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Syntheses, Characterizations, and X-ray Single-Crystal Structures of 1,8-Bis(trimethylsilylamino)naphthalene Aluminum Hydride and the Methyl Derivative

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Dedicated to Professor K. Mach

Keywords: Aluminum / Arene ligands / Structure elucidation

The reaction of 1,8-bis(trimethylsilylamino)naphthalene (LH_2) (**1**) with *n*BuLi yields the dilithium compound [1,8-$(Me_3SiN)_2C_{10}H_6$]$(Li)_2(thf)_3$ (**2**). Compound **1** reacts with $H_3Al{\cdot}NMe_3$ with elimination of hydrogen gas to produce [1,8-$(Me_3SiN)_2C_{10}H_6$]$AlH(NMe_3)$ (**3**), and the reaction of **2** with $MeAlCl_2$ leads to [1,8-$(Me_3SiN)_2C_{10}H_6$]Al(Me)thf (**4**). Compounds **3** and **4** are the first two aluminum mononuclear compounds to contain the 1,8-diaminonaphthalene ligand. These compounds were characterized by elemental analysis, NMR and IR spectroscopy, MS, and single-crystal X-ray structural analysis.

Introduction

Aluminum hydrides and their alkyl derivatives are involved in many aluminum-containing reactions, and thus are extraordinarily important in aluminum chemistry. Aluminum hydrides are good reducing agents and are used in a wide range of inorganic and organic transformations.[1] In addition, they are excellent precursors in the synthesis of alumoxanes by controlled hydrolysis,[2] and they can be used in the preparation of carbaalane clusters in conjunction with acetylenes or substituted acetylenes[3,4] and for the generation of amidoalane clusters from organic nitriles.[5] Recent research in our group showed that they can be used as very efficient starting materials in the preparation of aluminum chalcogenides[6–10] and also in the preparation of aluminum-containing heterocycles[11] by the elimination of H_2 gas. Alkylaluminum compounds are important cocatalysts used in polymerization reactions for the production of polypropylene, medium-to-low pressure polyethylene, and polybutadiene. They can also be converted into aluminum halides or oxides. A series of aluminum oxides and hydroxides was synthesized by the hydrolysis of alkylaluminum compounds,[12] and a very important product is methylaluminum oxide (MAO). MAO is a highly active cocatalyst for group 4 metallocenes and catalyzes ethylene and propylene polymerization.[13,14]

A bulky organic ligand is usually employed to stabilize the aluminum center both electronically and sterically. The introduction of a bulky organic ligand at the Al center can efficiently reduce the condensation of the resulting products. In recent years, a number of aluminum compounds with monovalent bulky chelating ligands have been reported, although there are not many aluminum compounds known that are supported by bivalent bulky ligands. In 1998, a series of new bivalent bulky 1,8-diaminonaphthalene ligands was synthesized.[15–19] The interest in these ligands is currently growing as a result of their specific steric and electronic properties, and these properties can efficiently control the geometry at the metal center. The known complexes containing these ligands, or naphthalene-based substrates, include main group (Al, Ge, In, Li, Na, Mg, Si, Sn, Tl) and transition-metal (Ni, Ti, Zr, Zn) derivatives.[16,20–27] Previously, aluminum mononuclear complexes were unknown, but herein we report the synthesis and characterization of bulky 1,8-bis(trimethylsilylamino)naphthalene (L) aluminum monohydride and its aluminum monomethyl derivative.

Results and Discussion

The reaction of 1,8-bis(trimethylsilylamino)naphthalene (LH_2) (**1**) with *n*BuLi leads to the starting material [1,8-

