Notes

tert-Butylaluminum Bis[1,2-bis(trimethylsilyl)hydrazide]: The First Alkylaluminum Dihydrazide

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*Summary: The reaction of di(tert-butyl)aluminum hydride with a mixture of 1,1- and 1,2-bis(trimethylsilyl)-hydrazine afforded colorless crystals of the title compound $Me_3CAl[N(SiMe_3)N(H)SiMe_3]_2$ (**1**) in 60% yield. **1** is a monomer in the solid state. Its aluminum atom has a coordination number of 5 and is side-on coordinated by both hydrazido ligands. Different Al−N distances of 1.814(2) and 2.072(2) Å are observed according to the different coordination by amido or amino nitrogen atoms, respectively.*

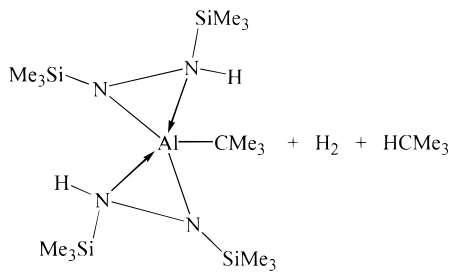
Introduction

Hydrazido derivatives of the elements of the third main group are of current interest[1−12] because they are suitable starting materials for the formation of aluminum or gallium nitride.[2,8,13] Different methods have been employed for their synthesis such as salt elimination reactions of element halides and lithium hydrazides[7,8,12] or alkane elimination reactions of trialkylaluminum or -gallium compounds and hydrazines.[1,2,4,5] In most of these cases dialkylelement monohydrazides were formed. Usually, these products were dimeric, showing one of three possible structures: (i) four-membered Al_2N_2 heterocycles with only one N atom of each hydrazido group in a bridging position and two exocyclic N−N bonds,[1,2,4,5,8] (ii) six-membered Al_2N_4 heterocycles with the N−N bonds included in the ring,[7,12] and (iii) a mixed form with Al_2N_3 heterocycles that contain an endocyclic and an exocyclic N−N bond.[12] Beside these dimers, further hydrazido aluminum and gallium compounds are known, which possess ladder type structures,[6] macrocycles,[3] or cage structures.[1,2,10] We report here on the first alkylaluminum dihydrazide.

Results and Discussion

In all experiments we started with a mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazine, which is easily available by the reaction of hydrazine with chlorotrimethylsilane[14] and contains both components in an almost equimolar ratio. Both isomers are in an equilibrium, and the rapid 1,2 shift of trimethylsilyl substituents was observed in the presence of butyllithium.[15] Nevertheless, this mixture is an excellent starting material for the synthesis of bis(trimethylsilyl)hydrazido derivatives in a high yield, and dilithium 1,2-bis(trimethylsilyl)hydrazide was isolated upon the reaction with *n*-butyllithium in 95% yield.[16] The reaction of di(*tert*-butyl)aluminum hydride with 2 equiv of that mixture yielded a colorless crystalline product, which, on the basis of its NMR spectroscopic characterization, was identified as *tert*-butylaluminum bis[1,2-bis(trimethylsilyl)hydrazide] **1** (eq 1). The ^1H NMR spectrum of com-

