatment of isolated samples of the aluminium diamide $[cis-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ with either $[H_3AlNMe_3]$ or N,N' -di-*t*-butylethylenediamine in OEt_2 at $25^\circ C$ results in the recovery of unreacted $[cis-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ and no formation of either the dialuminium amide $[(CH_2-\mu-NBu^t)_2(AlH_2)_2]$ or the aluminium triamide $[\{HN(Bu^t)CH_2CH_2NBu^t\}Al\{N(Bu^t)CH_2\}_2]$. This lack of reactivity of $[cis-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ and the absence of any $[cis-\{\mu-N(Bu^t)CH_2CH_2NBu^t\}AlH\}_2]$ being formed in the reactions of N,N' -di-*t*-butylethylenedia-

mine with $[\text{H}_3\text{AlNMe}_3]$ shows that $[\text{cis-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ is not involved in the reaction mechanism for the formation of $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$, $[(\text{CH}_2\text{-}\mu\text{-NBu}^t)_2(\text{AlH}_2)_2]$ or $[\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{Al}\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$.

The formation of the diamido-aluminium hydride $[\text{cis-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ from the reaction of the lithium amide $[\text{cis-}\{\text{Li}[\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Bu}^t]\}_2]$ with $[\text{H}_3\text{AlNMe}_3]$ precedes via the unstable lithium diamido-aluminium dihydride $\{\{\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{LiAlH}_2\}_n$, which eliminates LiH to give $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ and $[\text{cis-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$. The aluminium amides $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ and $[\text{cis-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ are also prepared in the same ratio from the thermal decomposition of the N,N' -di-*t*-butylethylenediamine adduct of LiAlH_4 , $\{\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Bu}^t\}\text{LiAlH}_4\}_n$, in benzene solution. This presumably, initially involves the elimination of molecular hydrogen by metallation of the secondary amines to give the lithium diamido-aluminium dihydride $\{\{\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{LiAlH}_2\}_n$ which may then spontaneously further eliminate LiH to give the diamido-aluminium hydrides $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ and $[\text{cis-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$. Given that the aluminium amides $[\text{trans-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ and $[\text{cis-}\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{AlH}\}_2]$ do not interconvert in OEt_2 and the *cis*-isomer is not formed from the reaction of N,N' -di-*t*-butylethylenediamine with $[\text{H}_3\text{AlNMe}_3]$, the decomposition of $\{\{\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{LiAlH}_2\}_n$ must involve an oligomer which assembles into the *cis*-isomer, the consequence of the structure of $\{\{\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t\}\text{LiAlH}_2\}_n$.

The insolubility of the adduct $\{\{\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Bu}^t\}\text{LiAlH}_4\}_n$ is in contrast to the related dimeric ethylenediamine and 1,4-diazabut-1-ene adducts $[\{\{\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{H})\text{Bu}^t\}\text{Li}(\mu\text{-H})_2\text{AlH}_2\}_2]$ [36] and $[\{\{\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHN}\text{Bu}^t\}\text{Li}(\mu\text{-H})_2\text{AlH}_2\}_2]$ [43] which are highly soluble species prepared from the reactions of the respective ligands with LiAlH_4 in diethyl ether, Scheme 6. Presumably the less bulky ethylenediamine ligand N,N' -di-*t*-butylethylenediamine results in the adduct forming a higher oligomeric or polymeric structure in the solid state or perhaps the compound may be ionic.

The mechanism for hydroalumination reactions of carbonyls and imines is generally believed to involve the initial coordination of the aluminium centre to the heteroatom followed by hydride transfer to the carbon atom via a cyclic four membered or similar transition state [46]. The crystal structures of $[\{\{\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{H})\text{Bu}^t\}\text{Li}(\mu\text{-H})_2\text{AlH}_2\}_2]$ and $[\{\{\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHN}\text{Bu}^t\}\text{Li}(\mu\text{-H})_2\text{AlH}_2\}_2]$ [46] show that the reason for the stability of these adducts with respect to metallation and hydrometallation is due to the ligands bearing the reactive secondary amine and imine functional groups coordinating to the lithium centres. The ligands chelate the lithium centres and two of the hydride substituents of the $[\text{AlH}_4]$ units also coordinate to the lithium centres forming the lithium aluminium tetrahydride dimers, the other two hydride substituents of the $[\text{AlH}_4]$ units are terminal, Fig. 9. This results in a cyclic $\text{Li}_2\text{Al}_2\text{H}_4$ ring of the type established for the lithium amido-aluminium hydride and lithium alkylaluminium hydride com-



Scheme 6.

plexes $[\{(\text{Me}_3\text{Si})_2\text{NAlH}(\mu\text{-H})_2\text{Li}(\text{Et}_2\text{O})_2\}_2]$ [48] and $[\{(\text{Me}_2\text{PhSi})_3\text{CAIH}(\mu\text{-H})_2\text{Li}(\text{THF})_2\}_2]$ [49]. The importance of the lithium cation in the stability of the imine functional group in the adduct $[\{\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHN}(\text{Bu}^t)\text{-Li}(\mu\text{-H})_2\text{AlH}_2\}_2]$ is that the approach of using LiAlH_4 instead of $[\text{H}_3\text{AlNMe}_3]$ as the hydride source in reduction/metallation reactions can lead to chemo-selectivity and the effective protection of the more reactive functional group by coordination to the lithium centre, leaving the secondary amine free to be metallated, which is the reverse case for the reaction of the 1,4-diazabicyclo[2.2.0]hexane with $[\text{H}_3\text{AlNMe}_3]$ or AlH_3 . In that sense, the metallation of secondary amines in the presence of reactive imines could be achieved by “protecting” the imine by the in situ coordination of imines in their reactions with LiAlH_4 . In this regard, group 1 metal hydroaluminates

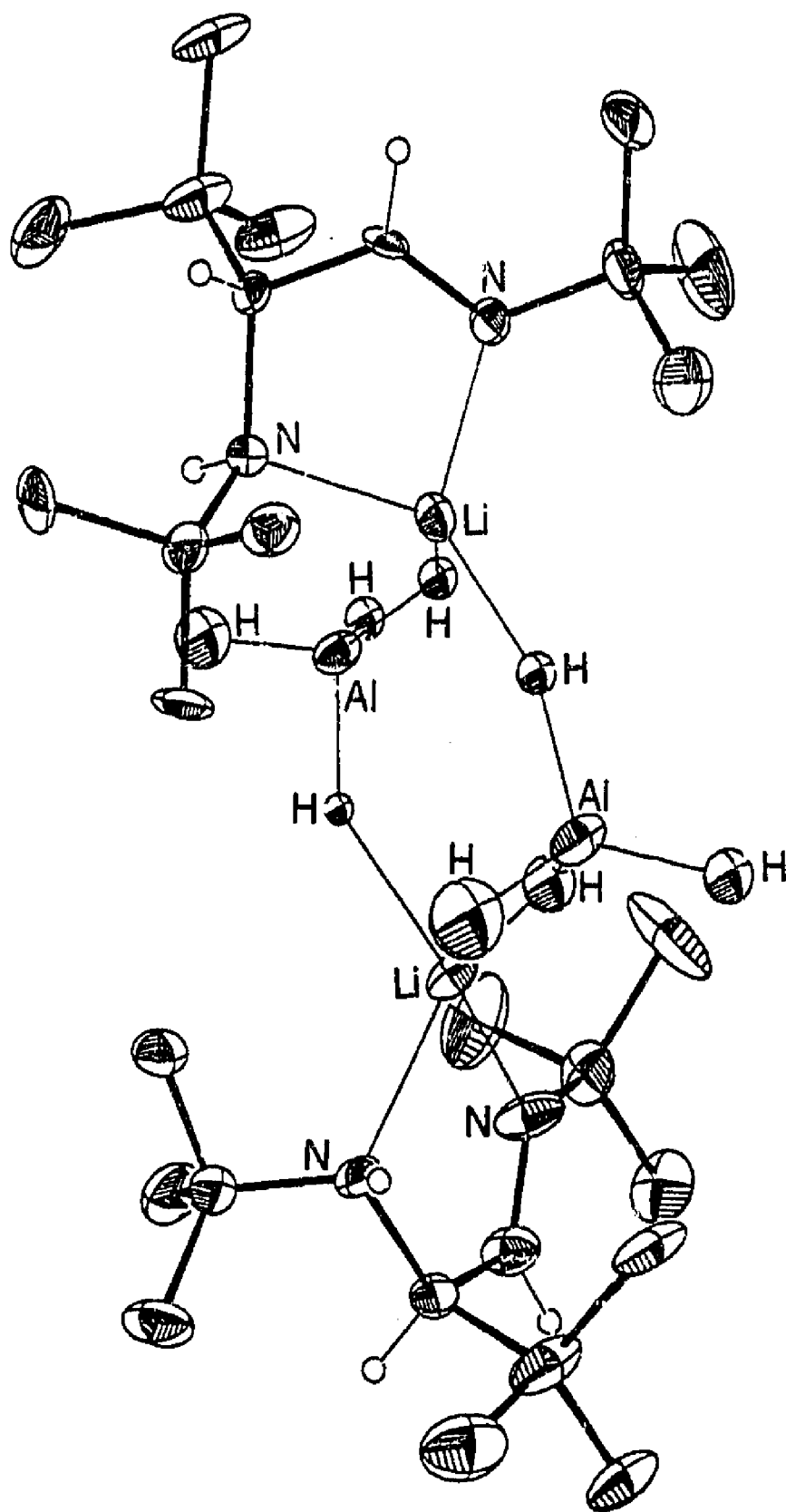


Fig. 9. Molecular structure of $[\{ \text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHN}(\text{Bu}^t) \} \text{Li}(\mu\text{-H})_2\text{AlH}_2]_2$. For clarity methyl hydrogen atoms are omitted.

may be useful protecting agents for imines in their reduction and metallation reactions.

