Syntheses and Structural Characterization of a $LAl(N_3)N[\mu\text{-}Si(N_3)(tBu)]_2NAl(N_3)L$ and a Monomeric Aluminum Hydride Amide LAlH(NHAr) (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-$iPr_2C_6H_3$)

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Reactions between the aluminum(I) monomer LAl (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-$iPr_2C_6H_3$) and organic azides (RN_3, R = $C_{10}H_{15}$ (adamantyl), Ph_3Si; $tBuSi(N_3)_3$) are reported. LAl reacted with the bulky azide RN_3 in toluene in a temperature range of −50 to 25 °C, resulting in the compound $LAl[(NR)_2N_2]$ (R = $C_{10}H_{15}$ (**1**), Ph_3Si (**2**)) instead of the expected Al═N multiple bond species, while the reaction with $tBuSi(N_3)_3$ gave $LAl(N_3)N[(\mu\text{-}Si(N_3)(tBu)]_2NAl(N_3)L$ (**3**). Compounds **1**−**3** have been fully characterized by mass spectrometry and IR and multinuclear NMR spectroscopy (^1H, ^{13}C, and ^{29}Si) as well as by single-crystal X-ray crystallography. The structural analysis of **1** and **2** reveals an AlN_4 planar five-membered ring compound, suggesting a [2 + 3] cycloaddition of the Al═N multiple bond species with a molecule of RN_3 despite the steric bulk of the L and R substituents. Compound **3** shows a bonding of the N_3 group to the Al and a formation of the N_2Si_2 central core, implying the migration of N_3 and a [2 + 2] cycloaddition in the reaction sequence. In addition, the solvent-free reaction of an aluminum dihydride $LAlH_2$ with $ArNH_2$ was also investigated at elevated temperatures (150−290 °C), and a monomeric aluminum hydride amide, LAlH(NHAr) (**4**), was obtained as the only isolable product. The Al−H and N−H groups of **4** are shown in the IR and ^1H NMR spectra. The corresponding X-ray structural analysis exhibits the Al−H and N−H bonds that are nearly arranged in position *trans* to the $Al-N_{NHAr}$ bond.

Introduction

The reactions of monovalent heavier group 13 compounds with organic azides are of general interest. In these reactions, an interaction between the metal center and the N_3 group results in an elimination of N_2 and the formation of a M−N bond with a multiple bond character.[1] Such M−N bonded species are highly reactive and can further react through dimerization,[2] by C−H bond activation,[3] by 1,3-dipolar addition,[4] and alternatively by cycloaddition with another molecule of azide.[5] More recently, we have reported on a reaction of LAl with Ar^*N_3 (L = $HC[(CMe)(NAr)]_2$, Ar* = 2,6-$Ar_2C_6H_3$, Ar = 2,6-$iPr_2C_6H_3$) at low temperatures. The initially formed imide LAlNAr* further reacts intramolecularly under C−H bond activated addition and [2 + 2] cycloaddition involving the methyl and phenyl group, respectively.[6] However, the reaction of $(Cp^*Al)_4$ with Me_3SiN_3 at elevated temperature yielded $Cp^*[(Me_3Si)_2N]AlN(\mu\text{-}AlCp^*)(\mu\text{-}Al[N(SiMe_3)_2])NAlCp^*_2$; the related mechanism is still under investigation.[3] These examples demonstrate an extensive reaction chemistry between heavier group 13 metal(I) species and organic azides. Moreover, it has been shown that the steric demand of the substituents at M (M(I) species) and N (organic azide) has a great influence on the formation of the products. Herein we report on the reaction of the aluminum(I) monomer LAl with the bulky azide RN_3 and the isolation of the AlN_4 five-membered-ring compound $LAl[(NR)_2N_2]$ (R = $C_{10}H_{15}$ (adamantyl) (**1**), $SiPh_3$ (**2**)). Treatment of LAl with $tBuSi(N_3)_3$, however, generates the compound $LAl(N_3)N[(\mu\text{-}Si(N_3)(tBu)]_2NAl(N_3)L$ (**3**), different from the previously reported results on related reactions. In addition, the investigation of the H_2 elimination reaction using an aluminum dihydride $LAlH_2$ and a primary amine $ArNH_2$ at elevated temperatures is also presented, in which a monomeric aluminum hydride amide, LAlH(NHAr) (**4**), was obtained as the only isolable product.

