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Syntheses of some bulky alkylalanes and alkyltrihydroaluminates: crystal structures of $[Li(THF)_2AlH_3C(SiMe_3)_2(SiMe_2NMe_2)]_2$, $Li(THF)_2Al_2H_5\{C(SiMe_3)_3\}_2$, $(Me_3Si)_3CAlH_2{\cdot}THF$ and the pyrazolato derivative $[LiAlH(C_3H_3N_2)_2C(SiMe_3)_3]_2$ (THF = tetrahydrofuran)

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Dedicated to Professor S. Pasynkiewicz in recognition of his notable contributions to organometallic chemistry, especially the chemistry of organoaluminium compounds, and of his work for the Federation of European Chemical Societies.

Abstract

The alkylaluminate $[Li(THF)_2AlH_3C(SiMe_3)_2(SiMe_2NMe_2)]_2$ (**3**), obtained by the reaction between $[LiC(SiMe_3)_2(SiMe_2NMe_2){\cdot}2THF]$ and $LiAlH_4$, has a cyclic structure like those of the compounds $[Li(THF)_2AlH_3R]_2$ ($R = C(SiMe_3)_3$ (**1**), or $C(SiMe_2Ph)_3$ (**2**)). The Al and Li atoms are linked by hydride bridges and the NMe_2 groups are not coordinated to metal centres. The compound **1** reacts (i) with one equivalent of $SiMe_3Cl$ to give the cyclic dialuminate $\overline{\mathrm{Li(THF)2(\mu\text{-}H)AlHR(\mu\text{-}H)AlHRH}}$ (**4**) (characterised by an X-ray study); (ii) with two equivalents of $SiMe_3Cl$ to give the alane–THF complex $(Me_3Si)_3CAlH_2{\cdot}THF$ (**5**); and (iii) with an excess of pyrazole to give $[LiAlH(C_3H_3N_2)_2C(SiMe_3)_3]_2$ (**7**), in which Al and Li atoms are linked by both hydride and pyrazolato bridges. The compound $(Me_2PhSi)_3CAlH_2{\cdot}THF$ (**6**) has been obtained by the reaction of **2** with two equivalents of $SiMe_3Cl$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkylalanes; Aluminium; Lithium; Pyrazolato

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1. Introduction

The selectivity of lithium tetrahydroaluminate, $LiAlH_4$, as a reducing agent in organic chemistry can be modified by the introduction of bulky substituents in place of hydrogen [1]. Alkyltrihydroaluminates are normally difficult to isolate because the species $[AlRH_3]^-$ readily rearrange in solution to give $[AlR_2H_2]^-$ and $[AlH_4]^-$ [2]. However, when the organic groups are large, stable alkyl- [3] and aryltrihydroaluminates [4] can be obtained, and these prove to be excellent reagents for the syntheses of further organoaluminium compounds [5,6]. In this paper we describe the synthesis and structure of the alkyltrihydroaluminate $[Li(THF)_2AlH_3C(SiMe_3)_2(SiMe_2NMe_2)]_2$ (**3**). We also describe the conversion of the alkyltrihydroaluminates $[Li(THF)_2AlH_3R]_2$, $R = C(SiMe_3)_3$ (**1**) or $C(SiMe_2Ph)_3$ (**2**), into the alkylalane–THF adducts **5** and **6** (THF = tetrahydrofuran). The few monoorganoalanes $RAlH_2$ that were described previously were all aryl derivatives, with $R = 2,4,6\text{-}Bu^t_3C_6H_2$ [6], $2,6\text{-}Mes_2C_6H_3$ (Mes = $2,4,6\text{-}Me_3C_6H_2$), $2,6\text{-}Trip_2C_6H_3$ (Trip = $2,4,6\text{-}Pr^i_3C_6H_2$) [4], $2\text{-}Me_2NC_6H_5$ [7], or $2,6\text{-}(Me_2N)_2C_6H_3$ [8], and the first in particular has been the source of much interesting chemistry [9]. The compounds **5** and **6** are the first monoalkylalanes to be characterised. The conversion of the compound **1** into **5** proceeds via the novel diorganodialuminate **4**, which has been structurally characterised. The pyrazolato compound **7**, in which the THF

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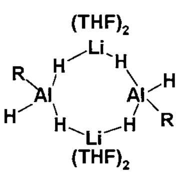
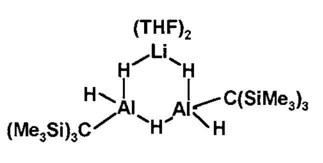
has been excluded from the coordination sphere of both lithium and aluminium, was obtained by treatment of the compound **1** with pyrazole.



