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Dialkylaluminum Hydrazides Derived from Free Hydrazine N_2H_4. Molecular Structures of $[(Me_3C)_2AlN_2H_3]_2$ and $[(Me_3C)_2Al]_4(N_2H_2)_2$

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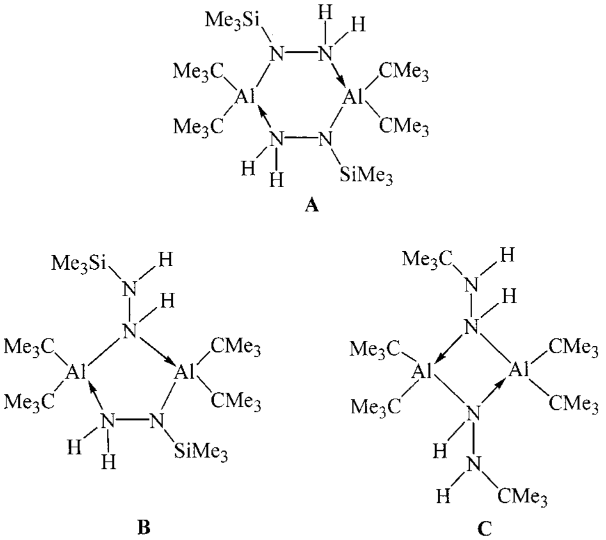
The reaction of di(*tert*-butyl)aluminum hydride with hydrazine N_2H_4 afforded the hydrazide $(Me_3C)_2AlN_2H_3$, **1**, by the release of elemental hydrogen. Compound **1** is a dimer in solution and in the solid state and possesses a six-membered Al_2N_4 heterocycle in a *twist* conformation with two intact N−N bonds. Further reaction of **1** with an excess of $HAl(CMe_3)_2$ yielded the tricyclic aluminum and nitrogen rich Al_4N_4 compound $[(Me_3C)_2AlN_2H_2]_2$-$[Al(CMe_3)_2]_2$, **2**, in which each N−N bond of a central six-membered Al_2N_4 ring similar to that of **1** is side-on-coordinated to an $Al(CMe_3)_2$ group. The structure of **2** may be interpreted as a dimer of the dialuminum hydrazide $(Me_3C)_2Al{-}NH{-}NH{-}Al(CMe_3)_2$.

Introduction

Chart 1



Hydrazido derivatives of the group 13 elements found considerable interest in recent literature because they are potentially useful as precursors for the formation of the corresponding element nitrides.[1−6] We are very interested in the syntheses and characterization of *tert*-butylaluminum hydrazides, which adopt three different types of structures depending on the steric demand of the substituents attached to nitrogen (Chart 1). Six-membered Al_2N_4 heterocycles **A** with two endocyclic N−N bonds were formed with trimethylsilylhydrazide as a ligand.[3] This compound rearranged upon sublimation in a vacuum by a shift of hydrogen atoms to give a five-membered Al_2N_3 heterocycle **B**, which had one exocyclic N−N bond.[3] A similar compound was obtained by employing the phenylhydrazido ligand.[3] Probably owing to steric overcrowding, a four-membered Al_2N_2 heterocycle **C** with two exocyclic N−N bonds was formed with *tert*-butylhydrazide as a ligand.[6] Most of the hydrazido compounds described in the literature[1−6] bear alkyl or silyl groups attached to their nitrogen atoms, probably owing to their better solubility in common organic solvents and their increased stability. Unsubstituted hydrazine N_2H_4 has been used as a reagent only in very few cases. The trimethylamine adduct of AlH_3 was reported to yield an insoluble, not well-characterized and dangerously explosive solid upon treatment with hydrazine.[7] Caution! This observation was verified in our group: the solid is thermally stable even in boiling toluene but explodes upon touch with a spatula under solvent-free conditions. Thus, its preparation should be avoided or only be done with the greatest care on a very small scale. Trimethylaluminum was reported to react with hydrazine by the release of methane and the formation of a solid which was characterized by

