Aluminium Hydrazides: Dimeric Bis(*tert*-butyl)aluminium Hydrazides with Six-Membered Al_2N_4 and Five-Membered Al_2N_3 Heterocycles

Werner Uhl,*[a] Jens Molter,[a] and Rainer Koch[b]

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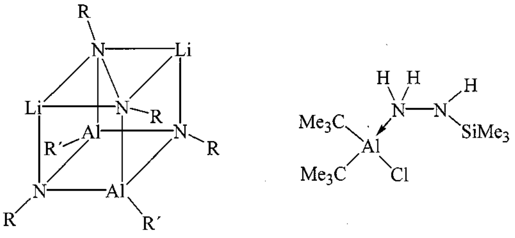
Treatment of the hydrazine adduct $(Me_3C)_2AlCl{\cdot}NH_2NHSiMe_3$ (**2**) with *n*-butyllithium afforded the colorless dialkylaluminium hydrazide $(Me_3C)_2AlN(SiMe_3)NH_2$ (**3**) by the release of butane and the precipitation of LiCl. Hydrazide **3** gave a dimer in solution and in the solid state. As shown by a crystal structure determination, a six-membered Al_2N_4 heterocycle with two intact endocyclic N–N bonds was formed by a head-to-tail dimerization. Upon sublimation of **3** in vacuum, a rearrangement was observed which gave an isomeric compound **4** after the migration of a hydrogen atom of a hydrazido ligand. The molecular core of **4** comprises a five-membered Al_2N_3 heterocycle, in which the Al atoms are bridged by one hydrazido ligand similar to **3**. The second ligand, however, has only one nitrogen atom in a bridging position with an exocyclic N–N bond. A similar compound (**5**) was obtained by the reaction of bis(*tert*-butyl)aluminium chloride with phenylhydrazine and *n*-butyllithium.

Introduction

Aluminium and gallium hydrazides found considerable interest in recent literature, because they are potentially useful as starting materials for the formation of the corresponding nitrides by chemical vapor deposition or by thermolysis of macroscopic samples. Several methods for the synthesis of those compounds were published, such as the treatment of hydrazines with trialkylelement compounds by the release of alkane,[1−3] the formation of hydrogen in a similar reaction by employing dialkylaluminium hydride[4] or $LiAlH_4$,[5] the reaction of lithium hydrazides with dialkylelement chlorides,[5,6] and the hydroalumination of azobenzene.[7] We tried to synthesize aluminium hydrazides by the reaction of dilithium bis(trimethylsilyl)hydrazide with dialkylaluminium chlorides. However, by partial cleavage of the N−N bonds, mixtures of products were formed from which cage compounds such as **1** were isolated in low yields (Scheme 1).[8] These cages contain a dimeric iminoalane, in which the Al_2N_2 heterocycle is bridged by a hydrazido ligand with an intact N−N bond. A heterocubane-type structure is formed by the addition of two lithium atoms. Boron hydrazides were obtained by the reaction of trimethylsilylhydrazine derivatives with boron halides[9] and the release of chlorotrimethylsilane. As was recently shown by our group, this method could not be applied to the synthesis of aluminium hydrazides.[10] Instead, bis(trimethylsilyl)hydrazine reacted with dialkylaluminium chlorides by dismutation to yield tris(trimethylsilyl)hydrazine and trimethylsilylhydrazine, which is thermally unstable[11] and was stabilized here by the formation of adducts **2** with the coordinatively unsaturated Al atoms (Scheme 1).[10] As is reported here, these adducts are excellent starting materials for the synthesis of aluminium hydrazides under mild conditions.



1 ($R = SiMe_3$; $R' = CMe_3$)

2

Scheme 1

Results and Discussion

Reaction of the Adduct $(Me_3C)_2AlCl{\cdot}NH_2NHSiMe_3$ with *n*-Butyllithium

A suspension of the adduct $(Me_3C)_2AlCl{\cdot}NH_2NHSiMe_3$ (**2**) in *n*-hexane was treated with an equimolar quantity of *n*-butyllithium at −30 °C. A clear solution was formed upon heating the mixture to room temperature, and LiCl precipitated slowly by stirring the solution over a period of 12h. As shown by NMR spectroscopy, adduct **2** was completely consumed, and two products were formed in the ratio of 10 (**3**) to 1. This ratio remained unchanged despite many attempts at recrystallization from different solvents and at different temperatures. We assumed that compound **3** may exist in equilibrium with another species and may for instance dissociate in solution. Indeed, the concentration of the by-product increased with temperature, and at 80 °C we observed a ratio of about 3 (**3**) to 1. The similar reactions of adduct **2** with methyl- or *tert*-butyllithium gave the product **3** only in very poor yields, but in all cases the by-product was detected in almost the same ratio by NMR spectro-

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[a] Fachbereich Chemie der Philipps Universität,
Hans-Meerwein-Straße, 35032 Marburg, Germany
Fax: (internat.) + 49-6421/282-8917
[b] Fachbereich Chemie der Carl von Ossietzky Universität,
Postfach 2503, 26111 Oldenburg, Germany

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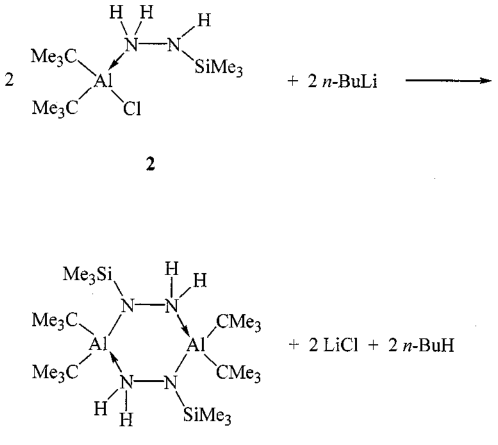
scopy. Some characteristics of this product are discussed below.