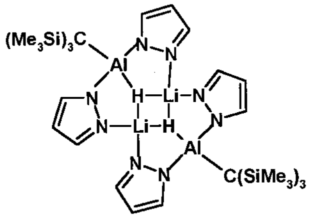


1 R = C(SiMe$_3$)$_3$, **2** R = C(SiMe$_2$Ph)$_3$ **4**

3 R = C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)

RAlH$_2$.THF

5 R = C(SiMe$_3$)$_3$, **6** R = C(SiMe$_2$Ph)$_3$



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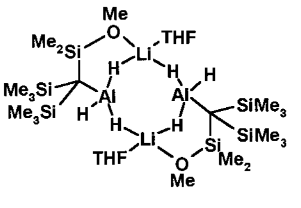

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2. Results and discussion

2.1. *Trihydroaluminates* ***1–3***

The syntheses of compounds **1** and **2** (Eq. (1)) have been described [3].

$$\mathrm{LiAlH_4 + LiR/THF \rightarrow Li(THF)_2AlH_3R + LiH} \qquad (1)$$

We made the dimethylamino compound **3** because we were intrigued to know whether it would adopt a structure like that of the methoxy analogue [Li(THF)AlH$_3$C(SiMe$_3$)$_2$(SiMe$_2$OMe)]$_2$ (**8**) [10], in which the lithium and aluminium centres are bridged by both hydride and the C–Si–O chain of the ligand. Compound **8** was previously reported to be monomeric [10], but closer examination of the crystal packing shows that it is better described as dimeric. The bond lengths and angles in the Li···H–Al bridges linking the Li(THF)AlH$_3$C(SiMe$_3$)$_2$(SiMe$_2$OMe) units are Al–H 1.65(7), Li–H 1.95(7) Å and Li–H–Al 162(4)°.

The synthesis of **3** was straightforward and crystals suitable for an X-ray structure determination were obtained from light petroleum. The structure showed considerable disorder within the organic groups, so we do not discuss the bond lengths and angles in detail. It is, however, clear that the structure is dimeric like those of the other lithium trihydroaluminates that have been characterised [3,4], with the NMe$_2$ groups not coordinated to Li unlike the OMe groups in **8**. The structure is shown in Fig. 1. The puckered eight-membered central ring is like that in **2**, i.e. the aluminium atoms are bent sharply out of the mean ring plane to give a chair conformation with the bulky alkyl substituents pointing in opposite directions. In contrast, the ring in the compound [Li(Et$_2$O)$_2$AlH$_3$N(SiMe$_3$)$_2$]$_2$ [11], containing the less sterically demanding N(SiMe$_3$)$_2$ group, is planar. We have not made any cryoscopic measurements but ^{6}Li nuclear Overhauser effect (nOe) experiments [12] and decoupled difference spectra show that the Li···H – Al bridges, and therefore probably the dimeric structure, are maintained in benzene solution. There is no indication that the Li atoms are near the protons of the NMe$_2$ groups. There is no simple explanation of