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elemental analysis to be $(Me_2Al)_2N_2H_2$ and which also was reported to tend toward spontaneous decomposition.[8] The ether adduct of tris(trimethylsilyl)aluminum reacted with hydrazine by cleavage of the N−N bond and the formation of a dimeric aluminum amide.[9] However, under certain circumstances explosive mixtures are formed.[9] We hoped to isolate more stable aluminum derivatives of hydrazine by the introduction of large substituents such as *tert*-butyl groups and treated di(*tert*-butyl)aluminum hydride with N_2H_4.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane over $LiAlH_4$, toluene and diisopropyl ether over Na/benzophenone). The trimeric di(*tert*-butyl)aluminum hydride and anhydrous hydrazine were obtained according to literature procedures.[10,11]

$[(Me_3C)_2AlNHNH_2]_2$ (1). An emulsion of anhydrous hydrazine (0.5 mL, 0.511 g, 15.97 mmol) in 25 mL of *n*-hexane was cooled to −100 °C and vigorously stirred. A solution of 2.266 g (15.96 mmol) of $(Me_3C)_2AlH$ in 25 mL of *n*-hexane was added. The mixture was slowly warmed to room temperature over a period of 1 day. A colorless solid precipitated, which was dissolved by the addition of toluene. The solution was filtered and cooled to −40 °C to obtain colorless crystals of compound **1**. Yield: 2.36 g (86%). Decompositon point (argon, closed capillary): 110 °C. Molar mass (cryoscopically in benzene): calcd 344.5; found 340. ^1H NMR (C_6D_6, 300 MHz): δ 2.90 (2 H, d, $^3J_{HH}$ = 5.2 Hz, br, NH_2), 1.97 (1 H, t, $^3J_{HH}$ = 5.2 Hz, br, NH), 1.10 (18 H, s, CMe_3). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 31.7 (s, C*Me*$_3$), 13.4 (AlC). IR (paraffin, CsBr plates, cm^{-1}): 3331 w, 3279 w, 3187 w ν(NH); 2922 vs, 2855 vs (paraffin); 1590 w $\delta(NH_2)$; 1461 vs, 1378 s (paraffin); 1362 m, 1275 m, 1182 m $\delta_s(CH_3)$; 1090 vw, 1000 w, 935 m $\nu_{as}(C_3C)$, ν(NN); 813 s $\nu_s(C_3C)$; 727 w, 684 m, 651 w, 619 m, 579 m, 538 w, 483 s ν(AlC), ν(AlN); 403 m, 387 w, 364 m $\delta(C_3C)$. Anal. Calcd for $C_{16}H_{42}Al_2N_4$: Al, 15.7; N, 16.3. Found: Al, 15.5; N, 16.0.

$[(Me_3C)_2AlN_2H_2]_2[Al(CMe_3)_2]_2$ (2). A cooled (−80 °C) suspension of compound **1** (2.11 g, 6.12 mmol) in 25 mL of toluene was treated with a solution of $(Me_3C)_2AlH$ (1.74 g, 12.27 mmol) in 40 mL of *n*-hexane. The mixture was warmed to room temperature over a period of 1 day. A colorless solid precipitated, which was filtered off and identified as pure **2**. The product may be recrystallized from a hot toluene/diisopropyl ether mixture. Yield: 2.15 g (56%). Decomposition point (argon, closed capillary): 160 °C. MS (EI): *m*/*z* 567 (80%, M^+ − *t*Bu). ^1H NMR (D_8-THF, 300 MHz): δ 2.67 (2 H, s, NH), 1.13 and 0.98 (each 18 H, s, CMe_3). ^{13}C NMR (D_8-THF, 75.5 MHz): δ 31.0 and 29.7 (CMe_3), 13.8 and 12.2 (AlC). IR (paraffin, CsBr plates, cm^{-1}): 3256 w ν(NH); 2923 vs, 2852 vs (paraffin); 1604 vw, 1587 vw $\delta(NH_2)$; 1464 vs, 1377 s (paraffin); 1363 m, 1306 vw, 1259 vw, 1201 m, 1186 w $\delta_s(CH_3)$; 1086 vw, 1002 w, 975 vw, 933 w, 886 m $\nu_{as}(C_3C)$, ν(NN); 811 m $\nu_s(C_3C)$; 722 w, 626 m, 604 m, 586 m, 535 w, 480 vw ν(AlC), ν(AlN); 442 w, 427 w $\delta(C_3C)$. Anal. Calcd for $C_{32}H_{76}Al_4N_4$: Al, 17.3; N, 9.0. Found: Al, 16.9; N, 9.1.