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Experimental Section

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside an Mbraun MB 150-GI glovebox filled with dry nitrogen where the calibrated values of O_2 and H_2O were strictly controlled below 1 ppm. All solvents were dried by standard methods prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received except for $ArNH_2$. $ArNH_2$ was distilled prior to use. The other compounds mentioned in this paper were prepared according to published procedures: Ph_3SiN_3,[2] LAl,[7] tBuSi$(N_3)_3$,[8] $LAlH_2$.[9] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^{1}H (300.13 and 500.13 MHz), ^{13}C (125.76 MHz), and ^{29}Si (99.36 MHz) NMR spectra were recorded on a Bruker AM 300 or 500 spectrometer and IR spectra on a Bio-Rad Digilab FTS-7 spectrometer. EI mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of $LAl[(NC_{10}H_{15})_2N_2]$ (1). Precooled toluene (30 mL) was added to a mixture of LAl (0.20 g, 0.45 mmol) and $C_{10}H_{15}N_3$ (0.16 g, 0.90 mmol) at −50 °C. The suspension was allowed to warm to room temperature and stirred for 12 h. A yellow solution developed. The solvent from the solution was removed in vacuo, and the residue was washed with *n*-hexane (5 mL) to afford a yellow crystalline solid of **1**. Yield: 0.29 g, 84%. Mp: 384 °C. ^{1}H NMR (500.13 MHz, D_8-toluene, 298 K, ppm): δ 1.06 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.18 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.24 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.25 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.33−1.49 (m), 1.77−1.84 (m), 2.22 (br) (15 H, $C_{10}H_{15}$), 1.62 (s, 2 × 3 H, β-CH_3), 3.32 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.88 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 5.20 (s, 1 H, γ-CH), 6.90−7.18 (m, 6 H, Ar-C_6H_3). ^{13}C{^{1}H} NMR (125.76 MHz, D_8-toluene, 298 K, ppm): δ 24.5, 24.6, 25.2, 25.5, 25.6, 29.2, 30.1, 31.0 ($CH(CH_3)_2$, β-CH_3), 36.9, 37.8, 44.6, 52.5, 53.6 ($C_{10}H_{15}$), 101.8 (γ-C), 124.9, 125.1, 127.8, 128.1, 129.2, 141.1, 143.0, 146.1 (Ar-C_6H_3), 171.8 (CN). EI-MS: *m/z* (%) 770.5 (100, [M$^+$]). Anal. Calcd (%) for $C_{49}H_{71}AlN_6$ (M_r = 771.13): C, 76.32; H, 9.28; N, 10.90. Found: C, 76.34; H, 9.24; N, 10.74. X-ray quality single crystals of **1**·Et_2O were grown from a mixture of solvents (Et_2O:*n*-hexane = 1:3) at 4 °C for one week.

Synthesis of $LAl[(NSiPh_3)_2N_2]$·PhMe (2·PhMe). The synthetic route is similar to that of **1**. LAl (0.44 g, 1 mmol) and Ph_3SiN_3 (0.60 g, 2 mmol) are used. After workup, a colorless solution developed. The solution was concentrated (ca. 5 mL), and to it *n*-hexane (10 mL) was added. The solution was kept at 4 °C for three weeks to afford X-ray quality crystals of **2**·PhMe. Yield: 0.89 g, 80%. Mp: 220 °C. ^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ 0.61 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 0.76 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 0.87 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.01 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.27 (s, 2 × 3 H, β-CH_3), 2.10 (s, 3 H, PhMe), 2.47 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.66 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.91 (s, 1 H, γ-CH), 6.96−7.26 (m, 41 H, Ar-C_6H_3, SiPh_3, PhMe). ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298 K, ppm): δ 21.4, 24.7, 25.0, 25.6, 28.3, 28.8 ($CH(CH_3)_2$, β-CH_3, PhMe), 102.3 (γ-C), 125.1, 125.8, 126.0, 128.0, 128.2, 128.5, 128.9, 129.2, 129.3, 137.2, 137.3, 137.5, 138.1, 140.7, 143.7, 145.8 (Ar-C_6H_3, SiPh_3, PhMe), 172.2 (CN). ^{29}Si NMR (99.36 MHz, C_6D_6, 298 K, ppm): δ −20.6, −15.1. EI-MS: *m/z* (%) 717.4 (100, [M$^+$ − Ph_3SiN_3]). Anal. Calcd (%) for $C_{72}H_{79}AlN_6Si_2$ (**2**·PhMe, M_r = 1111.62): C, 77.80; H, 7.16; N, 7.56. Found: C, 77.79; H, 7.25; N, 7.34.

Note: The reaction of LAl and $C_{10}H_{15}N_3$ (or Ph_3SiN_3) in a molar ratio of 1:1 even in the temperature range of −78 °C to room temperature still resulted in the formation of **1** (or **2**).