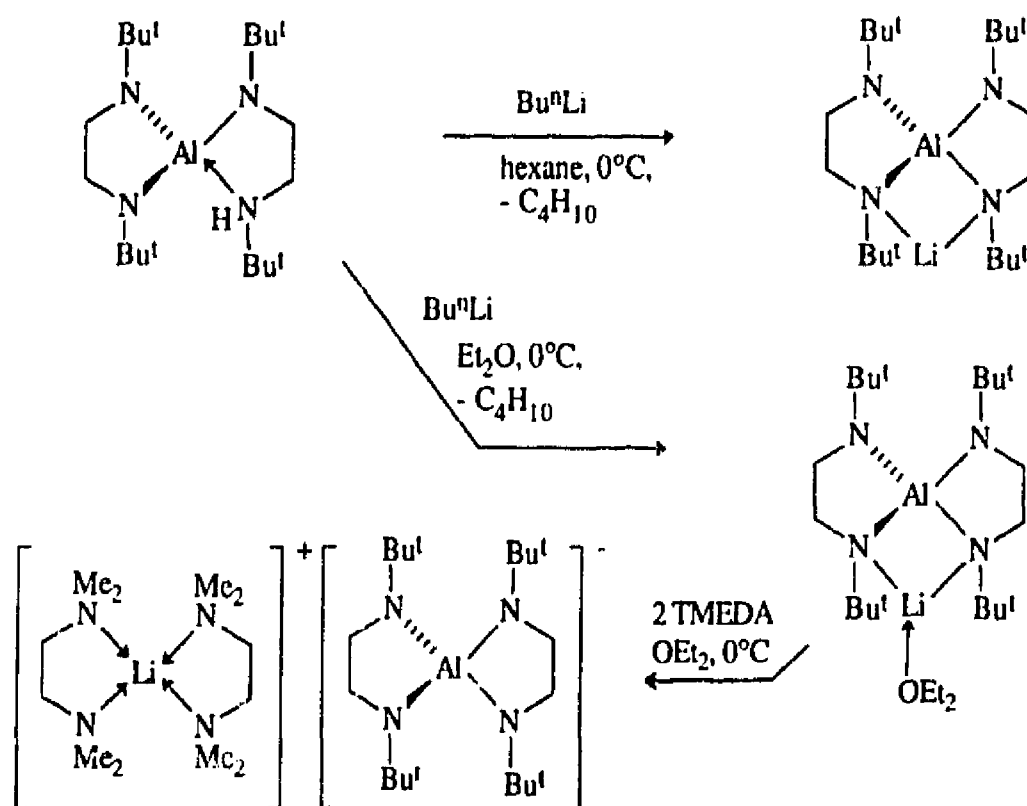
The lithium aluminium hydride adducts $[\{ \text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{H})\text{Bu}^t \} \text{Li}(\mu\text{-H})_2\text{AlH}_2]_2$ and $[\{ \text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHN}(\text{Bu}^t) \} \text{Li}(\mu\text{-H})_2\text{AlH}_2]_2$ decompose by extended heating in benzene solution by metallation and metallation/hydrometallation, respectively, yielding the stable lithium diamido-aluminium dihydride $[\{ \text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{H})\text{Bu}^t] \text{AlH}_2 \}_4]$. The stability of the tetrameric C-alkylated lithium diamido-aluminium dihydride $[\{ \text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{H})\text{Bu}^t] \text{AlH}_2 \}_4]$ is

$\text{CH}_2\text{NBu}^t\text{AlH}_2\}_4]$ is in contrast to the unsubstituted analogue $\{[\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\text{LiAlH}_2\}_n$ which decomposes at room temperature by elimination of LiH to give a mixture of isomers of the aluminium diamides [*cis*- $\{[\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\text{AlH}\}_2]$ and [*trans*- $\{[\mu\text{-N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\text{AlH}\}_2]$. Compound $\{[\text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{NBu}^t]\text{AlH}_2\}_4]$ is stable $>115^\circ\text{C}$ which can be accounted for by the added steric bulk of the ethylenediamide. An alternative synthesis of $\{[\text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{NBu}^t]\text{AlH}_2\}_4]$ has been achieved by the hydrometallation of the lithium amide [*cis*- $\{[\text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHNBu}^t]\}_2]$ by $[\text{H}_3\text{AlNMe}_3]$.

This field has been extended to the attempted synthesis of lithium diamido-aluminium dihydride and lithium tetraamido-aluminium complexes by the lithiation of the latent reactive secondary amide functionalities present in the complexes already discussed. This includes investigating an alternative synthesis of lithium diamido-aluminium dihydride $\{[\text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{NBu}^t]\text{AlH}_2\}_4]$ by the reaction of methyl lithium in OEt_2 with $\{[\text{HN}(\text{Bu}^t)\text{CH}_2\text{C}(\text{Bu}^t)\text{HNBu}^t]\text{AlH}_2\}_2]$. This approach has proved unsuccessful, giving a product tentatively formulated on the basis of IR and NMR spectroscopic data as $\{[\text{Li}[\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{NBu}^t]\text{AlHMe}\}_2]$, formed by the elimination of H_2 from the reactants rather than the expected elimination of methane.

This unexpected behaviour led to the lithiation reactions of the aluminium triamide $\{[\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\text{Al}\{[\text{N}(\text{Bu}^t)\text{CH}_2\}_2\}_2]$, the results are summarised in Scheme 7. The reaction of the aluminium triamide $\{[\text{HN}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\text{Al}\{[\text{N}(\text{Bu}^t)\text{CH}_2\}_2\}_2]$ with Bu^nLi in hexane and OEt_2 gives the monomeric lithium aluminium tetraamides as both solvent free and the OEt_2 adduct $[\text{Li}\{[\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\}_2\text{Al}]$ and $[\text{Et}_2\text{OLi}\{[\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\}_2\text{Al}]$, respectively. The reaction of the diethyl ether adduct $[\text{Et}_2\text{OLi}\{[\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\}_2\text{Al}]$ with two equivalents of the chelating nitrogen Lewis base TMEDA in OEt_2 affords the ionic complex $[\text{Li}(\text{TMEDA})_2][\text{Al}\{[\text{N}(\text{Bu}^t)\text{CH}_2\}_2\}_2]$.

The crystal structures of the unsolvated and OEt_2 solvated monomeric lithium aluminium tetraamides $[\text{Li}\{[\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\}_2\text{Al}]$ and $[\text{Et}_2\text{OLi}\{[\text{N}(\text{Bu}^t)\text{CH}_2\text{CH}_2\text{NBu}^t]\}_2\text{Al}]$ are shown in Figs. 10 and 11. The di-metallated ethylenediamide act as bidentate ligands, chelating the aluminium atoms, with one nitrogen centre of each ligand binding to a lithium centre. Four-fold coordination for the aluminium centres is achieved and they exhibit distorted tetrahedral $\text{N}(\text{amido})_2\{\mu\text{-N}(\text{amido})_2\}$ coordination environments. The lithium centres are two coordinate and three coordinate in the two structures, respectively. For the unsolvated species, the two coordinate $\text{N}\{\mu\text{-N}(\text{amido})_2\}$ bent coordination environment is unusually low and the additional coordination of the OEt_2 molecule is therefore achieved easily with little distortion of the molecule with the exception of the Li-N distances which are lengthened from $1.97(1)\text{--}2.00(1)\text{ \AA}$ for the two coordinate lithium to $2.043(8)\text{ \AA}$ for the three coordinate complex. The angle between the planes of the two chelate rings of $76.5^\circ\text{--}79.9^\circ$ in the two structures is presumably made acute by the lithium centres bridging two of the amido-nitrogen centres and distorts the geometry from the ideal orthogonal disposition. In contrast, the crystal structure of the ionic complex $[\text{Li}(\text{TMEDA})_2][\text{Al}\{[\text{N}(\text{Bu}^t)\text{CH}_2\}_2\}_2]$ shows that the anion exhibits chelate



Scheme 7.

rings which are close to orthogonal (91.4°), the anion being non-coordinating, Fig. 12.

