Inorg. Chem. **2001,** *40,* 121−124

Lithium Amidohydridoaluminates

Jochen Pauls and Bernhard Neumüller*

Fachbereich Chemie der Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Received April 26, 2000

The amidohydridometalates $[Li(THF)_4][HAl(NPh_2)_3]$ (**1**), $[Li(DME)_3][HAl\{N(CH_2Ph)_2\}_3]$ (**2**), and $[\{(THF)_3Li\}\{H_2Al(N^cHex_2)_2\}]\cdot0.5toluene$ (**3**·0.5toluene; $^cHex = C_6H_{11}$) have been prepared by reaction of the corresponding amines with $LiAlH_4$ in THF. For **2** recrystallization from DME is required to obtain crystals, suitable for X-ray diffraction. The new compounds have been characterized by elemental analyses, IR, NMR, and MS techniques, and X-ray structure analyses. According to this the anions of **1**, **2**, and **3**·0.5toluene possess distorted tetrahedral coordination spheres. In **3**·0.5toluene a Li···H contact of 184(4) pm was detected to complete the tetrahedral coordination of the Li^+ center.

Introduction

Lithium amidohydridoaluminates have become an interesting class of compounds in the past decade.[1] Although some derivatives were known from earlier publications,[2,3] it was two contributions of H. Nöth et al. in 1988[4] which gave a closer insight into these reactions. Further investigations of other authors followed.[5,6] One reason for this was the systematic reaction sequences and NMR investigations carried out to enlighten the reaction behavior of mixtures of $LiAlH_4$ and secondary amines. As a result of the two studies,[4] all four products of eqs 1−4 are

$$LiAlH_4 + HNR_2 \xrightarrow{THF} \underset{\mathbf{A}}{Li[H_3AlNR_2]} + H_2 \qquad (1)$$

$$Li[H_3AlNR_2] + HNR_2 \xrightarrow{THF} \underset{\mathbf{B}}{Li[H_2Al(NR_2)_2]} + H_2 \qquad (2)$$

$$Li[H_2Al(NR_2)_2] + HNR_2 \xrightarrow{THF} \underset{\mathbf{C}}{Li[HAl(NR_2)_3]} + H_2 \qquad (3)$$

$$Li[HAl(NR_2)_3] + HNR_2 \xrightarrow{THF} \underset{\mathbf{D}}{Li[Al(NR_2)_4]} + H_2 \qquad (4)$$

present when $LiAlH_4$ is treated with the amine. To isolate at least product **D**, it was necessary to add 4 equiv of amine. Additional parameters are solvent, temperature, and the bulk of the amine. Our interest was to isolate products of type **A**, **B**, or **C** in a simple procedure.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon. Purification and drying of the solvents were done using standard methods.[7] $LiAlH_4$ solutions in THF, $HNPh_2$, $HN(CH_2Ph)_2$, HN^cHex_2, and $AlCl_3$ were purchased from Aldrich.

The ^1H, ^{13}C, and ^{27}Al NMR spectra were recorded on Bruker AC 200 (^1H, ^{13}C) and AC 300 (^{27}Al) spectrometers. The standards were TMS (internal; ^1H, ^{13}C) and $[Al(H_2O)_6]^{3+}$ (external; ^{27}Al) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). For the EI mass spectra a Varian CH7a mass spectrometer (70 eV) was used. The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected).

