Syntheses and Structures of Intramolecularly Coordinated Azidoalanes

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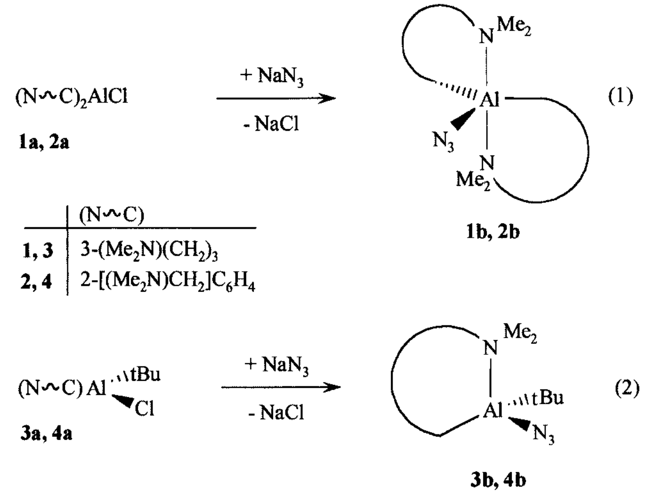
The four intramolecularly coordinated azidoalanes $R_2Al(N_3)$ and $RAl\textit{t}Bu(N_3)$ ($R = (CH_2)_3$-NMe_2 (**1b**, **3b**), 2-($Me_2NCH_2)C_6H_4$ (**2b**, **4b**)) were synthesized by reaction of the corresponding aluminum chlorides (**1a**−**4a**) with an excess of dry sodium azide in refluxing toluene or toluene/THF. The structures of the products were deduced from ^1H, ^{13}C, and ^{27}Al NMR spectra and were confirmed by X-ray structural determinations of **1a**, **1b**, and **2b**. The compounds of type **1** and **2** contain pentacoordinated Al atoms, whereas the alanes of type **3** and **4** show tetracoordination of the central Al atoms.

Introduction

The group 13 nitrides AlN, GaN, and InN are candidates for advanced microelectronic and optoelectronic devices such as light-emitting diodes and lasers and high-temperature and high-power devices, as well as chemical sensors, acoustic surface wave conductors, and isolating passivation layers.[1,2] Recently, group 13 metal azides containing a 3-(dimethylamino)propyl ligand, capable of intramolecular donor stabilization, were shown to be suitable single-source precursors for the deposition of AlN,[3] GaN,[4] and InN[5] at relatively low temperatures. To date, only a few monoazido alanes have been structurally characterized, namely $[R_2Al(N_3)]_3$ (R = Me, Et)[6] and $[EtClAl(N_3)]_3$[7] by vibrational spectroscopy and $[\{(SiMe_3)_2CH\}_2Al(N_3)]_3$[8] by single-crystal X-ray diffraction.[9] The compound with the bulky “disyl” ligand trimerizes via γ-nitrogen atoms and not like the others via α-nitrogen atoms. Recently, we reported the synthesis and characterization of $Me_2Al(N_3)NH_2\textit{t}Bu$ and $[Me_2N(CH_2)_3]_2Al(N_3)$ (**1b**).[3] These two Lewis acid/base adducts are the first known monomeric azidoalanes. We describe here the continuation of our investigations on intramolecularly Lewis-base-stabilized aluminum azides using the well-known and related ligands 3-(dimethylamino)propyl and 2-[(dimethylamino)methyl]phenyl.

Scheme 1



Results and Discussion

Syntheses. The new azidoalanes **1b**−**4b** (Scheme 1) were synthesized by reaction of the aluminum chlorides **1a**−**4a** with an excess of dry sodium azide in refluxing toluene or toluene/THF for several days. The gallium

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(9) $AlCl_2(N_3)$ (structure unknown): Wiberg, N.; Joo, W.-Ch.; Schmid, K. H. *Z. Anorg. Allg. Chem.* **1972**, *394*, 197.

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azides $[Me_2N(CH_2)_3]Ga(N_3)_2$ and $[Me_2N(CH_2)_3]GaR(N_3)$ (R = Me, *t*Bu)[4a] had been obtained earlier by a similar method. The syntheses of the aluminum compounds described here required higher temperatures and longer reaction times. The progress of the substitution reactions was followed by ^{27}Al NMR spectroscopy, the signals of the starting chlorides and the respective azides being well-separated (see discussion below). The synthesis of compound **1b** was reported in an earlier communication.[3] This azide was an unexpected product in the attempted preparation of $[Me_2N(CH_2)_3]Al(N_3)_2$ by reaction of the dichloride[10] $[Me_2N(CH_2)_3]AlCl_2$ and sodium azide. Instead of the expected diazido compound, the monoazide **1b** was isolated in about 50% yield (eq 3). Treatment of $[Me_2N(CH_2)_3]AlCl_2$ with

$$[Me_2N(CH_2)_3]AlCl_2 \xrightarrow{+\,NaN_3} \mathbf{1b} + Na[Al(N_3)_4] \quad (3)$$