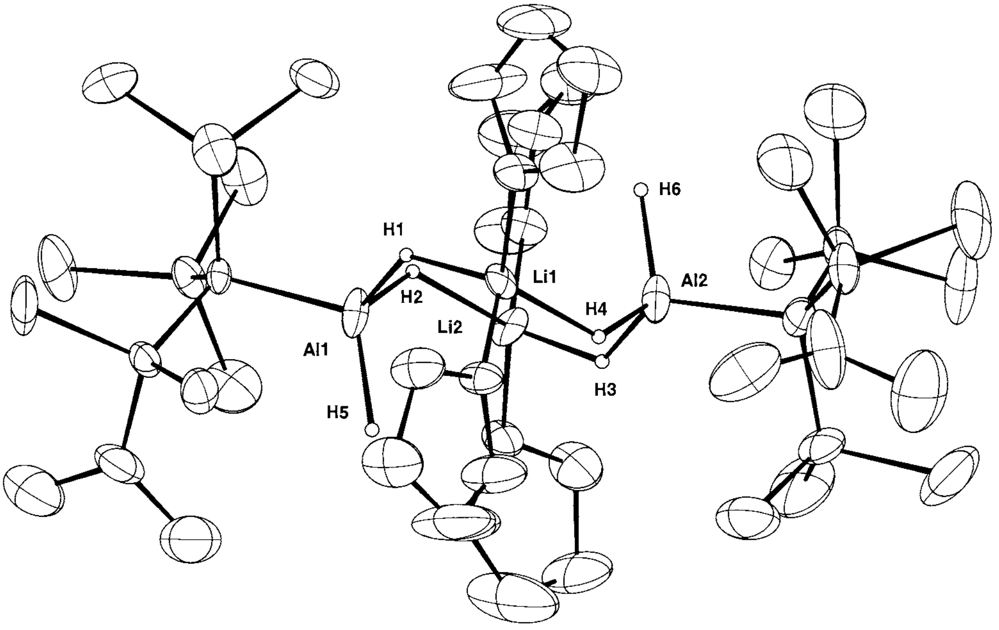

Fig. 1. Molecular structure of [Li(THF)$_2$AlH$_3$C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)]$_2$ (**3**).

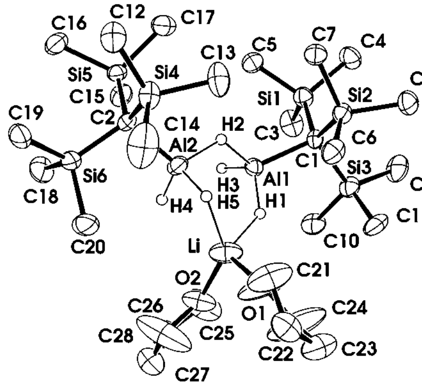

Fig. 2. Molecular structure of $Li(THF)_2Al_2H_5\{C(SiMe_3)_3\}_2$ (**4**).

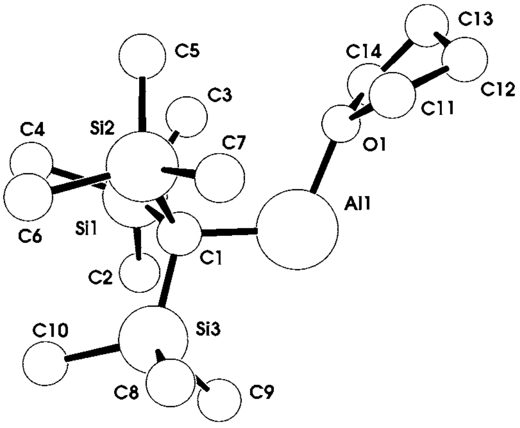

Fig. 3. Molecular structure of $(Me_3Si)_3CAlH_2{\cdot}THF$ (**5**).

why the NMe_2 group in **3** is not coordinated to lithium whereas the OMe group in **8** is. The gas-phase lithium affinity of dimethylamine is greater than that of methanol [13], so it would be expected that the ligand bearing the dimethylamino group would coordinate more strongly than that bearing methoxy. However, this is not the only factor in determining relative stabilities; in a chelate ring like that in **8**, the replacement of the $SiMe_2OMe$ group having planar coordination at oxygen by an $SiMe_2NMe_2$ group having pyramidal coordination at nitrogen leads to near-eclipsed methyl substituents on adjacent nitrogen and silicon atoms. It is probable that this destabilises the bridge structure for the NMe_2 derivative. It is noteworthy that in the compounds $(THF)_2\overline{LiC(SiMe_3)_2(SiMe_2X)}$, X = OMe [10] or NMe_2 [14], the endocyclic Li–C and Si–C bond lengths in the two compounds are similar but the Li–N and Si–N bond lengths (2.162(8) and 1.796(4) Å, respectively) are significantly larger than the Li–O and Si–O bond lengths (1.933(11) and 1.684(4) Å).

*2.2. Syntheses of the organoalanes **5** and **6***

When $SiMe_3Cl$ was added to a solution of compound **1** in toluene, a white precipitate of LiCl was formed immediately. This was filtered off and the NMR spectra of the filtrate suggested that it contained solely the alane **5**. The experiment was repeated with a sample of **1** made by the reaction shown in Eq. (1) but used without recrystallisation. The main product was again **5** but there was an impurity that gave a similar set of NMR signals. The impurity was separated from the main product **5** by fractional crystallisation and an X-ray study showed that it was compound **4**, a lithium complex of a hydride-bridged dialuminate anion. This suggests that it is an intermediate in the reaction sequence (2) and persists when there is a deficiency of $SiMe_3Cl$ in the reaction mixture.