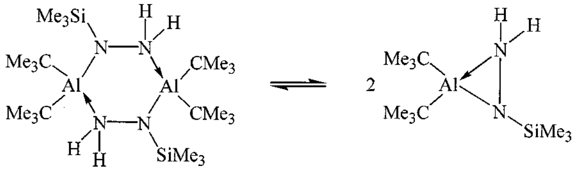
The mixture containing **3** as the main component was isolated in a yield of 69%. Compound **3** gave two singlets in the ^{1}H NMR spectrum, with an intensity ratio of 2:1 for the *tert*-butyl and trimethylsilyl hydrogen atoms. A single, broad resonance at $\delta = 4.32$ was assigned to the N−H protons. The integration gave one NH_2 group for each trimethylsilyl substituent, and thus one N−H proton had been removed from the adduct **2**. The composition of **3** as a dimeric dialkylaluminium hydrazide possessing a six-membered Al_2N_4 heterocycle was ascertained by a crystal structure determination (see below) and is depicted in Equation (1). As expected, the strong base *n*-butyllithium did not deprotonate the NH_2 moiety of adduct **2**, but the more acidic N−H proton of the NH($SiMe_3$) group, because an anion in this position is strongly stabilized by hyperconjugation[12] with the $SiMe_3$ substituent. The precipitation of lithium chloride led to the formation of an aluminium hydrazide, which gave a dimer owing to the presence of the NH_2 groups. The dimeric formula unit was also detected in benzene solution.



2

3

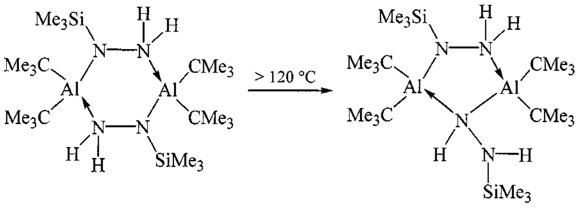
The by-product discussed above had two resonances for the $SiMe_3$ and CMe_3 hydrogen atoms in the intensity ratio of 1:2 ($\delta = 0.06$ and 1.29, respectively) similar to **3**, but two different resonances were now observed for two N−H protons at $\delta = 3.11$ and 2.68. In contrast to **3**, a strong dependence of the spectrum on temperature was observed. While the $SiMe_3$ singlet remained unchanged upon cooling of a solution in toluene to −80 °C, the resonance of the *tert*-butyl groups was split into two singlets ($\delta = 1.49$ and 1.24). The N−H protons gave a very broad resonance at +80 °C, which split into two resonances at about 50 °C. At 0 °C, two doublets were observed with chemical shifts of $\delta = 3.11$ and 2.68 and a coupling constant of $J = 4.6$Hz. We assume that this by-product results from partial dissociation of dimeric **3** into a monomeric species, which is favored in hot solutions [Equation (2)]. Its particular NMR data are in agreement with a three-membered AlN_2 heterocycle containing a dative $AlNH_2$ bond and a nonplanar environment of the negatively charged N atom, which is attached to the exocyclic trimethylsilyl group. A similar and still unpublished structure was recently observed by our group. The $SiMe_3$ substituent is thus neighbored by one hydrogen atom and one *tert*-butyl group, which causes the splitting of the corresponding resonances in the ^{1}H NMR spectrum. At higher temperature a rapid inversion of the configuration at that nitrogen atom occurs, which results in the equilibration of the hydrogen and the *tert*-butyl substituents in accordance with the observations in the temperature-dependent NMR spectra. The inversion barrier was estimated from these NMR data[13] to be about 65 kJ/mol. The low value of the molar mass of **3,** which was detected in benzene solution, may be caused by its partial dissociation. Other compounds are consistent with the NMR data. For instance, the dimeric aluminium hydrazide $[(Me_3C)_2$-Al−NH−$NHSiMe_3]_2$ may be formed by a hydrogen shift in both hydrazido ligands. A similar shift was observed with compound **3** as discussed below, but in all cases the rearrangement was observed with only one hydrazido ligand of the dimer, even at an elevated temperature, and a prolonged reaction time in solution was required. That hydrogen shift is irreversible, and it seems quite implausible that the completely rearranged product may exist in a temperature-dependent equilibrium in our NMR experiment. Besides the resonances discussed so far, other signals with a very low intensity are observed in the NMR spectra. These are either characteristic of compound **4** (next section) or could not be assigned to a particular species (two resonances of equal intensity at $\delta = 3.78$).