$$(Me_3C)_2AlH + 2\,N_2H_2(SiMe_3)_2 \longrightarrow \quad (1)$$



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(1) Peters, D. W.; Bourret, E. D.; Power, M. P.; Arnold, J. *J. Organomet. Chem.* **1999**, *582*, 108.
(2) Peters, D. W.; Power, M. P.; Bourret, E. D.; Arnold, J. *Chem. Commun.* **1998**, 753.
(3) Gibson, V. C.; Redshaw, C.; White, A. J. P.; Williams, D. J. *Angew. Chem.* **1999**, *111*, 1014; *Angew. Chem., Int. Ed.* **1999**, *38*, 961.
(4) Kim, Y.; Kim, J. H.; Park, J. E.; Song, H.; Park, J. T. *J. Organomet. Chem.* **1997**, *545−546*, 99.
(5) Cho, D.; Park, J. E.; Bae, B.-J.; Lee, K.; Kim, B.; Park, J. T. *J. Organomet. Chem.* **1999**, *592*, 162.
(6) Silverman, J. S.; Abernethy, C. D.; Jones, R. A.; Cowley, A. H. *Chem. Commun.* **1999**, 1645.
(7) Nöth, H.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, 1931.
(8) Neumayer, D. A.; Cowley, A. H.; Decken, A.; Jones, R. A.; Lakhotia, V.; Ekerdt, J. G. *Inorg. Chem.* **1995**, *34*, 4698.
(9) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 2717.
(10) Uhl, W.; Molter, J.; Koch, R. *Eur. J. Inorg. Chem*, **1999**, 2021.
(11) Uhl, W.; Molter, J.; Saak, W. *Z. Anorg. Allg. Chem.* **1999**, *625*, 321.
(12) Uhl, W.; Molter, J.; Koch, R. *Eur. J. Inorg. Chem.*, in press.
(13) Okumara, H.; Misawa, S.; Yoshida, S. *Appl. Phys. Lett.* **1991**, *59*, 1058.
(14) Wannagat, U.; Liehr, W. *Z. Anorg. Allg. Chem.* **1958**, *297*, 129.
(15) (a) Bailey, R. E.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 5369. (b) West, R.; Ishikawa, M.; Bailey, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 4648. (c) West, R.; Ishikawa, M.; Bailey, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 4068.
(16) Drost, C.; Jäger, C.; Freitag, S.; Klingebiel, U.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1994**, *127*, 845.

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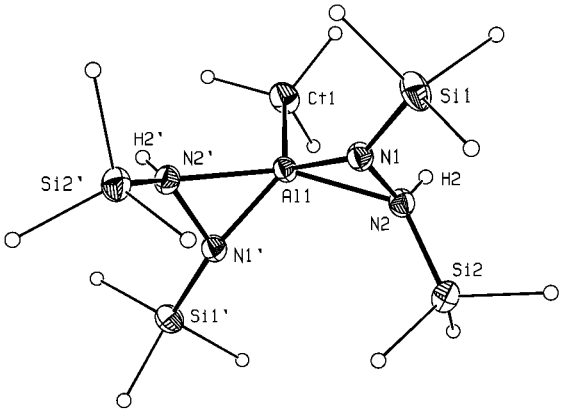

Figure 1. Molecular structure of **1**. The thermal ellipsoids are drawn at the 40% probability level. Methyl carbon atoms and the hydrogen atom attached to N2 are drawn with an arbitrary radius. Important bond lengths (Å) and angles (deg): Al1−N1 1.814(2), Al1−N2 2.072(2), Al1−Ct1 1.990(4), N1−N2 1.521(3), N1−Si1 1.708(2), N2−Si2 1.758(2), N1−Al1−N2 45.48(9), N1−Al1−N1′ 121.5(1), N1−Al1−N2′ 115.5(1), N1−Al1−Ct1 119.26(7), N2−Al1−N2′ 147.8(1), N2−Al1−Ct1 106.12(7), N2−N1−Al1 76.3(1), N1−N2−Al1 58.3(1) (N1′ and N2′ generated by 0.5 − *x*, 0.5 − *y*, *z*).

pound **1** showed a sharp resonance due to the N−H protons at δ 2.32, which is indicative of a terminal, nonbridging hydrogen atom. Two very narrow singlets of equal intensity were observed for the trimethylsilyl groups, and the integrated ratio verified that one *tert*-butyl group and two 1,2-bis(trimethylsilyl)hydrazido ligands were coordinated to each aluminum atom. In the IR spectrum, a sharp absorption at 3258 cm^{-1} was observed for the N−H group, also indicating that no hydrogen bridges occur in the molecule. Cryoscopic determination of the molar mass in benzene solution showed that the monomeric formula unit was present as shown schematically in eq 1. **1** is stable in solution at room temperature and dissolves readily in polar and nonpolar solvents such as tetrahydrofuran or *n*-pentane. Its sublimation in a vacuum at a bath temperature of 100 °C succeeded only with considerable decomposition.