$$\underset{\mathbf{1}}{[\mathrm{Li(THF)_2AlH_3R}]_2} + \mathrm{SiMe_3Cl} \rightarrow \underset{\mathbf{4}}{\mathrm{Li(THF)_2Al_2H_5R_2}} + \mathrm{LiCl} + \mathrm{SiHMe_3} \tag{2a}$$

$$\underset{\mathbf{4}}{\mathrm{Li(THF)_2Al_2H_5R_2}} + \mathrm{SiMe_3Cl} \rightarrow \underset{\mathbf{5}}{\mathrm{2AlRH_2{\cdot}THF}} + \mathrm{LiCl} + \mathrm{SiHMe_3} \tag{2b}$$

$$\mathrm{R = C(SiMe_3)_3}$$

We suggest that when samples of **1** are prepared by reaction (1) some lithium hydride cocrystallises with the product and that this reacts with $SiMe_3Cl$ faster than the intermediate **4**. The measured stoichiometry is therefore upset. The occluded LiH can be largely removed by repeated recrystallisation of **1** from light petroleum.

The reaction between the phenyl-substituted compound **2** and $SiMe_3Cl$ proceeds more cleanly to give good yields of the alane–THF adduct **6**.

*2.3. Structures of the compounds **4** and **5***

A satisfactory data set was collected from compound **5** but the structure proved to be extensively disordered. Bond lengths and angles are therefore unreliable and are not discussed further, but the atom connectivity, shown in Fig. 3, is quite clear. The compound is a THF adduct like those of the analogous dihalides [5c, 15a]. In spite of the large size of the $C(SiMe_3)_3$ group there is enough room around the aluminium to allow for the coordination of THF. The structure stands in contrast to those of the previously reported compounds $[RAlH_2]_2$, R = 2,4,6-$Bu^t_3C_6H_2$ [6], 2,6-$Mes_2C_6H_3$ or 2,6-$Trip_2C_6H_3$ [4], in which the steric requirements of the large planar aryl ligands are such that the THF is forced out of the coordination sphere of the aluminium.

There was much less disorder in the structure of **4** so that the hydrogen atoms attached to aluminium could be located. The structure is shown in Fig. 2 and bond lengths and angles are given in Table 1. The bond lengths within the central severely puckered six-membered ring are similar to those in **2** [5c] and in the related compounds $[Li(THF)_nAlH_3R]_2$ (R = 2,4,6-$Ph_3C_6H_2$, $n = 1.5$ or R = 2,4,6-$Bu^t_3C_6H_2$, $n = 2$) [4a], $[Li(TMEDA)AlH_4]_2$ (TMEDA = tetramethylethylenediamine) [12], and some complex lithium arylamido-substituted aluminates [15c]. The endocyclic and exocyclic Al–H bond lengths are the same within experimental error, showing that the AlH_3 fragment is little distorted by coordination to lithium. The large alkyl groups attached to aluminium are *trans* with respect to the mean ring plane. Intramolecular steric strain is shown by the variation in Al–C–Si angles indicating that the CSi_3 ligand cores are bent away from the Al–C axis. The long Li–H bonds and the wide range of H–Li–H angles in **4** and cyclic trihydroaluminates generally suggest that the lithium fragments are more weakly bound within the ring than are the aluminium fragments. We have previously described the diindium species corresponding to **4**, but the poor quality of the X-ray data meant that the endocyclic hydrogen atoms could not be located and this precluded discussion of the configuration of the central ring [16]. We are not aware of any previously characterised diorganodialuminate; the silver and potassium salts of the $[Al_2F_5\{C(SiMe_3)_3\}_2]^-$ anion have been described [15], but these have crystal structures quite different from that of the dialkylpentahydrodialuminate described here.

2.4. The pyrazolato compound **7**

In view of the widespread use of tris(pyrazolyl)borates as ligands in coordination chemistry [17], we considered that the synthesis of compounds containing related tridentate, lipophilic, anionic ligands $[RAl(C_3H_3N_2)_3]^-$ would be of interest. Though we have not yet succeeded in this aim, we have obtained a bis(pyrazolyl) derivative **7** by treatment of the trihydroaluminate **1** with three equivalents of pyrazole. The presence of a residual Al–H function has been demonstrated by IR spectroscopy, and an X-ray study has confirmed the molecular structure.