Synthesis of $[Li(THF)_4][HAl(NPh_2)_3]$, 1. An 8 mL portion of a 1 M $LiAlH_4$ solution in THF (8 mmol) was added to 8.46 g (50 mmol) of $HNPh_2$ dissolved in 50 mL of THF under evolution of H_2. The mixture was stirred for 12 h at 20 °C and 3 h under reflux. The solution was concentrated to 30 mL, and 10 mL of *n*-pentane was added. At 5 °C colorless needles of **1** were formed (5.56 g, 84%). Mp: 42 °C dec. ^1H NMR (THF-d_8, ppm): δ 1.18 (s, br, 1 H, Al−*H*), 1.65 (m, 10 H, CH_2, THF; sample loses THF during manipulation under a flow of Ar), 3.50 (m, 10 H, OCH_2, THF), 6.71−6.33 (m, 30 H, phenyl *H*). ^{13}C NMR (THF-d_8, ppm): δ 26.4 (CH_2, THF), 68.3 (OCH_2, THF), 118.2 (C^4, phenyl), 124.4 ($C^{2,6}$, phenyl), 129.8 ($C^{3,5}$, phenyl), 155.1 (C^1, phenyl). ^{27}Al NMR (THF-d_8, ppm): δ 100 ($W_{1/2} = 1040$ Hz). EI-MS: *m/z* (%) 168 (65) $(NPh_2)^+$, 91 (4) $(NPh)^+$, 77 (24) $(Ph)^+$, 72 (31) $(THF)^+$. IR (cm^{-1}): 2726 (w), 2665 (w), 2574 (w), 2499 (w), 2050 (w), 1909 (w), 1777 (s, ν(AlH)), 1684 (w), 1594 (vs), 1493 (vs), 1342 (s), 1283 (vs), 1209 (s), 1181 (s), 1153 (s), 1082 (m), 1068 (m), 1030 (vs), 1003 (m), 989 (s), 974 (m), 935 (s), 918 (m), 882 (s), 871 (s), 758 (vs), 745 (vs), 702 (vs), 690 (vs), 617 (w), 577 (m), 516 (vs), 439 (m, $\nu_{as}(AlN_3)$), 414 (m), 393 (m, $\nu_s(AlN_3)$), 339 (w), 317 (vw), 289 (vw), 279 (vw), 262 (vw). Anal. Calcd for $C_{44}H_{47}AlLiN_3O_2$ (sample loses two THF molecules during manipulation under a flow of Ar; M_r 683.80): C, 77.29; H, 6.93; N, 6.15; Al, 3.95; Li, 1.02. Found: C, 77.02; H, 6.79; N, 5.78; Al, 3.96; Li, 1.02.

Synthesis of $[Li(DME)_3][HAl\{N(CH_2Ph)_2\}_3]$, 2. A 10 mL portion of a 1 M $LiAlH_4$ solution in THF (10 mmol) was added to a solution of 7.89 g (40 mmol) of $HN(CH_2Ph)_2$ in 10 mL of THF at 20 °C under evolution of H_2. The color of the reaction mixture changed from red (color of the anion $[N(CHPh)_2]^-$) to orange to yellow. The solution was stirred for an additional hour, and its volume was then reduced to 10 mL. The colorless crystals, probably $[Li(THF)_4][HAl\{N(CH_2Ph)_2\}_3]$, were not suitable for X-ray crystallography. The solvent was removed under vacuum, and 20 mL of DME was added. At −20 °C colorless

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10.1021/ic000450s CCC: \$20.00