The formation of compound **1** may proceed either from the 2-fold attack of hydrazine molecules on di(*tert*-butyl)aluminum hydride by the release of 1 equiv of elemental hydrogen and 1 equiv of isobutane or from the β-elimination of isobutene and the release of 2 equiv of hydrogen. **1** was isolated in 60% yield. The mother liquor gave an oily residue after evaporation of the solvent, which showed many resonances of unknown products in its NMR spectrum. All attempts to replace the second *tert*-butyl group of *t*-Bu_2AlH and to synthesize trihydrazidoaluminum by treatment of **1** with an excess of hydrazine failed. In refluxing toluene only complete decomposition of **1** occurred, giving a mixture of several unknown products, none of which could be isolated in pure form. To replace the remaining N−H protons of the hydrazido ligands, we treated **1** with an excess of di(*tert*-butyl)aluminum hydride, but in no case did we observe complete deprotonation of the hydrazine. Reactions with equimolar quantities of bis(trimethylsilyl)hydrazine and the dialkylaluminum hydride gave mixtures of unknown products.

The molecular structure of **1** as depicted in Figure 1 contains a *tert*-butyl group and two 1,2-bis(trimethylsilyl)hydrazido ligands. It is a monomer in the solid state, and its central aluminum atom has a remarkable coordination sphere with side-on coordination of both hydrazido ligands. Thus, the aluminum atom has a coordination number of 5, and two three-membered AlN_2 heterocycles are formed. The hydrazido ligands are not in a plane (angles Ct1−Al1−N1 119.26(7)°; Ct1−Al1−N2 106.12(7)°). Nevertheless, the structure resembles more that of a distorted quadratic pyramid than that of a trigonal bipyramid. As expected, the nitrogen atom N2 bearing the N−H bond has a strongly distorted tetrahedral configuration, and the environment of the amido nitrogen atom N1 is not planar (sum of the angles is 347.4°). The hydrogen atom H2 and the silicon atom Si1 are directed toward the *tert*-butyl group. Thus the $SiMe_3$ substituents are on different sides of the heterocycle. This particular conformation may be caused by a steric interaction between the trimethylsilyl groups of one hydrazido ligand.

The Al−N distances differ markedly. Short Al−N bond lengths (Al1−N1 1.814(2) Å) are observed to the negatively charged nitrogen atoms N1, which are a little shorter than those observed for other aluminum (trimethylsilyl)hydrazides,[7,10,11,12] although they are still in the normal Al−N range.[17] Much longer distances (Al1−N2 2.072(2) Å) are observed to the neutral amino nitrogen atoms N2, which are characteristic for Al−N "dative"[17] bonds. The N−N bond length (1.521(3) Å) is a little longer than that in dimeric dialkylaluminum hydrazides published earlier,[1−12] but they are similar to those of other hydrazine derivatives.[16,18] The N−Si bond lengths depend on the charge of the nitrogen atom. Shorter distances (1.708(2) compared to 1.758(2) Å) are observed for the bond to the anionic nitrogen atom N1, which may be interpreted in terms of a hyperconjugative stabilization of the negative charge by a π interaction with the silicon atoms.

Experimental Section

All procedures were carried out under purified argon. *n*-Hexane was dried over $LiAlH_4$; pentafluorobenzene, over molecular sieves. Di(*tert*-butyl)aluminum hydride[19] and a mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazine[14] were obtained according to literature procedures.

Synthesis of Compound 1. A solution of 4.5 mL (3.649 g, 20.7 mmol) of an approximate 1:1 mixture of the 1,1 and 1,2 isomers of bis(trimethylsilyl)hydrazine in 25 mL of *n*-hexane was cooled to −30 °C and treated with 1.471 g (10.4 mmol) of di(*tert*-butyl)aluminum hydride in 25 mL of the same solvent. The solution was allowed to warm to room temperature and stirred for 5 days. The solvent was removed in vacuo. The residue was thoroughly evacuated at room temperature for 2 h and dissolved in 10 mL of pentafluorobenzene. Colorless crystals of **1** were obtained upon slow cooling to −40 °C. Yield: 2.69 g (60%). Dec (argon, sealed capillary): above 130 °C. Anal. Calcd for $C_{16}H_{47}N_4AlSi_4$ (434.90): Al, 6.2; N, 12.9.