Table 1
Selected bond lengths (Å) and angles (°) for $Li(THF)_2$-$Al_2H_5\{C(SiMe_3)_3\}_2$ (**4**)

Bond lengths			
Al–C [a]	1.990(5)		
Al1–H1	1.56(4)	Al1–H2	1.74(4)
Al2–H2	1.67(4)	Al2–H5	1.48(5)
Al1–H3	1.62(5)	Al2–H4	1.51(6)
Li–H1	2.00(5)	Li–H5	1.87(4)
Li–O1	1.864(11)	Li–O2	1.909(11)
C1,2–Si [a]	1.881(5)	Si–Me [a]	1.880(6)
Bond angles			
Li–H1–Al1	139(3)	H2–Al2–H5	100(2)
H1–Al1–H2	97(2)	Al2–H5–Li	108(3)
Al–H2–Al2	123(2)	H5–Li–H1	90(2)
Al1–C1–Si1	105.6(2)	Al2–C2–Si4	108.5(2)
Al1–C1–Si2	110.3(2)	Al2–C2–Si5	108.7(2)
Al1–C1–Si3	103.6(2)	Al2–C2–Si6	104.0(2)
C–Al–H [a]	115(2)	Si–C–Si [a]	112.0(3)
Me–Si–Me [a]	105.9(7)	C–Si–Me [a]	112.7(3)

[a] Average value with precision of individual measurements indicated in parentheses.

The structure is shown in Fig. 4, and the most important bond lengths and angles are given in Table 2. The species in the solid state are centrosymmetric dimers in which each aluminium is linked to two lithium centres by mixed pyrazolato–hydride bridges similar to the mixed bridges in **8**. The hydride–pyrazolato bridges are arranged on either side of the planar Li_2H_2 ring so that bulky substituents at aluminium point away from the centre of the molecule. The positions of the hydrogen atoms are not located precisely enough to reveal whether the Li–H bond length (1.99(4) Å) is significantly longer than those in $LiAlBu^t_3H$ (1.92(3) Å) [18] or **2** (1.93(4) Å). The Al–C, Al–N and Li–N [19] bond lengths appear to be normal. The C–N bond lengths in the two independent pyrazole rings are identical within experimental error and show that the shorter, more electron-rich, C–N bonds are adjacent to lithium. The corresponding C–C bonds in the independent rings are also identical. The angles at lithium are highly distorted from tetrahedral with N–Li–N 142° and H–Li–H 86°. The configuration at aluminium is much less distorted, but the C–Al–N angles (118–119°) are well above and the N–Al–H angles (100°) well below the tetrahedral value, probably as a consequence of intramolecular steric repulsion from the bulky silyl-substituted alkyl groups. The Si–C–Si, Me–Si–Me and C–Si–Me angles are also normal. In compounds **2**, **4** and **7**, the Si–C1 and Si–Me bonds lengths are similar, as expected from the previously established relation between bond lengths in compounds containing the $M–C(SiMe_3)_3$ fragment and the electronegativity of M [20]. The shortest Li···Me contact (to C9) is 3.38 Å, so there is no evidence for so-called agostic interactions that have been much discussed [19,21].

It is noteworthy that although compound **7** was made in the presence of THF, there is no coordinated THF in the crystalline product. We noted previously [12b] that when the compound $[Li(TMEDA)_2][AlH_4]$ (which contains separated cations and anions in the solid state) was dissolved in THF/TMEDA there was evidence from nOe experiments for Li···H–Al as well as Li–TMEDA or Li–THF interactions in solution, showing that Al–H-containing groups displace donor ligands, at least transiently, from the coordination sphere of lithium. Similarly the coordination sphere of Li in **7** comprises two pyrazole ligands and two Al–H fragments; the THF coordinated to lithium in the starting aluminate **1** is displaced.