sodium azide in toluene gave only traces of **1b**. The presence of THF was necessary to achieve quantitative formation of **1b** according to eq 3. However, in contrast to the case of gallium, the aluminum diazido compound could not be isolated from the reaction mixture. The azide **1b**, a volatile, low-melting solid, is a potential single-source precursor for the deposition of AlN films,[3] and a straightforward synthesis of **1b** was needed. Chloride **1a**, prepared by the reaction of 2 equiv of $Li(CH_2)_3NMe_2$ with aluminum trichloride in 84% yield, gave **1b** on reaction with NaN_3. The analogous bromide $[Me_2N(CH_2)_3]_2AlBr$ (**1c**), which is accessible by a similar route, also was tested as a starting material. In principle it makes no difference if the chloride or the bromide is used (eq 1, Scheme 1); the reaction times needed rather are a function of the solvent used. With a 2:1 toluene/THF mixture the substitution is complete within 15 h, whereas in pure toluene more than 60 h is required, probably due to the higher solubility of NaN_3 in the presence of THF.

The starting compounds required for the syntheses of azides equipped with the "one-arm phenyl" ligand (**2b** and **4b**) were published recently.[11] Applying the method used for the chloride **4a**[11] and the gallane $[Me_2N(CH_2)_3]Ga$*t*$Bu(Cl)$,[4a] we prepared **3a** by reaction of $[Me_2N(CH_2)_3]AlCl_2$[10] and 1 molar equiv of *t*-BuLi.

The four azides **1b**−**4b** are not pyrophoric, are not explosive, and sublime or distill in the range of 60−140 °C under high vacuum.

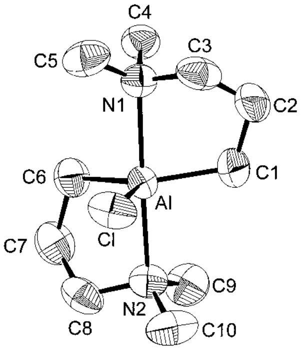

Figure 1. Molecular structure of **1a** (thermal ellipsoids at 50% probability).

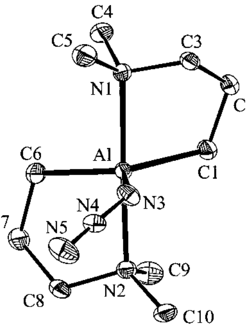

Figure 2. Molecular structure of **1b** (Platon;[22] thermal ellipsoids at 30% probability).

Table 1. Crystal Data, Data Collection Parameters, and Convergence Results for 1a, 1b, and 2b

	1a	1b[a]	2b
formula	$C_{10}H_{24}AlClN_2$	$C_{10}H_{24}AlN_5$	$C_{18}H_{24}AlN_5$
fw	234.70	241.32	337.41
cryst syst	orthorhombic	monoclinic	orthorhombic
space group (No.)	*Pcab* (61)	$P2_1/n$ (14)	$P2_12_12_1$ (19)
a, Å	11.024(6)	7.234(1)	9.048(2)
b, Å	15.062(8)	11.236(1)	10.007(1)
c, Å	16.557(8)	17.525(3)	20.844(3)
β, deg	90	100.409(12)	90
U, Å^3	2749(3)	1401.0(3)	1887.2(9)
Z	8	4	4
d_{calc}, g cm^{-3}	1.134	1.144	1.187
μ, cm^{-1}	3.13	1.3	9.77
θ_{max}, deg	26.0	25.6	71.9
cryst dimens, mm^3	0.5 × 0.5 × 0.5	0.20 × 0.20 × 0.51	0.28 × 0.48 × 0.60
λ, Å	0.710 73	0.710 73	1.541 84
no. of rflns	2699	12795	9234
no. of indep rflns	2699	2466	3733
abs cor	empirical		empirical
transmissn (min/max)	0.836/0.768		0.999/0.872
no. of indep obs rflns	1994 ($I > 2.0\sigma(I)$)	2051 ($I > 2.0\sigma(I)$)	1893 ($I > 1.0\sigma(I)$)
no. of vars	224	241	217
R	0.037	0.051	0.055
R_w ($w^{-1} = \sigma^2(F_o)$)			0.045
wR2	0.086	0.092	
GOF	1.040	1.024	0.888
resid electron dens, e Å^{-3}	0.211	0.309	0.331

[a] Data taken from ref 3.

