

# Planar Dimeric Six-Membered Spirane Aluminum Hydrazide: Synthesis and X-ray Crystal Structure of $[\text{LAlN}(\text{Me})\text{NH}]_2$ ( $\text{L} = \text{HC}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})(\text{CMe})\}_2$ )

S. Shravan Kumar,<sup>†</sup> Sanjay Singh,<sup>†</sup> Fan Hongjun,<sup>‡</sup> Herbert W. Roesky,<sup>\*,†</sup> Denis Vidović,<sup>†</sup> and Jörg Magull<sup>†</sup>

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany, and Theoretische Chemie, Universität Siegen, D-57068 Siegen, Germany

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**Summary:** The reaction between stoichiometric amounts of  $\beta$ -diketiminato-stabilized aluminum dihydride and methylhydrazine affords reddish brown crystals of a planar dimeric spirane aluminum hydrazide complex,  $[\text{LAlN}(\text{Me})\text{NH}]_2$  (**2**).

## Introduction

Until now much of the aluminum structural chemistry was focused on the synthesis of aluminum amides<sup>1</sup> and aluminum imides.<sup>2</sup> They are found to be excellent precursor for aluminum nitride.<sup>3</sup> In combination with CVD formed diamond film, aluminum nitride is a promising piezoelectric material for acoustic wave (SAW) application.<sup>3k</sup> Fetter et al.<sup>4</sup> reported the reaction between hydrazine and trimethylamine alane, but were unsuccessful in the synthesis of aluminum hydrazides. Further work with hydrazine-aluminum compounds was hampered by their shock sensitivity. Only in the past few years has there been a gradual upsurge in the synthesis of hydrazine derivatives of aluminum,<sup>5–21</sup> as

they are found to be potential precursor not only in the formation of aluminum- and nitrogen-containing rings and cages<sup>5–9</sup> but also in the formation of aluminum nitride by chemical vapor deposition or by the thermalolysis of macroscopic samples.<sup>3</sup> The hydrazine derivatives have been prepared either by treatment of hydrazines with trialkylaluminum compounds, which eliminates alkanes,<sup>5–7,14,16</sup> or by reaction of hydrazines with dialkylaluminum hydrides<sup>8</sup> or  $\text{LiAlH}_4$ ,<sup>11</sup> which eliminates hydrogen. Furthermore, they are prepared by reaction of lithiated hydrazines with dialkylaluminum chlorides<sup>11,12</sup> or by hydroalumination of azobenzene with an arylaluminum dihydride.<sup>13</sup> These compounds usually are dimeric, containing a four-membered  $\text{Al}_2\text{N}_2$ ,<sup>5,6,12,14,16</sup> a five-membered  $\text{Al}_2\text{N}_3$ ,<sup>13,15</sup> or a six-membered  $\text{Al}_2\text{N}_4$  heterocycle,<sup>11,15,20</sup> respectively. The  $\text{Al}_2\text{N}_2$  dimers exist as *cis* and *trans* isomers, and the  $\text{Al}_2\text{N}_4$  rings can adopt a *chair* and *twist-boat* conformation. In our exploration of the reactivity of the Al–H bonds as well as of aluminum hydrazide compounds we have studied the reaction between  $\text{LAlH}_2$  ( $\text{L} = \text{HC}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N})(\text{CMe})\}_2$ ), which contains the bulky  $\beta$ -diketiminato ligand, and methylhydrazine, which resulted in the formation of a structurally characterized planar

\* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

<sup>†</sup> Universität Göttingen.

<sup>‡</sup> Universität Siegen.