Crystal Structure Determinations. Single crystals were obtained by recrystallization from toluene/*n*-hexane (**1**, 20/−40 °C) and toluene/diisopropyl ether (**2**, reflux/room temperature). The X-ray data collections were performed on the STOE IPDS system (**1**) and the four-circle diffractometer CAD-4 (**2**) with graphite-monochromated Mo Kα radiation. The crystals (**1**, 0.2 mm × 0.3 mm × 0.4 mm; **2**, 0.5 mm × 0.5 mm × 0.3 mm) were mounted in perfluorinated polyether. The intensity data were collected at 213 K in the 2θ ranges 3.8−51.9° (**1**) and 4.8−50.6° (**2**), spanning the octants $-21 \le h \le 21$, $-7 \le k \le 7$, $-27 \le l \le 27$ and $-10 \le h \le 0$, $-12 \le k \le 12$, $-13 \le l \le 13$, respectively. A total of 2138 independent reflections was collected for compound **1** (3622 for **2**). All structures were solved by direct methods using the program system SHELXTL PLUS[12] and refined with the SHELXL-97[12] program via full-matrix least-squares calculations based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms of methyl groups were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}(C)$; N−H hydrogen atoms were taken from difference Fourier maps and refined isotropically. The crystallographic data and details of the final *R* values are provided in Table 1. Conventional *R* factors (R1) are based on *F* using reflections with $F > 4\sigma(F)$ (1806 reflections for **1**, 2677 for **2**); weighted *R* factors (wR2) are based on F^2. The number of refined parameters was 122 (**1**) and 253 (**2**). The molecules of compound **1** were located on a crystallographic 2-fold rotation axis perpendicular to the central heterocycle. The equatorial hydrogen atoms of the hydrazido groups were statistically disordered and had occupancy factors of 0.5. The molecule of compound **2** resided on a crystallographic center of symmetry. The nitrogen atoms and N−H hydrogen atoms were statistically disordered (occupancy factors 0.53 and 0.47) and adopted positions below and above the molecular plane.

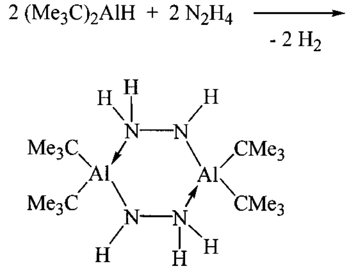
Table 1. Crystallographic Data for **1** and **2**

	1	**2**
chemical formula	$C_{16}H_{42}Al_2N_4$	$C_{32}H_{76}Al_4N_4$
fw	344.5	624.9
space group	$C2/c$	$P\bar{1}$
a (pm)	1738.9(1)	940.8(1)
b (pm)	591.79(3)	1082.6(1)
c (pm)	2249.6(1)	1169.4(1)
α (deg)	90.0	82.25(1)
β (deg)	108.695(7)	69.57(1)
γ (deg)	90.0	71.77(1)
V (10^{-30} m^3)	2193(2)	1059.7(2)
Z	4	2
temp (K)	213	213
λ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.043	0.979
μ (mm^{-1})	0.136	0.133
R1 [a]	0.0508	0.0530
wR2 [b]	0.1599	0.1518

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ ($F > 4\sigma(F)$). [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$ (all data).