X-ray Structural Analyses. Molecular Structures of 1a and 1b. The chloroalane **1a** crystallizes in the orthorhombic space group *Pcab*, and the azidoalane **1b**[3] crystallizes in the monoclinic space group $P2_1/n$ with no unusual intramolecular contacts in each case (Figures 1 and 2 and Tables 1 and 2). The coordination geometries around the Al centers reflect distorted trigonal bipyramids with the two amine N-donor atoms at the apical positions and the alkyl carbon atoms of the propyl groups as well as Cl and N3 (of the azide), respectively, in the equatorial plane. The N1−Al1−N2 axes are very close to linearity. The angles C1−Al−C6 for both compounds (**1a** and **1b**) are 136°, larger than the ideal value of 120° as a result of the steric requirements of the chelating aminopropyl ligands. The Al−Cl bond distance of 2.224(1) Å (**1a**) is comparable to the mean Al−N distance of 2.18 Å in $(HMe_2N)_2$-

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[11] Müller, J.; Englert, U. *Chem. Ber.* **1995**, *128*, 493.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a, 1b, and 2b

		Compound **1a**			
Al−N1	2.210(2)	Al−N2	2.189(2)	Al−Cl	2.224(1)
Al−C1	1.981(3)	C1−C2	1.529(3)	C2−C3	1.518(4)
C3−N1	1.486(3)	Al−C6	1.989(2)	C6−C7	1.533(3)
C7−C8	1.515(4)	C8−N2	1.487(3)		
N1−Al−N2	176.2(1)	N1−Al−Cl	91.3(1)	N1−Al−C1	83.6(1)
Al−N1−C3	101.1(2)	N2−Al−Cl	92.5(1)	N2−Al−C6	84.0(1)
Al−N2−C8	102.0(2)	Cl−Al−C1	111.1(1)	Cl−Al−C6	112.9(1)
C1−Al−C6	136.0(2)				
		Compound **1b**			
Al−N1	2.167(2)	Al−N2	2.199(2)	Al−N3	1.897(2)
N3−N4	1.191(2)	N4−N5	1.145(2)	Al−C1	1.982(2)
C1−C2	1.534(3)	C2−C3	1.514(2)	C3−N1	1.483(2)
Al−C6	1.991(2)	C6−C7	1.536(3)	C7−C8	1.518(3)
C8−N2	1.483(3)				
N1−Al−N2	178.3(1)	N1−Al−N3	89.6(1)	N3−N4−N5	176.9(2)
N1−Al−C1	84.0(1)	Al−N1−C3	101.7(1)	N2−Al−N3	91.5(1)
N2−Al−C6	84.1(1)	Al−N2−C8	102.7(1)	N3−Al−C1	111.7(1)
N3−Al−C6	112.4(1)	C1−Al−C6	135.9(1)		
		Compound **2b**			
Al−N1	2.168(5)	Al−N2	2.209(4)	Al−N3	1.864(6)
N3−N4	1.161(6)	N4−N5	1.153(7)	Al−C10	1.985(5)
C10−C11	1.429(7)	C11−C16	1.510(8)	C16−N1	1.469(7)
Al−C20	1.988(6)	C20−C21	1.397(7)	C21−C26	1.507(7)
C26−N2	1.512(7)				
N1−Al−N2	176.9(2)	N1−Al−N3	85.8(2)	N3−N4−N5	175.5(7)
N1−Al−C10	82.0(2)	Al−N1−C16	101.2(3)	N2−Al−N3	91.3(2)
N2−Al−C20	80.1(2)	Al−N2−C26	100.2(3)	N3−Al−C10	113.9(2)
N3−Al−C20	120.4(2)	C10−Al−C20	125.6(2)		

$AlCl_3$.[12] The azido unit of **1b** shows a characteristic bending (Al−N3−N4 = 133.1(1)°) and is almost linear (N3−N4−N5 = 176.9(2)°). The Al−N3 bond length of 1.897(2) Å compares well with the values of 1.901(1) and 1.864(6) Å for $Me_2(N_3)Al(NH_2tBu)$[3] and **2b**, respectively, which represent the only known structurally characterized monoazido alanes to date. The $Al-N_{azide}$ bonds in $(N_3)_3Al(py)_3$ of 1.952(3), 1.953(2), and 2.007(3) Å are significantly longer.[3] The donor−acceptor bonds of **1a** (2.189(2) and 2.210(2) Å) are insignificantly longer than those of the azide **1b** (2.167(2) and 2.199(2) Å). Compounds **1a** and **1b** both exhibit two fused five-membered metallacyclic rings, each in an expected envelope conformation. The "flap" atoms are C3 and C8 for both alanes. Two envelope conformations could lead to several isomers, depending on the "bending directions" of the carbon tips. The one adopted by **1a** and **1b** could be called an *exo*/*exo* isomer, i.e., C3 and C8 are both bent toward the chloride or the azide, respectively. A similar conformation is adopted by the related chlorogallane $[Me_2N(CH_2)_3]_2GaCl$.[13] The related azidoindane $[Me_2N(CH_2)_3]_2In(N_3)$, however, exhibits an *exo*/*endo* orientation. However, in contrast to **1a** and **1b**, this indium compound is associated in the solid state via linear bridging azide units, similar to the related halides $[Me_2N(CH_2)_3]_2InX$ (X = Br, I).[13]