3

Rearrangement of 3

Owing to the unknown structure of the by-product in all isolated samples of **3**, we tried to purify this product by sublimation under vacuum. Sublimation occurred at a temperature of 120−140 °C at 10^{-3} Torr. However, NMR spectroscopy showed that a new product (**4**) was formed in a yield of 97% [Equation (3)]. Compound **4** was also obtained by heating solutions of **3** in benzene at 70 °C for 12 h. According to the NMR spectroscopic characterization and crystal structure determination, a hydrogen shift occurred with one of the hydrazido ligands so that each of its nitrogen atoms was attached to one hydrogen atom. The size of the central heterocycle changed. A five-membered ring was now observed with one bridging hydrazido ligand similar to compound **3** and one rearranged hydrazido group, only one nitrogen atom of which is in a bridging position. The latter hydrazido group has an intact N−N bond with an exocyclic NH($SiMe_3$) group.



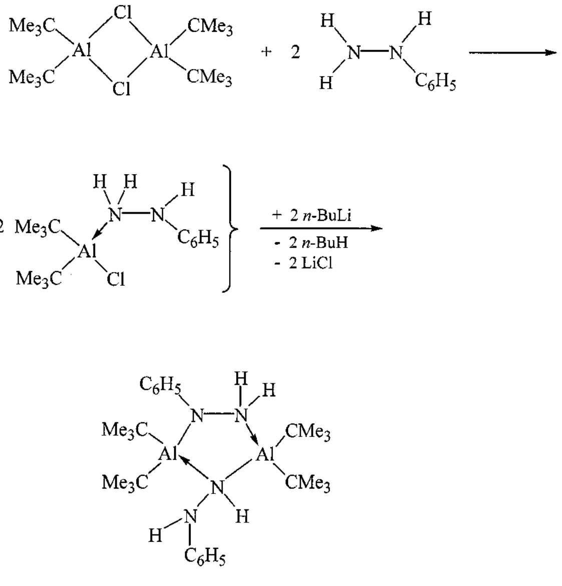
3 **4**

Owing to this particular molecular symmetry, which is retained in solution, we obtained a more complicated ^{1}H NMR spectrum. The $SiMe_3$ substituents, one attached to an endocyclic and the other bonded to an exocyclic nitrogen atom, gave rise to two resonances. Four different *tert*-butyl groups resulted owing to the chiral environment of the bridging nitrogen atom. Similarly, all N−H protons are chemically different and give rise to two AX spin systems by vicinal or geminal H−H coupling. The downfield resonances were assigned to the NH_2 group, because of their larger coupling constants and smaller differences in their chemical shifts. To the best of our knowledge, a similar rearrangement of a hydrazido ligand in oligomeric aluminium or gallium compounds has never been observed before. However, the shift of hydrogen atoms and silyl groups was observed in disilylhydrazine derivatives, where this process seems to be catalyzed by bases and leads to an equilibration of the 1,1- and 1,2-substituted species.[14]

Reactions with Phenylhydrazine

Phenylhydrazine is insoluble in hexane, and all reactions were carried out in toluene as solvent. Treatment of bis(*tert*-butyl)aluminium chloride with phenylhydrazine yielded a colorless precipitate, which was soluble in warm toluene and which probably contained an adduct similar to compound **2** described above. It was not isolated here, but directly treated with *n*-butyllithium at room temperature. The ^{1}H NMR spectrum of the crude reaction product, which was obtained after filtration and evaporation of the solvent, showed that in contrast to the reaction of the trimethylsilyl derivative described above, a six-membered heterocycle was not formed. Instead, a rearranged compound analogous to **4** containing a five-membered heterocycle in its molecular center was obtained under mild conditions [**5**, Equation (4)]. After recrystallization from a mixture of toluene and *n*-hexane, colorless crystals of **5** were isolated. The NMR spectra of **5** were similar to those of compound **4** with four different *tert*-butyl resonances and two AX spin-systems of the N−H protons. Although we changed the reaction conditions such as temperature and solvents systematically, we never found any evidence for the formation of an intermediate analogous to **3** with a six-membered Al_2N_4 heterocycle.

Crystal Structures of Compounds 3, 4 and 5



5

Compound **3** crystallizes with two independent molecules in the unit cell, each of which is localized on a crystallographic center of symmetry. Both molecules are similar, and therefore only one of the molecular structures is depicted in Figure1. They possess centrosymmetric six-membered Al_2N_4 heterocycles in their molecular centers, in which two hydrazido ligands bridge both aluminium atoms. Each Al atom has an Al−N bond to a N−$SiMe_3$ group and is further attached to one NH_2 group by a dative Al−N interaction. The heterocycles adopt a chair conformation. Similar structures with an endocyclic N−N bond are rare. One derivative was recently published by the group of Nöth with the compound $[Me_2AlN(SiMe_3)NH(CMe_3)]_2$.[5] Two six-membered Ga_2N_4 heterocycles were observed in the compound $[MeGa(\mu\text{-}NHNC_6H_5)_2GaMe]_2$, which adopts an overall hexagonal prismatic structure.[1] In most cases, however, only one nitrogen atom of the hydrazido group bridges two Al or Ga atoms with the N−N bond in an exocyclic position and the formation of E_2N_2 (E = Al, Ga) and Ga_3N_3 heterocycles.[1,3,4]

