Synthesis and Structures of Hydrazinoalanes and Hydrido(hydrazino)aluminates☆

Heinrich Nöth* and Thomas Seifert

Institute of Inorganic Chemistry, University of Munich,
Meiserstraße 1, D-80333 München, Germany
Fax: (internat.) +49(0)89/5902-451
E-mail: H.Noeth@lrz.uni-muenchen.de

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Several monomeric dimethylaluminium hydrazide ether adducts $Et_2O/THF \times Me_2AlNR–NR'R''$ (**5–7**) were obtained by deprotonating the respective hydrazines with *n*BuLi, followed by reaction with Me_2AlCl. The hydrazines Ph(H)N–$N(SiMe_3)_2$ and *t*Bu(H)N–N(H)$SiMe_3$ react with $LiAlH_4$ in the presence of either ether or THF with the formation of dimeric lithium hydrazino(hydrido)aluminates, e.g. **8** and **9**. Their structures depend on the number of acidic hydrogen atoms bonded to the nitrogen atoms of the starting hydrazine. The hydrazine Ph(H)N–$N(SiMe_3)_2$ (**1**) reacts with $LiAlH_4$ to form monometallated $LiAlH_3[(Ph)N–N(SiMe_3)_2] \times 2\ Et_2O$ (**8**) with elimination of one equivalent of H_2. The molecule is dimeric and features an $(AlHLiH)_2$ eight-membered ring. In contrast, the reaction of *t*Bu(H)N–N(H)$SiMe_3$ with $LiAlH_4$ in the presence of THF leads to the formation of dimeric 2 THF × $LiAlH_2[(tBu)N–N(SiMe_3)]$ (**9**) with a central $(AlNN)_2$ six-membered ring. A dimeric aluminium hydrazide **10** was obtained by allowing *t*Bu(Li)N–N(H)$SiMe_3$ to react with Me_2AlCl in a hexane/toluene solution. The structure of **10** features a six-membered Al_2N_4 ring in chair conformation.

Introduction

In recent years great progress has been achieved in the structural chemistry of alkali metal hydrazides[1]. Among the structural principles such as "laddering" and "stacking"[2], well known for alkali metal amides, additional arrangements such as "butterfly" or "side-on" coordination play an important role in the structure of the hydrazides. However, the structural chemistry of the amino alanes is mainly determined by the steric requirements of the organyl groups as well as by additional ligands. There are subtle differences; for example, $(Me_2AlNMe_2)_2$ possesses a planar four-membered Al_2N_2 ring while a six-membered Al_3N_3 ring was observed for $(Me_2AlNHMe)_3$, which exists in either a chair or a "skew-boat" conformation[3]. Furthermore, the structural motifs found for imidoalanes vary from heterocubanes, e.g. $(PhAlNPh)_4$, to different kinds of bridged or fused cage structures[4]. To date, much of the structural chemistry of group-13 elements has focused on amides and imides[8][15]. In contrast, information on the hydrazido derivatives is still scarce, even though a renewed interest in the investigation of these compounds in the last few years can be noted[5]. Since the synthesis and structural knowledge of borylated hydrazines are well developed[5a][5b][5c][5d], we present here work related to new hydrazinoalanes and hydrazino(hydrido)aluminates.

Results and Discussion

Preparation and NMR-Spectroscopic Characterization

Among the various possible routes to hydrazinoalanes only two have been pursued in this study, the metathesis of R_2AlCl with a lithium hydrazide and secondly the reaction of $LiAlH_4$ with a hydrazine. Four alkyl-, phenyl- and silyl-substituted hydrazines, **1**−**4**, were deprotonated by *n*BuLi and the Li compounds were allowed to react with Me_2AlCl. The deprotonation of **1**−**3** (Eq. 1) was carried out in the presence of donor molecules. A conceivable Si−N bond cleavage with formation of Me_3SiCl for reactions (1) and (2), well-known for the reaction of aminosilanes with aluminium trihalides[6], was not observed. However, the alkyl-substituted hydrazide **10** was obtained from a hexane/toluene solution (Eq. 2). Furthermore the deprotonation of **1** and **4** with $LiAlH_4$ proceeded smoothly with H_2 evolution producing the hydrazino(hydrido)aluminates **8** and **9** (Eqs. 3 and 4).

The use of ether as a solvent or cosolvent for reactions (1) and (3) was due to the fact that lithiated phenyl hydrazides and $LiAlH_4$, respectively, are only sparingly, if at all, soluble in both aliphatic and aromatic hydrocarbons. This proved to be essential for good yields.

Although several aluminium hydrazides have already been investigated[5e][5f][5g], no ^{27}Al-NMR data have so far been reported. However, ^{27}Al-NMR spectroscopy is a useful tool not only for monitoring the course of the reaction but also for obtaining structural information. Thus, the formation of **5**, **6** and **7** (Eq. 1) can be readily deduced from ^{27}Al-NMR spectroscopy. Resonances at $\delta = 151$ (**5**), $\delta = 165$ (**6**) and $\delta = 170$ (**7**), with half widths of 5600−6100 Hz, are indicative of asymmetrically tetracoordinated aluminium centers[7], and the chemical shifts are comparable with those of dimeric dialkylaluminium amides, e.g. $[iBu_2AlNC_6H_{12}]_2$[8]. The ^{1}H- and ^{13}C-NMR spectra of **5**, **6** and

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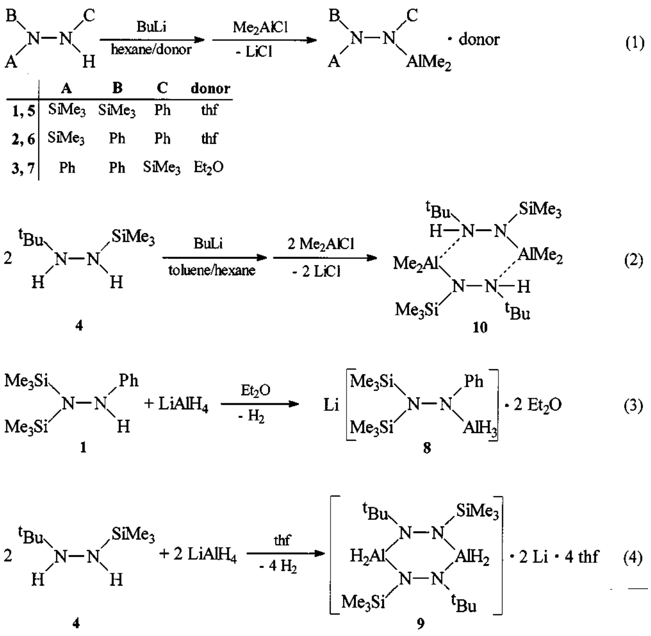
Scheme 1



	A	B	C	donor
1, 5	SiMe3	SiMe3	Ph	thf
2, 6	SiMe3	Ph	Ph	thf
3, 7	Ph	Ph	SiMe3	Et2O

7 show one resonance for the methyl groups residing at the aluminium atom, indicating free rotation about the Al−N bond at room temperature.