Reaction of thiomorpholine with $[\text{H}_3\text{AlNMe}_3]$ in OEt_2 affords the metallated species $[\text{H}_2\text{Al}\{\mu\text{-N}(\text{CH}_2\text{CH}_2)_2\text{S}\}]_2$ which in the solid state is a dimer with bridging amido centres. These molecules are then weakly associated via long intermolecular $\text{Al} \cdots \text{S}$ interactions at $3.26(1) \text{ \AA}$ [7].

4. Gallane phosphide and chloride derivatives

In developing suitable precursors for the formation of hydride/phosphide gallium complexes we have prepared $[\text{Cy}_3\text{PGaH}_2\text{Cl}]$. This reacts with $[\text{Li}(\text{PCy}_2)(\text{THF})_n]$ affording $[\{\text{H}_2\text{Ga}(\mu\text{-PCy}_2)\}_3]$ which crystallises with the inner core of the complex in a twist boat conformation, Fig. 13. The gallium phosphide is of interest in relation to the generation of thin films of group 13/15 semiconductor materials using single-source precursors of the general type $\text{L}_n\text{MEL}'_n$ that feature the desired 1:1 stoichiometry of the elements [51]. Related compounds include a trimeric aluminium phosphide $[(\text{Et}_2\text{-}\mu\text{-P})\text{AlH}_2]_3$ [52], two monomeric base-stabilised phosphide (and arsenide) species, $[\text{Me}_3\text{NAl}\{(\text{P or As})(\text{mesityl})_2\}\text{H}_2]$ [53] and an amidogallane $[(\text{H}_2\text{Ga-}\mu\text{-NH}_2)_3]$ [54]. Theoretical studies on the geometries, stabilities and bond energies of $[\text{H}_2\text{MEH}_2\text{M}'\text{H}_2\text{E}'\text{H}_2]$, $\text{M, M}' = \text{Al or Ga}$, $\text{E, E}' = \text{P or As}$, cyclic species are also noteworthy [55].

The chlorogallane $[\text{Cy}_3\text{PGaH}_2\text{Cl}]$ is thermally robust (dec. $> 164^\circ\text{C}$) as is the dichlorogallane $[\text{Cy}_3\text{PGaHCl}_2]$ (dec. $> 184^\circ\text{C}$). Both are accessible by redistribution reactions involving $[\text{Cy}_3\text{PGaH}_3]$ and $[\text{Cy}_3\text{PGaCl}_3]$ and via anhydrous HCl reacting

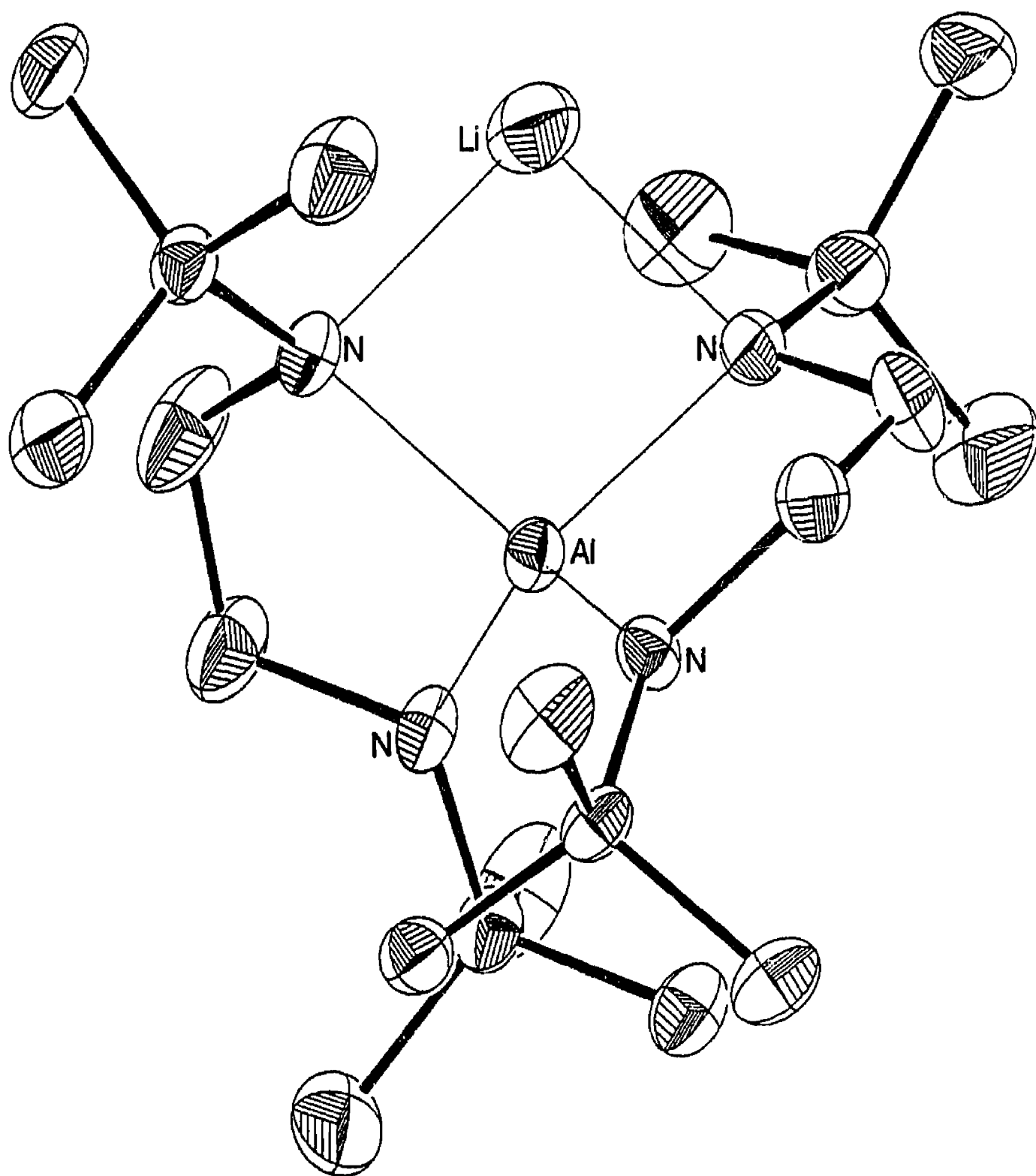


Fig. 10. Molecular structure of $[\text{Li}\{\text{N}(t\text{-Bu})\text{CH}_2\text{CH}_2\text{N}t\text{-Bu}\}_2\text{Al}]$. For clarity hydrogen atoms are omitted.

with $[\text{Cy}_3\text{PGaH}_3]$. Similar compounds have been prepared for the trimethylamine adduct system [56]. The reaction of $[\text{Cy}_3\text{PGaH}_3]$ with HgCl_2 (ratio 1:2) affords a mixture of compounds, $[\text{Cy}_3\text{PGaH}_n\text{Cl}_{3-n}]$, $n=1-3$. In contrast the aluminium analogue $[\text{Cy}_3\text{PAIH}_2\text{Cl}]$ is readily prepared by reacting $[\text{Cy}_3\text{PAIH}_3]$ with HgCl_2 [57]. Lewis base free chlorogallane, $[\text{GaH}_2\text{Cl}]_2$, is accessible from GaCl_3 and Me_3SiH , but it requires stringent synthetic requirements including exclusion of air, and it decomposes at room temperature [58].

In benzene solvents containing mixtures of $[\text{Cy}_3\text{PGaH}_n\text{Cl}_{3-n}]$, $n=1-3$, there is no chloride/hydride redistribution between the $[\text{MH}_3\text{Cl}_{3-n}]$ moieties, unlike in