Table 1. Crystallographic Data of **1**, **2**, and **3**·0.5Toluene

	1	**2**	**3**·0.5toluene
empirical formula	$C_{52}H_{63}AlLiN_3O_4$	$C_{54}H_{73}AlLiN_3O_6$	$C_{39.5}H_{74}AlLiN_2O_3$
fw	828.00	894.11	658.95
cryst size (mm)	0.6 × 0.25 × 0.2	0.4 × 0.4 × 0.3	0.6 × 0.5 × 0.4
a (pm)	1053.3(2)	2352.7(4)	1992.0(1)
b (pm)	2627.8(7)	1365.4(2)	
c (pm)	1725.8(3)	1660.5(1)	2129.7(1)
β (deg)	99.05(2)		
space group	$P2_1/n$ (no. 14)[16]	$Pna2_1$ (no. 33)	$P\bar{4}2_1c$ (no.114)
V (pm^3 × 10^6)	4717(2)	5334(1)	8450.8(7)
Z	4	4	8
ρ_{calcd} (g/cm^3)	1.166	1.113	1.036
temp (K)	193	193	203
2θ range (deg)	4.6−50.0	4.6−50.0	6.0−120.0
hkl values	$0 \leq h \leq +12$ $-31 \leq k \leq 0$ $-20 \leq l \leq +20$	$-20 \leq h \leq +27$ $-12 \leq k \leq +12$ $-15 \leq l \leq +19$	$-22 \leq h \leq +3$ $-22 \leq k \leq +22$ $-23 \leq l \leq +23$
radiation	Mo Kα	Mo Kα	Cu Kα
μ (cm^{-1})	0.9	0.9	6.7
no. of reflns	8997	8576	9175
no. of unique reflns (R_{int})	8294 (0.0446)	8308 (0.0454)	4443 (0.0549)
no. of reflns with $F_o > 4\sigma(F_o)$	2864	3500	3349
no. of params	568	567	429
Flack param		−0.1(1)	0.1(1)
R_1 [$F_o > 4\sigma(F_o)$]^a	0.0947	0.0978	0.0853
wR_2	0.2592	0.3011	0.2542
weight factor a^c	0.0988	0.141	0.1624
weight factor b^c	0	0	3.6
min/max electron residue (e/pm^3 × 10^{-6})	−0.26/0.26	−0.38/0.49	−0.28/0.24

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$. ^{c} $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

crystals of **2** could be obtained (7.46 g, 83%). Mp: 62−67 °C dec. ^{1}H NMR (THF-d_8, ppm): δ 1.58 (s, br, 1 H, Al−*H*), 3.12 (s, 12 H, NC*H*$_2$), 3.29 (s, 12 H, OC*H*$_2$, DME), 3.89 (s, 18 H, OC*H*$_3$, DME), 6.80−7.23 (m, 30 H, phenyl *H*). ^{13}C NMR (THF-d_8, ppm): δ 52.8 (N*C*H$_2$), 58.7 (O*C*H$_2$), 72.5 (O*C*H$_3$), 125.0 (*C*^{4}, phenyl), 127.5 (*C*$^{2/6}$, phenyl), 129.6 (*C*$^{3/5}$, phenyl), 147.1 (*C*^{1}, phenyl). ^{27}Al NMR (THF-d_8, ppm): δ 120 ($W_{1/2}$ = 835 Hz). EI-MS: *m*/*z* (%) 196 (12) $[N(CH_2Ph)_2]^+$, 106 (60) $(HNCH_2Ph)^+$, 91 (100) $(C_7H_7)^+$. IR (cm^{-1}): 2677 (w), 1947 (w), 1870 (w), 1810 (w), 1698 (sh, br, ν(AlH)), 1649 (sh, br, ν(AlH)), 1638 (br, ν(AlH)), 1597 (m), 1344 (s), 1310 (m), 1276 (m), 1243 (m), 1190 (m), 1159 (w), 1122 (s), 1082 (s), 1045 (s), 1027 (s), 984 (w), 953 (s), 903 (m), 866 (s), 841 (w), 810 (m), 698 (s), 608 (s), 570 (m), 479 (m), 463 (m), 432 (m, ν_{as}(AlN$_3$)), 401 (m, ν_s(AlN$_3$)), 336 (m), 256 (vw). Anal. Calcd for $C_{54}H_{73}AlLiN_3O_6$ (sample loses one DME molecule during manipulation under a flow of Ar; M_r 803.99): C, 74.70; H, 7.90; N, 5.23; Al, 3.36; Li, 0.86. Found: C, 74.46; H, 7.66; N, 5.31; Al, 3.46; Li, 0.88.