For the dimeric compound **10** a ^{27}Al-NMR chemical shift of $\delta = 141$ is observed with a half width of 2200 Hz. The ^{1}H-NMR data at room temperature reveal two resonances for the methyl groups attached to the aluminium center in accordance with its structure in the solid state. In contrast, the ^{13}C-NMR spectrum shows only a single resonance for the $Al(CH_3)_2$ group at room temperature, but at −60°C two resonances for the methyl groups can be detected in the ^{13}C NMR. Because there is no temperature-dependent line broadening, this behavior is thus best interpreted as being due to a coincidentally equal chemical shift at room temperature.

The ^{27}Al-NMR data of **8** and **9** suggest the formation of a tetracoordinated H_3Al- and a H_2Al- species, respectively, by analogy to $[tripAlH_3LiOEt_2]_n$[9] (trip = 2,4,6-iPr$_3C_6H_2-$), $[2,6\text{-}t\mathrm{Bu}_2C_6H_3OAlH_3Li(OEt_2)_2]_2$ and $(mentO)_2AlH_2Li(THF)_2$[10] (ment = 2-iPr-5-MeC$_6$H$_9$−). The ^{27}Al-NMR spectrum of **8** in deuteriobenzene solution consists of a quadruplet at $\delta = 110$ [^{1}J(Al, H) = 178 Hz]. However, the ^{7}Li-NMR resonance shows a half width of 12 Hz and it was not possible to resolve an Li−H coupling in the temperature range of −80°C to room temperature. Until recently, little information had been reported on ^{1}J(Li, H) coupling constants, and we are aware of only two examples, 10.5 Hz for $[(Me_3Si)_2N]_2AlH_2Li(OEt_2)_2$[11a] and 8.4 Hz for [Cp*IrH3Li(pmdta)] (pmdta = pentamethylethylenetriamine)[11b], both smaller than the observed half width for **8**.

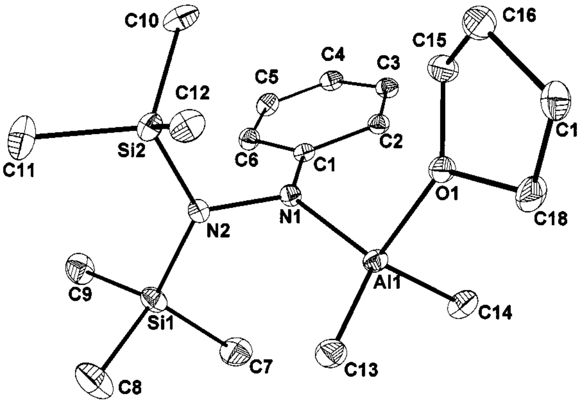
The spectrum of **9** shows a ^{27}Al-NMR resonance at $\delta = 119$ with a half width of 1520 Hz. Even at −80°C it was not possible to observe a ^{1}J(Al, H) coupling as for compound **8**. In addition, the ^{7}Li-NMR spectrum shows a broad resonance with a half width of 30 Hz.

Molecular Structures

The Aluminium Hydrazide $Me_2Al(Ph)N-N(SiMe_3)_2 \times$ THF (**5**)

Compound **5** crystallizes in the orthorhombic system, space group $Pna2_1$ with four molecules in the unit cell. Figure 1 depicts the molecular structure.

Figure 1. ORTEP plot of the aluminium hydrazide **5**; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level



The aluminium atom is tetracoordinated by one oxygen, one nitrogen and two carbon atoms. However, the bond angles reveal a significant distortion from an ideal tetrahedral array as indicated by bond angles N1−Al1−C13 of 115.9(1)°, O1−Al1−C13 of 102.2(1)° and C13−Al1−C14 of 114.7(1)°, respectively. The Al−O distance is larger than the Al−N distance with a difference of 0.063 Å. The sum of bond angles, Σ, at the oxygen atom and the two nitrogen atoms is close to 360° (O1: 357.8°, N1: 358.3°, N2: 360.0°). Therefore, the nitrogen atoms N1 and N2 can be considered as being essentially sp^2-hybridized and this seems also to hold for the oxygen atom. Nevertheless, the latter geometry can also be readily explained in terms of ion-dipole interactions between the metal ion and the THF molecule[12].

While the N−N bond length is 1.469(3) Å, we note that the planes around the nitrogen atoms stand almost orthogonal to one another, as shown by the interplanar angle C1N1Al1/Si1N2Si2 of 85.2°. The phenyl group is twisted against the plane N2N1Al1 by 20.8°. Although the N−N−Si bond angles differ from one another by up to 8.4°, the Si−N bond lengths of 1.742(2) Å and 1.746(2) Å are equal to within the 3σ standard deviation.

The Aluminium Hydrazide $Me_2Al(Ph)N-N(Ph)SiMe_3 \times$ THF (**6**)

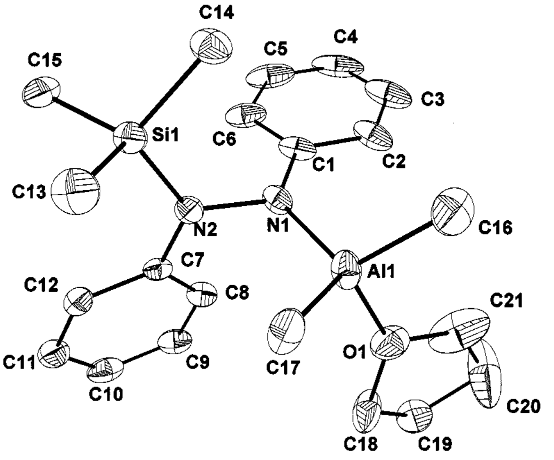
Compound **6** crystallizes in the monoclinic system, space group Cc with four molecules in the unit cell. The molecular structure is shown in Figure 2.