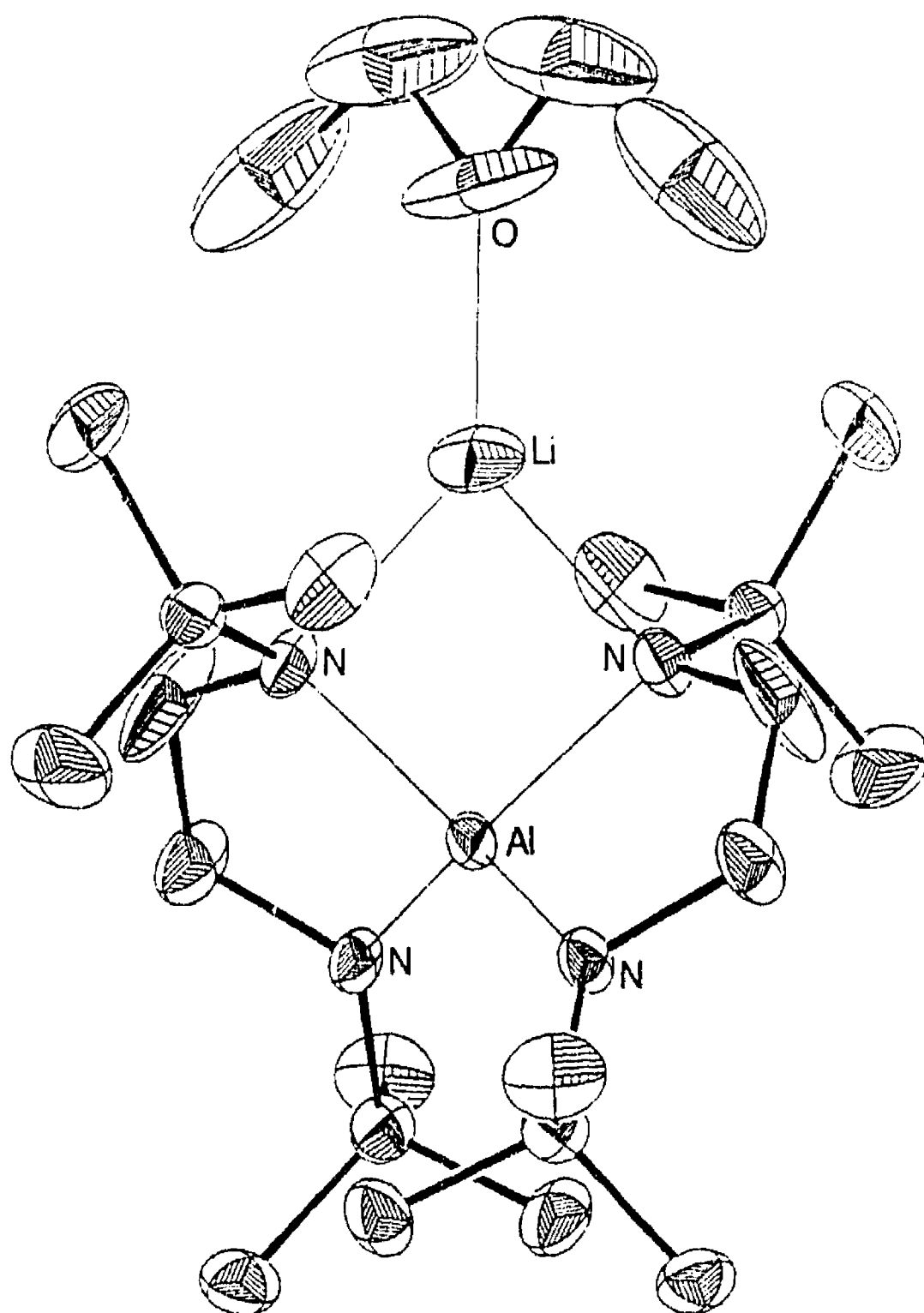


Fig. 11. Molecular structure of $[\text{Et}_2\text{OLi}\{\text{N}(t\text{-Bu})\text{CH}_2\text{CH}_2\text{N}(t\text{-Bu})_2\text{Al}]$. For clarity hydrogen atoms are omitted.

THF. However, in both benzene and toluene, phosphine exchange prevails. The ^{31}P NMR spectrum for an equimolar mixture of $[\text{Cy}_3\text{PGaH}_2\text{Cl}]$ and $[\text{Cy}_3\text{PGaH}_3]$ in toluene comprises a single resonance at 6.8 ppm. On cooling coalescence occurs at -50°C followed by two resonances at -80°C , corresponding to the two species, $[\text{Cy}_3\text{PGaH}_2\text{Cl}]$ and $[\text{Cy}_3\text{PGaH}_3]$ (Eq. (1), $k = 3.1 \times 10^3 \text{ s}^{-1}$, $\Delta G^\ddagger = 9.4 \text{ kcal mol}^{-1}$).



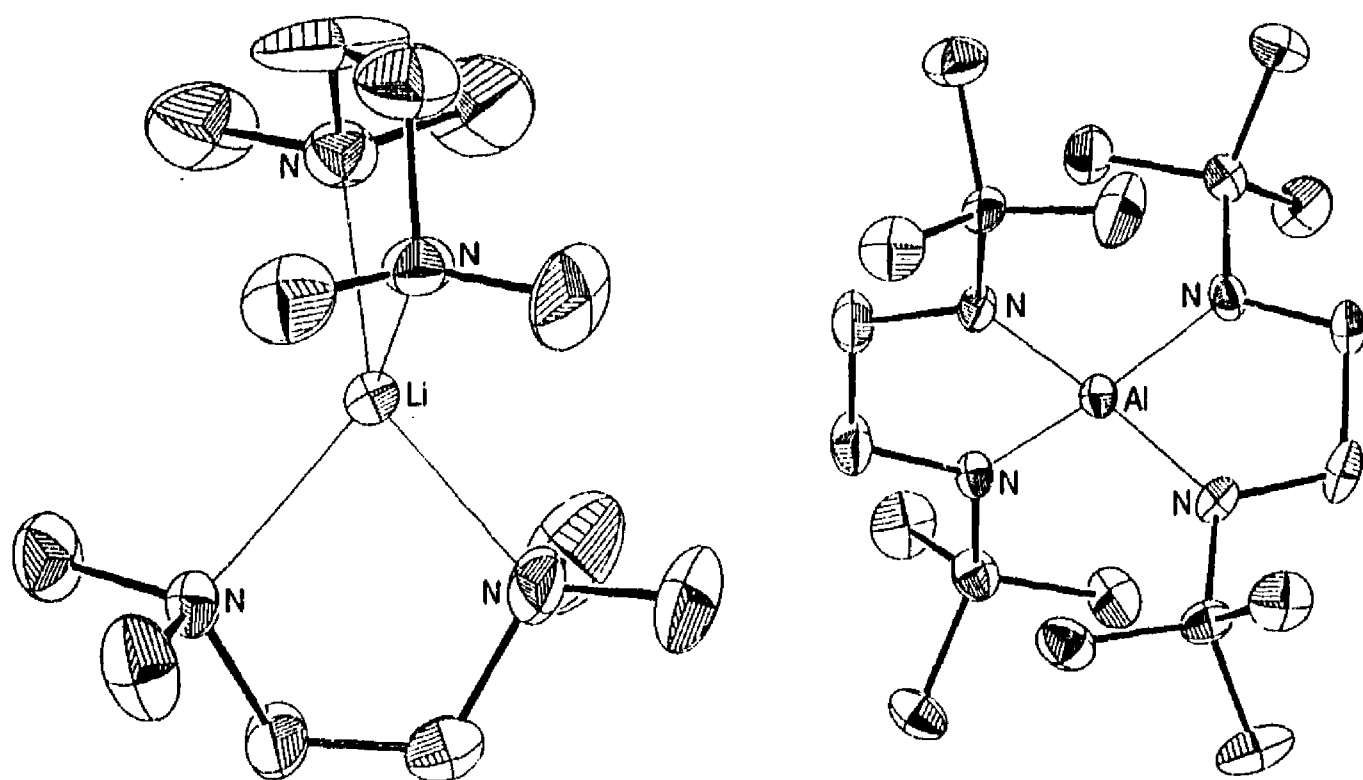


Fig. 12. Molecular structure of cation and anion of $[\text{Li}(\text{TMEDA})_2][\text{Al}\{\text{N}(t\text{-Bu})\text{CH}_2\}_2]_2$. For clarity hydrogen atoms are omitted.

5. Metal-group 16 complexes derived from alane and gallane

Reaction of $[\text{H}_3\text{AlNMe}_3]$ with $p\text{-Bu}^t\text{-calix[4]arene}$ yields a divergent receptor system arising from linking two calix[4]arenes through the O-rims by two metal centres, Scheme 8 [59]. Similarly trimethylaluminium completely metallates all the O-phenolic centres of calix[n]arene, $n=4$ [60], and Ref. [61], but now yielding aluminium rich monocalixarene species with some residual methyl groups attached to the metal centres. The divergent receptor molecule is a model system for the binding of calix[4]arene to aluminium oxide surfaces, and the reaction generating it relates to the use of $[\text{H}_3\text{AlNMe}_3]$ in removing surface hydroxyl groups of alkyl functionalised silica [62].

The symmetrical O-dimethylated calixarene, 1,3-dimethyl ether $p\text{-Bu}^t\text{-calix[4]arene}$, yields an isomeric mixture of monomeric five coordinate metalocalixarene species when treated with $[\text{H}_3\text{AlNMe}_3]$ in toluene [63]. Oxygen centres of the dimetallated calixarene are bound to the metal centre with the hydride either exo- or endo- to the cavity formed by the polyphenol, Scheme 8. The exo-isomer is converted to the thermodynamically favoured endo- in the presence of $[\text{H}_3\text{AlNMe}_3]$, with the chloro-analogue of the exo-isomer, formed exclusively from the reaction of the same calixarene with AlCl_3 , preferentially affording the exo-hydrido isomer when treated with NaH . The exo-hydrido isomer has been structurally authenticated for a single crystal, as has the analogous compound with a methyl group exo- to the cavity which is the only isomer formed on treating the same calixarene with AlMe_3 [60]. No reaction is evident when 1,3-dimethyl ether $p\text{-Bu}^t\text{-calix[4]arene}$ is treated with either two equivalents of $[\text{H}_3\text{GaNMe}_3]$, or with two equivalents of gallium trichloride.