Synthesis of [{(THF)$_3$Li}{H$_2$Al(N^{c}Hex$_2$)$_2$}]·0.5Toluene, 3·0.5Toluene. A 10 mL portion of a LiAlH$_4$ solution in THF (10 mmol) was added to 7.29 g (40 mmol) of HN^{c}Hex$_2$ at 20 °C under evolution of H$_2$. The reaction mixture was stirred for 2 d at 20 °C and 3 h under reflux. The solution was reduced under vacuum to a viscous oil. The oil was dissolved in 1 mL of THF and 30 mL of toluene. At −20 °C colorless plates of **3**·0.5toluene could be obtained (4.01 g, 61%). Mp: 258 °C dec. ^{1}H NMR (THF-d_8, ppm): δ 0.52 (s, br, 2 H, Al−*H*), 0.69−1.52 (m, 40 H, C*H*$_2$, ^{c}Hex), 1.69 (m, 5 H, C*H*$_2$, THF; sample loses THF and toluene during manipulation under a flow of Ar), 2.20 (0.5 H, C*H*$_3$, toluene), 2.50 (m, 4 H, NC*H*), 3.52 (m, 5 H, OC*H*$_2$, THF), 6.97−7.10 (m, 1 H, phenyl *H*, toluene). ^{13}C NMR (THF-d_8, ppm): δ 21.4 (*C*H$_3$, toluene), 26.3 (THF, *C*H$_2$), 27.5 (*C*^{4}H$_2$, ^{c}Hex), 28.4 (*C*$^{3/5}$H$_2$, ^{c}Hex), 38.5 (*C*$^{2/6}$H$_2$, ^{c}Hex), 57.9 (*C*^{1}H, ^{c}Hex), 68.1 (O*C*H$_2$, THF), 125.6 (*C*^{4}, toluene), 128.8 (*C*$^{2/6}$, toluene), 129.5 (*C*$^{3/5}$, toluene), 138.0 (*C*^{1}, toluene). ^{27}Al (THF-d_8, ppm): δ 108 ($W_{1/2}$ = 2067 Hz). EI-MS: *m*/*z* (%) 181 (1) (HN^{c}Hex$_2$)$^+$, 138 (5) $(AlN_2C_6H_{11}/NC_9H_{16})^+$. IR (cm^{-1}): 2727 (m), 2665 (m), 2500 (vw), 2359 (vw), 2226 (vw), 2130 (vw), 1939 (vw), 1777 (vs, ν(AlH)), 1619 (vs, br, ν(LiHAl)), 1348 (s), 1336 (s), 1303 (m), 1257 (s), 1179 (m), 1146 (vs), 1099 (vs), 1073 (vs), 1046 (vs), 983 (m), 956 (vs), 916 (m), 891 (vs), 846 (s), 765 (vs), 685 (m), 639 (w), 608 (s), 554 (s), 521 (m), 480 (m), 426 (m, ν_{as}(AlN$_2$)), 392 (m, ν_s(AlN$_2$)), 360 (w), 341 (w), 306 (m), 282 (m), 229 (w), 206 (m), 129 (m). Anal. Calcd for $C_{28}H_{54}AlLiN_2O$ (sample loses two THF molecules and toluene during manipulation under a flow of Ar; M_r 468.67): C, 71.76; H, 11.61; N, 5.98; Al, 5.76; Li, 1.48. Found: C, 71.99; H, 11.49; N, 6.27; Al, 5.98; Li, 1.37.

X-ray Structure Determinations of 1, 2, and 3·0.5Toluene. The crystals (all taken directly from the mother liquor) were covered with a perfluorinated ether and mounted on the top of a glass capillary under the flow of cold gaseous nitrogen. The orientation matrix and the preliminary cell dimensions were determined from 15 reflections. The instruments were two CAD4 four-circle diffractometers (Enraf-Nonius; Mo Kα radiation (**1** and **2**, λ = 71.073 pm); Cu Kα radiation (**3**·0.5toluene, λ = 154.178 pm) with graphite-monochromated radiation. The final cell parameters were determined from 25 high-angle reflections.