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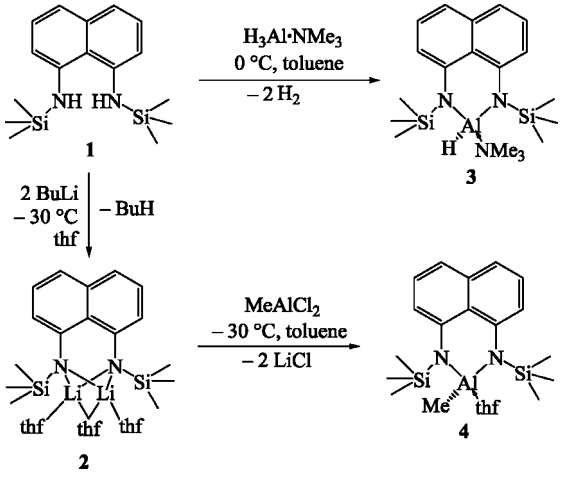
$(Me_3SiN)_2C_{10}H_6](Li)_2(thf)_3$ (**2**). Synthesis of [1,8-$(Me_3SiN)_2$-$C_{10}H_6$]AlH(NMe_3) (**3**) was accomplished by the reaction of LH_2 (**1**) with $H_3Al{\cdot}NMe_3$ at 0 °C in high yield. The compound [1,8-$(Me_3SiN)_2C_{10}H_6$]Al(Me)thf (**4**) was prepared from the reaction of **2** in situ with $MeAlCl_2$ at –30 °C. Compounds **3** and **4** (Scheme 1) are both mononuclear aluminum compounds containing the 1,8-diaminonaphthalene ligand (L). Only one aluminum compound of the form $L(AlMe_2)_2$ is known to contain the 1,8-diaminonaphthalene ligand,[25] and it is a binuclear compound synthesized by the reaction of LH_2 (**1**) with $AlMe_3$. We found, whether in a ratio of 1:1 or 1:2, the reaction of compound **1** with $AlMe_3$ always leads to $L(AlMe_2)_2$. Mononuclear LAlMe compounds are unknown. This is explained by the fact that after the formation of the $LH(AlMe_2)$ intermediate, the second Me group at the same Al center is not reactive enough to interact with the other proton of the ligand to eliminate another molecule of methane. In the reaction of **1** with $H_3Al{\cdot}NMe_3$, only mononuclear LAlH(NMe_3) (**3**) was obtained independently whether the reaction was conducted in the ratio of 1:1 or 1:2. This is due to the reactivity of the second hydride at the same Al center, which is high enough to interact with the other proton of the ligand to result in the elimination of H_2 gas. Consequently, the question as to whether it is possible to prepare the mononuclear methylaluminum compound of the general form LAlMe is raised. To prepare LAlMe, we used $LLi_2(thf)_3$ (**2**) and $MeAlCl_2$ as the starting materials. This reaction involved the elimination of two molecules of LiCl, and we successfully prepared the mononuclear methylaluminum compound LAl(Me)thf (**4**). The lithium salt **2** was prepared in situ at –30 °C, and the reaction with $MeAlCl_2$ was conducted also at –30 °C. Compounds **3** and **4** are soluble in common solvents such as toluene, dichloromethane, and tetrahydrofuran, and they can be kept in the glove box for several months without decomposition.



Scheme 1. Preparation of compounds **3** and **4**.

Compounds **3** and **4** were characterized by multinuclear NMR and IR (for **3**) spectroscopy, MS (EI), and elemental analysis. The presence of an Al–H bond in **3** is evident from the analysis of the IR spectrum. The broad IR band around 1869 cm^{-1} was assigned to the Al–H stretching frequency, which compares well with the known value of 1860 cm^{-1}.[28] In the ^1H NMR spectra of compounds **3** and **4**, resonances in the ranges from δ = 6.6 to 7.2 ppm and δ = 0.3 to 0.1 ppm in the ratio of 6:18 are present, which were assigned to the $C_{10}H_6$ and $SiMe_3$ groups, respectively. They confirm the existence of the backbone of the 1,8-bis(trimethylsilylamino)naphthalene ligand. In the ^1H NMR spectrum of **3**, the resonance at δ = 2.66 ppm suggests the existence of the NMe_3 group. In the ^1H NMR spectrum of **4**, the resonances at δ = 3.79 and 1.57 ppm in a ratio of 1:1 were assigned to the thf molecule coordinated to the aluminum center, and the resonance at δ = –0.55 ppm indicates the existence of the Al–Me bond in the molecule. The ^{13}C NMR spectra of **3** and **4** for the arene part exhibit almost the same resonances for both compounds.

Compounds **3** (Figure 1) and **4** (Figure 2) crystallize in the orthorhombic system *Ama*2 and in the monoclinic system $P2_1/n$, respectively. In both structures, the aluminum centers have a tetrahedral environment. The tetrahedral aluminum center in **3** indicates the existence of an H atom. Compounds **3** and **4** have almost the same Al–N bond lengths (av. 1.828 Å for **3** and 1.830 Å for **4**), whereas the Al–N bonds in the binuclear compound $L(AlMe)_2$ are much longer (av. 2.00 Å). The Al centers in $L(AlMe_2)_2$ are much more crowded than those in mononuclear **3** and **4**.[25] Thus, the two Al centers in $L(AlMe_2)_2$ are in close proximity, which results in the longer bond lengths of the Al–N bonds in $L(AlMe_2)_2$ in comparison to those in **3** and **4**. In the binuclear structure of $L(AlMe_2)_2$, it is obvious that the two Me groups at the same aluminum atom have different chemical environments. One Me group is near the naphthalene ligand and the other Me group is positioned away from the arene ring (δ = –0.11 and –1.14 ppm).[25] There is only one Me group at the aluminum atom in mononuclear **4**, which results in only one chemical shift. The Al→N2 bond