Results and Discussion

$[(Me_3C)_2AlNHNH_2]_2$ (1). Anhydrous hydrazine is insoluble in most organic solvents. Therefore, vigorously stirred emulsions of N_2H_4 in *n*-hexane were employed in the reactions described here. Furthermore, treatment of hydrazine with *tert*-butylaluminum hydride at room temperature gave mixtures of several unknown products, none of which could be isolated in pure form. However, very selective reactions were observed upon cooling of the emulsions to low temperature (−100 °C) prior to the addition of the aluminum hydride. Both components precipitated under these conditions, and the reaction occurred only upon slow warming to room temperature (eq 1). As shown by NMR spectroscopy, the product **1** was quantitatively formed without any detectable byproduct. **1** is insoluble in *n*-hexane and was dissolved by the addition of toluene to the reaction mixture. The crystalline product was isolated after cooling of the mixture to −40 °C in 86% yield. In the ^1H NMR spectrum



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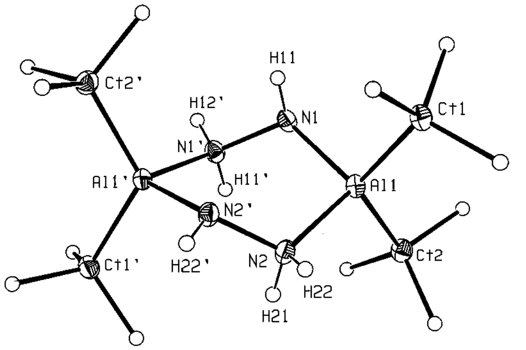


Figure 1. Molecular structure and numbering scheme of **1**. The thermal ellipsoids are drawn at the 40% probability level. Methyl hydrogen atoms are omitted for clarity, and methyl carbon atoms and N−H hydrogen atoms are shown with arbitrary radius.

it showed a singlet of the *tert*-butyl groups and two resonances of the chemically different N−H protons of the hydrazido ligand in an intensity ratio of 2 to 1, which, owing to H−H coupling across the N−N bond, split into a doublet and a triplet. Compound **1** is dimeric in benzene solution as was shown by cryoscopic molar mass determination. It is thermally stable up to 110 °C; above that point slow decomposition occurred to yield a gray, amorphous powder. Also, bulk material up to 3 g decomposes slowly without indication of a strong exothermic process, and no spontaneous decomposition was observed at room temperature upon mechanical treatment. In air, slow decomposition occurred, probably owing to hydrolysis, to give a colorless oil. Sublimation afforded only a small quantity of an unknown secondary product, which could not be identified. The formation of $[(Me_3C)_2AlNH_2]_2$ could be excluded owing to a comparison of the NMR data ($\delta = 1.15$ for *tert*-butyl and $\delta = 2.10$ for N−H protons; intensity ratio 18 to 1) with those reported in the literature.[14] All observations concerning the stability of **1** indicate so far that it does not have the hazardous properties of the hydrazine derivatives described above and can be handled and used for further experiments. Its higher thermal stability may be caused by the "dilution" of the hydrazido groups by two bulky *tert*-butyl substituents on each aluminum atom.