The intensities were corrected for Lorentz and polarization effects (for cell parameters and collection of the intensities, see Table 1). The structures were solved by direct methods (**1** and **3**·0.5toluene, SHELXTL[8]) and the Patterson method (**2**, SHELXTL-Plus[9]). The structures were refined against F^2 by full-matrix least-squares using SHELXL-97.[10] Empirical absorption corrections were performed for all data sets. The positions of the hydrogen atoms (except the Al-bonded H atoms, which were freely refined) were calculated for ideal positions and refined with a common displacement parameter. The calculations of the bond lengths, bond angles, and U_{eq} values were performed using the program PLATON.[11] The final *R* values were influenced by the disorder behavior mainly of the solvent molecules. However, the standard deviations of the distances and angles were acceptable. Splitted positions were used in **1** (C921 and C931, 0.7 (occupation parameter); C922 and C932, 0.3) and **3**·0.5toluene (C721 and C731, 0.6; C722 and C732, 0.4). The Li$^+$ center in **2** is surrounded by three DME ligands. Two DME molecules occupy two major and two minor positions. The

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minor position is represented only weakly and could not be included into the refinement (C79−C80 fixed bond length of 154 pm).

Results and Discussion

Addition of $\mathrm{LiAlH_4}$ solutions to the amines $\mathrm{HNPh_2}$, $\mathrm{HN(CH_2Ph)_2}$, and $\mathrm{HN^cHex_2}$ in THF at room temperature leads to $\mathrm{H_2}$ evolution. Even with an excess of $\mathrm{HNPh_2}$ and reflux conditions, only the 3-fold nitrogen-substituted aluminate **1** was observed (eq 5). Because the crystals of $[\mathrm{Li(THF)_4}][\mathrm{HAl\{N(CH_2Ph)_2\}_3}]$ were not suitable for X-ray analysis, we changed the solvent to DME (eq 6). Under these conditions (eq 6) only two H atoms were substituted by the treatment of $\mathrm{LiAlH_4}$ with $\mathrm{HN^cHex_2}$ (eq 7). Recrystallization from THF/toluene mixtures gives colorless crystals of **3**·0.5toluene. Both the steric demand and the basicity of $\mathrm{HN^cHex_2}$ are significantly different from the properties of $\mathrm{HNPh_2}$ and $\mathrm{HN(CH_2Ph)_2}$, respectively.

$$\mathrm{LiAlH_4} + 3\mathrm{HNPh_2} \xrightarrow{\text{THF, 20 °C}} \underset{\mathbf{1}}{[\mathrm{Li(THF)_4}][\mathrm{HAl(NPh_2)_3}]} + 3\mathrm{H_2} \quad (5)$$

$$\mathrm{LiAlH_4} + 3\mathrm{HN(CH_2Ph)_2} \xrightarrow{\text{THF, 20 °C}} [\mathrm{Li(THF)_4}][\mathrm{HAl\{N(CH_2Ph)_2\}_3}] + 3\mathrm{H_2} \quad (6)$$

$$[\mathrm{Li(THF)_4}][\mathrm{HAl\{N(CH_2Ph)_2\}_3}] \xrightarrow{\text{DME}} \underset{\mathbf{2}}{[\mathrm{Li(DME)_3}][\mathrm{HAl\{N(CH_2Ph)_2\}_3}]}$$

$$\mathrm{LiAlH_4} + 2\mathrm{HN^cHex_2} \xrightarrow{\text{THF, 20 °C}} \underset{\mathbf{3}}{[\{\mathrm{Li(THF)_3}\}\{\mathrm{H_2Al(N^cHex_2)_2}\}]} + 2\mathrm{H_2} \quad (7)$$

Interestingly the reactions of $\mathrm{HN(CH_2Ph)_2}$ with reducing agents such as $\mathrm{Li^nBu}$ or $\mathrm{LiAlH_4}$ lead to an intensive red solution as in the case of reaction 6 as well as in the formation of $[\mathrm{R_2AlN(CH_2Ph)_2}]_2$[12] caused by the presence of small amounts of the anion $[\mathrm{N(CHPh)_2}]^-$.[13]