Synthesis of $LAl(N_3)N[\mu$-Si$(N_3)(t$Bu$)]_2NAl(N_3)L$ (3). A precooled toluene solution (10 mL) of tBuSi$(N_3)_3$ (0.11 g, 0.5 mmol) was added to a toluene solution (20 mL) of LAl (0.22 g, 0.5 mmol) at −50 °C. The mixture was stirred and allowed to warm to room temperature. The color of the solution changed from red to yellow, and finally to colorless. After stirring for an additional 12 h, the solution was concentrated (ca. 5 mL), and to this solution *n*-hexane (15 mL) was added. The colorless crystalline solid of **3** was immediately formed and collected by filtration (0.10 g). The filtrate was stored at 4 °C for three weeks to afford another crop of X-ray quality crystals of **3**·PhMe (0.17 g). Total yield: 0.26 g, 83% of **3**. Mp: 320 °C. ^{1}H NMR (300.13 MHz, D_8-toluene, 298 K, ppm): δ 0.27 (s, 18 H, *tBu*), 1.07 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.14 (d, 8 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.21 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.64 (s, 4 × 3 H, β-CH_3), 3.16 (sept, 4 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.26 (sept, 4 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 4.76 (s, 2 × 1 H, γ-CH), 6.94−7.20 (m, 12 H, Ar-C_6H_3). ^{13}C{^{1}H} NMR (125.76 MHz, D_8-toluene, 298 K, ppm): δ 1.36 (*tBu*), 22.5, 23.0, 24.2, 24.6, 24.8, 27.1, 28.6, 29.1, 32.0 ($CH(CH_3)_2$, β-CH_3), 94.3 (γ-C), 123.5, 125.1, 127.9, 128.1, 137.4, 141.3, 142.7, 144.4 (Ar-C_6H_3), 172.2 (CN). ^{29}Si NMR (99.36 MHz, D_8-toluene, 298 K, ppm): δ −21.5, −20.8. EI-MS: *m/z* (%) 1255 (30, [M$^+$]), 1198 (100, [M$^+$ − tBu]). IR (KBr plate, Nujol mull, cm^{-1}): ν 2113, 2076 (m, N_3). Anal. Calcd (%) for $C_{66}H_{100}Al_2N_{18}Si_2$ (M_r = 1255.79): C, 63.12; H, 8.03; N, 20.01. Found: C, 63.08; H, 8.08; N, 20.04.

Synthesis of LAlH(NHAr) (4). A mixture of $LAlH_2$ (1.34 g, 3 mmol) and $ArNH_2$ (0.57 mL, 3 mmol), with stirring, was slowly heated to ca. 150 °C for 1 h. H_2 evolution was observed and ceased after 1 h. When cooled to room temperature, the solidified product was dissolved in toluene (15 mL). The solvent from the solution was removed in vacuo, and the residue was washed with *n*-hexane (2 × 2 mL), affording the light yellow crystalline solid of **4** (yield >95%). Mp: 134 °C. ^{1}H NMR (300.13 MHz, D_8-toluene, 298 K, ppm): δ 0.95 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.10 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.11 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.13 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.26 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.55 (s, 2 × 3 H, β-Me), 2.43 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 2.93 (s, 1 H, NH), 3.32 (sept, 4 × 1 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 4.97 (s, 1 H, γ-CH), 5.50 (br, 1 H, Al-H), 6.69−6.72, 6.92−7.10 (m, 9 H, Ar-C_6H_3). ^{13}C{^{1}H} NMR (125.76 MHz, D_8-toluene, 298 K, ppm): δ 23.4, 24.4, 24.5, 24.6, 24.7, 25.2, 28.4, 28.7, 28.9 ($CH(CH_3)_2$, β-CH_3), 97.9 (γ-C), 117.5, 123.0, 124.6, 125.0, 125.6, 128.2, 128.5, 129.2, 129.3, 135.4, 137.5, 140.7, 144.0, 144.5, 145.3 (Ar-C_6H_3), 170.6 (CN). EI-MS: *m/z* (%): 621 (22, [M$^+$]), 578 (100, [M$^+$ − *i*Pr]). IR (KBr plate, Nujol mull, cm^{-1}): ν 1821 (w, Al-H), 3358 (w, N-H). Anal. Calcd (%) for $C_{41}H_{60}AlN_3$ (M_r = 621.93): C, 79.18; H, 9.72; N, 6.76. Found: C, 79.12; H, 9.74; N, 6.61. X-ray single crystals of **4**·PhMe were obtained by recrystallization of **4** from a mixture of toluene and *n*-hexane (3:2).

X-ray Structure Determination and Refinement. The crystallographic data for compounds **1**·Et_2O, **2**·PhMe, and **3**·PhMe were collected on a Stoe IPDS II-array detector system and for compound **4**·PhMe on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector. In both cases graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used. All structures were solved by direct methods

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(8) The compound tBuSi$(N_3)_3$ was prepared using tBuSiCl$_3$ and excess NaN_3 with reference to that of Ph_3SiN_3 in ref 2. The physical and spectroscopic data are shown here: colorless liquid, mp −10 °C; ^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm) δ 0.70; IR (KBr plate, Nujol mull, cm^{-1}) ν 2185, 2156 (vs, N_3).