The exo- to endo-isomerisation is unlikely to be an intramolecular process and

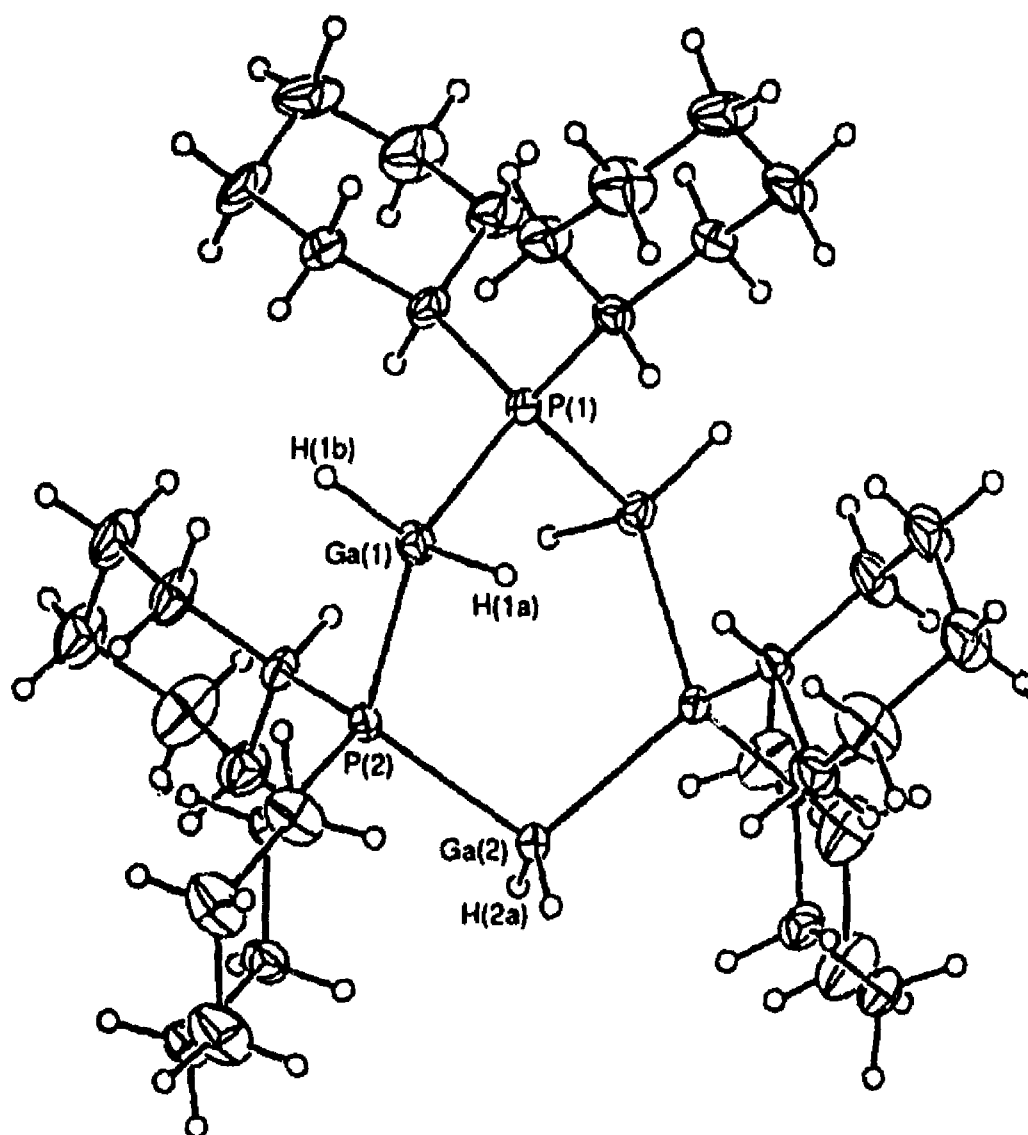
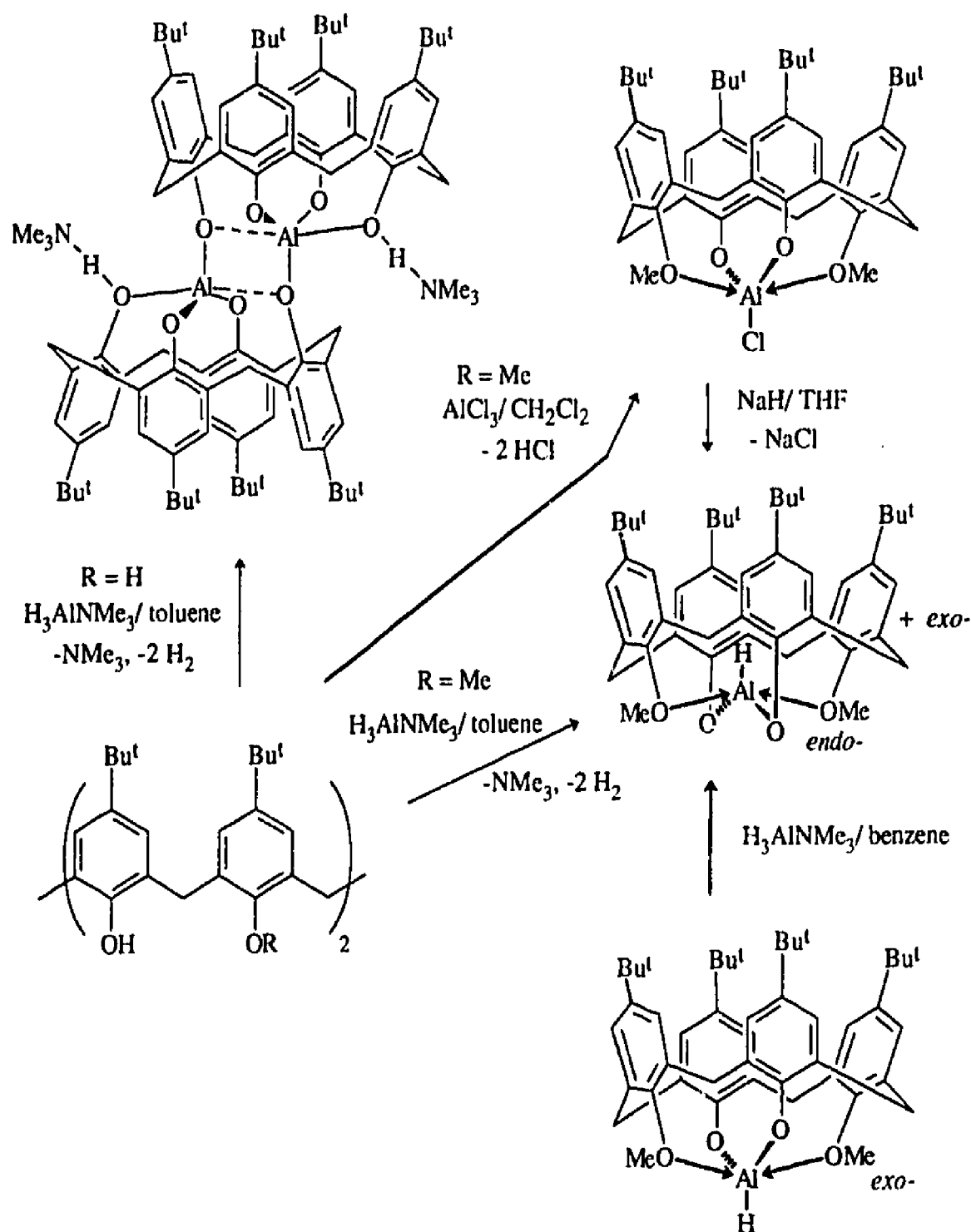


Fig. 13. Molecular structure of $[H_2Ga(\mu-PCy_2)]_3$ showing atom numbering schemes. Selected bond length (Å) and angles ($^\circ$). Ga1–P1 2.402(3); Ga2–P2 2.380(3); Ga1–P2 2.375(3) Ga1–H1 1.76(9) needs more.

may involve the formation of the ubiquitous $[AlH_4]^-$ species and an aluminium calixarene cation when formed from the exo-isomer in the presence of $[H_3AlNMe_3]$. The exo-isomer preferentially hydrolyses under mild conditions and forms an inclusion complex with methylene chloride, Fig. 14. Molecular mechanics of both isomers makes the endo-isomer 21 kcal mol^{-1} more favourable than the exo-isomer, in accordance with the kinetic versus thermodynamic considerations for both compounds.