1−**3** are air-sensitive colorless solids. The ^{1}H NMR spectra in THF-d_8 exhibit broad singlets for the Al−H resonances at 1.18 (**1**), 1.58 (**2**), and 0.52 (**3**) ppm. The neutral species such as $[\mathrm{HAlN^iPr}]_6$ give a signal at 4.57 ppm,[14] while the metalate ions in $[\{\mathrm{(THF)Li}\}\{\mathrm{H_2AlN(H)R}\}\{\mathrm{HAl[N(H)R]_2(NR)}\}\{\mathrm{Li(THF)_3}\}]$ (R = Dipp; **7**)[6] exhibit a resonance at 0.29 ppm, supporting our findings for **1**−**3**. The ^{27}Al signals measured in THF-d_8 are broad and independent of the temperature (VT ^{27}Al NMR investigations for all three metalate ions) and were observed at 100 (**1**), 120 (**2**), and 108 (**3**) ppm (line width; see the Experimental Section). This fits well to the results obtained during ^{27}Al NMR studies for the reactions of small secondary amines with $\mathrm{Li[AlH_4]}$.[4]

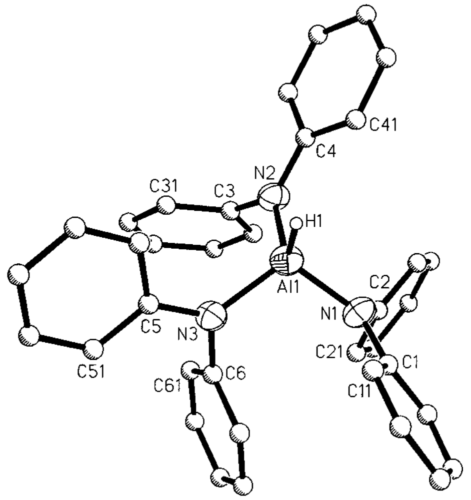

Figure 1. Molecular structure of the anion of **1**. The ellipsoids have a probability level of 50%. Carbon atoms are shown as spheres, and the hydrogen atoms (except Al−H) are omitted for clarity.

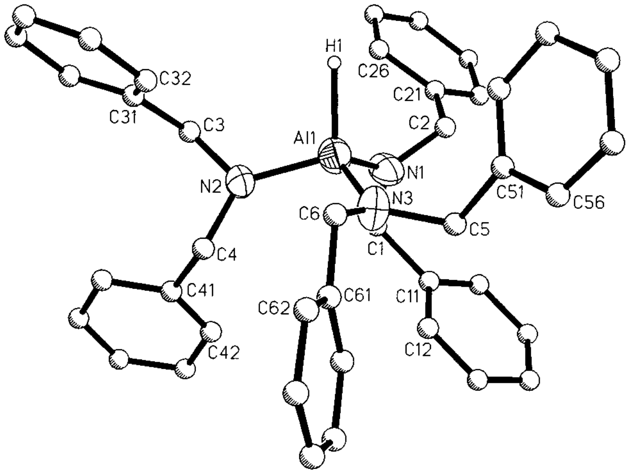

Figure 2. Molecular structure of the anion of **2** (for an explanation, see Figure 1).

The Al−H absorption in **1** was observed in the IR spectra at 1777 cm^{-1}. For **2** three reproducible bands at 1698, 1649, and 1638 cm^{-1} were found, indicating already a bridging character of the hydride functions to Li$^+$ caused by the loss of DME. In **3**·0.5toluene a terminal Al−H bond is responsible for the absorption at 1777 cm^{-1}. The Li−H−Al bridge was assigned to the broad band at 1619 cm^{-1}. The values for the terminal Al−H bonds are somewhat lower than those of the bands in neutral complexes ($[\mathrm{HAlNR}]_n$, 1795−1870 cm^{-1}) due to the negative charge[14] and are comparable with the absorptions measured for $[\{\mathrm{(Et_2O)_2Li}\}\{\mathrm{H_2Al[N(SiMe_3)_2]_2}\}]$ (1754 cm^{-1})[5] and **7**[6] (1786 cm^{-1}).