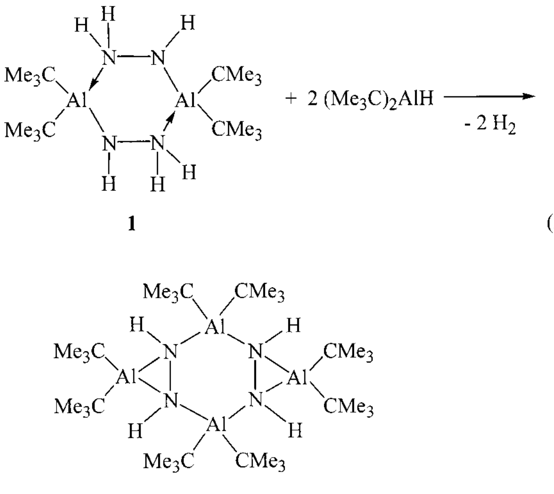
The molecular structure of **1** is depicted in Figure 1. Two aluminum atoms are bridged by two N_2H_3 groups with intact N−N bonds to give a six-membered Al_2N_4 heterocycle. Not a chair conformation was ascertained as for the compound $[(Me_3C)_2AlN(SiMe_3)NH_2]_2$,[3] but a *twist* conformation was observed, which may be stabilized by a steric interaction among the four bulky *tert*-butyl groups in positions 1 and 4 of the ring. Four almost equidistant Al−N distances (195.0 pm, Table 2) were detected. In contrast, dimeric aluminum hydrazides obtained before usually gave clearly separated Al−N bond lengths of about 188 pm (polar covalent bond, tricoordinated nitrogen atom) and about 200 pm (dative bond, tetracoordinated nitrogen atom).[3,5] The value observed for **1** is between these ideal distances, which may be caused by the disorder of the molecule as described in the Experimental Section. The N−N bond lengths (149.1 pm on average) are similar to those observed for other dimeric aluminum hydrazides with endocyclic N−N bonds.[3]

Table 2. Selected Bond Lengths (pm) and Angles (deg) for Compounds **1** and **2**

$[(Me_3C)_2AlNHNH_2]_2$, **1**[a]			
Al(1)−N(1)	195.1(2)	Al(1)−N(1)−N(1)′	116.8(1)
Al(1)−N(2)	194.9(2)	Al(1)−N(2)−N(2)′	116.8(1)
N(1)−N(1)′	149.3(4)	N(1)−Al(1)−N(2)	102.9(1)
N(2)−N(2)′	148.9(4)		
$[(Me_3C)_2AlN_2H_2]_2[Al(CMe_3)_2]_2$, **2**[b]			
Al(1)−N(1)	194.1(7)/197.0(6)	Al(1)−N(1)−N(2)′	120.5(8)/121.4(7)
Al(1)−N(2)	195.9(7)/195.2(7)	Al(1)−N(2)−N(1)′	120.8(8)/121.4(7)
Al(2)−N(1)	196.9(7)/194.6(6)	Al(1)−N(1)−Al(2)	153.8(7)/152.9(6)
Al(2)−N(2)′	194.8(7)/195.7(7)	Al(1)−N(2)−Al(2)′	153.7(7)/153.5(6)
N(1)−N(2)′	157.7(14)/153.2(12)	N(1)−Al(1)−N(2)	98.2(3)/97.2(3)
		N(1)−Al(2)−N(2)′	47.5(4)/46.2(3)
		N(1)−N(2)′-Al(2)	67.0(4)/66.5(3)
		N(2)′-N(1)−Al(2)	65.6(4)/67.3(3)

[a] N(1)′, N(2)′ generated by $-x + 1, y, -z + {}^{1}/_{2}$. [b] N(1)′, N(2)′, Al(2)′ generated by $-x + 2, -y, -z$; disordered N_2 groups.

$[(Me_3C)_2AlNHNH]_2[\mu\text{-}Al(CMe_3)_2]_2$ (2). All hydrazido derivatives obtained so far had further substituents attached to their N−N bonds. In contrast, compound **1** is far less sterically shielded. Therefore, we hoped to achieve a further reaction and to obtain an aluminum-rich new compound when we treated **1** with an excess of di(*tert*-butyl)aluminum hydride. Both components were combined in toluene and *n*-hexane at −80 °C, and the mixture was slowly warmed to room temperature (eq 2). The product **2** is insoluble in that solvent mixture and precipitated as a colorless solid. It was filtered off and recrystallized from a hot mixture of toluene and diisopropyl ether. Owing to the low solubility in benzene, its molar mass in solution could not be detected by cryoscopy. It showed two singlets for chemically different *tert*-butyl groups in the ^{1}H NMR spectrum and only one resonance for the N−H protons at $\delta = 2.67$. The intensity ratio was 9 to 9 to 1, which verified that di(*tert*-butyl)aluminum groups were added to the molecule and had replaced one N−H hydrogen atom of each hydrazido group. Compound **2** is easily soluble in THF and does not crystallize from those solutions upon cooling to −40 °C. Heating of such solutions to 40 or 50 °C led to the interesting observation that the product precipitated; it dissolves again on cooling to room temperature. After evaporation of the solvent, pure **1** was recovered quantitatively. We suppose that a weak adduct of **2** and THF was formed at lower temperature, perhaps accompanied by dissociation and the formation of monomers. Upon heating, this adduct loses its THF molecules and the