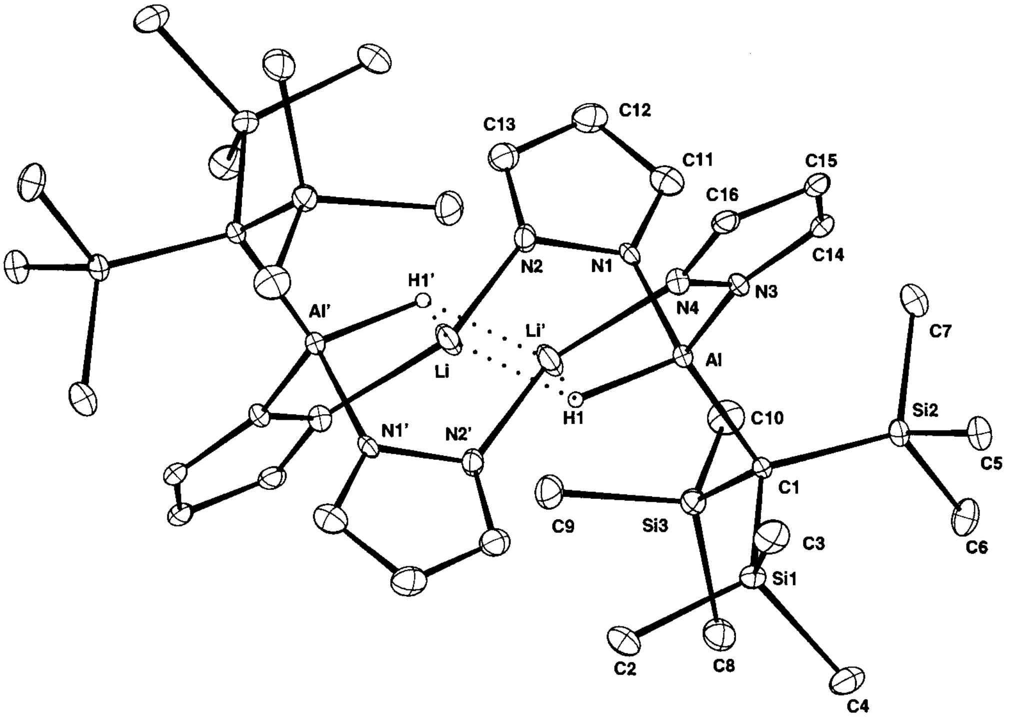

Fig. 4. Molecular structure of $[LiAlH(C_3H_3N_2)_2C(SiMe_3)_3]_2$ (**7**).

3. Experimental

All manipulations were made in Schlenk tubes with flame-dried glassware and argon as blanket gas. Solvents were distilled over Na–K and stored over potassium mirrors. Except where indicated, samples for NMR spectroscopy were in C_6D_6 and data were recorded at 300.13 (^1H), 75.43 (^{13}C), 99.4 (^{29}Si) and 130.44 (^{27}Al) MHz. Chemical shifts are relative to $SiMe_4$ (H, C, Si), aq. LiCl (Li) and aq. $Al(NO_3)_3$ (Al). EI mass spectra were obtained at 70 eV. Molar quantities of compounds **1**–**3** are for dimers.

*3.1. $Li(THF)_2Al_2H_5\{C(SiMe_3)_3\}_2$ (**4**) and $(Me_3Si)_3CAlH_2{\cdot}THF$ (**6**)*

Chlorotrimethylsilane (0.54 cm^3, 4.24 mmol) was added dropwise at room temperature (r.t.) to a solution of **1** (1.76 g, 2.13 mmol) in light petroleum (b.p. 40–60°C, 10 cm^3) and the mixture stirred for 15 min, then filtered. The volume of the filtrate was reduced to 4 cm^3, then the solution was kept at 5°C. The small crop (ca. 0.21 g) of colourless air- and moisture-sensitive block-like crystals that separated were shown by an X-ray study to be the dialuminate **4**. δ(H): 0.52 (54H, s, $SiMe_3$), 1.37 and 3.65 (8H, m, THF). δ(C): 5.6 ($SiMe_3$), 25.3 and 68.1 (THF). δ(Si): -3.7. δ(Li): -2.1. A second larger crop of crystals, which were needle-like, consisted of the alane **5** (0.56 g, 40%). Anal found: C, 50.2, H, 10.5. $C_{14}H_{37}AlOSi_3$ Anal. Calc. C, 51.4, H, 9.8. IR: (Al–H cm^{-1}) 1784 s, br. δ(H): 0.45 (27H, s, $SiMe_3$), 0.9 and 3.6 (4H, broad m, THF). δ(C): 5.2 ($SiMe_3$), 24.9 and 74.0 (THF). δ(Al): 150, $\Delta\nu_{1/2}$ 3 kHz. δ(Si): -3.8.