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Table 1. Crystallographic Data for Compounds 1·Et$_2$O, 2·PhMe, 3·PhMe, and 4·PhMe

	1·Et$_2$O	**2**·PhMe	**3**·PhMe	**4**·PhMe
formula	$C_{53}H_{81}AlN_6O$	$C_{72}H_{79}AlN_6Si_2$	$C_{73}H_{108}Al_2N_{18}Si_2$	$C_{48}H_{68}AlN_3$
fw	845.22	1111.57	1347.91	714.03
temp (K)	133(2)	133(2)	133(2)	200(2)
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	*Pbca*	*P*2(1)/*n*	$P\bar{1}$	$P\bar{1}$
a (Å)	17.413(1)	14.476(3)	12.923(1)	10.071(2)
b (Å)	21.173(1)	22.773(5)	16.568(1)	11.630(2)
c (Å)	26.774(1)	18.766(4)	19.751(1)	19.851(4)
α (deg)			102.65(1)	91.56(3)
β (deg)		93.20(3)	99.84(1)	90.86(3)
γ (deg)			99.24(1)	110.81(3)
V (Å^3)	9871(1)	6177(2)	3978(1)	2172(1)
Z	8	4	2	2
ρ_c (Mg/m^3)	1.137	1.195	1.125	1.427
μ (mm^{-1})	0.084	0.119	0.118	0.110
F(000)	3696	2376	1452	1020
θ range (deg)	1.52−25.01	1.41−24.99	1.76−25.17	3.52−22.47
index ranges	$-20 \leq h \leq 20$	$-17 \leq h \leq 16$	$-12 \leq h \leq 15$	$-10 \leq h \leq 10$
	$-23 \leq k \leq 25$	$-25 \leq k \leq 26$	$-19 \leq k \leq 19$	$-12 \leq k \leq 12$
	$-30 \leq l \leq 31$	$-22 \leq l \leq 22$	$-23 \leq l \leq 23$	$-21 \leq l \leq 21$
no. of reflns collected	91 750	62 011	40 310	9308
no. of indep reflns (R_{int})	8688 (0.0571)	10 804 (0.0903)	13 529 (0.0561)	5648 (0.0761)
no. of data/restraints/params	8688/0/562	10 804/0/735	13 529/1/853	5648/0/488
GoF/F^2	1.036	1.025	1.082	1.015
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0418, 0.1057	0.0480, 0.1183	0.0629, 0.1770	0.0495, 0.1318
R1,[a] wR2[b] (all data)	0.0586, 0.1124	0.0608, 0.1258	0.0837, 0.1925	0.0615, 0.1464
largest diff peak/hole (e·Å^{-3})	0.203/−0.265	0.491/−0.413	1.177/−0.845	0.258/−0.234

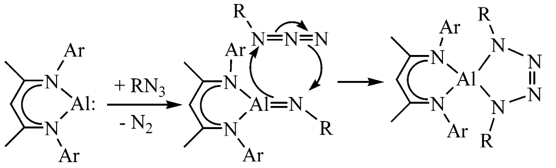
[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$.

(SHELXS-96)[10] and refined against F^2 using SHELXL-97.[11] All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically except for those of toluene molecules in **2**·PhMe and **3**·PhMe, which were refined isotropically using a part treatment (the PhMe molecule was located in two positions with the respective 0.50 occupation) for **2**·PhMe and a rigid model of benzene and distance restraints treatment for **3**·PhMe. Thus, the residual electronic density of the difference Fourier synthesis in **3**·PhMe is somewhat high (1.177 e·Å^{-3}). We were not able to improve this value by the collection of the reflection data on another diffractometer. All hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms, except for the Al-H hydrogen in **4**, which was located by difference Fourier synthesis and refined isotropically. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1.