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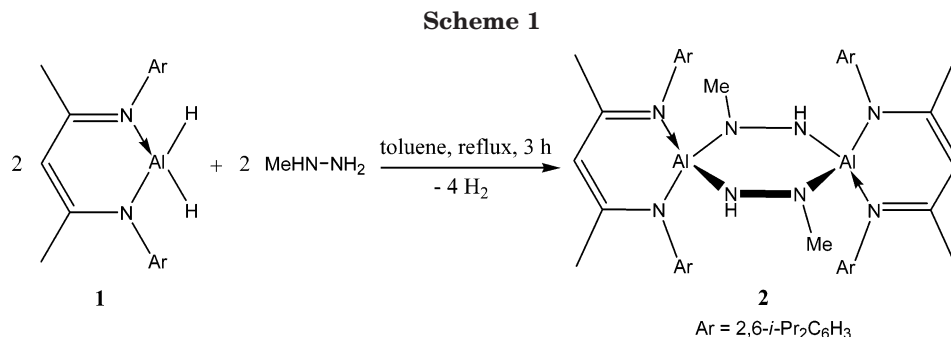
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dimeric spirane aluminum hydrazide, [LAlN(Me)NH]<sub>2</sub> (**2**). Theoretical studies using the DFT-B3LYP method have served to explain the planarity and the stability of the six-membered Al<sub>2</sub>N<sub>4</sub> ring in **2**.

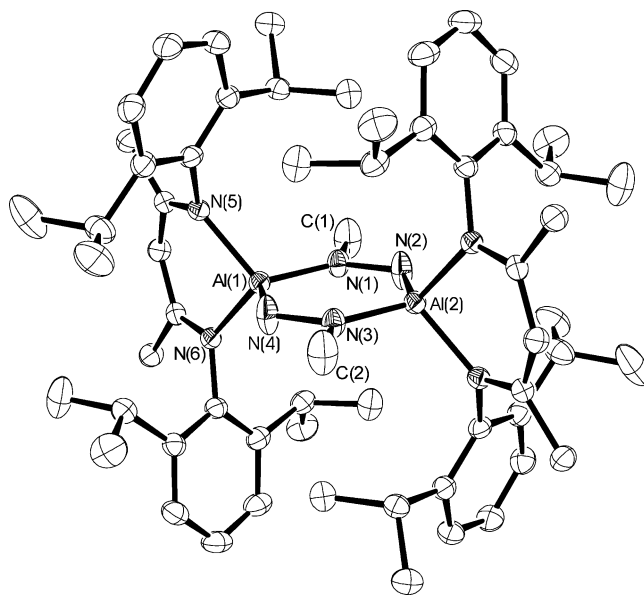
### Results and Discussion

The reaction between stoichiometric amounts of **1** and methylhydrazine in toluene refluxing solution gave compound **2** with elimination of H<sub>2</sub> (Scheme 1). During the reaction the color of the solution changed from colorless to reddish brown, and this color is sustained during the course of the reaction. All appropriate workup details for the experiment gave reddish brown crystals of **2** as the only isolable compound. No reaction was observed when the reaction was attempted at room temperature. The air- and moisture-sensitive compound **2** was characterized by multinuclear NMR spectroscopy, mass spectrometry, IR spectroscopy, and elemental analysis. In the <sup>1</sup>H NMR spectrum the *NMe* protons resonate at  $\delta$  2.10 and the *NH* proton at  $\delta$  0.21. Compound **2** is centrosymmetric and has two septets corresponding to the *CH* proton of the isopropyl groups ( $\delta$  3.46 and 3.25). In the EI mass spectrum the most intense peak (*m/z* 976) corresponds to the dimer, which is indicative of the stability of the Al<sub>2</sub>N<sub>4</sub> ring, and a small peak related to the monomer appears at *m/z* 488. In the IR spectrum a weak band was observed at 3440 cm<sup>-1</sup>, which can be attributed to the N–H stretching frequency.

The molecular structure of **2** in the solid state was determined by X-ray crystal structural analysis. An ORTEP plot of **2** is shown in Figure 1. Compound **2** crystallizes in the triclinic space group *P* $\bar{1}$  with one-half of the molecule and one-half of the *n*-hexane molecule in the asymmetric unit. It is a spirane molecule in which the six-membered Al<sub>2</sub>N<sub>4</sub> ring is connected by  $\beta$ -diketiminato ligands at each of the aluminum centers. Compound **2** has a planar Al<sub>2</sub>N<sub>4</sub> ring. It contains a centrosymmetric dimer with an inversion center. The aromatic groups are dangling above and below the six-membered ring, and they are slightly inclined toward the vertical axis of the six-membered ring. The aluminum atom is tetracoordinate, connected to the four nitrogen atoms in a distorted tetrahedral array. Two methyl groups present on N(1) and N(3) are anti-periplanar to each other. The hydrogen atoms on two nitrogen atoms were freely refined on two split positions with half-occupancy. The Al–N bond lengths [Al(1)–N(1) 1.787(2) Å, N(2)–Al(2) 1.804(2) Å] within the planar Al<sub>2</sub>N<sub>4</sub> ring of **2** are shorter in comparison to those of [Me<sub>2</sub>AlN(SiMe<sub>3</sub>)N(*t*Bu)H]<sub>2</sub> (1.874(2) and 2.016(2) Å),<sup>11</sup> [(Me<sub>3</sub>C)<sub>2</sub>AlN(SiMe<sub>3</sub>)NH<sub>2</sub>]<sub>2</sub> (1.867(2) and