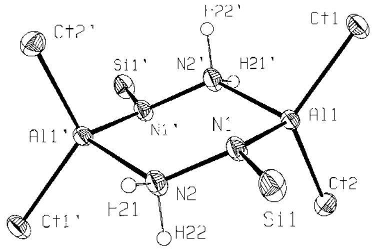


Figure 1. Molecular structure and numbering scheme of compound **3**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; hydrogen atoms with arbitrary radius; selected bond lengths [pm] and angles [°]: Al1−N1 186.7(1), Al1−N2 200.4(1), N1−N2 148.2(1), N1−Si1 174.4(1), Al2−N3 187.8(1), Al2−N4 199.8(1), N3−N4 148.3(2), N3−Si2 175.1(1); N2−Al1−N1 102.96(5), Al1−N1−N2 114.39(8), Al1−N1−Si1 131.14(6), N2−N1−Si1 109.23(8), N1−N2−Al1 126.69(8), N4−Al2−N3 102.84(5), Al2−N3−N4 111.80(8), Al2−N3−Si2 129.74(6), N4−N3−Si2 114.27(9), N3−N4−Al2 120.02(9)

The N−N bond lengths (148.2 pm on average) are similar to those usually observed in hydrazine derivatives,[15] in aluminium hydrazides[2−5,8,10] or in dilithium bis(trimethylsilyl)hydrazide.[16] The Al−N distances (187.2 and 200.1 pm) differ strongly. As expected, longer ones were observed for the dative[17] bonds Al1−N2′ and Al2−N4′. The N atoms N2 and N4 of the NH_2 groups have a distorted tetrahedral coordination sphere, while the tricoordinated nitrogen atoms N1 and N3 attached to the Al and Si atoms deviate only slightly from planarity, with sums of the bond angles of 354.8° and 355.8°. As can be expected with a hyperconjugative interaction, the N−Si bond lengths are short (174.7 pm).

The compounds **4** (Figure 2), an isomer of **3**, and **5** (Figure 3) have five-membered Al_2N_3 heterocycles in their molecular centers. One hydrazido ligand bridges both Al atoms in a similar manner as in compound **3** with an intact NH_2 group, but only one nitrogen atom of the second ligand is in a bridging position, while the second nitrogen atom is part of an exocyclic $NH(SiMe_3)$ group. Thus, one hydrogen atom of the NH_2 group moved, and each N atom is attached to one H atom. To the best of our knowledge, a similar structure has not yet been observed. The heterocycles adopt a twisted conformation, as can be derived from the torsion angles in the ring[18] (clockwise starting with N1−N2: 34.9°, −25.3°, 7.5°, 6.8°, −25.0° of **4**; 45.4°, −34.1°, 8.4°, 9.3°, −32.1° of **5**).

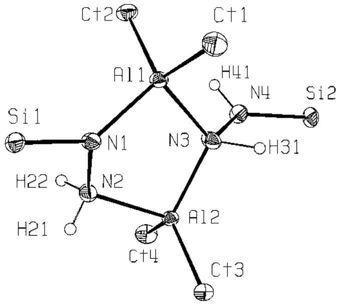


Figure 2. Molecular structure and numbering scheme of compound **4**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; hydrogen atoms with arbitrary radius; selected bond lengths [pm] and angles [°]: Al1−N1 188.5(2), Al1−N3 201.1(2), Al2−N2 200.3(2), Al2−N3 193.2(2), N1−N2 148.7(2), N3−N4 143.4(2), N1−Si1 174.4(2), N4−Si2 173.09(8); N1−Al1−N3 95.88(7), Al1−N3−Al2 112.64(7), N3−Al2−N2 93.34(7), Al2−N2−N1 115.2(1), N2−N1−Al1 114.0(1), Al1−N3−N4 116.2(1), Al2−N3−N4 115.2(1), Al1−N1−Si1 134.67(8), N2−N1−Si1 109.5(1)

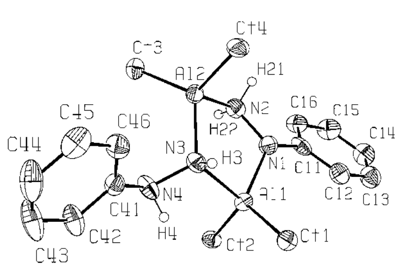


Figure 3. Molecular structure and numbering scheme of compound **5**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; hydrogen atoms with arbitrary radius; selected bond lengths [pm] and angles [°]: Al1−N1 193.9(3), Al1−N3 201.5(3), Al2−N2 205.9(2), Al2−N3 192.2(3), N1−N2 142.5(4), N3−N4 144.8(4), N1−C11 140.8(4), N4−C41 143.7(4); N1−Al1−N3 92.3(1), Al1−N3−Al2 113.3(1), N3−Al2−N2 93.3(1), Al2−N2−N1 109.7(2), N2−N1−Al1 115.7(2), Al1−N3−N4 108.5(2), Al2−N3−N4 114.5(2), Al1−N1−C11 124.5(2), N2−N1−C11 111.9(3)