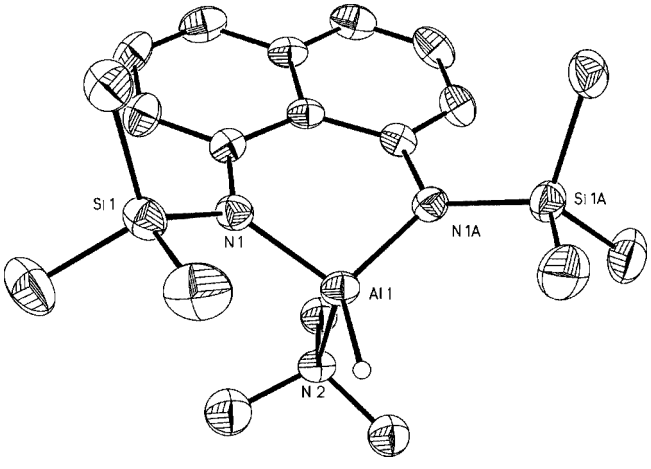


Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity, while the hydrogen atom on the aluminum atom was set. Selected bond lengths [Å] and angles [°]: Al1–N1 1.828(2), Al1–N1A 1.828(2), Al1–N2 2.021(3), N1–Si1 1.744(2); N1–Al1–N1A 102.95(13), N1–Al1–N2 106.85(8), N1A–Al1–N2 106.86(8).

length (2.021 Å) in **3** and the Al→O bond length (1.920 Å) in **4** are longer than the normal σ bonds of compounds containing Al–N and Al–O moieties.

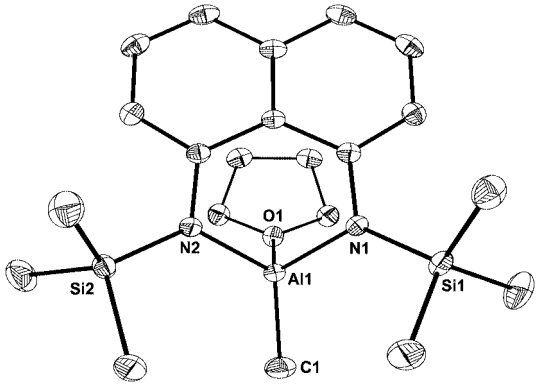


Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1–N1 1.8298(13), Al1–N2 1.8311(12), Al1–O1 1.9202(11), Al1–C1 1.9482(16); N1–Al1–N2 100.82(6), N1–Al1–O1 101.88(5), N2–Al1–O1 100.33(5), N1–Al1–C1 121.37(7), N2–Al1–C1 125.87(7), O1–Al1–C1 102.09(7).

Conclusions

Herein, we described the syntheses, characterizations, and X-ray structures of aluminum hydride and methyl compounds supported by the 1,8-bis(trimethylsilylamino)naphthalene ligand. The resulting compounds are interesting precursors for the preparation of new aluminum compounds.

Experimental Section

[1,8-(Me$_3$SiN)$_2$C$_{10}$H$_6$]AlH(NMe$_3$) (3): To a solution of [1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$] (3.02 g, 10 mmol) in toluene (40 mL) at 0 °C was added dropwise H$_3$Al·NMe$_3$ (1 M in toluene, 10 mL, 10 mmol). The resulting solution was stirred and warmed to room temperature. After additional stirring for 2 h, the solution was evaporated to dryness in vacuo, and the residue was washed with cold *n*-hexane (2 × 5 mL) to yield crystalline **3** (3.29 g, 85%). M.p. 213 °C. ^{1}H NMR (500.13 MHz, CDCl$_3$, 298 K): δ = 0.30 (s, 18 H, Si-*Me*), 2.66 (s, 9 H, N*Me*$_3$), 6.70 (m, 2 H, C$_{10}$*H*$_6$), 7.25–7.45 (m, 4 H, C$_{10}$*H*$_6$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$, 298 K): δ = 2.91 (Si-*Me*), 47.60 (N*Me*$_3$), 116.19 (*C*H, *C*$_{10}$H$_6$), 118.54 (*C*H, *C*$_{10}$H$_6$), 125.32 (*C*, *C*$_{10}$H$_6$), 137.98 (*C*H, *C*$_{10}$H$_6$), 144.75 (*C*, *C*$_{10}$H$_6$), 150.64 (*C*N, C$_{10}$H$_6$) ppm. ^{29}Si NMR (99.36 MHz, CDCl$_3$, 298 K): δ = –0.55 ppm. IR (KBr, plate): $\tilde{\nu}$ = 1869 (m, AlH) cm^{-1}. MS (EI): *m*/*z* (%) = 387 (16) [M]$^+$, 328 (100) [M – NMe$_3$]$^+$. C$_{19}$H$_{34}$AlN$_3$Si$_2$ (387.64): calcd. C 58.87, H 8.84, N 10.84; found C 57.76, H 8.62, N 10.44.