Its aluminium atom is tetracoordinated by the oxygen atom of one molecule of THF, one nitrogen atom and two

Table 1. Selected bond lengths [Å] and angles [°] of **5**, **6**, **7** and **10**

	5	**6**	**7**	**10**
Al−N	1.869(2)	1.863(3)	1.847(2)	N1: 2.016(2) N2: 1.874(2)
Al−C	C13: 1.960(2) C14: 1.970(2)	C16: 1.955(4) C17: 1.947(8)	C16: 1.975(2) C17: 1.973(3)	C1: 1.982(2) C2: 1.981(2)
N−N	1.468(2)	1.449(3)	1.446(2)	1.486(2)
N−Si	Si1: 1.746(2) Si2: 1.742(2)	1.766(3)	1.746(2)	1.764(2)
Σ N1/N2	358.3/360.0	360.0/360.0	359.6/359.9	323.3/359.9
C−Al−C	114.7(1)	102.1(7)	116.0(1)	106.7(1)
N−N−Al	118.1(1)	114.2(2)	116.1(1)	122.7(1)

Figure 2. The molecular structure of the aluminium hydrazide **6** in ORTEP representation; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level



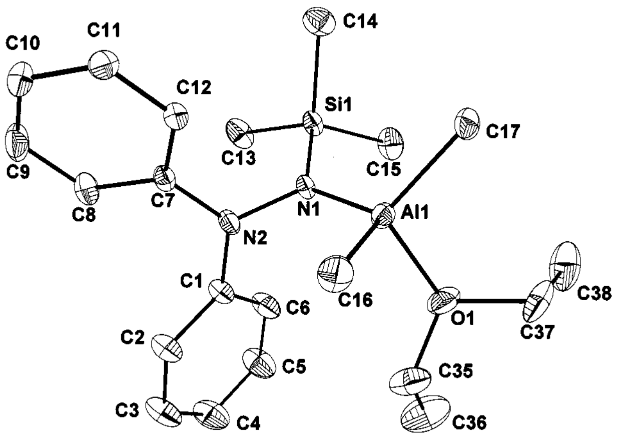
carbon atoms of the methyl groups. The Al−N and Al−O bond lengths of 1.863(3) Å and 1.879(3) Å, respectively, are very similar to each other, in contrast to those in compounds **5** and **7**. Both nitrogen atoms are tricoordinated in a planar environment, the sum of bond angles, Σ, amounting to 360.0° both for N1 and N2. Even the oxygen atom shows a tricoordinate-planar environment.

It is found that the planes around the nitrogen atoms are even closer to perpendicular in comparison with **5**, as demonstrated by the torsion angle C1−N1−N2−C7 of 89.7°. Moreover, the N−N distance of 1.449(3) Å is noticeably shorter than that determined for compound **5**, differing by 0.019 Å. In contrast to **5**, the Si−N bond of 1.766 Å is slightly lengthened (0.020 Å). The phenyl groups are twisted by 3.2° at N1 and 17.4° at N2 with respect to the N2N1Al and N1N2Si plane, respectively, in accordance with the N−C distances of 1.396(4) Å and 1.405(4) Å, indicating N−C π bonding.

The Aluminium Hydrazide $Me_2AlN(SiMe_3)-NPh_2 \times Et_2O$ (**7**)

Compound **7** crystallizes in the triclinic system, space group $P\bar{1}$. There are two independent molecules in the unit cell whose structural parameters differ only insignificantly. Therefore we depict only one of these in Figure 3.

Figure 3. ORTEP plot of the aluminium hydrazide **7**; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level



The tetracoordinated aluminium atom shows again a distorted tetrahedral array as described for compound **5**. The geometry at both nitrogen atoms is almost planar with a sum of bond angles, Σ, of 359.6° for N1 and 359.9° for N2. The Al−N distance of 1.847(2) Å in **7** is slightly shorter than in compounds **5** or **6**. The Al−O bond length of 1.928(2) Å is comparable with that in compound **5**, despite the weaker base strength of diethyl ether.

The N−N bond length of 1.446(2) Å corresponds to that found in compound **6**. The planes at the nitrogen atoms Si1N1Al1/C1N2C7 are again close to perpendicular (the interplanar angle is 81.2°) and both phenyl groups are twisted against the plane around N2 by 27.5° and 28.3°, respectively. The Si−N bond length of 1.746 (2) Å is comparable to that in compound **5**.

The Lithium Hydrazino(hydrido)aluminate $LiAlH_3[(Ph)N-N(SiMe_3)_2] \times 2\ Et_2O$ (**8**)

The colorless prisms of **8** belong to the triclinic system, space group $P\bar{1}$. There are two molecules $LiAlH_3[(Ph)N-N(SiMe_3)_2] \times 2\ Et_2O$ in the unit cell which are symmetry-related by a crystallographical inversion center in the midpoint of an $(LiH_2Al)_2$ eight-membered ring as shown in Figure 4. For molecular parameters of compounds **8** and **9** see Table 2.

Thus, two hydrazidoaluminate units are linked by two H−Li−H bridges. The resulting eight-membered ring shows a striking feature: six atoms build up exactly a plane, without significant deviation. Two hydrogen atoms, H1c and H1ca, lie 0.36 Å above and below this plane, respectively.

The aluminium atom is almost tetrahedrally coordinated by three (one terminal and two bridging) hydrogen atoms and one nitrogen atom. The lithium atom is also tetracoordinated by two oxygen atoms and two hydrogen atoms in a slightly distorted tetrahedral array as indicated by the O1−Li1−O2 bond angle of 116.9(3)°. The Al−H bond lengths are 1.50(4) Å for the terminal hydrogen atom and

Figure 4. ORTEP representation of the lithium hydrazino(hydrido)aluminate **8** including selected hydrogen atoms; the ethyl groups of the ether molecules are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level

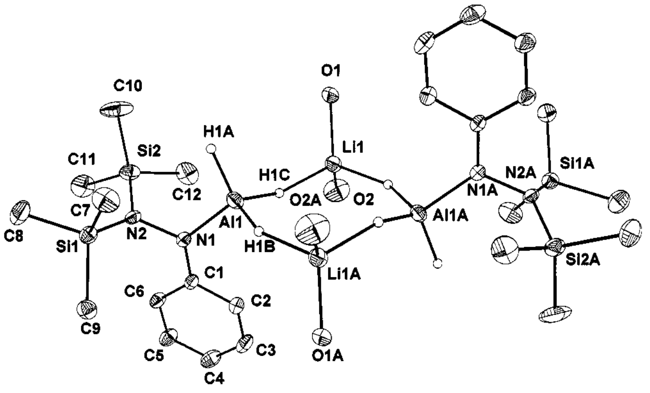
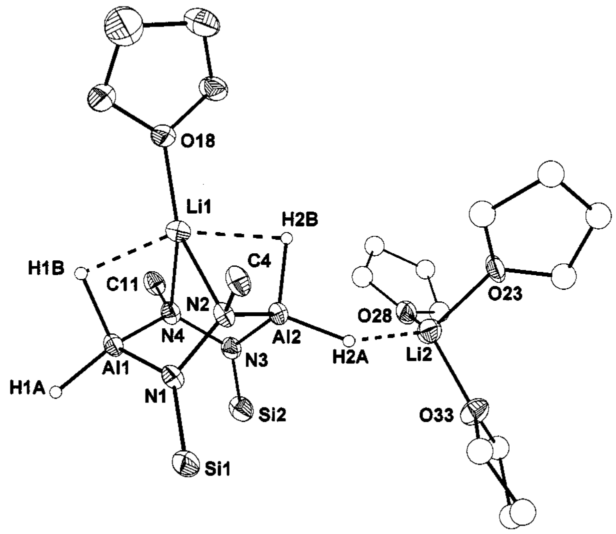