The exocyclic N−N bond of compound **4** is shorter (N3−N4 143.4 pm) than the endocyclic one (N1−N2 148.7 pm), which resembles that of the hydrazido bridges in **3**. The reverse situation was observed for the phenylhydrazine derivative **5**, which had the shortest N−N bond in the ring (N1−N2 142.5 pm; N3−N4 144.8 pm). This observation may reflect the different charge separation in the molecules with a more effective charge-transfer to the phenyl group than to the trimethylsilyl group. Indeed, the phenyl groups are almost ideally in plane with the N−N bonds to allow mesomeric stabilization (torsion angles N1−N2−C11−C12 167.2°, N1−N2−C11−C16 −15.0°; −162.8° and 20.7° for the second phenyl group). The C−N bond to the anionic nitrogen atom [140.8(4) pm] is slightly shorter than that to the exocyclic nitrogen atom [143.7(4) pm]. The N−Si bonds of **4** are similar (N1−Si1 174.4 pm and N4−Si2 173.1 pm) and comparable with those observed for **3**. Each Al atom of both compounds is coordinated by two N atoms with alternating short and long bond lengths. The distances to the bridging nitrogen atom N3 are very similar [201.3 (Al1) and 192.7 pm (Al2) on average for both compounds **4** and **5**], but the distances to the hydrazido bridges differ with larger separations to the phenyl hydrazido group (**4**: Al1−N1 188.5 pm; Al2−N2 200.3 pm; **5**: Al1−N1 193.9 pm; Al2−N2 205.9 pm).

Quantum Mechanical Calculations

Two of the main issues of the preceding experimental findings are the rearrangement of compound **3** to give the five-membered ring **4** and the appearance of a by-product with an AlN_2 ring core. Previous studies on aluminium-containing molecules have shown that the application of the HF/6−31G* method/basis set combination gives good agreement with experimental structural data.[8,19,20] Larger basis sets led only to a slight improvement of the description of geometries and their use is not essential for our investigation.[19,20] We extended our current study to including density functional theory methods (in particular the hybrid functional approach Becke3LYP) and, where applicable, also to second-order perturbation theory (MP2) in order to assess the performance of the above methods for the calculation of relative energies. These studies were restricted to those compounds which had methyl instead of *tert*-butyl groups and *N*-silyl (SiH_3) instead of *N*-trimethylsilyl substituents (**3a**, **4a**).

The rearrangement of compound **3** which may exist in both a chair or a twist-boat conformation leads to the five-membered ring **4**. When considering a second migration, a four-membered ring, **6**, is formed with two rearranged hydrazido groups and only one nitrogen atom of each ligand bridging both Al atoms. The results of the Hartree−Fock and B3LYP calculations are summarized in Figure 4 and Table 1. It can be seen clearly that once again the Hartree−Fock-predicted geometrical data of **3a** and **4a** agree well with the experimental structures. The same is true for the DFT-calculated geometry which is slightly better for contacts not involving Al. As for the relative energies of the four isomeric structures, both methods give the same energetic ordering with almost identical differences separating the compounds: The five-membered ring **4a** is found to be the most stable isomer, followed by the chair conformation of **3a**. The least likely structures are the twist-boat conformation of **3a** and the Al_2N_2 heterocycle **6**. These data suggest that the rearrangement of **3** will indeed lead to **4**, which is thermodynamically favored over the former and over the completely rearranged compound **6**.

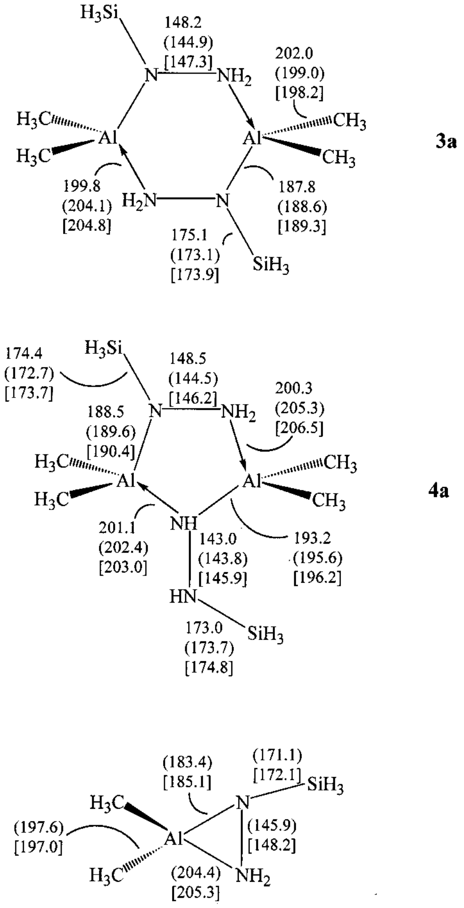
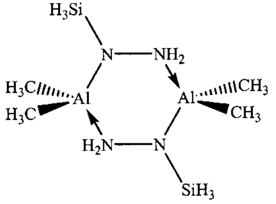
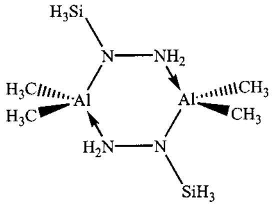
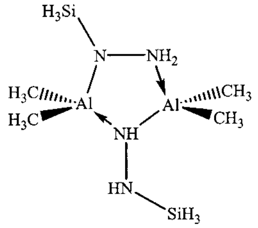
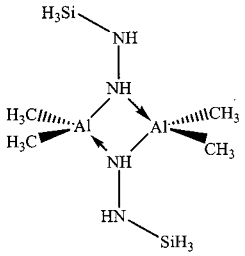