(17) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993.
(18) (a) Bode, K.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *40*, 1. (b) Dielkus, S.; Drost, C.; Herbst-Irmer, R.; Klingebiel, U. *Angew. Chem.* **1993**, *105*, 1689; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1625. (c) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Chem. Soc. A* **1970**, 318. (d) Morino, Y.; Iijima, T.; Murata, Y. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 46. (e) Bode, K.; Drost, C.; Jäger, C.; Klingebiel, U.; Noltemeyer, M.; Zak, Z. *J. Organomet. Chem.* **1994**, *482*, 285.
(19) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37.

Anal. Found: Al, 6.0; N, 12.9. Molar mass (in benzene by cryoscopy): found 440. ^{1}H NMR (C_6D_6, 300 MHz): δ 2.32 (2 H, s, NH), 1.21 (9 H, s, CMe_3), 0.196 and 0.192 (each 18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 32.5 (CMe_3), 11.7 (AlC), 1.4 and 0.0 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 14.8 and 2.0. IR (CsBr plates, paraffin, cm^{-1}): 3258 m νNH; 2923 vs, 2854 vs, 2726 w, 2697 w, 1463 vs, 1377 s paraffin; 1297 s, 1250 vs δCH_3; 1184 vw, 1049 vs, 1003 m νCC, νNN; 873 vs, 839 vs, 802 vs ρCH_3(Si), νC_3C; 749 vs ρCH_3(Si); 682 s ν_{as}SiC; 646 s, 597 s, 544 m, 462 w ν_sSiC, νAlC, νAlN, νSiN; 407 m, 384 w, 371 w, 343 m, 326 s δSiC, δC_3C.

Crystal Structure Determination. Single crystals of **1** were obtained on cooling of a saturated solution in pentafluorobenzene to −15 °C. The crystallographic data were collected with a CAD-4 four-circle diffractometer. $C_{16}H_{47}N_4AlSi_4$, orthorhombic, *Pccn*, no. 56,[20] $Z = 4$, temperature 212(2) K, $D_{calcd} = 1.007$ g/cm^3, $a = 11.950(1)$ Å, $b = 12.387(1)$ Å, $c = 19.381(1)$ Å, $V = 2868.9(4)\cdot10^{-30}$ m^3, $\mu = 0.245$ mm^{-1}, crystal dimensions $0.41 \times 0.37 \times 0.25$ mm, radiation Mo Kα, graphite monochromator, 2θ range $4.7° \le 2\theta \le 50.1°$, index ranges $-14 \le h \le 2$, $-14 \le k \le 2$, $-19 \le l \le 23$; number of unique reflections 2540; number of parameters 141. The structure was solved by direct methods and refined with the program SHELXL-97[21] by a full-matrix least-squares method based on F^2. R1 (1991 reflections $I > 2\,\sigma(I)$) = 0.0567; wR2 (all data) = 0.1585; max./min. residual electron density = 0.792/−0.294 × 10^{30} e/m^3. The atoms Al1 and Ct1 are located on a crystallographic 2-fold rotation axis, in consequence of which the methyl carbon atoms of the *tert*-butyl group are statistically disordered over two positions. The hydrogen atoms of the methyl groups were refined on ideal positions by employing the riding model. The position of the hydrogen atom H2 was taken from a difference Fourier map; it was refined isotropically without restrictions.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-143180.

OM000330S

(20) Hahn, T., Ed. *International Tables for Crystallography, Space-Group Symmetry*; Kluwer Academic Publishers: Dordrecht, 1989; Vol. A.

(21) *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-RAY Instruments Inc.: Madison, WI, 1990. Sheldrick, G. M. *SHELXL-93*, Program for the Refinement of Structures; Universität Göttingen, 1993.