Figure 5. ORTEP plot of **9** including selected hydrogen atoms; the methyl groups on C4, C11 (*t*Bu); Si1 and Si2 ($SiMe_3$) are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level



1.58(4) Å and 1.61(4) Å for the bridging hydrogen atoms. The Li−H atom distances of 1.86(4) Å and 1.85(4) Å are longer than those to the aluminium atoms but clearly shorter than in ionic LiH (2.08 Å)[13]. The Al−N bond length of 1.869(3) Å corresponds to that found in the aluminium hydrazide $Me_2Al(Ph)N-N(SiMe_3)_2$ × THF (**5**). The hydrazide unit in **8** shows the same tendencies in bond lengths and angles as described for compound **5**. Both nitrogen atoms are almost sp^2-hybridized with sum of bond angles, Σ, of 359.1° for N1 and 358.3° for N2. Furthermore the planes around the nitrogen atoms are almost perpendicular to one another, as indicated by the torsion angle C1−N1−N2−Si1 of 81.3°. The phenyl group is twisted slightly against the plane around N1 (N2Al1C1) by 11.1°.

Table 2. Selected bond lengths [Å] and angles [°] of **8** and **9**

	8	**9**
Al−N	1.869(3)	N1: 1.843(3)/N3: 1.841(3) N2: 1.871(3)/N4: 1.895(3)
Al−H	1.50(4)−1.61(4)	1.54(3)−1.61(3)
N−N	1.460(4)	N1: 1.508(3)/N3: 1.504(4)
Li−H	1.85(4)−1.86(4)	Li1: 2.09(3)/2.26(4) Li2: 1.89(4)
N−Si	Si1: 1.730(3) Si2: 1.735(3)	Si1: 1.707(3) Si2: 1.705(3)
Σ N1 (N3)	359.1	358.6 (357.6)
Σ N2 (N4)	358.3	356.1 (354.8)

The Lithium Hydrazino(hydrido)aluminate $LiAlH_2[(tBu)N-N(SiMe_3)]$ × 2 THF (**9**)

Compound **9** crystallizes in the monoclinic system, space group $P2_1/n$, with four molecules in the unit cell. It should be noted that due to some disorder of the THF molecules the carbon atoms of the THF molecules around Li2 were refined only isotropically.

The most remarkable feature of compound **9**, depicted in Figure 5, are two differently coordinated lithium atoms. Li1 is tricoordinated by the nitrogen atoms of the *t*BuN groups of the $(Al-N-N)_2$ six-membered ring and one oxygen atom of a THF molecule, whereas Li2 is tetracoordinated by three oxygen atoms and one hydrogen atom of an AlH_2 unit.

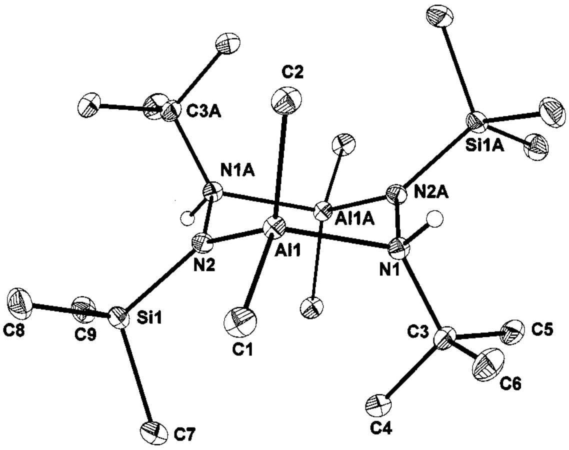
In addition, Li1 exhibits two close contacts with two hydrogen atoms of the AlH_2 units with distances of 2.09(3) Å (for H1b) and 2.26(4) Å (for H2b). Taking these contacts into account, we arrive at pentacoordination with a distorted trigonal-bipyramidal array with the hydrogen atoms in apical positions. This is an unexpected situation, because usually the most electronegative partners occupy the apices of the trigonal bipyramid. The deviation from the ideal trigonal-bipyramidal array is indicated by the bond angle H1b−Li1−H2b of 153(2)°. It should be noted that the Li1−N distances [2.278(7) Å and 2.213(7) Å] are longer than the Li1−O18 distance [1.920(6) Å] in accordance with the larger effective radius of the nitrogen atoms compared to the oxygen atom.

The aluminium atoms are not bonded symmetrically to the neighboring nitrogen atoms. Due to the electron-releasing properties of the $SiMe_3$ group, the corresponding Al−N bond lengths, Al1−N1 and Al2−N3 are shortened. For example, Al1−N1 and Al1−N4 differ by 0.052 Å. Comparing the sum of bond angles, Σ, at the nitrogen atoms, we found in accordance with the aluminium−nitrogen bond lengths, that the Σ of N1 (358.6°) and N3 (357.6°) are closer to 360° than those of N2 (356.1°) and N4 (354.8°) (neglecting the Li···N interaction), which are slightly pyramidalized. It is particularly noteworthy that the N−N bond lengths of 1.508(3) Å (N1−N2) and 1.504(4) Å (N3−N4) are quite long. One reason for this is certainly the twisted planes around the nitrogen atoms, as indicated by the interplanar angles Al1N1Si1/Al2N2C4 (75.0°) and Al2N3Si2/Al1N4C11 (78.3°), causing a repulsion of the π electrons at the nitrogen atoms. But surely the most significant factor in the elongation of the N−N bond is the four-coordination observed for N2 and N4. Finally, we note comparatively short N−Si bond lengths of 1.707(3) Å (Si1−N1) and 1.705(3) Å (Si2−N3), respectively.

The Aluminium Hydrazide [$Me_2AlN(SiMe_3)-N(tBu)H]_2$ (**10**)

The solvent-free compound **10** crystallizes in the orthorhombic system, space group *Pbca*, with 8 molecules in the unit cell. The molecular structure is depicted in Figure 6.