2.004(1) Å),<sup>15</sup> [(Me<sub>3</sub>C)<sub>2</sub>AlNHNH<sub>2</sub>]<sub>2</sub> (1.951(2) Å),<sup>20</sup> and [(Me<sub>3</sub>C)<sub>2</sub>AlNHNH]<sub>2</sub>[ $\mu$ -Al(CMe<sub>3</sub>)<sub>2</sub>] (1.941(7)–1.970(6) Å).<sup>20</sup> The sum of the bond angles of N(1) and N(3), which are bonded to the methyl groups, is 359.99°, indicating the trigonal planar geometry. For N(2) and N(4) the sum of the bond angles is 337.45°, showing clearly the pyramidal arrangement.

The theoretical calculations were carried out to explain the planarity of the nitrogen centers in the Al<sub>2</sub>N<sub>4</sub> ring of compound **2**. The DFT-B3LYP method was employed within Gaussian 98,<sup>22</sup> selecting 6-311g(d,p) as basis sets unless otherwise specified. The geometry of compound **2** was optimized (6-311g for phenyl, and CHMe<sub>2</sub> in L was replaced by H). The planar nitrogen center and other structural parameters were successfully reproduced and the average bond length deviation is less than 0.02 Å, thus showing the reliability of the theoretical method. According to the classic chemical bond theory and VSEPR model, nitrogen with its coordination number three adopts a pyramidal geometry. However, in compound **2** there are two planar Al–N(Me)N centers. Several model molecules (AlH<sub>2</sub>(H<sub>2</sub>O)(NH<sub>2</sub>), AlH<sub>2</sub>(H<sub>2</sub>O)(NMe<sub>2</sub>), AlH<sub>2</sub>(H<sub>2</sub>O)N(NH<sub>2</sub>)<sub>2</sub>, AlCl<sub>2</sub>–



**Figure 1.** Molecular structure of **2** with 50% thermal ellipsoid probability. Hydrogen atoms and the hexane molecules are omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Al(1)–N(1) 1.787(2), N(1)–N(2) 1.445(2), N(2)–Al(2) 1.804(2), Al(1)–N(5) 1.939(2), N(6)–Al(1)–N(5) 93.92(7), N(5)–Al(1)–N(1) 112.23(8), Al(1)–N(1)–N(2) 126.66(13), Al(1)–N(1)–C(1) 124.61(15), C(1)–N(1)–N(2) 108.72(17), N(1)–N(2)–Al(2) 123.54(13), N(1)–Al(1)–N(4) 109.79(8).

(H<sub>2</sub>O)(NHNH<sub>2</sub>) were studied theoretically in order to find the reason for the planarity of the nitrogen centers in **2**. It was observed that the geometry optimization gives a planar nitrogen center. These results show that the nitrogen center forms a triangular planar arrangement when bonded to aluminum and two other atoms. Thus the planar nitrogen center in **2** is due to the Al–N bond character rather than the presence of the sterically bulky ligands and other steric interactions. Moreover we also calculated the curve when the planar nitrogen center in AlH<sub>2</sub>(H<sub>2</sub>O)N(NH<sub>2</sub>)<sub>2</sub> is distorted artificially (torsion angle 180°) to a pyramidal conformation (torsion angle 130°). The total energy change is only 0.95 kcal/mol, which is small compared with that of a hydrogen bond interaction. This may explain the pyramidal geometry at the Al–NHN center in compound **2**, as the steric interaction prefers a staggered NH–NMe conformation rather than an eclipsed one.