Molecular Structure of 2b. The azidoalane **2b** crystallizes in the space group $P2_12_12_1$ with no unusual intermolecular contacts (Figure 3). The metal center is distorted trigonal bipyramidal coordinated. Two carbon atoms (C10, C20) and the azide nitrogen atom N3 form the equatorial plane, whereas the two amino nitrogen atoms N1 and N2 are in apical positions. The N1−Al−N2 axis is close to linearity (176.9(2)°), and the three angles in the equatorial plane sum up to 360°. The deviation from an ideal trigonal-bipyramidal geometry may be described by the tilt angle of 101° between the least-squares plane N1, Al, N2, and N3[14] and the equatorial plane. The linear N_3 group (N3−N4−N5 = 175.5(7)°) is bent in a similar way (Al−N3−N4 = 139.5(5)°) as that of **1b** discussed earlier. The two donor−acceptor bond lengths of 2.168(5) Å (Al−N1) and 2.209(4) Å (Al−N2) match well those of the chloride **1a** and of the azide **1b**. The closely related alane $[2-(Me_2NCH_2)C_6H_4]_2AlMe$[11] exhibits with 2.245(2) and 2.290(2) Å significantly longer Al−N bonds, but it is known that Al−N bond lengths are very sensitive to substituent effects and, therefore, cover quite a large range.[15]

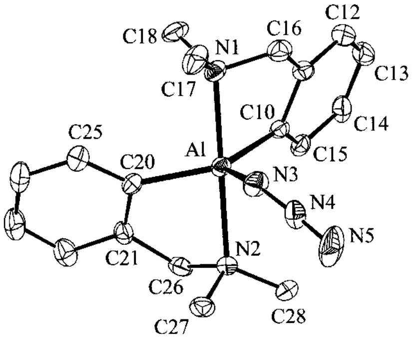

Figure 3. Molecular structure of **2b** (Platon;[22] thermal ellipsoids at 30% probability).

Compound **2b** contains two fused five-membered rings, each in an envelope conformation. Compared

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[12] Ahmed, A.; Schwarz, W.; Weidlein, J.; Hess, H. *Z. Anorg. Allg. Chem.* **1977**, *434*, 207.

[13] Schumann, H.; Seuss, T. D.; Just, O.; Weimann, R.; Hemling, H.; Gorlitz, F. H. *J. Organomet. Chem.* **1994**, *479*, 171.

[14] Orthogonal distances from the least-squares plane (Å): N1, 0.008(4); Al, 0.015(1); N2, 0.007(4); N4, 0.000(4).

[15] Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: Weinheim, Germany, 1993; Chapter 1.

with the alanes of type **1**, however, the "flap" atoms of **2b** are the nitrogen ring atoms; i.e., N1 and N2 are displaced 0.77 and 0.84 Å outside their respective planes (Al−C10−C11−C16 and Al−C20−C21−C26). The difference between the "one-arm phenyl" ligand and its aminopropyl counterpart obviously is a consequence of the rigidity of the aryl systems incorporated into the chelate. As in the case of **1a** and **1b**, the envelope conformations give rise to several isomers, depending on the "bending directions" of the nitrogen tips. The one adopted by **2b** could be called an *endo*/*exo* isomer, i.e., N1 is bent toward the gap between the two aromatic rings (*endo*), whereas N2 is bent in the opposite direction (*exo*). A related *endo*/*exo* isomer was revealed by single-crystal analysis of $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlMe$.[11]

Spectroscopy. The pentacoordination of aluminum in **1** and **2** is revealed by NMR spectroscopy. At ambient temperature, the azide **1b** shows C_2 symmetry with respect to the NMR time scale (500 MHz instrument); i.e., three different CH_2 groups and two different NMe groups. This gives rise to five ^{13}C and eight ^{1}H resonances. In the ^{1}H NMR spectrum the differences between two multiplets of one CH_2 group increase from $AlCH_2-$ ($\Delta = 0.10$ ppm) to $-CH_2-$ ($\Delta = 0.35$ ppm) and $-H_2CN$ ($\Delta = 0.71$ ppm). The starting compounds **1a** and **1c** exhibit similar NMR patterns. Temperature-dependent measurements using a 200 MHz NMR instrument were undertaken for **1a** and **1b**. In the case of the two proton resonances for the NMe units the coalescence temperature is about 300 K. Above 330 K a simple spectrum is obtained, i.e., on the NMR time scale the symmetry of the molecule is C_{2v}, indicating a fast equilibrium between the possible isomers. Neither the presence of a coordinating solvent (THF-d_8) nor the variation of the concentration of the solutions interferes with this process; the temperature of coalescence is unaffected. These results, together with the unchanged chemical shifts of the ^{27}Al atoms (see below), are strong evidence for the persistence of 5-fold-coordinated Al species in solution.