Mass spectra of **1**, **2**, and **3**·0.5toluene give as the highest mass only a signal of the corresponding amine fragment $\mathrm{NR_2}$ caused by the salt character of the compounds.

The structures of **1** and **2** consist of separate cations $[\mathrm{Li(THF)_4}]^+$ or $[\mathrm{Li(DME)_3}]^+$ and monohydridotriamidoaluminate anions $[\mathrm{HAl(NPh_2)_3}]^-$ or $[\mathrm{HAl\{N(CH_2Ph)_2\}_3}]^-$ (Figures 1 and 2). **3** possesses a Li···H bridge leading to a distorted tetrahedral coordination sphere of the Li$^+$ ion with three THF ligands and one $[\mathrm{H_2Al(N^cHex_2)_2}]^-$ ligand (Figure 3). The Al−H bonds in **1**−**3** are in the typical range of about 150−175 pm (see Table 2). The coordination polymer $[\mathrm{Li\{HAl(NEt_2)_3\}}]_n$[4] (**4**) possesses an Al−H bond of 152 pm, and the dihydridoaluminate $[\{\mathrm{(Et_2O)_2Li}\}\{\mathrm{H_2Al[N(SiMe_3)_2]_2}\}]$[5] (**5**) one of 161 pm (mean). The

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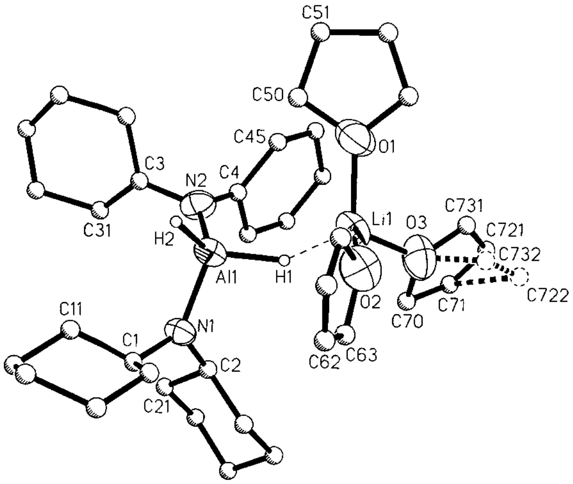

Figure 3. Molecular structure of the ion pair in **3**·0.5toluene with disorder behavior of one THF ligand (for further explanations, see Figure 1).

average value for the Al−H distance in **7** is 161 pm.[6] For the Li···H contact 184(4) pm was measured, corresponding well with the mean values in **4** (195 pm), **5** (178 pm), **6**, and **7** (189 pm). A more detailed discussion of the bonds, involving the H atoms bound to Al, is not possible because of the standard deviations of the Al−H and Li···H distances. The average Al−N bond distance of 187 pm in **1** lies between a characteristic terminal Al−N function of about 182 pm and a μ_2-bridging Al−N function of about 189 pm. A suitable comparison is the Al−N bond lengths in **2** (183 pm, terminal) or **3** (182 pm, terminal) and in $[\{(THF)_2Li\}\{Al(NC_5H_{10})_4\}]$ (183 pm, terminal; 189 pm, μ_2-bridging).[15] μ_3-Bridging NR groups were found, for example, in $[\{(THF)Mg\}\{HAlN^{t}Bu\}_3]$ (191 pm) and $[\{(THF)_3Ca\}\{HAlN^{t}Bu\}_3]$ (190 pm).[3b] In all three cases, **1**, **2**, and **3**·0.5toluene, the N atoms possess a trigonal planar environment. This is a typical behavior for N atoms in terminal Al−N bonds and was observed in silylamido groups (e.g., **5**),[5] in alkylamido groups (e.g., $[\{(THF)_2Li\}\{Al(NMe_2)_4\}]$),[4a] and for N atoms integrated in heterocycles (e.g., $[Al(NC_4H_8)_3]_2$; $[\{(THF)_2Li\}\{Al(NC_5H_{10})_4\}]$).[15]