Results and Discussion

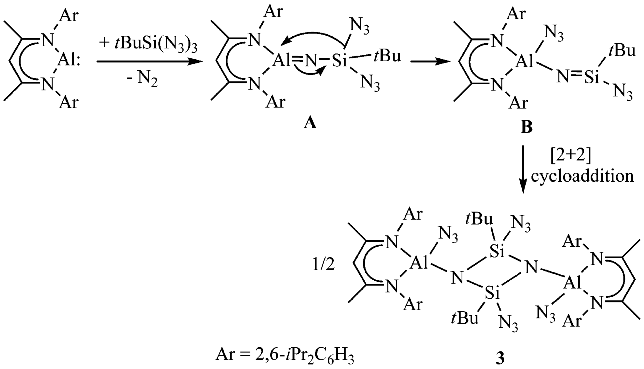
Reactions of LAl with RN$_3$ (R = C$_{10}$H$_{15}$ (adamantyl), Ph$_3$Si) and tBuSi(N$_3$)$_3$. The reaction of LAl with 2 equiv of bulky azide and RN$_3$ in toluene in the temperature range −50 to 25 °C resulted in the formation of the five-membered-ring compound LAl[(NR)$_2$N$_2$] (R = $C_{10}H_{15}$ (**1**), Ph$_3$Si (**2**)), a result similar to that in the previously reported reaction of LAl with the less bulky Me$_3$SiN$_3$.[5] Treatment of such a mixture in 1:1 molar ratio in a lower temperature range (−78 to 25 °C) in an attempt to isolate a LAlNR species was not successful, and LAl[(NR)$_2$N$_2$] was always formed as the only isolable product. This indicates that the steric bulk of the $C_{10}H_{15}$ and Ph$_3$Si substituents is still not sufficient enough to stabilize the LAlNR monomer; instead, such Al=N multiple bonded species further react under [2 + 3] cycloaddition with another molecule of the azide (Scheme 1). Undoubtedly, in view of our work in this field,[5−7] the alternation of the bulky azide further evidences the high reactivity of the Al=N multiple bonded species despite the steric bulk of the substituents at both Al and N atoms. Further exploration of the reaction of LAl with tBuSi(N$_3$)$_3$ interestingly led under similar conditions to LAl(N$_3$)N[μ-Si(N$_3$)(tBu)]$_2$NAl(N$_3$)L (**3**). This result is completely different from the previously reported ones.[2−6] Here we were able to deduce that the formation of **3** may proceed through the initial N$_2$ elimination to yield the Al=N multiple bonded intermediate **A**. **A** further rearranges under migration of one N$_3$ group from the Si to the Al atom to form the N=Si species **B**. Finally **B** reacts in a [2 + 2] cycloaddition to yield **3** (Scheme 2). Obviously, the high reactivity of **A** initiates this intramolecular N$_3$ migration. Moreover, the chelating character and the bulk of L at Al compared to those of the N$_3$ and tBu groups at N may be

Scheme 1



R = C$_{10}$H$_{15}$ **1**, Ph$_3$Si **2**
Ar = 2,6-iPr$_2$C$_6$H$_3$

Scheme 2



Ar = 2,6-iPr$_2$C$_6$H$_3$

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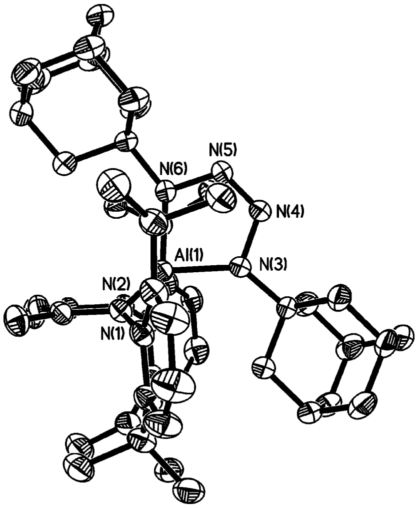

Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

responsible for the different reaction products. This proposed rearrangement can be compared to the result reported on the 1,3-dipolar addition of Me_3SiN_3 to the Ga=N multiple bonded intermediate.[4] Compounds containing the N=Si double bond are known,[12] and [2 + 2] cycloaddition reactions of these systems have been well documented.[13]

Compounds **1** and **2** were obtained in high yield as a yellowish crystalline solid and colorless crystals, respectively. The latter crystallized with a toluene molecule. **1** has a high melting point (384 °C), and EI-MS indicates the highest peak for the molecular ion. In contrast, **2** melts at 220 °C, and the most intense peak in the EI-MS of **2** was observed corresponding to the $LAlNSiPh_3$ fragment without any other related ions indicative of the composition of **2** in the gas phase.

The single-crystal X-ray diffraction studies clearly reveal that **1** and **2** both have an AlN_4 five-membered-ring structure. The molecular structures of **1** and **2** are shown in Figures 1 and 2. Selected bond lengths and angles are listed in Table 2. In the structures of **1** and **2**, the Al center is involved as part of two fused rings (AlC_3N_2 and AlN_4) that are in almost orthogonal array (dihedral angle: 90.6° **1**; 87.1° **2**). The AlN_4 ring exhibits a perfect plane (least-squares plane $\Delta = 0.0069$ Å **1**; 0.0188 Å **2**). The corresponding parameters within this plane (Al−N: 1.818(1), 1.854(1) Å **1**; 1.842(2), 1.871(2) Å **2**; N−N: 1.390(2), 1.272(2), 1.391(2) Å **1**; 1.412(2), 1.259(2), 1.427(2) Å **2**) indicate that the AlN_4 ring in **1** is more densely packed than that in **2**. This may give rise to the difference of the above-mentioned physical properties between **1** and **2**. The Al−N bond lengths within the AlN_4 ring are a little shorter compared to that in the $AlNC_2$ ring (1.876(2) Å), which is formed by [2 + 2] cycloaddition of an Al=N and the C=C bond of a phenyl ring.[6]