In addition to the expected resonances of the aromatic ring (ABCD spin system), the azide **2b** shows four broad singlets in the ^{1}H NMR spectrum; two for the diastereotopic protons of CH_2 and two for the NMe groups. Accordingly, these groups give only one sharp ^{13}C resonance (CH_2) and two broad ones (NMe) in the ^{13}C NMR spectrum. At higher temperature (70 °C; toluene-d_8, 500 MHz instrument) the CH_2 and the NMe groups each give only one singlet in the ^{1}H NMR spectrum, while at −80 °C these groups result in four doublets (CH_2) and four singlets (NMe). The related compounds **2a** and $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlMe$ were investigated in detail by variable-temperature ^{1}H NMR spectroscopy.[11] As deduced from these experiments, the equilibrium geometry corresponds to an *endo*/*exo* configuration (C_1 point group), in accordance with the structure of the methylalane in the solid state. The dynamic behavior in solution was explained by assuming two processes. First, an envelope inversion converts an *endo*/*exo* isomer into an *exo*/*endo* species, which results in a C_2-symmetrical molecule. Second, there is an interchange of the two chelating ligands, i.e., an interconversion of the two C_2-symmetrical enantiomers, which results in a C_{2v}-symmetrical molecule on time average. The spectra of **2b** fully resemble those of the chloride **2a**. Therefore, we assume the same dynamic processes in solution.

Table 3. ^{27}Al NMR Shifts (ppm)

	a	b
1	118	109
2	96[a]	87
3	158	145
4	145	134

[a] Taken from ref 11.

The asymmetrically substituted alanes **3** and **4** (C_1 point group) show the expected NMR signals; for example, **3a** and **3b** give six multiplets for the three CH_2 groups, with separation trends similar to those found for the alanes of type **1**, plus two singlets for the NMe_2 and one for the *t*Bu group in the ^{1}H NMR spectra. A respective pattern can be seen in the ^{13}C NMR spectra.

^{27}Al NMR spectroscopy often is used to deduce the coordination number of aluminum. Besides the number of ligands, the electronic nature of the substituents governs the ^{27}Al NMR chemical shifts.[16] The δ (^{27}Al) values for **1**−**4** are compiled in Table 3. Inspection of the data in Table 3 shows that the compounds with pentacoordination resonate in the range of 87−118 ppm, whereas the signals for the substances **3** and **4**, with only tetracoordinated centers, are found at lower field strength (134−158 ppm). The resonances of the chlorides **1a** and **2a** are deshielded by 9 ppm compared with their azide counterparts **1b** and **2b**, respectively. In addition, the "exchange" of two aminopropyl ligands in **1a** and **1b** by two "one-arm phenyl" substituents (**2a** and **2b**) is accompanied by an upfield shift of 22 ppm. Similar effects can be seen with the compounds **3a**, **3b**, **4a**, and **4b**. The chloride/azide substitution results in a difference of 13 ppm for the **3a**/**3b** couple and 11 ppm for the **4a**/**4b** couple, whereas the "propyl/phenyl" exchange yields 13 ppm for the chlorides **3a**/**4a** and 11 ppm for the azides **3b**/**4b**. The ^{27}Al shift is affected neither by the change of the solvent, i.e., THF instead of toluene-d_8, nor by a variation of the concentration of the substance, as was found for the compounds **1a** and **1b**.

Experimental Section

All procedures were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures, distilled, and stored under nitrogen and molecular sieves (4 Å). NaN_3 was dried at 110 °C under high vacuum for 12 h. The reagents $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlCl$ (**2a**),[11] $[2\text{-}(Me_2NCH_2)C_6H_4]Al\textit{t}BuCl$ (**4a**),[11] $Li(CH_2)_3NMe_2$,[17] and $[Me_2N(CH_2)_3]AlCl_2$[10b] were prepared according to the literature methods.

NMR spectra were obtained on a Varian Unity 500 at ambient temperature (^{1}H, 499.843 MHz; ^{27}Al, 130.195 MHz; ^{13}C, 125.639 MHz) and calibrated against residual protons of the deuterated solvents. ^{1}H and ^{13}C chemical shifts are reported relative to TMS and ^{27}Al values relative to the external standard $[Al(acac)_3]$ in C_6D_6. As a result of the electric quadrupole moment of the ^{27}Al nucleus, not all of the carbon atoms bound to aluminum could be detected in ^{13}C NMR experiments. The assignments of the ^{1}H and ^{13}C NMR signals were made either with the aid of $^{1}H/^{13}C$-HMQC experiments

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(**1c** and **3b**) or according to the literature.[11] The IR spectra were recorded on a Perkin-Elmer FTIR 1720x in toluene. Mass spectra were obtained on a Finnigan MAT 95 (70 eV). Elemental analyses (C, H, N) were measured on either a Carlo-Erba elemental analyzer (Model 1106) or an Elementar Vario EL. Melting points were obtained in sealed glass capillaries under N_2 and are uncorrected.