Figure 6. ORTEP representation of **10**; hydrogen atoms, except on the nitrogen atoms, are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level



10 forms a centrosymmetric dimer with an $(AlN_2)_2$ six-membered ring in chair conformation with the methyl groups in axial (C2) and equatorial (C1) positions. The aluminium atom is tetracoordinated to carbon atoms of the methyl groups and two nitrogen atoms in a distorted tetrahedral array. The fairly long Al−N1 distance of 2.016(2) Å indicates a coordination of the nitrogen atom N1 across its lone pair of electrons to the aluminium atom. This is supported by the sum of bond angles of N1, neglecting the Al···N1 interaction, of 323.3°, indicating clearly a pyramidal geometry with (*S*) configuration at N1 and (*R*) configuration at its symmetry equivalent, N1A. In contrast to that, the Al−N2 bond length of 1.872(2) Å is comparable to those found in **5**, **6** and **7**. However, N2 shows a trigonal-planar geometry with a sum of bond angles of 359.9°.Due to sp^3 hybridization of N1, the N−N bond length of 1.486(2) Å is slightly lengthened compared to the monomeric ether adducts **5**−**7**.

Discussion

The ether adducts **5**, **6** and **7** are the first structurally characterized monomeric aluminium hydrazides. It should be noted that in all three reported compounds the β-nitrogen atom of the hydrazide unit is not involved in coordination to the aluminium center due to the fact that this nitrogen atom is sterically and electronically less suited for coordination than atom N1. As previously shown for alkali metal hydrazides[1g], oligomerization can be inhibited by suitable donor molecules coordinating to the metal center, thus preventing the formation of additional metal−nitrogen interactions. One reason for this is certainly the planarity at the nitrogen atoms that decreases the basicity of the R_2N group. The Al−N bond lengths of **5**, **6** and **7** are comparable to those in aluminium amides with tetracoordinated aluminium atoms and tricoordinated nitrogen atoms[14]. These bond lengths vary from 1.869(2) Å in **5** to 1.847(2) Å in **7**. Although the weaker donor ability of diethyl ether in contrast to THF is expected to lead to longer Al−O distances, the Al−O bond length of 1.928(2) Å in compound **7** is comparable to that found in **5** [1.932(2) Å]. The reason for the short Al−N bond of **7** may be the higher acidity of the nitrogen atom, due to the neighboring $SiMe_3$ group. This effect is also observed in compound **10**. Therefore, the metallation took place at the silyl-substituted nitrogen atom. The Al−N bond length of 1.874(2) Å is somewhat longer than in the ether adducts **5**, **6** and **7**, but reasonably shorter than the Al−N bond length of 2.016(2) Å of the coordinating nitrogen atom in compound **10**, which compares well to those found in alane amines such as $Me_2ClAl(NHBz_2)$ (Bz = benzyl)[15a] or $Me_3Al(NHBz_2)$[15b]. In contrast to the solvates **5**, **6** and **7**, the β-nitrogen atom of the aluminium hydrazide **10** is also involved in coordination to the aluminium atom. Dimeric **10** forms a six-membered Al_2N_4 ring in chair conformation with the *tert*-butyl groups in axial positions. These results differ from the structural observations recently reported for the dimeric aluminium hydrazide, $[Me_2Al-\mu\text{-}N(H)NMe_2]_2$[5e], which forms an $(AlN)_2$ four-membered ring in a *trans* configuration in the solid state with tetracoordinated aluminium and nitrogen atoms and therefore with fairly long Al−N bond lengths of 1.958(3) Å and 1.953(3) Å. This structural feature is already known for amino alanes, e.g. $[Np_2Al-N(H)Ph]_2$ (Np = Me_3CCH_2-)[16] or $[iBu_2AlNC_6H_{12}]_2$[8].

The structure of the hydrazino(hydrido)aluminate **9** can be readily derived from the aluminium hydrazide **10**. The six-membered ring in chair conformation may be slightly twisted due to the coordination of two facing nitrogen atoms to one lithium center. The two nitrogen atoms are slightly pyramidalized, but the sum of their bond angles (356.1°, 354.8°) is still close to 360°, suggesting an Li···N-p_z interaction which is in accordance with the fairly long Li−N bond lengths of 2.278(7) Å and 2.213(7) Å, respectively. The most striking feature of compound **9** is the fact that this lithium atom faces the ring directly above its center, completing its coordination sphere by one molecule of THF and two additional Li···H contacts, while the lateral lithium atom Li2 is solvated by three THF molecules, contacting the ring via a hydrogen bond. In contrast to **9**, the hydrazino(hydrido)aluminate **8** forms an $(LiHAlH)_2$ eight-membered ring. This characteristic feature was also observed for $[(Me_3Si)_2NAlH_3Li(OEt_2)_2]_2$[11a] and $[(2,6\text{-di-}tBu)C_6H_3OAlH_3Li(OEt_2)_2]_2$[10]. The β-nitrogen atom is neither involved in coordination with the aluminium atom nor the lithium atom. The Al−N bond lengths of both compounds, **8** and **9**, ranging from 1.841(3) Å to 1.895(3) Å, are typical for tetracoordinated aluminium and tricoordinated nitrogen atoms and comparable to those found in $[(Me_3Si)_2$-

Table 3. Crystal data and data related to data collection and structure solution

Compound	**5**	**6**	**7**	**8**	**9**	**10**
chem. formula	$C_{18}\,H_{37}\,Al\,N_2\,O\,Si_2$	$C_{21}\,H_{33}\,Al\,N_2\,O\,Si$	$C_{42}\,H_{70}\,Al_2\,N_4\,O_2\,Si_2$	$C_{20}\,H_{46}\,Al\,Li\,N_2\,O_2\,Si_2$	$C_{30}\,H_{72}\,Al_2\,Li_2\,N_4\,O_4\,Si_2$	$C_9\,H_{25}\,Al\,N_2\,Si$
formula weight	380.66	384.56	773.16	436.69	676.94	216.38
cryst. size [mm]	0.2 × 0.3 × 0.4	0.3 × 0.3 × 0.4	0.1 × 0.2 × 0.3	0.1 × 0.2 × 0.2	0.40 × 0.50 × 0.60	0.2 × 0.3 × 0.3
cryst. system	orthorhombic	monoclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	$Pna2_1$	Cc	P1bar	P1bar	$P2_1/n$	$Pbca$
a [Å]	13.7263(3)	10.2097(2)	9.21590(10)	10.8302(2)	11.928(2)	12.473(2)
b [Å]	14.0198(3)	13.8731(4)	14.8404(2)	11.645	20.066(4)	13.147(2)
c [Å]	11.9554(1)	16.4523(4)	18.20120(10)	12.3135(2)	18.555(4)	16.295(3)
α [°]	90	90	84.962(1)	89.18(1)	90	90
β [°]	90	93.16(1)	77.664(1)	76.57(1)	105.377(8)	90
γ [°]	90	90	74.633(1)	74.23(1)	90	90
V [Å^3]	2300.70(7)	2326.76(10)	2343.63(4)	1451.69(4)	4282.1(14)	2672.1(8)
Z	4	4	2	2	4	8
ρ (calcd.), [Mg/m^3]	1.099	1.098	1.096	0.999	1.050	1.076
μ [mm^{-1}]	0.200	0.150	0.149	0.167	0.157	0.209
F(000)	832	832	840	480	1488	960
index range	$-15 \le h \le 15$, $-15 \le k \le 15$, $-13 \le l \le 11$	$-11 \le h \le 11$, $-15 \le k \le 11$, $-19 \le l \le 19$	$-10 \le h \le 10$, $-17 \le k \le 17$, $-20 \le l \le 20$	$-12 \le h \le 8$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-13 \le h \le 13$, $-22 \le k \le 22$, $-21 \le l \le 21$	$-14 \le h \le 15$, $-17 \le k \le 16$, $-21 \le l \le 21$
2θ [°]	47.62	48.82	49.42	49.42	47.64	58.70
T [K]	183	183	183	183	193	183
refl. collected	10043	5407	11342	7101	18550	14679
refl. unique	3203	3215	6014	3778	6266	2881
refl. observed (4σ)	3114	3100	5495	3291	4752	2395
R (int.)	0.0264	0.0225	0.0253	0.0303	0.0301	0.0369
no. variables	225	279	503	295	417	130
weighting scheme[a] x/y	0.0300/0.8165	0.0189/2.2622	0.0405/1.1897	0.0219/2.0060	0.0819/7.8740	0.0420/1.4158
GOF	1.083	1.150	1.090	1.145	1.025	1.108
final R (4σ)	0.0278	0.0412	0.0396	0.0608	0.0747	0.0392
final $wR2$	0.0688	0.0959	0.0992	0.1321	0.1814	0.0925
larg. res. peak [e/Å^3]	0.158	0.152	0.270	0.296	0.590	0.288