Figure 4. Selected bond lengths [pm] of compounds **3a**, **4a** and of the monomer of **3a** (experimental data without brackets, HF/6−31G* data in round brackets, B3LYP/6−31G* data in square brackets)

Table 1. Calculated relative energies [kJ/mol] with HF/6−31G* ZPVE corrections of compounds **3a**, **4a**, and **6**

Compound	HF/6-31G*	B3LYP/6-31G*
 **3a** chair conformation	0.0	0.0
 **3a** twistboat conformation	7.4	8.4
 **4a**	-2.4	-2.0
 **6**	7.8	9.0

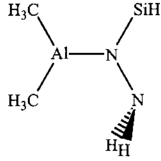
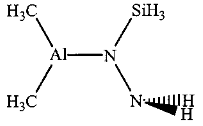
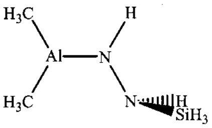
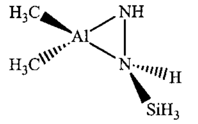
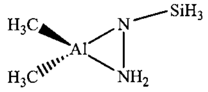
The existence of the second molecule which is in equilibrium with **3** [Equation (2)] and which is probably a monomer was also examined by means of quantum chemical methods. Five isomeric structures of this monomeric compound were calculated at the HF, the B3LYP and the MP2 level of theory (Table 2, structural parameters Figure 4). The most stable isomer is indeed the three-membered ring structure which has been previously assumed. It is favored over the next stable molecules by almost 20 kJ/mol. These results clearly show that if dissociation of **3** occurs, it will form the above-mentioned AlN_2 heterocycle. However, this process is calculated to be endothermic by almost 150 kJ/mol at 0 K. The entropy advantage reduces this difference to a surmountable barrier of 72 kJ/mol at 298 °C (laboratory conditions).

It is interesting to note that the HF and the DFT approach are both suitable for the examination of the compounds reported here. Not only are the calculated geometries of comparable quality, but the relative HF and B3LYP energies of both series of monomeric and dimeric structures are also very close. This finding confirms previous observations with similar calculations.[19]

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene with Na/benzophenone; *n*-hexane with $LiAlH_4$). The adduct **2**, bis(trimethylsilyl)hydrazine and $(Me_3C)_2AlCl$ were synthesized as described in refs.[10,11,21]. Phenylhydrazine (Aldrich) was distilled prior to use, and the solution of *n*-butyllithium in *n*-hexane (Aldrich) was used without further purification.

Table 2. Calculated relative energies [kJ/mol] with HF/6−31G* ZPVE corrections of the monomeric isomers

Compound	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
	0.0	0.0	0.0
	0.6	-0.6	0.6
	6.5	7.0	13.1
	17.6	18.5	10.2
	-17.4	-17.1	-20.0

Synthesis of (μ-2,2-Dihydro-1-trimethylsilylhydrazido-1κN^1:2κN^2)-(μ-2,2-dihydro-1-trimethylsilylhydrazido-2κN^1:1κN^2)bis[di(*tert*-butyl)aluminium] (3): A cooled (−30 °C) suspension of the adduct **2** (1.52g, 5.43mmol) in *n*-hexane (40mL) was treated with a solution of *n*-butyllithium in hexane (1.6 M, 3.4mL, 5.43mmol). The mixture was slowly warmed to room temperature, stirred for 12 h, filtered and concentrated. The residue was dissolved in a small volume of *n*-hexane. Colorless crystals of **4** (0.91g, 69%) were obtained on cooling the solution to −50 °C. − M.p. (argon, sealed capillary): 192 °C (dec.). − ^{1}H NMR (C_6D_6, 300MHz, 298K): δ = 0.15 (s, 18 H, $SiMe_3$), 1.11 (s, 36 H, CMe_3), 4.32 (s, 4 H, NH_2). − ^{13}C NMR (C_6D_6, 100.6MHz): δ = 0.25 ($SiMe_3$), 16.2 (AlC), 31.9 (C*Me*$_3$). − IR (CsBr, paraffin): ν = 3272 (w) cm^{-1}, 3243 (w), 3215 (w), 3201 (vw, νNH), 2925 (vs), 2855 (vs), 2726 (w), 2700 (w, paraffin, νCH_3), 1564 (m, δNH), 1462 (vs), 1378 (s, paraffin) 1285 (m), 1255 (s), 1231 (s, δCH_3), 1177 (w), 1000 (m), 972 (m), 955 (m), 901 (s, νC_3C), 868 (s), 836 (vs), 810 (s), 747 (s, ρCH_3) 677 (w, ν_{as}SiC) 626 (m, ν_sSiC), 579 (m), 547 (m), 511 (w), 493 (w, νAlC, νAlN), 403 (w), 357 (w, δSiC). − MS (EI); *m/z* (%): 431.3 (41) [$M^+ - C_4H_9$], 244.0 (58) [1/2 M^+]. − $C_{22}H_{58}Al_2N_4Si_2$ (488.86): calcd. Al 11.0; found Al 10.8. − Mol. mass: 450 (cryoscopically in benzene). − NMR characterization of the by-product: ^{1}H NMR ([D$_8$]toluene, 300MHz, 353K): δ = 0.08 (s, 18 H, $SiMe_3$), 1.23 (s, 36 H, CMe_3), 2.86 (br., 2 H, NH_2). − ^{1}H NMR ([D$_8$]toluene, 300MHz, 273K): δ = 0.06 (s, 9 H, $SiMe_3$), 1.29 (s, 18 H, CMe_3), 2.68 and 3.11 (each d, $^2J_{HH}$ = 4.6Hz, 1 H, NH). − ^{1}H NMR ([D$_8$]toluene, 300MHz, 193K): δ = 0.04 (s, 9 H, $SiMe_3$), 1.24 and 1.49 (each s, 9 H, CMe_3), 2.73 and 3.05 (each s, br., 1 H, NH).