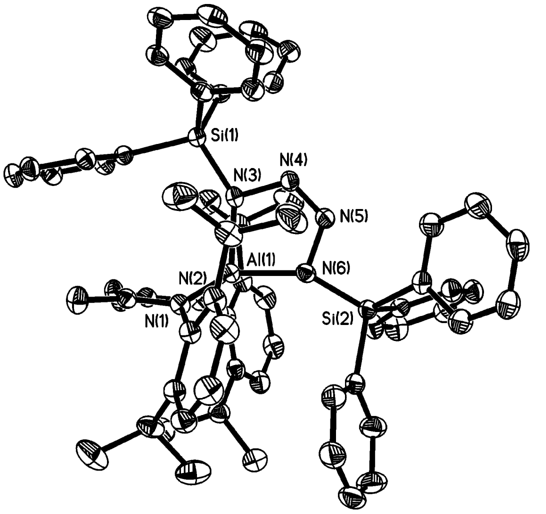

Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

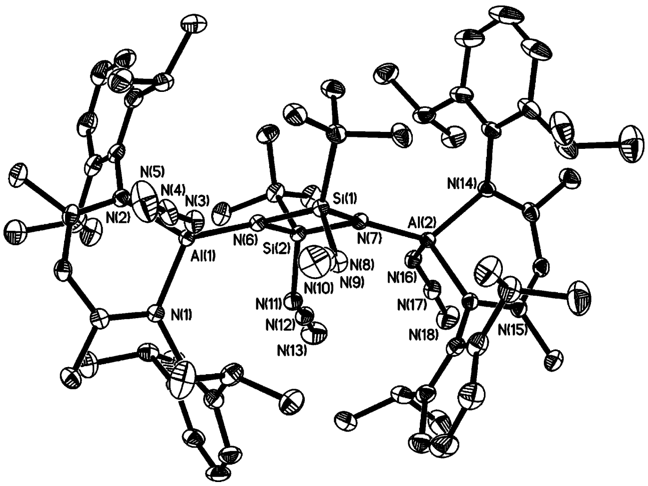

Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1·Et_2O and 2·PhMe

	1·Et_2O	**2**·PhMe		**1**·Et_2O	**2**·PhMe
Al(1)−N(1)	1.907(1)	1.892(2)	N(1)−Al(1)−N(2)	95.38(5)	96.99(7)
Al(1)−N(2)	1.895(1)	1.896(2)	N(3)−Al(1)−N(6)	85.08(5)	87.38(8)
Al(1)−N(3)	1.818(1)	1.871(2)	Al(1)−N(6)−N(5)	110.96(9)	108.94(12)
Al(1)−N(6)	1.854(1)	1.842(2)	N(6)−N(5)−N(4)	115.99(12)	117.51(15)
N(3)−N(4)	1.391(2)	1.412(2)	N(5)−N(4)−N(3)	115.63(11)	117.22(16)
N(4)−N(5)	1.272(2)	1.259(2)	N(4)−N(3)−Al(1)	112.31(9)	108.77(12)
N(5)−N(6)	1.390(2)	1.427(2)			

Compound **3** is a colorless crystalline solid that has a good solubility in toluene and benzene but a poor one in *n*-hexane. It has a high melting point (320 °C). EI-MS data (*m/z* (%): 1255 (30, $[M^+]$), 1198 (100, $[M^+ - tBu]$)) are consistent with the formulation of **3**, which was unambiguously established by single-crystal X-ray diffraction. This indicates a thermal stability of **3**, although this compound contains four N_3 groups.

Compound **3** crystallizes with two half toluene molecules in space group $P\bar{1}$. The molecular structure of **3** is shown in Figure 3. Selected bond lengths and angles are listed in Table 3. In the structure of **3**, each Al atom is coordinated by the chelating β-diketiminato L and one N_3 group and one N atom from the Si_2N_2 ring and appears in a distorted tetrahedral geometry. The central Si_2N_2 ring is formed in an approximate square (Si−N:

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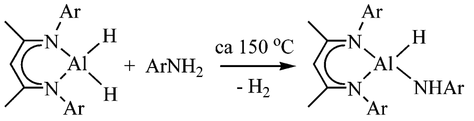
Table 3. Selected Bond Distances (Å) and Angles (deg) for 3·PhMe

Al(1)−N(1)	1.912(3)	Al(1)−N(2)	1.909(3)
Al(1)−N(3)	1.839(3)	Al(1)−N(6)	1.808(2)
N(6)−Si(1)	1.748(2)	N(6)−Si(2)	1.734(2)
Si(1)−N(7)	1.737(2)	Si(2)−N(7)	1.749(2)
Al(2)−N(7)	1.812(2)	Al(2)−N(16)	1.851(3)
Al(2)−N(14)	1.902(3)	Al(2)−N(15)	1.921(3)
N(3)−N(4)	1.190(4)	N(4)−N(5)	1.150(4)
N(8)−N(9)	1.227(4)	N(9)−N(10)	1.139(4)
N(11)−N(12)	1.223(4)	N(12)−N(13)	1.140(4)
N(16)−N(17)	1.207(4)	N(17)−N(18)	1.151(4)
N(1)−Al(1)−N(2)	97.07(11)	N(3)−Al(1)−N(6)	101.16(12)
Si(1)−N(6)−Si(2)	88.37(11)	N(6)−Si(1)−N(7)	91.66(12)
Si(1)−N(7)−Si(2)	88.22(11)	N(6)−Si(2)−N(7)	91.72(11)
N(7)−Al(2)−N(16)	102.90(11)	N(14)−Al(2)−N(15)	97.55(11)
N(3)−N(4)−N(5)	176.0(3)	N(8)−N(9)−N(10)	174.6(4)
N(11)−N(12)−N(13)	174.6(4)	N(16)−N(17)−N(18)	176.7(3)