### Experimental Section

All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Compound **1**<sup>23</sup> was prepared as described in the literature. NMR spectra were recorded on a Bruker AM 200 instrument, and the chemical shifts are reported with reference to TMS. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, Göttingen, Germany. A suitable crystal of compound **2** was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **2** were collected on a STOE IPDS II diffractometer at 133(2) K. The measurement was made with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods using SHELXS-97<sup>24</sup>

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and refined against  $F^2$  on all data by full-matrix least squares with SHELXL-97.<sup>25</sup> All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from *International Tables for X-Ray Crystallography*.<sup>26</sup>

**Synthesis of 2.** To a solution of LAIH<sub>2</sub> (0.50 g, 1.12 mmol) in toluene (30 mL) was added dropwise a solution of methylhydrazine (0.103 g, 2.24 mmol) in toluene (10 mL) at room temperature. The resultant solution was stirred for 0.5 h before refluxing it for 3 h. During the reaction evolution of H<sub>2</sub> was observed. After the removal of all volatiles the residue was extracted with *n*-hexane (20 mL). The resultant solution was kept for crystallization at room temperature for 24 h to give reddish brown crystals of **2**. Yield: 0.41 g, 76% with respect to **1**. Mp: 297–299 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.17–7.11 (m, 12 H, Ar), 4.91 (s, 2 H,  $\gamma$ -CH), 3.46 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 4 H, CHMe<sub>2</sub>), 3.25 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 4 H, CHMe<sub>2</sub>), 2.10 (s, 6 H, NMe), 1.57 (s, 12 H, CMe), 1.41 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12 H, CHMe<sub>2</sub>), 1.35 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 12 H, CHMe<sub>2</sub>), 1.12 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12 H, CHMe<sub>2</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12 H, CHMe<sub>2</sub>), 0.21 (s, 2 H, NH). <sup>13</sup>C NMR (125.13 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  161.48 (CN), 144.88–123.55 (Ar), 94.26 ( $\gamma$ -C), 45.64 (NMe), 31.9, 28.6 (CHMe<sub>2</sub>), 28.3, 25.16, 23.39, 22.99 (CHMe<sub>2</sub>), 20.74 (Me). IR (KBr, Nujol):  $\tilde{\nu}$  3440 (w), 1622, 1552, 1261, 1096, 1020, 800, 721 cm<sup>-1</sup>. EIMS (70 eV): *m/z* (%): 976 (100) [M<sup>+</sup>], 488 (12) [M<sup>+</sup> – Al – L – N(Me)NH]. Anal. (%) Calcd for C<sub>60</sub>H<sub>90</sub>Al<sub>2</sub>N<sub>8</sub> (979.39): C, 73.58; H, 9.47; N, 11.44. Found: C, 73.10; H, 9.20; N, 10.98.

Crystallographic data for compound **2**·C<sub>6</sub>H<sub>14</sub> (C<sub>66</sub>H<sub>104</sub>Al<sub>2</sub>N<sub>8</sub>):  $M_r = 1063.53$ , triclinic,  $P\bar{1}$ ,  $a = 9.054(5)$  Å,  $b = 13.218(7)$  Å,  $c = 13.446(8)$  Å,  $\alpha = 87.23(5)^\circ$ ,  $\beta = 80.54(4)^\circ$ ,  $\gamma = 78.99(4)^\circ$ ,  $V = 1558.04(15)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.134$  Mg m<sup>-3</sup>,  $3.08^\circ \leq 2\theta \leq 49.76^\circ$ ,  $T = 133(2)$  K,  $\lambda = 0.71073$  Å,  $\mu = 0.092$  mm<sup>-1</sup>,  $F(000) = 582$ ,  $-10 \leq h \leq 10$ ,  $-14 \leq k \leq 15$ ,  $-15 \leq l \leq 15$ , 28 288 reflns collected, 5222 were independent and were used in the structure refinement of 348,  $R1 = 0.0495$  ( $I > 2\sigma(I)$ ),  $wR2 = 0.1388$  (all data), min./max. residual electron density 0.636/–0.493 e<sup>-</sup>Å<sup>-3</sup>.

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**Supporting Information Available:** Single-crystal X-ray structural data of compound **2** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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