Hydrometallation involving alane and gallane is of interest in organic synthesis and can result in novel structures. Reaction of $O=CBu_2^t$ with excess $[H_3MNMe_3]$, $M=Al$ or Ga , yields dimeric $[H_2M\{\mu-OC(H)Bu_2^t\}]_2$. For the aluminium compound association prevails in the solid via two symmetrical bridging hydrides between single aluminium centres from different dimers such that the metal centres are either four or five coordinate, as distorted tetrahedra or square pyramids, Scheme 9 [64]. Related dimeric compounds with bridging alkoxides have been prepared by the reaction of alane or gallane in OEt_2 with one equivalent of $HOBu^t$. A second equivalent gives similar dimeric species with one of the hydrides replaced by a terminal alkoxide [65]. In addition, the reaction of $[H_3AlNMe_3]$ with HOR,



Scheme 8.

$\text{R} = \text{C}_6\text{H}_2(\text{Bu}^t)_2 - 2,6 - \text{Me} - 4$ forms a monomeric species $[\text{H}_2\text{Al}(\text{OR})\text{NMe}_3]$ or its dimer involving hydride bridges in the solid state [66].

The use of alane and gallane in synthesis is worthy of mention in the context of hydrometallation/reduction in general and the difference in selectivity of the two reagents. Preliminary results show promise with $[\text{H}_3\text{GaNMe}_3]$ selectively reducing the carbonyl group in 4-bromophenacyl bromide, with $[\text{H}_3\text{Al}(\text{quinuclidine})]$ effecting the same reduction but with concomitant cleavage of the adjacent C–Br bond [67]. Related to this, is the combined metallation and reduction of 1,1,1,5,5,5-hexafluoropentane-2,4-dione using $[\text{H}_3\text{AlNMe}_3]$, the bi-metallic complex isolated being based on $^-\text{OC}(\text{CF}_3)=\text{CH}-\text{CH}(\text{CF}_3)\text{O}^-$, whereas for $[\text{H}_3\text{GaNMe}_3]$ selective reduction of both carbonyl groups prevails yielding a bi-metallic complex but now based on *rac*- $^-\text{OCH}(\text{CF}_3)-\text{CH}_2-\text{CH}(\text{CF}_3)\text{O}^-$ [68]. Indiscriminate C–O

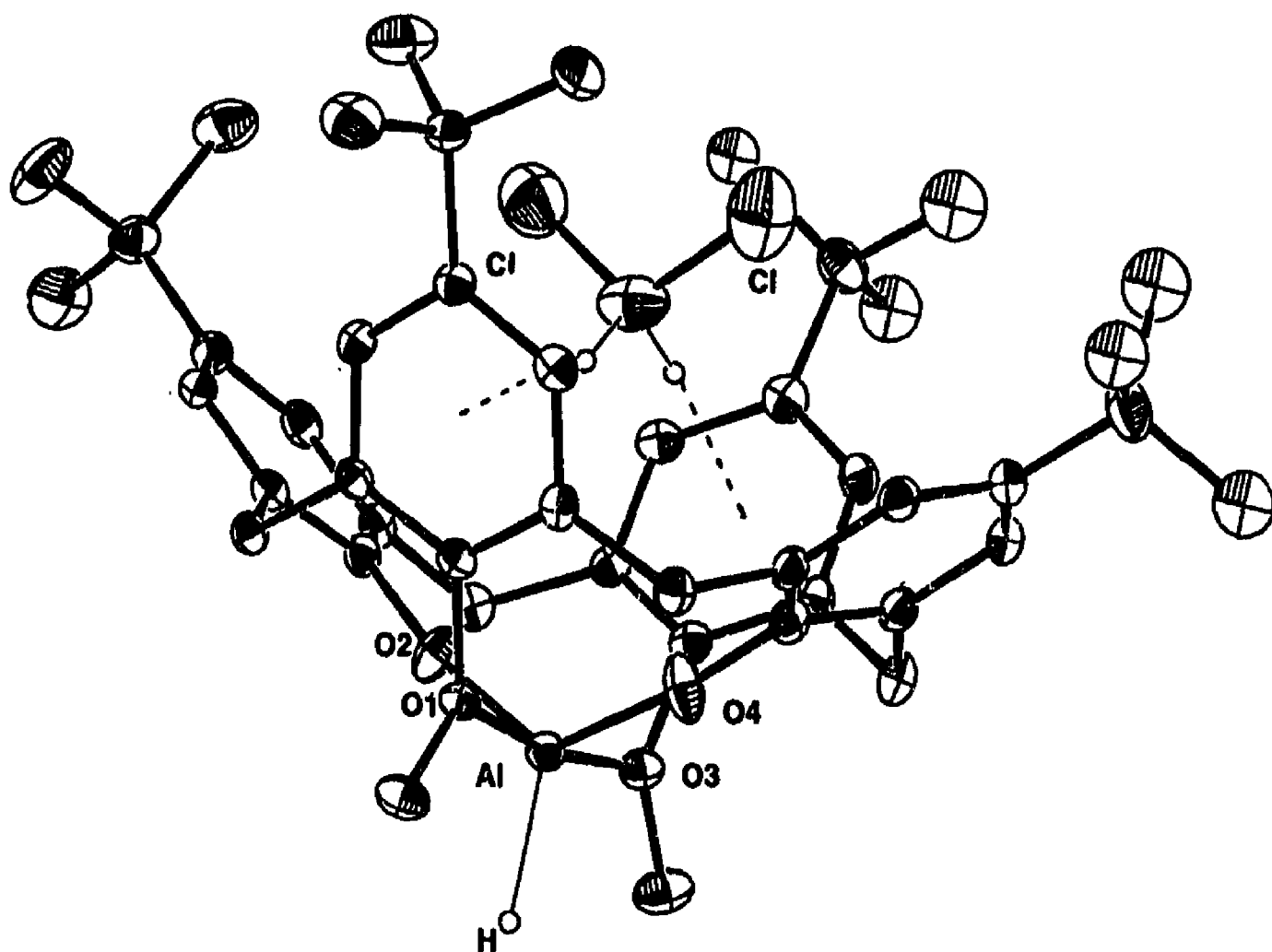
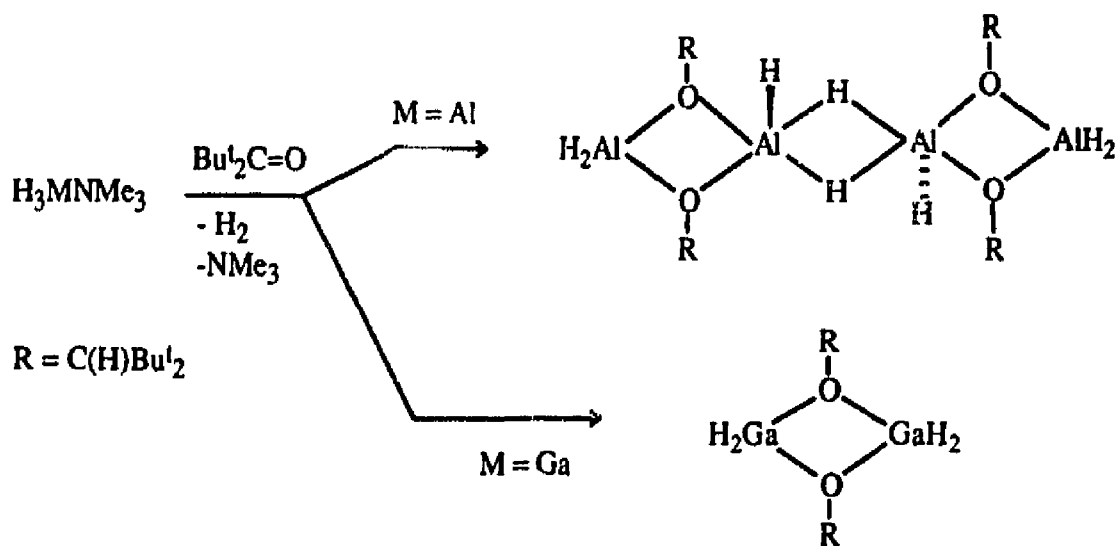


Fig. 14. Exo-isomer of the product derived from reaction of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene with [H₃AlNMe₃], with a methylene chloride in the cavity.