1 (2)

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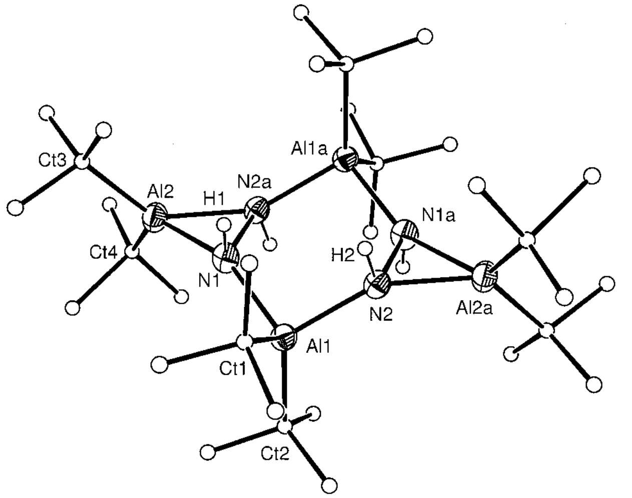

Figure 2. Molecular structure and numbering scheme of **2**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms of methyl groups are omitted for clarity, and carbon atoms are shown with arbitrary radius. Only one N_2H_2 group is drawn for each disordered hydrazido ligand.

insoluble product **2** is re-formed. Compound **2** decomposes only upon heating to 160 °C to yield a gray powder similar to the decomposition of **1**, and slow hydrolysis was observed on contact with air. No sensitivity to mechanical shock was observed.

A crystal structure determination of **2** revealed a singular tricyclic structure (Figure 2) with a central six-membered Al_2N_4 heterocycle and two intact N−N bonds similar to compound **1**. Both hydrazido groups were side-on-coordinated by dialkylaluminum ligands to give two three-membered AlN_2 heterocycles. A similar side-on coordination of aluminum atoms to hydrazido groups was observed before for the alkylaluminum bis(hydrazido) derivative $Me_3C{-}Al[N(SiMe_3)NH(SiMe_3)]_2$.[5] The six-membered heterocycle adopts an almost ideal chair conformation. Its Al−N distances (195.6 pm on average, Table 2) are similar to those observed for **1**. Owing to the disorder of the nitrogen atoms with positions above and below the average molecular plane, the N−N bond lengths could not be determined unambiguously. A short and somewhat unreasonable bond length of 141.7 pm on average results when the nitrogen atoms are taken from the same side of the molecular plane, while distances of 155.5 pm on average are obtained for the chair form of the heterocycle. This is longer than usually observed in aluminum hydrazides,[1−3] but similar distances were observed in dilithium hydrazides[15] or in heterocubane type molecules such as $Li_2(AlR)_2(NSiMe_3)_4$,[4] which have one intact N−N bond across one of their faces. All these molecules contain hydrazido dianions and are thus very similar to compound **2**, which makes the longer distance more probable. The Al−N distances in the three-membered heterocycle (195.5 pm on average) are indistinguishable from those of the six-membered central ring. Owing to the short N−N bond a very acute angle of 46.9° at the aluminum atom Al2 was observed. Both AlN_2 triangles and the average plane of the Al_2N_4 ring are almost coplanar, and the angle between the normals of these planes is only 18.6°.

Acknowledgment. We are grateful to the Fonds der Chemischen Industrie for generous financial support.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determinations are also available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-147183 (**1**) and CCDC-147184 (**2**).

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