Conclusions

The treatment of $LiAlH_4$ with sterically demanding secondary amines gives defined products. With $HNPh_2$ and $HN(CH_2Ph)_2$ the anion $[HAl(NR_2)_3]^-$ is dominating while $HN^{c}Hex_2$ leads to the anion $[H_2Al(NR_2)_2]^-$. In the solid state **1** and **2** form separate ions. An ion pair with a Li···H contact is the structural motif in **3**. The result, obtained in reactions of $LiAlH_4$:HNR_2 of 1:4 (molar equivalents) is influenced mainly by the basicity and the bulkiness of HNR_2.

Table 2. Selected Bond Lengths (pm) and Angles (deg) in **1**, **2**, and **3**·0.5Toluene

		1			
Al1−H1	159(4)	N1−Al1−N2	109.2(2)	Al1−N1−C1	122.8(4)
Al1−N1	187.9(5)	N1−Al1−N3	107.3(2)	Al1−N1−C2	119.5(4)
Al1−N2	186.8(6)	N2−Al1−N3	108.9(2)	C1−N1−C2	116.3(5)
Al1−N3	186.4(5)	H1−Al1−N1	113(1)	Al1−N2−C3	119.0(4)
		H1−Al1−N2	109(1)	Al1−N2−C4	125.1(4)
		H1−Al1−N3	109(1)	C3−N2−C4	115.8(5)
				Al1−N3−C5	125.5(4)
				Al1−N3−C6	119.4(4)
				C5−N3−C6	115.0(4)
		2			
Al1−H1	168(7)	N1−Al1−N2	114.6(4)	C1−N1−C2	112.1(7)
Al1−N1	182.1(8)	N1−Al1−N3	110.9(4)	Al1−N1−C1	124.6(6)
Al1−N2	181.6(7)	N2−Al1−N3	106.9(4)	Al1−N1−C2	123.0(6)
Al1−N3	184.3(9)	H1−Al1−N1	110(2)	C3−N2−C4	111.5(7)
		H2−Al1−N2	105(3)	Al1−N2−C3	120.1(6)
		H3−Al1−N3	109(3)	Al1−N2−C4	128.1(6)
				C5−N3−C6	110.7(7)
				Al1−N3−C5	122.4(6)
				Al1−N3−C6	122.5(7)
		3·0.5toluene			
Al1−H1	160(4)	N1−Al1−N2	118.5(2)	O1−Li1−O2	105.6(5)
Al1−H2	171(4)	N1−Al1−H1	104(2)	O2−Li1−O3	111.7(6)
Al1−N1	183.3(4)	N1−Al1−H2	103(2)	O1−Li1−O3	112.3(6)
Al1−N2	181.6(4)	N2−Al1−H1	102(2)	C1−N1−C2	115.0(4)
Li1···H1	184(4)	N2−Al1−H2	112(2)	Al1−N1−C1	129.4(4)
		H1−Al1−H2	118(2)	Al1−N1−C2	115.6(3)
		Li1···H1−Al1	135(3)	C3−N2−C4	115.4(6)
				Al1−N2−C3	116.2(5)
				Al1−N2−C4	128.3(5)

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of bond lengths and angles, hydrogen positional and isotropic displacement parameters, and non-hydrogen anisotropic displacement parameters for **1**, **2**, and **3**·0.5toluene. This material is available free of charge via the Internet at http://pubs.acs.org

IC000450S

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