[a] $w^{-1} = \sigma^2 F_o{}^2 + (xP)^2 + yP$; $P = (F_o{}^2 + 2F_c{}^2)/3$.

$NAlH_3Li(OEt_2)_2]_2$ and $[(Me_3Si)_2N]_2AlH_2Li(OEt_2)_2$[11a]. The average Li−H bond length for **8** is 1.86 Å and is distinctly shorter than in lithium hydride (2.08 Å)[13]. This is also true for Li2 [1.89(4) Å] in compound **9**, but additionally we note two fairly long Li−H contacts of 2.09(3) Å and 2.26(4) Å of the trigonal-bipyramidal-coordinated lithium atom Li1.

Conclusion

The most significant general result derived from the structure determinations of aluminium hydrazides is that the hydrazine units adopt planar geometries in which the lone pairs are orientated orthogonally. Moreover, the aluminium centers prefer OEt_2 or THF as a coordination partner over the NRR′ unit of the hydrazino group. This occurs only when Et_2O or THF is excluded in the preparation.

One can envisage that aluminium hydrazides $Me_2Al-NR-NR'SiMe_3$ and $Me_2Al-NR-N(SiMe_3)_2$ will decompose at higher temperatures with loss of $SiMe_4$, with the formation of oligomeric clusters of the type $[MeAl-NR-NR']_n$ or $[MeAl-NR-N(SiMe_3)]_m$. These may then decompose into AlN at sufficiently high temperatures, as has recently been shown for some gallium organylhydrazides[5i][5h]. This aspect has not yet been investigated nor have we made attempts to prepare tris(hydrazino)alanes $Al(NR-NR'R'')_3$ which may be associated (small R groups) or monomeric (bulky R groups). Provided that the two amino groups of the hydrazino units remain in a perpendicular orientation new structural coordination patterns can be realized.

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Experimental Section

General Remarks: All reactions were performed under argon using Schlenk techniques. Solvents were dried by conventional methods ($LiAlH_4$, potassium/benzophenone, P_4O_{10}) and stored under argon. The compounds $PhNH-NH_2$, Ph_2N-NH_2 × HCl, Ph(H)N−N(H)Ph × HCl, *n*-butyllithium, Me_3SiCl, 2 M solution of Me_2AlCl in hexane, Me_3SiCl, C_6D_6 and [D_8]toluene were used as purchased. $Ph(H)N-N(SiMe_3)_2$ (**1**), $Ph(H)N-N(Ph)SiMe_3$ (**2**), $Ph_2N-N(H)SiMe_3$ (**3**) and $H(tBu)N-N(H)SiMe_3$ (**4**)[17] were prepared according to literature methods.

Elemental analyses of the compounds were often unreliable, most likely as a result of the formation of silicon carbide or to their hydrolytic sensibility. In addition, they lose coordinated solvent quite readily. Therefore, the purities were checked by the interpretation of the ^{1}H-NMR signals and the single signal found in the ^{27}Al-NMR spectra.

X-ray Structure Analysis (see Table 3): All crystals had to be handled carefully under argon, preferably in a glove box or in a closed Schlenk system. Once the selected crystals were covered with oxygen-free perfluoroether oil, they were mounted in a glass capillary or on a glass fibre and transferred to the goniometer head of Siemens P4 diffractometer (Mo-K_α radiation, $\lambda = 0.71063$ Å, graphite monochromator) equipped with a CCD detector, and cooled in the cold stream of the Siemens LT2 device. Determination of the unit-cell parameters was performed with the data of reflections collected with a total of 75 frames, taking 15 frames each with ω rotation of 0.3° for five different settings. The axes calculated for the unit cell were checked by recording the reflections in the 100, 010 and 001 planes. The final unit-cell parameters were calculated from the whole set of observed reflections. Data collection was performed in a standard manner with an exposure time of 10 s per frame and a 0.3° difference in φ orientation. Data reduction was performed with the program SAINT[18], and the structure was solved by direct methods or by the sharpened Patterson method as implemented in the SHELXTL system[19]. The SHELX97 program[20] was used for the final refinement. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically in calculated positions as a riding model. Further details of the crystal structure determinations are deposited at the Cambridge Crystallographic Data Centre and may be obtained by quoting the depository numbers CCDC-101834 (**5**), -101835 (**6**), -101836 (**7**), -101837 (**8**), -101838 (**9**), -101839 (**10**), the names of the authors and the journal citation.