Synthesis of (μ-2,2-Dihydro-1-trimethylsilylhydrazido-1κN^1:2κN^2)-(μ-1,2-dihydro-2-trimethylsilylhydrazido-1κN^1:2κN^1)bis[di(*tert*-butyl)aluminium] (4): Compound **5** (1.12g, 2.29mmol) was sublimed in vacuo (10^{-3} Torr) at a bath temperature of 120−140 °C to yield the pure product **6**. In a similar procedure, **6** was obtained directly from the crude product of the synthesis of **5** (1.09g, 97%). − M.p. (argon, sealed capillary): 56 °C. − ^{1}H NMR (C_6D_6, 300MHz): δ = 0.11 and 0.13 (each s, 9 H, $SiMe_3$), 1.10, 1.15, 1.20 and 1.26 (each s, 9 H, CMe_3), 2.78 and 3.15 (each d, $^3J_{HH}$ = 5.3Hz, 1 H, NH of the 1,1-bridging hydrazido ligand), 3.94 and 4.13 (each d, $^2J_{HH}$ = 11Hz, 1 H, NH of the 1,2-bridging hydrazido ligand). − ^{13}C NMR (C_6D_6, 75.5MHz): δ = 0.1 and −0.1 ($SiMe_3$), 14.3 and 18.3 (AlC), 31.94, 32.68 and 32.73 (C*Me*$_3$, the first resonance has double the intensity of the last two signals). − IR (CsBr, paraffin): ν = 3397 (w) cm^{-1}, 3277 (vw), 3248 (w), 3206 (vw, νNH), 2953 (vs), 2924 (vs), 2853 (vs), 2834 (vs), 2764 (w), 2729 (w), 2704 (w), 2625 (vw) paraffin, νCH; 1568 (m, δNH) 1466 (vs), 1377 (s, paraffin), 1358 (s), 1296 (w), 1254 (vs, δCH_3), 1209 (m), 1179 (w), 1113 (sh), 1045 (s), 1003 (m), 953 (m), 937 (m, νC_3C), 895 (vs), 839 (vs), 810 (vs), 748 (s, ρCH_3), 719 (m), 675 (m), 652 (s, ν_{as}SiC), 627 (m), 615 (m), 604 (m, ν_sSiC, νSiN), 575 (m), 550 (m), 517 (m), 476 (m), 467 (sh), 421 (m), 401 (m, νAlC, νAlN), 347 (w, δSiC). − MS (EI); *m/z* (%): 431.7 (18) [$M^+ - C_4H_9$], 244.2 (33) [1/2 M^+]. − $C_{22}H_{58}Al_2N_4Si_2$ (488.86): calcd. Al 11.0; found Al 10.9. − Mol. mass: 478 (cryoscopically in benzene).

Synthesis of (μ-2,2-Dihydro-1-phenylhydrazido-1κN^1:2κN^2)(μ-1,2-dihydro-2-phenylhydrazido-1κN^1:2κN^1)bis[di(*tert*-butyl)aluminium] (5): A solution of of bis(*tert*-butyl)aluminium chloride (3.27g, 18.5mmol) in toluene (20mL) was added to a cooled (0 °C) solution of phenylhydrazine (2.00g, 18.5mmol) in toluene (40mL). The mixture was warmed to room temperature and stirred until the precipitate was completely dissolved. A mixture of a solution of *n*-butyllithium in *n*-hexane (1.6 M, 11.6mL, mmol) and toluene (20mL) was added. After stirring at room temperature for 5 h, LiCl was filtered off, and the solvent was removed under vacuum. The residue was treated with a mixture of toluene and *n*-hexane (50mL, 1:1) and filtered. The filtrate was concentrated and gave the colorless product **5** (2.77g, 60%) upon cooling to 0 °C. − M.p. (argon, sealed capillary): 146 °C. − ^{1}H NMR (C_6D_6, 300MHz): δ = 0.99, 1.16, 1.23 and 1.32 (each s, 9 H, CMe_3), 3.96 (d, $^3J_{HH}$ = 3.1Hz, 1 H, NH of the 1,2-bridging hydrazido ligand), 4.44 and 4.64 (each d, $^2J_{HH}$ = 10.7Hz, 1 H, NH of the 1,2-bridging hydrazido ligand), 5.48 (d, $^3J_{HH}$ = 3.1Hz, 1 H, NH of the 1,1-bridging hydrazido ligand), 6.64, 6.68, 6.70, 6.74, 6.80, 6.82 and 6.86 (all phenyl, not able to to assign further owing to the overlap of resonances), 7.28 and 7.13 (pseudo-t, line distance 7.7Hz). − ^{13}C NMR (C_6D_6, 75.5MHz): δ = 33.1, 33.5, 33.8 and 34.4 (C*Me*$_3$), 113.5, 114.5, 120.9, 123.4, 131.9, 132.0, 151.0 and 155.0 (all phenyl), AlC not detected. − IR (CsBr, paraffin): ν = 3394 cm^{-1} (w), 3349 (w), 3218 (w), 3183 (w), 3132 (vw, νNH), 2956 (vs), 2924 (vs), 2854 (vs), 2730 (w), 2701 (w, paraffin, νCH), 1600 (m, phenyl), 1578 (m, δNH), 1463 (vs), 1378 (s, paraffin), 1308 (m), 1259 (s, δCH_3), 1220 (m), 1180 (w), 1155 (w), 1091 (vw), 1082 (w), 1040 (w), 986 (m), 930 (w), 870 (m), 809 (m), 749 (s), 723 (w, νCN, νC_3C, ρCH_3), 686 (s), 675 (m), 601 (w, δphenyl), 564 (w), 539 (m), 523 (w), 464 (w), 435 (w, νAlC, νAlN), 412 (w), 371 (vw), 338 (w, δC_3C). − MS (EI); *m/z* (%): 439.3 (1) [$M^+ - C_4H_9$], 325.1 (100) [$M^+ - 3\ C_4H_9$], 248.0 (5) [1/2 M^+]. − $C_{28}H_{50}Al_2N_4$ (496.69): calcd. Al 10.9; found Al 10.6.