Table 2
Selected bond lengths (Å) and angles (°) for $[LiAlH(C_3H_3N_2)_2C(SiMe_3)_3]_2$ (**7**)

Bond lengths			
Li–N [a]	1.956(8)	Li–H [a]	1.99(4)
Al–N1	1.901(4)	Al–N3	1.887(4)
Al–H	1.64(4)	Al–C	1.985(4)
Si–C [a]	1.893(4)	Si–Me	1.876(5)
N–N	1.382(5)[a]	C–C	1.364(6), 1.381(6)
C–N(Li)	1.328(5)[a]	C–N(Al)	1.355(5) [a]
N1–C11	1.354(5)	N2–C13	1.327(5)
Bond angles			
H–Li–H′	86.3(16)	Li–H–Li′	93.6(16)
N2–Li–N4′	142.5(5)	Li–H–Al	116(2) [a]
N2–Li–H1′	113.4(12)	N4′–Li–H1′	90.3(12)
N2–Li–H1	90.2(11)	N4–Li–H1	121.4(12)
C–Al—H	110.8(13)	N1–Al–N3	104.28(16)
C–Al–N1	118.31(17)	N3–Al–H	100.0(13)
C–Al–N3	119.74(17)	N1–Al–H	100.6(13)
Si–C–Si [a]	110.8(2)	Si1–C–Al	104.9(2)
Me–Si–Me	105.0(2)	Si2–C–Al	112.7(2)
C–Si–Me	113.5(2)	Si3–C–Al	106.6(2)

[a] Average value with precision of individual measurements indicated in parentheses.

Table 3
X-ray structure determinations

	3	4	5	7
Chemical formula	$C_{38}H_{98}Al_2Li_2N_2O_4Si_6$	$C_{28}H_{75}Al_2LiO_2Si_6$	$C_{14}H_{37}AlOSi_3$	$C_{32}H_{68}Al_2Li_2N_8Si_6$
Formula weight	883.6	673.3	332.7	801.3
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	*Fdd*2 (no. 43)	$P2_1/n$ (no. 14)	*Pbcn* (no. 60)	$P\bar{1}$ (no. 2)
a (Å)	19.419(4)	9.188(1)	26.757(9)	8.969(4)
b (Å)	33.500(6)	23.652(6)	11.846(3)	9.077(4)
c (Å)	33.699(6)	20.235(3)	13.466(3)	15.455(10)
α (°)	90	90	90	76.59(4)
β (°)	90	92.90(1)	90	76.58(4)
γ (°)	90	90	90	76.15(3)
U (Å^3)	21922(7)	4392(1)	4268(2)	1167(1)
Z	16	4	8	1
μ (mm^{-1})	0.22	0.25	0.26	0.25
R_1, wR_2 $I>2\sigma(I)$	0.089, 0.217	0.066, 0.152	0.088, 0.240	0.053, 0.125
All data	0.118, 0.244	0.122, 0.189	0.157, 0.282	0.080, 0.139
Measured/independent reflections/R_{int}	6777/3434/0/0536	6502/6073/0.0366	7379/3745/0.0737	3234/3234/ -

3.2. $(Me_2PhSi)_3CAlH_2\cdot THF$ (**6**)

Me_3SiCl (0.32 g, 2.94 mmol) was added to a solution of **2** (1.51 g, 1.26 mmol) in toluene (30 cm^3) and the mixture was stirred for 20 h. The solvent was removed and the residue was washed with hexane (20 cm^3) then extracted with toluene. The extract was filtered through Celite and stored at 10°C to give needles of the alane **6** (0.67 g, 50%), m.p. 152°C (softens 91°C). IR (Al–H cm^{-1}) 1857s, 1809w. Anal. found: C, 67.0; H, 8.5. $C_{29}H_{43}AlOSi_3$ Anal. Calc: C, 67.2; H, 8.3. δ(H): 0.66 (18H, s, $SiMe_2$), 0.93 (4H, m, THF), 3.39 (4H, m, THF), 4.65 (2H, broad s, AlH), 6.98–7.09 (9H, m, *m*-and *p*-H), 7.70(6H, m, *o*-H). δ(C): 4.5 ($SiMe_3$), 25.1 (THF), 74.5 (THF), 127.3, 128.3, 136.5, 143.6 (Ph). The signal from the quaternary carbon was not observed. δ(Al): 158, $\Delta\nu_{1/2}$ 8 kHz. δ(Si): -8.6. *m*/*z* 518 (3%, M), 503 (3, M–Me), 445 (10, RAlH), 429 (10, RAl–Me), 403 (100, RH–Me).