Dimethylaluminium N-Phenyl-N′,N′-bis(trimethylsilyl)hydrazide −Tetrahydrofuran (**5**): A solution of *n*BuLi in hexane (7.4 ml, 11.5 mmol) was slowly added dropwise to a stirred solution of Ph(H)N−N(SiMe$_3$)$_2$ (2.91 g, 11.5 mmol) in tetrahydrofuran (20 ml). The mixture was kept at reflux until butane evolution had ceased. Then one equivalent of a 1 M solution of dimethylaluminium chloride in heptane (11.5 mmol) was slowly added at −69°C. After warming to room temperature, the mixture was stirred for 48 h. The solvent was removed and the residue was dissolved in 20 ml of hexane. After removal of insoluble material (LiCl) by filtration, the filtrate was stored at −20°C. Colorless single crystals which were suitable for an X-ray structure investigation could be isolated after a few days. Yield 3.45 g (79%); m.p. 86°C (dec.). − ^{1}H NMR (C$_6$D$_6$, 270 MHz): $\delta = -0.32$ (s, 6 H, AlMe$_2$); 0.34 (s, 18 H, SiMe$_3$); 0.91 (t, 4 H, THF); 3.45 (t, 4 H, THF); 6.73 [t, ^3J(H,H) = 7.1 Hz, 1 H, *p*-Ph]; 7.05 [d, ^3J(H,H) = 8.1 Hz, 2 H, *o*-Ph]; 7.28 [t, ^3J(H,H) = 7.5 Hz, 2 H, *m*-Ph]. − ^{13}C NMR (C$_6$D$_6$, 100 MHz) $\delta = -7.8$ (AlMe$_2$); 2.8 (SiMe$_3$); 24.65 (THF); 71.3 (THF); 113.1 (*o*-Ph); 115.1 (*p*-Ph); 128. 8 (*m*-Ph); 157.9 (*i*-Ph). − ^{29}Si NMR (C$_6$D$_6$ 54 MHz): $\delta = 7.1$. − ^{27}Al NMR (hexane, 70 MHz): $\delta = 151$ ($h_{1/2} = 5570$ Hz). − C$_{18}$H$_{37}$AlN$_2$OSi$_2$ (380.66): calcd. C 56.79, H 9.82, N 7.36, Al 7.09; found C 53.85, H 9.22, N 6.79, Al 7.12.

Dimethylaluminium N,N′-Diphenyl-N′-trimethylsilylhydrazide−Tetrahydrofuran (**6**): A solution of *n*BuLi in hexane (4.5 ml, 7.1 mmol) was slowly added to a stirred solution of Ph(H)N−N(Ph)SiMe$_3$ (1.83 g, 7.1 mmol) in 40 ml of tetrahydrofuran. The mixture was heated to reflux for 1 h until butane evolution had ceased. After cooling to −69°C, one equivalent of a 1 M solution of dimethylaluminium chloride in heptane (7.1 mmol) was added slowly and the mixture was allowed to attain room temperature and was stirred further for 12 h. The solvent was then removed and the residue dissolved in 50 ml of hexane. After removal of insoluble material (LiCl), the filtrate was stored at −20°C. After 2 weeks, colorless single crystals had separated. Yield 2.16 g (80%); m.p. 97°C. − ^{1}H NMR (C$_6$D$_6$, 400 MHz): $\delta = -0.46$ (s, 6 H, AlMe$_2$); 0.42 (s, 9 H, SiMe$_3$); 0.87 (m, 4 H, THF); 3.41 (m, 4 H, THF); 6.74 [t, ^3J(H,H) = 7.2 Hz, 1 H, *p*-Ph]; 6.77 [t, ^3J(H,H) = 7.5 Hz, 1 H, *p*-Ph]; 6.95 [d, ^3J(H,H) = 7.2 Hz, 2 H, *o*-Ph]; 7.02 [d, ^3J(H,H) = 7.5, 2 H, *o*-Ph]; 7.13 [t, ^3J(H,H) = 7.2 Hz, 2 H, *m*-Ph]; 7.22 [t, ^3J(H, H) = 7.5 Hz, 2 H, *m*-Ph]. − ^{13}C NMR (C$_6$D$_6$, 100 MHz): $\delta = 0.5$ (AlMe$_2$); 1.5 (SiMe$_3$); 24.7 (THF); 71.6 (THF); 113.1 (*o*-Ph); 115.4 (*o*-Ph); 116.3 (*p*-Ph); 117.9 (*p*-Ph); 128.8 (*m*-Ph); 129.3 (*m*-Ph); 152.1 (*i*-Ph); 156.1 (*i*-Ph). − ^{27}Al NMR (C$_6$D$_6$, 104 MHz): $\delta = 165$ ($h_{1/2} = 6100$ Hz). − ^{29}Si NMR (C$_6$D$_6$, 79 MHz): $\delta = 10.3$. − C$_{21}$H$_{33}$AlN$_2$OSi (384.56): calcd. C 65.24, H 9.12, N 7.25, Al 7.02; found C 62.38, H 8.70, N 7.45, Al 7.14.

Dimethylaluminium N′,N′-Diphenyl-N-trimethylsilylhydrazide −Diethyl Ether (**7**): A solution of *n*BuLi in hexane (4.2 ml, 6.6 mmol) was slowly added dropwise to a stirred solution of (Ph)$_2$N−N(H)SiMe$_3$ (1.67 g, 6.5 mmol) in 40 ml of diethyl ether. The mixture was heated to reflux until butane evolution had ceased. After cooling to −69°C, one equivalent of a 1 M solution of dimethylaluminium chloride in heptane (6.5 mmol) was added slowly. This mixture was allowed to reach room temperature and was stirred for another 12 h. The solvent was removed in vacuo and the residue was treated with 40 ml of hexane. After insoluble material (LiCl) had been removed, the filtrate was kept at −20°C. Four weeks later colorless single crystals were isolated. Yield 1.46 g (56%); m.p. 61°C. − ^{1}H NMR (C$_6$D$_6$ 400 MHz): $\delta = -0.45$ (s, 6 H, AlMe$_2$); 0.27 (s, 9 H, SiMe$_3$); 0.59 (t, 6 H, Et$_2$O); 3.25 (q, 4 H, Et$_2$O); 6.73 [t, ^3J(H,H) = 7.4 Hz, 2 H, *p*-Ph]; 7.11 [t, ^3J(H,H) = 7.4 Hz, 4 H, *m*-Ph]; 7.48 [d, ^3J(H,H) = 7.4 Hz, 4 H, *o*-Ph]. − ^{13}C NMR (C$_6$D$_6$, 100 MHz): $\delta = -0.5$ (AlMe$_2$); 2.6 (SiMe$_3$); 1.4 (Et$_2$O); 66.1 (Et$_2$O); 119.6 (*o*-Ph); 119.71 (*p*-Ph); 128.6 (*m*-Ph); 150.0 (*i*-Ph). − ^{27}Al NMR (C$_6$D$_6$, 104 MHz): $\delta = 170$ ($h_{1/2} = 5770$ Hz). − ^{29}Si NMR (C$_6$D$_6$, 79 MHz): $\delta = 0.0$. − C$_{21}$H$_{35}$AlN$_2$OSi (386.58): calcd. C 65.24, H 9.12, N 7.25, Al 6.98; found C 63.38, H 8.70, N 7.45, Al 6.84.