Chlorobis[3-(dimethylamino)propyl]aluminum (1a). A suspension, prepared with $Li(CH_2)_3NMe_2$[17] (9.31 g, 100.0 mmol) in 200 mL of Et_2O, was added dropwise to a solution of $AlCl_3$ (6.66 g, 49.9 mmol) in 200 mL of Et_2O at −78 °C. The dry-ice bath was removed, and the reaction mixture was stirred overnight. The solution was filtered, and after removal of volatiles at ambient temperature, **1a** crystallized as large, colorless needles (9.81 g, 84%, mp 54 °C). Anal. Calcd for $C_{10}H_{24}AlClN_2$ (234.75): C, 51.17; H, 10.31; N, 11.93; Al, 11.49. Found: C, 49.21; H, 9.80; N, 11.53; Al, 11.86. HRMS: *m/z* calcd for $C_{10}H_{24}Al^{35}ClN_2$ 234.1444, found 234,1476. MS: *m/z* 234 (M^+, 4), 199 ($M^+ - Cl$, 6), 148 ($M^+ - C_5H_{12}N$, 72). ^1H NMR (toluene-d_8, 293 K): δ 0.13 (m, 4H, $AlCH_2$), 1.46 (m, 2H, $-CHH-$), 1.72 (m, 4H, NC*H*H, $-CHH-$), 1.95 (s, broad, 12H, NCH_3), 2.71 (m, 2H, NCH*H*). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 1.69 (broad, $AlCH_2$), 20.85 ($AlCH_2CH_2$), 44.98 (broad, NCH_3), 60.92 (NCH_2). ^{27}Al NMR (toluene-d_8): δ 118 ($h_{1/2} = 1750$ Hz).

Azidobis[3-(dimethylamino)propyl]aluminum (1b). Method A. A solution of **1a** (5.00 g, 21.3 mmol) in 100 mL of toluene and 50 mL of THF were added to NaN_3 (2.76 g, 42.5 mmol), and the mixture was heated at reflux for 15 h. After removal of the solvent under vacuum, the residue was purified by sublimation (100 °C, 10^{-4} Torr) with a −15 °C cold finger. **1b** was obtained as small, colorless crystals (4.72 g, 92%). **Method B.** A mixture of NaN_3 (3.16 g, 48.6 mmol) and **1c** (1.36 g, 4.9 mmol) in 40 mL of toluene was heated at reflux for 64 h. The reaction mixture was filtered, and the solid was washed with two 10 mL portions of toluene. After removal of the solvent under high vacuum, trap-to-trap distillation (60−70 °C, 10^{-3} Torr) gave pure **1b** as a colorless liquid (0.94 g, 80%), which slowly solidified on storage at −15 °C. Anal. Calcd for $C_{10}H_{24}AlN_5$ (241.31): C, 49.77; H, 10.03; N, 29.02; Al, 11.18. Found: C, 48.19; H, 10.08; N, 29.26; Al, 11.05. HRMS: *m/z* calcd for $C_{10}H_{24}AlN_5$ 241.1847, found 241,1848. MS: *m/z* 241 (M^+, 7), 199 ($M^+ - N_3$, 32), 155 ($M^+ - C_5H_{12}N$, 100), 113 ($C_5H_{12}AlN^+$, 9). ^1H NMR (C_6D_6): δ −0.15 (m, 2H, AlC*H*H), −0.05 (m, 2H, AlCH*H*), 1.38 (m, 2H, $AlCH_2C$*H*H), 1.60 (s, broad, 6H, N(C*H*$_3$)(CH_3)), 1.67 (m, 2H, NC*H*H), 1.73 (m, 2H, $AlCH_2CH$*H*), 2.05 (s, broad, 6H, N(CH_3)(C*H*$_3$)), 2.38 (m, 2H, NCH*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.25 (broad, $AlCH_2$), 20.99 ($AlCH_2CH_2$), 43.46 (broad, N(CH_3)(CH_3)), 45.51 (broad, N(CH_3)(CH_3)), 61.73 (NCH_2). ^{27}Al NMR (C_6D_6): δ 109 ($h_{1/2} = 1550$ Hz). IR (toluene; $\nu_{as}(N_3)$, cm^{-1}): 2113.

Bromobis[3-(dimethylamino)propyl]aluminum (1c). $Li(CH_2)_3NMe_2$ (2.48 g, 26.6 mmol) was added to a solution of $AlBr_3$ (3.55 g, 13.3 mmol) in 50 mL of toluene at −78 °C. The dry-ice bath was removed, and the reaction mixture was stirred overnight and subsequently filtered. The solid was washed with two 10 mL portions of toluene. After removal of volatiles at ambient temperature, sublimation (60 °C, 10^{-3} Torr) gave pure **1c** (3.02 g, 81%, mp 82−84 °C). Anal. Calcd for $C_{10}H_{24}AlBrN_2$ (279.20): C, 43.02; H, 8.67; N, 10.03. Found: C, 42.95; H, 8.72; N, 10.60. HRMS: *m/z* calcd for $C_{10}H_{24}AlBrN_2$ 278.0938, found 278.0938. MS: *m/z* 278 (M^+, 5), 263 ($M^+ - CH_3$, 3), 235 ($M^+ - C_3H_7$, 31), 199 ($M^+ - Br$, 25), 192 ($M^+ - C_5H_{12}N$, 100), 87 ($C_5H_{13}N^+$, 16), 86 ($C_5H_{12}N^+$, 17). ^1H NMR (C_6D_6): δ 0.09 (m, 2H, AlC*H*H), 0.20 (m, 2H, AlCH*H*), 1.45 (m, 2H, $AlCH_2C$*H*H), 1.65 (m, 2H, NC*H*H), 1.77 (m, 2H, $AlCH_2CH$*H*), 1.95 (s, broad, 12H, NCH_3), 2.88 (m, 2H, NCH*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.89 (broad, $AlCH_2$), 20.56 ($AlCH_2CH_2$), 44.99 (broad, NCH_3), 60.47 (NCH_2). ^{27}Al NMR (C_6D_6): δ 118 ($h_{1/2} = 1750$ Hz).