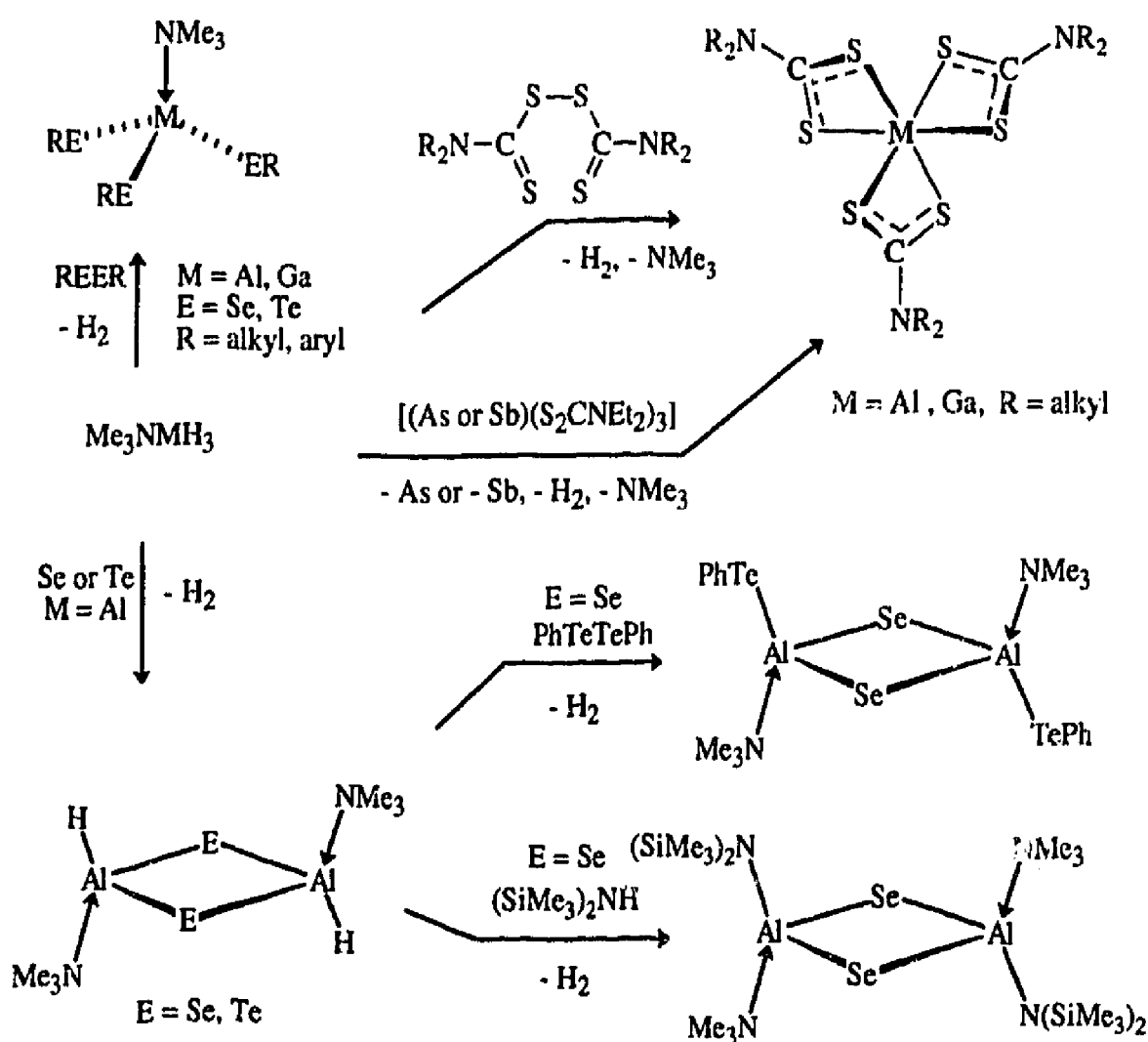
Scheme 9.

cleavage of styrene oxide occurs in the presence of [H₃Al(quinuclidine)], but with [H₃GaPCy₃] regio-selective C–O cleavage ensures at the secondary C-centre [67]. Functional group reduction using [H₃AlNEt₃] has been explored [69].

Treatment of 2-diethylaminoethanethiol hydrochloride with LiMH₄, M = Al, Ga, in OEt₂ or THF generates the five coordinate species [HM(SCH₂CH₂NEt₂)₂], M = Al or Ga, authenticated as isostructural, chiral five coordinate species in the solid,

with N-donor groups occupying apical positions of trigonal bipyramidal metal centres [7].

Cleavage of E–E bonds, E = S, Se or Te, in di-organo-dichalcogens or in the element themselves by alane or gallane is a simple way of generating mixed group 13/16 compounds. Such compounds are in general of interest as potential precursors for generating films of binary metal chalcogenides with useful electronic and optoelectronic properties [70], and as selective reagents in synthesis [71]. Reaction of $(ER)_2$, E = Se or Te, with $[H_3MNMe_3]$, M = Al or Ga, yields trimethylamine adducts of the tris(selenolato- or tellurolato-)metal(III) species, $[Me_3NM(ER)_3]$, M = Al, E = Se, R = Et, Ph, CH_2Ph , E = Te, R = Ph; M = Ga, E = Se, R = Ph, Scheme 10 [72]. These are four coordinate, monomeric species. The mechanism of the reaction yielding hydrogen as the byproduct is complex but most likely proceeds via initial complexation of a group 16 donor yielding a hypervalent metal centre which is common for alane, and only transient species for gallane. Contrary to the literature, bulky groups attached to group 13 metal centres are not essential to gain access to low order aggregates of chalcogenidoaluminium(III) species, at least in the presence of a Lewis base; rather a small hydrido group and a trimethylamine attached to the metal centre are seemingly more effective in limiting the degree of association to dimeric species, cf. tetramers for bulky alkyl groups [73]. Related to this chemistry is the formation of Bu_2AlER (R = alkyl, E = S, Se, Te) from $(ER)_2$ using Bu_2AlH [74].



Scheme 10.

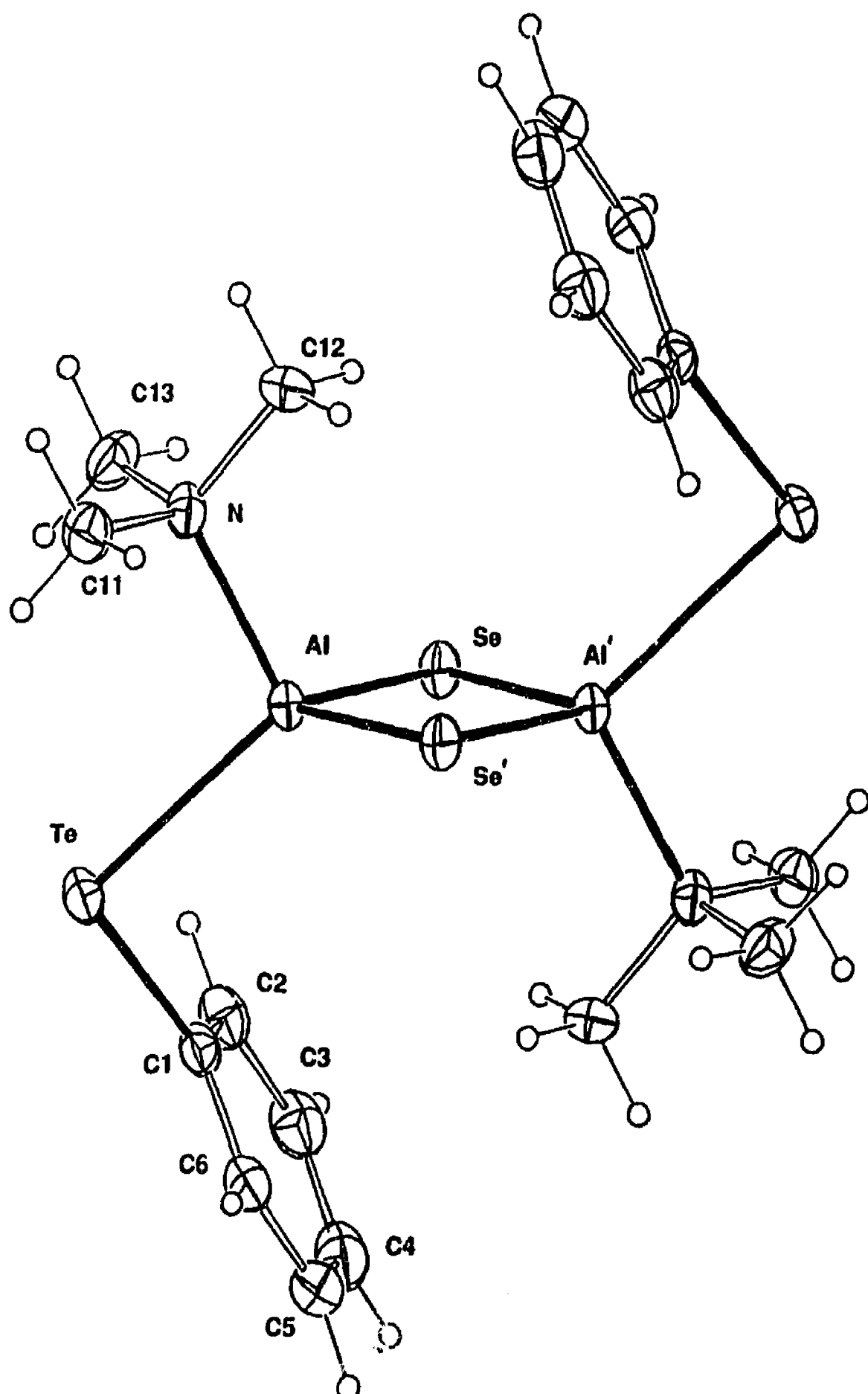


Fig. 15. Crystal structure of *trans*-[(Me₃N(PhTe)Al(μ-Se))₂]. Selected distances [Å] and angles [°]: Al–Te 2.610(2); Al–Se 2.359(2); Al–Se' 2.347(2); Al–N 1.951(5); Te–Al–Se, N, Se' 117.16(7), 102.1(1), 117.31(7); Se–Al–N, Se' 107.2(2), 103.63(6); Se–Al–Se' 103.9(2); Al–Se–Al' 76.37(6).