Lithium Trihydrido[N-phenyl-N′,N′-bis(trimethylsilyl)hydrazino]aluminate−Diethyl Ether(1/2) (**8**): A 1.75 M solution of LiAlH$_4$ in diethyl ether (3.7 ml, 6.5 mmol) was slowly added at −69°C to a stirred solution of Ph(H)N−N(SiMe$_3$)$_2$ (1.63 g, 6.5 mmol) in 30 ml of diethyl ether. After the mixture had attained room temperature, it was heated to reflux for 1 h. A small amount of insoluble material, which proved to be compound **3**, was filtered off and the filtrate was stored at −20°C. Colorless single crystals of **8** formed within a week. Yield 2.33 g (82%); m.p. 93°C. − ^{1}H NMR (C$_6$D$_6$, 270 MHz): $\delta = 1.99-4.71$ (s, br., 3 H, AlH$_3$); 0.34 (s, 18 H, SiMe$_3$); 0.95 [t, ^3J(H,H) = 7.0 Hz, 12 H, Et$_2$O]; 3.32 [q, ^3J(H,H) = 7.0 Hz, 8 H, Et$_2$O]; 6.69 [t, ^3J(H,H) = 7.1 Hz, 1 H, *p*-Ph]; 7.08−7.34 (m, 4 H, *o,m*-Ph). − ^{13}C NMR (C$_6$D$_6$, 100 MHz): $\delta = 2.4$ (SiMe$_3$); 14.8 (Et$_2$O); 65.6 (Et$_2$O); 112.6 (*o*-Ph); 118.6 (*p*-Ph); 129.1 (*m*-Ph); 158.6 (*i*-Ph). − ^{27}Al NMR (C$_6$D$_6$, ^{1}H-decoupled, 70 MHz): $\delta = 110$ ($h_{1/2} = 87$ Hz). − ^{27}Al NMR (C$_6$D$_6$, ^{1}H-coupled, 70 MHz): $\delta = 110$ [q, ^1J(Al,H) = 178 Hz]. − ^{29}Si NMR (C$_6$D$_6$, 54 MHz): $\delta = 6.2$. − ^{7}Li NMR (C$_6$D$_6$, 105 MHz): $\delta = 0.40$ ($\Delta h_{1/2} = 12$ Hz). − IR (hostaflon): $\tilde{\nu} = 1781$ cm^{-1} (vs, br., Al−H). − C$_{20}$H$_{46}$AlLiN$_2$O$_2$Si$_2$ (436.69): calcd. C 55.00, H 10.63, N 6.42, Al 6.18; found C 52.16, H 9.82, N 6.73, Al 6.28.

Lithium [N′-tert-Butyl-N-trimethylsilylhydrazino](μ-N,N′-dihydrido)aluminate−Tetrahydrofuran (2/4) (**9**): A solution of *t*Bu(H)N−N(H)SiMe$_3$ (1.79 g, 11.2 mmol) in 20 ml of THF was slowly added to a stirred 1.58 M solution of LiAlH$_4$ in THF (7.08 ml, 11.2 mmol). Stirring was continued at 50°C for 4 h. A small amount of insoluble material was removed by filtration, and the filtrate was then kept at −20°C. After 5 d, colorless crystals had formed, which were not suitable for an X-ray structure investigation. Recrystallization from diethyl ether provided single crystals of **9**. Yield 1.97 g (52%); m.p. 83°C (dec.). − ^{1}H NMR ([D$_8$]toluene, 400 MHz): δ = 0.54 (s, 18 H, $SiMe_3$); 1.43 (m, 16 H, THF); 1.61 (s, 18 H, *t*Bu); 3.58 (m, 16 H, THF). − ^{13}C NMR ([D_8]toluene, 100 MHz): δ = 5.1 ($SiMe_3$); 25.7 (THF); 32.2 (*t*Bu); 56.9 (*t*Bu); 68.4 (THF). − ^{27}Al NMR ([D_8]toluene, 104 MHz): δ = 119 ($h_{1/2}$ = 1520 Hz). − ^{29}Si NMR (THF, 54 MHz): δ = −2.0. − ^{7}Li NMR ([D_8]toluene, 155 MHz): δ = 0.35 ($h_{1/2}$ = 30 Hz). − IR (hostaflon): $\tilde{\nu}$ = 1723 cm^{-1} (s, br., Al−H), 1652 (m, br., Al−H). − $C_{15}H_{36}AlLiN_2O_2Si$ (338.47): calcd. C 53.22, H 10.74, N 8.28, Al 7.97; found C 47.55, H 9.33, N 7.20, Al 7.91.

Dimethylaluminium N-tert-Butyl-N′-(trimethylsilyl)hydrazide (**10**): A solution of *n*BuLi in hexane (6.4 ml, 10.0 mmol) was slowly added to a stirred solution of *t*Bu(H)N−N(H)$SiMe_3$ in 50 ml of toluene. The mixture was heated to reflux for 1 h until the butane evolution had ceased. After cooling to −50°C, one equivalent of a 1 M solution of dimethylaluminium chloride in heptane (10.0 mmol) was slowly added. Work up by analogy to **9**. Colorless single crystals of **10** were isolated after a week. Yield 1.58 g (73%), m.p. 126°C. − ^{1}H NMR (C_6D_6, 25°C, 400 MHz): δ = −0.33 (s, 3 H, AlMe); −0.24 (s, 3 H, AlMe); 0.26 (s, 9 H, $SiMe_3$); 1.13 (s, 9 H, *t*Bu); 4.04 (s, br., 1 H, NH). − ^{1}H NMR (C_6D_6, 80°C): δ = −0.35 (s, br., 6 H, $AlMe_3$). − ^{13}C NMR (C_6D_6, 25°C, 100 MHz): δ = 1.4 ($AlMe_2$); 3.8 ($SiMe_3$); 28.4 (*t*Bu); 59.7 (*t*Bu). − ^{13}C NMR ([D_8]toluene, −60°C, 100 MHz): δ = 1.2 ($AlMe_2$); 1.6 ($AlMe_2$). − ^{29}Si NMR (C_6D_6, 54 MHz): δ = 15.2. − ^{27}Al NMR (C_6D_6, 104 MHz): δ = 141 ($h_{1/2}$ = 2200 Hz). − IR (Nujol, Hostaflon): $\tilde{\nu}$ = 3246 cm^{-1} (s, N−H), 1380, 1365 (s, *t*Bu). − $C_9H_{25}AlN_2Si_2$ (216.38): calcd. C 49.95, H 11.65, N 12.95, Al 12.47; found C 46.33, H 10.38, N 11.67, Al 12.35.

☆ Dedicated to Prof. Dr. *W. Simson* on the occasion of his 60th birthday.

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