3.3. $[Li(THF)_2AlH_3C(SiMe_3)_2(SiMe_2NMe_2)]_2$ (**3**)

A solution of $[LiC(SiMe_3)_2(SiMe_2NMe_2)\cdot 2THF]$ (1.1 g, 2.7 mmol) in THF (40 cm^3) was added dropwise to a solution of $LiAlH_4$ (0.20 g, 5.3 mmol) in THF (25 cm^3) at r.t. and the mixture was stirred for 17 h. The excess of $LiAlH_4$ was filtered off and the solvent removed from the colourless filtrate. The solid residue was extracted with light petroleum (45 cm^3), and the extract filtered then concentrated and kept at 5°C to give colourless crystals of **3** (1.1 g, 95%), m.p. 181–185 °C. Anal. found: C, 51.2; H, 11.2; N 2.8. $C_{38}H_{98}Al_2Li_2N_2O_4Si_6$ Anal. Calc. C, 51.7; H, 11.2; N, 3.2. IR: (Al–H) 1741 cm^{-1}. δ(H): 0.48 (12H, s, $SiMe_2$), 0.55 (36H, s, $SiMe_3$), 1.39 (8H, m, THF), 2.67 (12H, s, NMe_2), 3.63 (8H, m, THF). δ(C): 2.9 ($SiMe_2$), 5.2 ($SiMe_3$), 25.4 (THF), 41.2 (NMe_2), 68.7 (THF). δ(Li): -0.2. δ(Al{H}): 115 $\Delta\nu_{1/2}$ 570 Hz. δ(Si): -4.4 ($SiMe_3$), -2.8 ($SiMe_2$). The signal from the quaternary carbon was not observed because of rapid quadrupolar relaxation, but a broad signal from the hydridic protons attached to aluminium was found between δ 2.7 and 4.0 by a ^{6}Li nOe experiment. The ^{27}Al spectrum was too broad for the measurement of the coupling constant J_{AlH}, but the presence of Al–H coupling was shown by subtraction of the $^{27}Al\{^1H\}$ from the ^{27}Al spectrum.

3.4. $[LiAlH(C_3H_3N_2)_2C(SiMe_3)_3]_2$ (**7**)

Toluene (25 cm^3) was added to a solid mixture of **1** (0.54g, 0.66 mmol) and pyrazole (0.27 g, 3.93 mmol) at r.t. Some gas was evolved immediately and more upon addition of THF (5 cm^3). The mixture was heated under reflux for 2 h, then allowed to cool and filtered. The solvent was removed from the filtrate to leave a colourless glass, which was crystallised from hot toluene–THF (100:1) to yield colourless plates of **7** (0.37 g, 71%), m.p. 283–284°C (dec., softens 150°C). Anal. found: C, 47.9; H, 8.2; N, 14.1. $C_{16}H_{34}AlLiN_4Si_3$ Anal. Calc. C, 48.0; H, 8.5; N, 14.0. IR: (Al–H) 1644 cm^{-1} br. δ(H) (C_6D_6–THF-d_8) 0.34 (27H, s, $SiMe_3$), 6.22 (2H, s, pz), 7.83 (4H, br s, pz). δ(C): 6.0 ($SiMe_3$), 104.0, 128.3, 140.7 (pz). δ(Li): 0.79. δ(Al): 125, $\Delta\nu_{1/2}$ 1.7 kHz. δ(Si): -3.3.

3.5. Crystallography

Data were recorded at 173(2) K on a CAD4 diffractometer by use of Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Further details are given in Table 3. Structure analysis was by direct methods (SHELXS-86) and refinement by full least-squares on all data (SHELXL-93). In the structure of compound **3** the $C(SiMe_3)_2(SiMe_2NMe_2)$ groups were disordered, 86:14 or 65:35 with lower occupancy sites located for Si and included with isotropic thermal parameters and Si···Si non-bonding distances constrained to be equal. Terminal Al–H atoms were freely refined and bridging H atoms refined with chemically equivalent distances constrained to be equal. For **4**, hydride H atoms were located on a difference map and freely refined. The Si atoms attached to C2 were disordered 90:10; the lower occupancy Si sites were left isotropic and the attached methyl H atoms omitted. In the structure of **5** the Al was disordered 69:31 over two sites with different orientations of the $C(SiMe_3)_3$ group, and for each of these orientations the Si atoms were disordered 53:16 and 21:10 over two sets of positions sharing common C sites. The sum of the occupancies of the four sets of Si atom sites was constrained to be equal to 1.0. Methyl H atoms were included for the major occupancy arrangement only. Hydride H atoms were located on a difference map and refined with Al–H bonds constrained to be equal. Atom H1 was common to both Al sites whereas H2 corresponded to the major site only. For **7** the hydride H atoms were freely refined with isotropic thermal parameters. In all structures non-H atoms were anisotropic and, except where indicated, H atoms were included in riding mode with $U_{iso}(H)$ equal to 1.2 $U_{eq}(C)$ or 1.5 $U_{eq}(C)$ for methyl groups.

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