Azidobis{2-[(dimethylamino)methyl]phenyl}aluminum (2b). A mixture of NaN_3 (8.47 g, 130.3 mmol) and **2a** (4.22 g, 12.8 mmol) in 120 mL of toluene was heated at reflux for 140 h. The reaction mixture was filtered, and the solid was washed with two 10 mL portions of toluene. After removal of the solvent under high vacuum, sublimation (140 °C, 10^{-3} Torr) gave pure, crystalline **2b** (3.25 g, 76%). Single crystals suitable for X-ray diffraction were obtained from Et_2O at −20 °C (mp 147−149 °C). Anal. Calcd for $C_{18}H_{24}AlN_5$ (337.41): C, 64.08; H, 7.17; N, 20.76. Found: C, 64.14; H, 7.39; N, 21.50. MS: *m/z* 337 (M^+, 2), 322 ($M^+ - CH_3$, 13), 295 ($M^+ - N_3$, 27), 203 ($M^+ - C_9H_{12}N$, 21), 135 ($C_9H_{13}N^+$, 57), 134 ($C_9H_{12}N^+$, 47), 91 ($C_7H_7^+$, 69), 58 ($C_3H_8N^+$, 100). ^1H NMR (C_6D_6): δ 2.04 (s, broad, 6H, N(C*H*$_3$)(CH_3)), 2.23 (s, broad, 6H, N(CH_3)(C*H*$_3$)), 3.26 (s, broad, 2H, C*H*H), 3.65 (s, broad, 2H, CH*H*), 6.91 (m, 2H, 3-H), 7.20 (m, 4H, 4,5-H), 7.63 (m, 2H, 6-H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 45.18 (broad, NCH_3), 46.05 (broad, NCH_3), 66.63 (CH_2), 125.90 (CH), 126.05 (CH), 127.65 (CH), 138.31 (C-6), 147.07 (C-2), 147.4 (broad, C-*ipso*). ^{27}Al NMR (C_6D_6): δ 87 ($h_{1/2}$ = 4400 Hz). IR (toluene; $\nu_{as}(N_3)$, cm^{-1}): 2124.

***tert*-Butylchloro[3-(dimethylamino)propyl]aluminum (3a).** A 1.7 M solution of *t*-BuLi in pentane (13.0 mL, 22.1 mmol) was added to $[Me_2N(CH_2)_3]AlCl_2$ (4.06 g, 22.1 mmol) dissolved in 120 mL of Et_2O at −78 °C. The dry-ice bath was removed, and the solution was stirred overnight. Subsequently, volatiles were distilled under high vacuum at ambient temperature. The residue was extracted with hexane (60 mL). The solution was filtered, and the solid was washed with two 10 mL portions of hexane. After removal of the solvent from the extracts under high vacuum, trap-to-trap distillation (70−80 °C, 10^{-3} Torr) yielded **3a** (3.81 g, 81%) as a colorless liquid. Further purification was effected by short-path distillation (60 mm Vigreux, bp 42−45 °C, 10^{-3} Torr) (3.11 g, 66%). HRMS: *m/z* calcd for $C_9H_{21}AlClN$ 205.1178, found 205.1179. MS: *m/z* 205 (M^+, 1), 170 ($M^+ - Cl$, 5), 148 ($M^+ - C_4H_9$, 100), 58 ($C_3H_8N^+$, 92). ^1H NMR (C_6D_6): δ 0.21 (m, 2H, $AlCH_2$), 1.14 (s, 9H, $C(CH_3)_3$), 1.30 (m, 1H, $AlCH_2C$*H*H), 1.53 (m, 1H, NC*H*H), 1.70 (s, 3H, NCH_3), 1.73 (m, 1H, $AlCH_2CH$*H*), 1.99 (s, 3H, NCH_3), 2.18 (m, 1H, NCH*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.40 (broad, $AlCH_2$), 20.66 ($AlCH_2CH_2$), 29.63 ($C(CH_3)_3$), 43.43 (NCH_3), 46.43 (NCH_3), 63.70 (NCH_2). ^{27}Al NMR (C_6D_6): δ 158 ($h_{1/2} = 1700$ Hz).