1.734(2), 1.737(2), 1.748(2), 1.749(2) Å; N−Si−N: 91.66(12), 91.72(11)°; Si−N−Si: 88.37(11), 88.22(11)°; $\Delta = 0.0101$ Å). A notable feature is that the two *t*Bu groups bound to Si atoms are arranged on one side of the Si_2N_2 ring, whereas the N_3 groups are located on the opposite side of the ring. This structural character is hardly observed among the known Si_2N_2 ring compounds[13] and gives rise to the two LAl moieties bonded to the respective N atom also in a position *syn* to the Si_2N_2 ring due to the steric effect caused by the two *t*Bu groups, whereas the two N_3 groups at the respective Al center are arranged in *trans* position. The Al−N bond lengths range from 1.808(2) to 1.921(3) Å (Al−N_β-diketiminato = 1.902(3)−1.921(3) Å; Al−N_{N3} = 1.839(3)−1.851(3) Å; Al−N_{Si2N2} = 1.808(2)−1.812(2) Å). The Al−N_β-diketiminato bond lengths are close to those in **1** and **2** (1.895(1)−1.907(1) Å), and the Al−N_{N3} bond distances are a little shorter than those terminal ones in R_2AlN_3 (R = 2-(Me_2NCH_2)-C_6H_4, 1.864(6) Å; $(CH_2)_3NMe_2$, 1.897(2) Å)[14] and $Me_2Al(N_3)NH_2t$Bu (1.901(1) Å).[15] The Al−N_{Si2N2} bond lengths compare well with those in Cp*{$(Me_3Si)_2N$}AlN(*μ*-AlCp*)(*μ*-Al{$N(SiMe_3)_2$})$NAlCp*_2$ (1.781−1.819 Å).[3] The N−N bond lengths (1.139(4)−1.227(4) Å) and N−N−N angles (174.6(4)−176.7(3)°) of the N_3 groups are consistent with those in the literature.[14,15] The IR spectrum confirms the characteristic frequencies of the terminal N_3 groups (2113, 2076 cm^{-1}).

Solvent-Free Reaction of $LAlH_2$ with $ArNH_2$. Among the syntheses of heavier group 13 imido compounds, the reaction of monovalent group 13 metal species with organic azides can be considered as a direct synthetic route under the elimination of N_2,[16] although the high reactivity of such monomeric species can cause a variety of products. One of the classic routes,[17] the reaction of group 13 metal hydride and/or alkyl ($R'MR_2$, R = organic group or H) with primary amine $R''NH_2$, has been widely studied. Work in this field has been extensively reported by Nöth,[18] Power,[19] Roesky,[20] and Schulz.[21] In these reactions, the $[R'MR(NHR'')]_m$ is thought to be an intermediate in the formation of the corresponding metal imide $[R'MNR'']_n$ ($m, n \geq 2$) with regard to the stepwise elimination of H_2 or alkane, whereas the orthometalation in some cases is observed resulting in C−H activated derivatives.[19a,b] However, $[R'MR(NHR'')]_m$ is thermally unstable. Studies on these systems have shown that its stability is strongly influenced by the steric bulk of R′ and R″ at both M and N atoms, especially in the case of R = H.[17] $[R_2Al(NHt\mathrm{Bu})]_2$ (R = H or D) is stable only at room temperature.[18] [Mes*AlH(*μ*-NHR*)]$_2$ containing bulky substituents R* = CH_2Mes, $SiPh_3$, Mes = 2,4,6-$Me_3C_6H_2$, and Mes* = 2,4,6-$t\mathrm{Bu}_3C_6H_2$ decomposes in the range 125 to 200 °C to the corresponding aluminum imides.[19d] Recent studies on the reaction of $Me_3N·AlH_3$ and $ArNH_2$ indicate that the $Me_3N·AlH(NHAr)_2$ intermediate gives under reflux in pentane [ArHNAl(H)-*μ*-NHAr]$_2$ and $Me_3N·Al(NHAr)_3$, respectively.[21] Nonetheless, there are only a few of such compounds known, and they are only sparingly studied by X-ray structural analysis.[22] Herein we show the preparation and structural characterization of the monomeric compound LAlH(NHAr) (**4**) derived from a solvent-free reaction of $LAlH_2$ and $ArNH_2$.