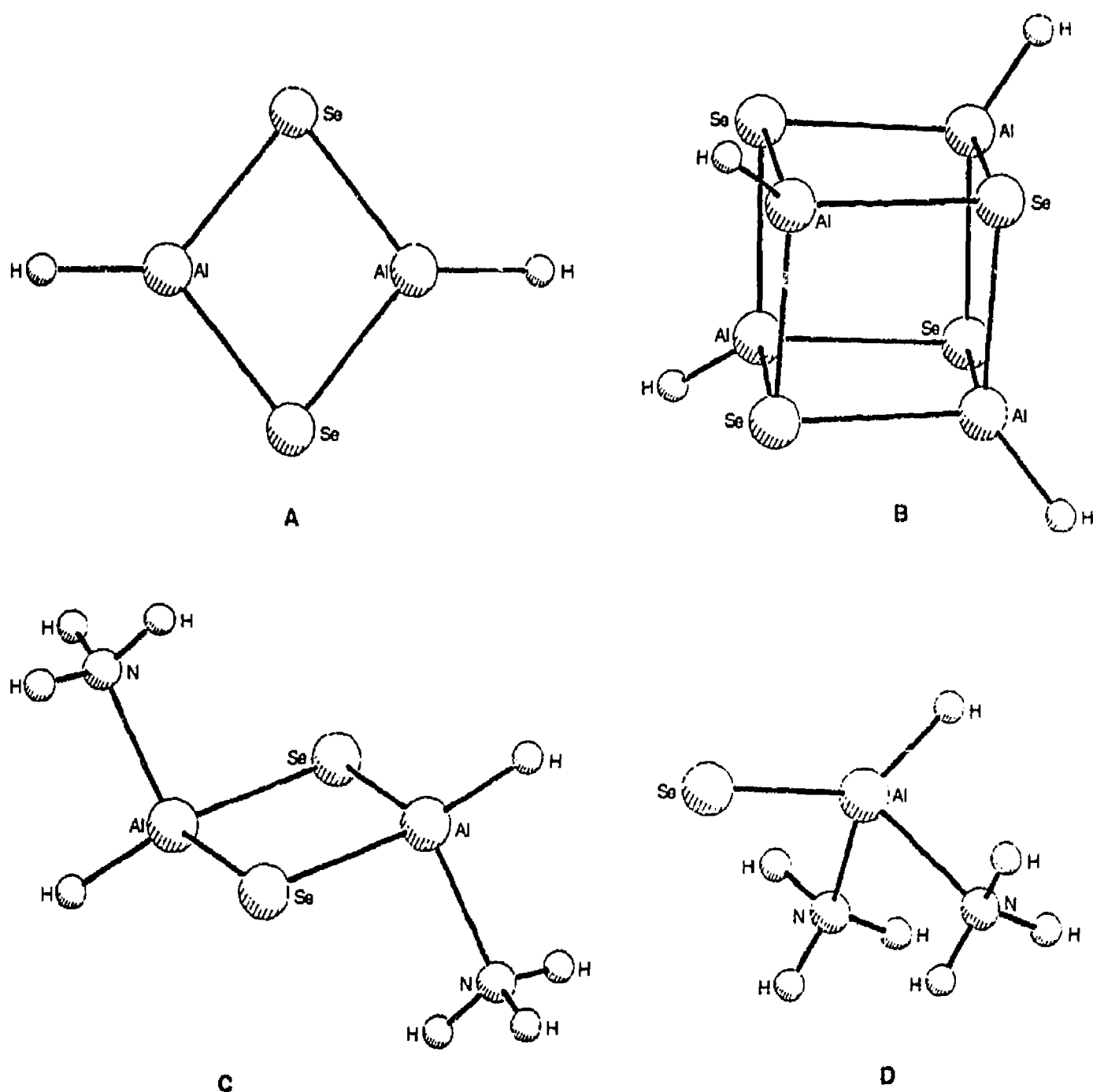


Fig. 16. Computed structures of model chalcogenidoalanes. (A) $[\{HAl(\mu-Se)\}_2]$, (B) $[\{HAl(\mu_3-Se)\}_4]$, (C) $[\{H_3N(H)Al(\mu-Se)\}_2]$, (D) $[(H_3N)_2(H)AlSe]$.

Thiuram disulfide, $(Et_2NCS_2)_2$ reacts with $[H_3MNMe_3]$, $M = Al$ or Ga , to give the corresponding tris(dithiocarbamato)metal(III) species, Scheme 10. The same products are also formed for the reaction of these hydrides with tris(dithiocarbamato)arsenic- or antimony-(III), with the extrusion of elemental arsenic or antimony [75].

Elemental selenium or tellurium react with $[H_3AlNMe_3]$ in toluene affording the bis-trimethylamine adduct of the dimeric chalcogenidoalane, $[\{HAl(\mu-E)\}_2]$ isolated as the *trans*-isomer, $E = Se, Te$, Scheme 10 [76]. These reactions offer a direct route to a new class of compound under mild conditions and in modest yield. The compounds can be regarded as tertiary amine stabilised adducts of the simplest selenido- and tellurido-aluminium(III) species. Reaction of *trans*- $[\{Me_3N(H)Al(\mu-Se)\}_2]$ with Ph_2Te_2 gives the novel mixed chalcogen species, *trans*- $[\{Me_3N(PhTe)Al(\mu-Se)\}_2]$, Fig. 15, or with $HN(SiMe_3)_2$ the mixed chalcogen/

amide species, *trans*-[$\{\text{Me}_3\text{N}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Al}(\mu\text{-Se})\}_2]$, Scheme 10. Elemental Se or Te with $[\text{H}_3\text{GaNMe}_3]$ results in decomposition to elemental gallium [75].

Ab initio molecular orbital calculations on model species relevant to the above dimers have been performed, albeit for NH_3 rather than NMe_3 , with the computed structures for selenium shown in Fig. 16. The calculations show that N-donor Lewis base solvated dimeric species are the most favourable products of the species investigated for both the selenide and telluride cases. Further association of the unsolvated dimers, $[\{\text{HAl}(\mu\text{-E})\}_2]$, to tetramers, $[\{\text{HAl}(\mu_3\text{-E})\}_4]$, gives association energies of -10.17 ($\text{E}=\text{Se}$) and -5.42 kcal mol^{-1} ($\text{E}=\text{Te}$). The formation of Lewis base solvated dimers, $[\{\text{H}_3\text{N}(\text{H})\text{Al}(\mu\text{-E})\}_2]$, from the unsolvated dimers has association energies of -32.51 ($\text{E}=\text{Se}$) and -30.80 kcal mol^{-1} ($\text{E}=\text{Te}$). The monomeric species bearing two Lewis base donors, $[(\text{H}_3\text{N})_2(\text{H})\text{AlE}]$, are 12.29 ($\text{E}=\text{Se}$) and 5.53 kcal mol^{-1} ($\text{E}=\text{Te}$) less stable than the Lewis base solvated dimers and free amine.

6. Conclusion

Recent developments in the chemistry of Lewis base adducts of alane and gallane have been driven mainly by their possible applications in synthesis and materials science. Significant differences between the chemistry of these adducts have emerged which relate to (a) the ability of alane but not gallane to readily form hyper-valent species, gallium achieving four-fold coordination whereas aluminium prefers five-fold coordination; (b) the frailty of the Ga–H bond relative to the Al–H bond; and (c) the polarising influence/back bonding participation of the d^{10} core for gallium.

Exploitation of the different reactivities of various functional groups towards alane and gallane has yet to be realised; our preliminary observations clearly show that gallane has greater selectivity over alane. This may also prevail for other types of aluminium and gallium hydrides. Developing single source precursors for CVD technology including heterobimetallic species capable of delivering metal alloys has its merit, as has the use of hydrides in surface modification, both in wet chemistry and under UHV conditions. Incorporating trimethylsilyl groups into ligands attached to aluminium and gallium has scope in CVD technology in assisting the degradation process via elimination of trimethylsilane.

Alane and gallane adducts of arsine and stibine, and of the heavier group 16 elements have yet to be developed. Then there is the reaction of alane and gallane in general with other main group elements, beyond the limited work to date on the reaction of selenium and tellurium with alane. Alane has been used to form novel calixarene complexes within the realms of supramolecular chemistry. Further advances here are likely in the area of generating other divergent receptor molecules with oxo-metal clusters at the base of two or more calixarenes.

Application of theoretical chemistry to give insight into synthetic targets has been shown to be a powerful research tool. Indeed, this approach may prove useful in the major challenge of developing metal hydride chemistry of indium.[37,47,50]

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