Crystal Structure Determinations: Single crystals of the compounds **3** and **4** were obtained by recrystallization from *n*-hexane. Compound **5** was recrystallized from a mixture of toluene and *n*-hexane. Crystal data and structure refinement parameters are given in Table3.[24] Compound **4** showed a disorder of the exocyclic N4−$SiMe_3$ group. Its atoms were refined in split positions with occupancy factors of 0.70 and 0.30. The atoms of the minor com-

Table 3. Crystal data, data collection parameters and structure refinement of compounds **3**, **4** and **5**

	3	**4**	**5**
Formula	$C_{22}H_{58}Al_2N_4Si_2$	$C_{22}H_{58}Al_2N_4Si_2$	$C_{28}H_{50}Al_2N_4$
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$; No. 2[22]	$P2_1/c$; No. 14[22]	$I2/a$; No. 15[22]
Z	2	4	16
Temperature [°C]	−80	−80	−80
$d_{calcd.}$ [g/cm^3]	1.012	1.023	1.069
a [pm]	1097.4(1)	903.5(2)	3196.4(1)
b [pm]	1235.5(1)	1764.6(4)	1175.18(4)
c [pm]	1248.4(1)	2013.5(4)	3375.01(8)
α [°]	102.38(1)	90	90
β [°]	92.83(1)	98.76(3)	103.092(3)
γ [°]	102.69(1)	90	90
V [10^{-30} m^3]	1604.7(3)	3173(1)	12348.0(7)
μ [mm^{-1}]	0.146	0.182	0.115
Crystal size [mm]	0.90 × 0.68 × 0.44	0.55 × 0.50 × 0.50	0.35 × 0.30 × 0.24
Diffractometer		Stoe-IPDS	
Radiation		Mo-K_α, graphite monochromator	
2Θ range [°]	$5.38 \le 2\Theta \le 52.2$	$4.1 \le 2\Theta \le 52.0$	$4.0 \le 2\Theta \le 52.0$
Index ranges	$-13 \le h \le 13$ $-15 \le k \le 15$ $-15 \le l \le 15$	$-11 \le h \le 11$ $-21 \le k \le 21$ $-24 \le l \le 24$	$-39 \le h \le 38$ $-14 \le k \le 14$ $-38 \le l \le 38$
Independent reflections	5820	6159	11331
Reflections $F > 4\sigma(F)$	4911	4677	6137
Parameters	305	320	707
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ [$F > 4\sigma(F)$]	0.0340	0.0395	0.0596
$wR^2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (all data)	0.0982	0.1176	0.1687
Max./min. residual [10^{30} e/m^3]	0.34/−0.21	0.35/−0.28	0.72/−0.42

ponent were refined isotropically with restrictions of bond lengths and angles. Two *tert*-butyl groups of compound **5** (CT4 and CT7) were rotationally disordered, the methyl groups were refined with restrictions of bond lengths and angles and occupancy factors of 0.64 and 0.36. Program: SHELXTL-Plus, SHELXL-93[23] solutions by direct methods; full-matrix refinement with all independent structure factors.

Quantum Chemical Calculations: The Hartree−Fock[25] method (including electron correlation at the MP2(fc) level of theory) and the Becke3LYP[26] approach in combination with the 6−31G* basis set were used to optimize the ground-state structure and to characterize the bonding situation. The located structures were confirmed as minima through calculation and analysis of the vibrational frequencies (HF/6−31G*). The energies given in Tables1 and 2 include the scaled zero-point vibrational energy corrections. All calculations were carried out with the GAUSSIAN 98 system of programs.[27]

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