A mixture of $LAlH_2$ and 1 equiv of $ArNH_2$ in the absence of solvent was treated at elevated temperature (150 °C) until H_2 evolution ceased. This reaction smoothly afforded a monomeric aluminum hydride amide, LAlH(NHAr) (**4**), as a light yellow crystalline solid in almost quantitative yield (>95%) (eq 1).



(1)

4

Ar = 2,6-*i*$Pr_2C_6H_3$

Compound **4** is soluble in aromatic solvents, but sparingly soluble in such hydrocarbons as *n*-pentane and *n*-hexane. It melts at 134 °C. The most intense peak in the EI-MS of **4** appeared at *m/z* 578 [$M^+ - i$Pr], and the signal at *m/z* 621 (22%) was assigned to the molecular ion [M^+]. In the ^1H NMR spectrum, a singlet at 3.01 ppm corresponds to the N-H proton resonance

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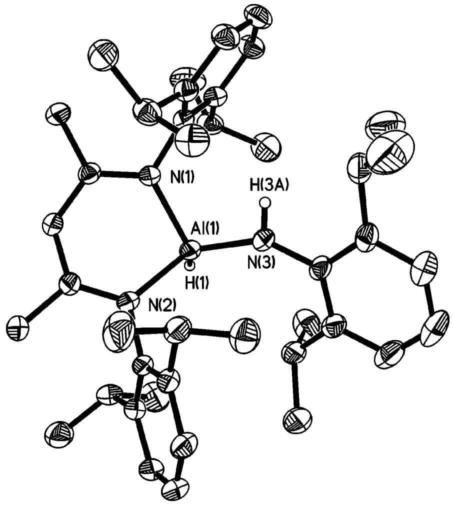

Figure 4. Molecular structure of **4**. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms of the L ligand and Ar group are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 4·PhMe

Al(1)−N(1)	1.905(2)	Al(1)−N(2)	1.922(2)
Al(1)−N(3)	1.817(2)	Al(1)−H(1)	1.482
N(1)−Al(1)−N(2)	95.57(8)	N(3)−Al(1)−H(1)	119.1

and one broad resonance centered at 5.50 ppm to the Al-H proton, characteristic for amidoaluminum hydrides.[22a] The IR spectrum clearly shows the respective N-H (3358 cm^{-1}) and Al-H (1821 cm^{-1}) absorption bands.

The structural analysis revealed **4** as monomeric with the coordination of the aluminum center completed by the chelating β-diketiminato ligand, one NHAr group, and one H atom in a distorted tetrahedral geometry. The molecular structure of **4** is shown in Figure 4. Selected bond lengths and angles are listed in Table 4. The Al−H bond length (1.482 Å) is located in the range 1.37−1.75 Å observed for terminal aluminum hydrides.[21−23] The Al−N$_{\mathrm{NHAr}}$ bond length (1.817(2) Å) is shorter than those of Al−N$_{\beta}$-diketiminato bonds (1.905(2), 1.922(2) Å). The Al−H and N−H bonds are nearly arranged in *trans* position to the Al−N$_{\mathrm{NHAr}}$ bond.

Compound **4** contains the Al-H and N-H functionalities, which are commonly thought to be highly reactive. Therefore, **4** was further treated at higher temperatures (150−290 °C) for 5 h; however, no H_2 gas evolution was observed. The melting point and spectroscopic (IR, ^{1}H NMR) measurements indicated that, during the heating, compound **4** did not change its composition.

Conclusion

In summary, LAl reacts with bulky azide RN_3 to yield the five-membered ring compound LAl[(NR)$_2$N$_2$] (R = $C_{10}H_{15}$ (**1**), Ph$_3$Si (**2**)), while with *t*BuSi(N$_3$)$_3$ LAl(N$_3$)N-[μ-Si(N$_3$)(*t*Bu)]$_2$NAl(N$_3$)L (**3**) is formed. The former appears to proceed by a [2 + 3] cycloaddition of a reactive LAl=NR species and an azide molecule, although the L and R substituents are rather bulky. The latter may occur with a further rearrangement of LAl=NSi(*t*Bu)(N$_3$)$_2$ (**A**) to LAl(N$_3$)N=Si(*t*Bu)(N$_3$) (**B**) and finally is completed by [2 + 2] cycloaddition. The steric demand of the β-diketiminato ligand L at Al and the R group at N hinders the oligomerization of the Al=N intermediates; however, the Al=N system is reactive enough to allow the cyclic addition, the N$_3$ migration, or the C−H activation. In some cases this is influenced by the reaction temperature.[6] In contrast, the reaction of LAlH$_2$ with ArNH$_2$ yields only the monomeric aluminum hydride amide LAlH(NHAr) (**4**). Further condensation of **4** at elevated temperatures was not observed.

Acknowledgment. We are grateful for financial support of the Göttinger Akademie der Wissenschaften.

Supporting Information Available: CIF files for compounds **1**·Et$_2$O, **2**·PhMe, **3**·PhMe, and **4**·PhMe are available free of charge via the Internet at http://pubs.acs.org.

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