Azido-*tert*-butyl[3-(dimethylamino)propyl]aluminum (3b). A mixture of NaN_3 (7.60 g, 116.9 mmol) and **3a** (2.41 g, 11.7 mmol) in 100 mL of toluene was heated at reflux for 88 h. The reaction mixture was filtered, and the solid was washed with two 10 mL portions of toluene. After removal of the solvent under high vacuum, trap-to-trap distillation (75−85 °C, 10^{-3} Torr) gave pure **3b** as a colorless liquid (1.39 g, 56%). Anal. Calcd for $C_9H_{21}AlN_4$ (212.28): C, 50.92; H, 9.97; N, 26.39. Found: C, 51.29; H, 10.55; N, 26.97. HRMS: *m/z* calcd for $C_9H_{21}AlN_4$ 212.1582, found 212.1583. MS: *m/z* 212 (M^+, 1), 170 ($M^+ - N_3$, 3), 155 ($M^+ - C_4H_9$, 100), 58 ($C_3H_8N^+$, 22). ^1H NMR (C_6D_6): δ 0.02 (m, 1H, AlC*H*H), 0.10 (m, 1H, AlCH*H*), 1.09 (s, 9H, $C(CH_3)_3$), 1.19 (m, 1H, $AlCH_2C$*H*H), 1.43 (m, 1H, NC*H*H), 1.53 (s, broad, 3H, NCH_3), 1.58 (m, 1H, $AlCH_2CH$*H*), 1.79 (s, broad, 3H, NCH_3), 1.93 (m, 1H, NCH*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −1.89 (broad, $AlCH_2$), 20.77 ($AlCH_2CH_2$), 29.49 ($C(CH_3)_3$), 43.14 (NCH_3), 45.50 (NCH_3), 63.92 (NCH_2). ^{27}Al NMR (C_6D_6): δ 145 ($h_{1/2} = 1850$ Hz). IR (toluene; $\nu_{as}(N_3)$, cm^{-1}): 2125.

Azido-*tert*-butyl{2-[(dimethylamino)methyl]phenyl}aluminum (4b). A mixture of NaN_3 (14.08 g, 216.6 mmol) and **4a** (5.75 g, 22.7 mmol) in 150 mL of toluene was heated at reflux for 90 h. The reaction mixture was filtered, and the solid was washed with two 10 mL portions of toluene. After removal of the solvent under high vacuum, trap-to-trap distillation (110−120 °C, 10^{-3} Torr) gave pure **4b** as a colorless liquid (4.99 g, 85%). The compound crystallized slowly at room temperature (mp 38−41 °C). Anal. Calcd for $C_{13}H_{21}AlN_4$ (260.32): C, 59.98; H, 8.13; N, 21.52. Found: C, 59.20; H, 8.40; N, 22.07. HRMS: *m/z* calcd for $M^+ - C_4H_9$ ($C_9H_{12}AlN_4$) 203.0877, found 203.0879. MS: *m/z* 203 ($M^+ - C_4H_9$, 33), 135

($C_9H_{13}N^+$, 98), 134 ($C_9H_{12}N^+$, 76), 91 ($C_7H_7^+$, 91), 58 ($C_3H_8N^+$, 100). ^{1}H NMR (C_6D_6): δ 1.15 (s, 9H, C(CH_3)$_3$), 1.57 (s, 3H, NCH_3), 1.84 (s, 3H, NCH_3), 2.73 (d, J = 14.0 Hz, 1H, CH_2), 3.28 (d, J = 14.0 Hz, 1H, CH_2), 6.74 (m, 1H, 3-H), 7.15 (m, 2H, 4,5-H), 7.70 (m, 1H, 6-H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 29.36 (C(CH_3)$_3$), 44.27 (NCH_3), 45.47 (NCH_3), 67.05 (CH_2), 124.36 (CH), 127.39 (CH), 128.57 (CH), 137.66 (C-6), 143.82 (C-2). ^{27}Al NMR (C_6D_6): δ 134 ($h_{1/2}$ = 2900 Hz). IR (toluene; $\nu_{as}(N_3)$, cm^{-1}): 2129.

X-ray Structure Determination of $C_{18}H_{24}AlN_5$ (1a). Geometry and intensity data were collected with Mo Kα radiation at −70 °C on a Siemens Stoe AED2 diffractometer equipped with a graphite monochromator (λ = 0.710 73 Å). A summary of crystal data, data collection parameters, and convergence results is compiled in Table 1. An empirical absorption correction (ψ scans) was applied.[18] The structure was solved by direct methods and refined with all data based on F^2.[19] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were located in a difference Fourier map and refined anisotropically.

X-ray Structure Determination of $C_{18}H_{24}AlN_5$ (1b). See reference 3.

X-ray Structure Determination of $C_{18}H_{24}AlN_5$ (2b). Geometry and intensity data were collected with Cu Kα radiation at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator (λ = 1.541 84 Å). A summary of crystal data, data collection parameters, and convergence results is compiled in Table 1. An empirical absorption correction (ψ scans) was applied.[18] The structure was solved by direct methods[20] and refined on structure factors with the local version of the SDP program suite.[21] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were not refined but included isotropically as riding on the corresponding carbon atoms (C−H = 0.98 Å, $U_{iso}(H) = 1.3[U_{eq}(C)]$).

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Supporting Information Available: Listings of the bond lengths and angles, atomic coordinates, and displacement parameters (7 pages). Ordering information is given on any current masthead page.

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