[1,8-(Me$_3$SiN)$_2$C$_{10}$H$_6$]Al(Me)thf (4): To a solution of [1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$] (3.02 g, 10 mmol) in thf (40 mL) at –30 °C was added dropwise *n*BuLi (2.5 M, 8 mL, 20 mmol). The mixture was stirred and warmed to room temperature. After additional stirring for 1 h, all volatiles were removed in vacuo and toluene (40 mL) was added to the solid residue. The solution was cooled to –30 °C and MeAlCl$_2$ (1 M, 10 mL, 10 mmol) was added. The resulting solution was warmed to room temperature and stirred for 2 h. After workup, the insoluble LiCl was removed by filtration, and the residue was dried in vacuo and washed with cold *n*-hexane (2 × 5 mL) to yield solid **4** (2.94 g, 71%). M.p. 154–155 °C. ^{1}H NMR (500.13 MHz, CDCl$_3$, 298 K): δ = –0.55 (s, 3 H, Al-*Me*), 0.23 (s, 18 H, Si-*Me*), 1.57 [m, 4 H, O(CH$_2$C*H*$_2$)$_2$], 3.79 [m, 4 H, O(C*H*$_2$CH$_2$)$_2$], 6.63 (m, 2 H, C$_{10}$*H*$_6$), 7.01–7.05 (m, 4 H, C$_{10}$*H*$_6$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$, 298 K): δ= 2.70 (Si-*Me*), 24.93 [O(CH$_2$*C*H$_2$)$_2$], 69.78 [O(*C*H$_2$CH$_2$)$_2$], 116.68 (*C*H, *C*$_{10}$H$_6$), 118.21 (*C*H, *C*$_{10}$H$_6$), 125.17 (*C*, *C*$_{10}$H$_6$), 137.66 (*C*H, *C*$_{10}$H$_6$), 144.15 (*C*, *C*$_{10}$H$_6$), 151.01 (*C*N, C$_{10}$H$_6$) ppm. ^{29}Si NMR (99.36 MHz, CDCl$_3$, 298 K): δ = –1.12 ppm. MS (EI): *m*/*z* (%) = 342 (100) [M – thf]$^+$. C$_{21}$H$_{35}$AlN$_2$OSi$_2$ (414.67): calcd. C 60.83, H 8.51, N 6.76; found C 58.94, H 7.99, N 6.93. The slight difference in the found and calculated analytical data is due to the extreme moisture sensitivity of the product.

X-ray Structure Determination of 3 and 4: Suitable crystals of **3** and **4** were mounted on a glass fiber and coated with paraffin oil. Data for **3** was obtained with a STOE-IPDS II image-plate diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data for **4** was collected with a Bruker SMART 1000 CCD diffractometer. The structures were solved by direct methods by using SHELXS-97[29] and refined against F^2 on all data by using full-matrix least-squares with SHELXL-97.[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms connected to carbon atoms were included at geometrically calculated positions and refined by using a riding model (Table 1).

CCDC-645712 (**3**) and -644929 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free

Table 1. X-ray crystallographic data for **3** and **4**.

	3	**4**
Empirical formula	C$_{19}$H$_{33}$AlN$_3$Si$_2$	C$_{21}$H$_{35}$AlN$_2$OSi$_2$
Formula weight	386.64	414.67
Temperature [K]	133(2)	133(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Ama*2	*P*2$_1$/*n*
a [Å]	18.5497(19)	7.2999(8)
b [Å]	12.2030(7)	16.7801(18)
c [Å]	10.1856(7)	19.187(2)
α [°]	90	90
β [°]	90	94.074(4)
γ [°]	90	90
V [Å^3]	2305.6(3)	2344.3(4)
Z	4	4
$D_{calcd.}$ [Mg m^{-3}]	1.114	1.175
Absorption coefficient [mm^{-1}]	0.199	0.202
F(000)	836	896
θ range for data collection [°]	2.20 to 24.80	1.61 to 30.50
Index ranges	$-21 \le h \le 21$	$-10 \le h \le 10$
	$-14 \le k \le 14$	$-23 \le k \le 23$
	$-12 \le l \le 12$	$-27 \le l \le 27$
Reflections collected	16394	49652
R_{int}	0.0837	0.0424
Data/restraints/parameters	2050/1/127	7143/0/251
Goodness-of-fit on F^2	0.890	1.037
Final R_{int} [$I > 2\sigma(I)$]	R_1 = 0.0327	R_1 = 0.0392
	wR_2 = 0.0623	wR_2 = 0.0939
R_{int} (all data)	R_1 = 0.0471	R_1 = 0.0646
	wR_2 = 0.0654	wR_2 = 0.1087
Largest difference peak and hole [e Å^{-3}]	0.182 and –0.204	0.456 and –0.299

of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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