Syntheses and Structures of Intramolecularly **Coordinated Azidoalanes**

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The four intramolecularly coordinated azidoalanes $R_2Al(N_3)$ and $RAltBu(N_3)$ (R = (CH₂)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, ¹³C, and ²⁷Al 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,^{$\overline{4}$} and InN^{$\overline{5}$} at relatively low temperatures. To date, only a few monoazido alanes have been structurally characterized, namely [R₂Al- $(N_3)]_3$ (R = Me, Et)⁶ and [EtClAl(N₃)]₃⁷ by vibrational spectroscopy and [{(SiMe₃)₂CH}₂Al(N₃)]₃⁸ by singlecrystal X-ray diffraction.⁹ The compound with the bulky

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"disyl" ligand trimerizes via γ -nitrogen atoms and not like the others via α -nitrogen atoms. Recently, we reported the synthesis and characterization of Me₂Al- $(N_3)NH_2tBu$ 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.

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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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 ²⁷Al 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 dichloride¹⁰ $[Me_2N(CH_2)_3]AlCl_2$ 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

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

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-(CH₂)₃NMe₂ with aluminum trichloride in 84% yield, gave **1b** on reaction with NaN₃. 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 NaN₃ 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 [Me₂N(CH₂)₃]-Ga*t*Bu(Cl),^{4a} we prepared **3a** by reaction of [Me₂N(CH₂)₃]-AlCl₂¹⁰ 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.

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 Ndonor 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



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	Collect	ion	
Parameters,	and Co	nverge	ence	Results	for	1a
	1b	o. and 2	2b			

	,		
	1a	1b ^{<i>a</i>}	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)	$P2_1/n(14)$	$P2_{1}2_{1}2_{1}$ (19)
a, Å	11.024(6)	7.234(1)	9.048(2)
<i>b</i> , Å	15.062(8)	11.236(1)	10.007(1)
<i>c</i> , 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)
Ζ	8	4	4
$d_{\rm calc}$, g cm ⁻³	1.134	1.144	1.187
μ , cm ⁻¹	3.13	1.3	9.77
$\theta_{\rm max}$, deg	26.0	25.6	71.9
cryst dimens,	0.5 imes 0.5 imes	0.20 imes 0.20 imes	0.28 imes 0.48 imes
mm ³	0.5	0.51	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	0.836/0.768		0.999/0.872
(min/max)			
no. of indep	1994 (<i>I</i> >	2051 (I >	1893 (<i>I</i> >
obs rflns	$2.0\sigma(I)$	$2.0\sigma(I)$	$1.0\sigma(I)$
no. of vars	224	241	217
R	0.037	0.051	0.055
$R_{\rm w} (w^{-1} = \sigma^2(F_{\rm o}))$			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.

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

		Compour	nd la		
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)				
		Compour	nd 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)		
		Compour	nd 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)		

AlCl₃.¹² The azido unit of **1b** shows a characteristic bending $(Al-N3-N4 = 133.1(1)^\circ)$ and is almost linear $(N3-N4-N5 = 176.9(2)^{\circ})$. 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-Nazide 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 [Me₂N(CH₂)₃]₂GaCl.¹³ The related azidoindane [Me₂-N(CH₂)₃]₂In(N₃), 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



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

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 N3¹⁴ and the equatorial plane. The linear N₃ group (N3- $N4-N5 = 175.5(7)^{\circ}$ is bent in a similar way (Al-N3- $N4 = 139.5(5)^\circ$) 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-(Me2-NCH₂)C₆H₄]₂AlMe¹¹ 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

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

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⁽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 $[2-(Me_2NCH_2)C_6H_4]_2AlMe.^{11}$

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 CH₂ groups and two different NMe groups. This gives rise to five ¹³C and eight ¹H resonances. In the ¹H NMR spectrum the differences between two multiplets of one CH₂ group increase from AlCH₂- ($\Delta = 0.10$ ppm) to -CH₂- ($\Delta = 0.35$ ppm) and $-H_2CN$ ($\Delta = 0.71$ ppm). The starting compounds **1a** and 1c exhibit similar NMR patterns. Temperaturedependent 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 $C_{2\nu}$, 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 ²⁷Al 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 ¹H NMR spectrum; two for the diastereotopic protons of CH₂ and two for the NMe groups. Accordingly, these groups give only one sharp ¹³C resonance (CH₂) and two broad ones (NMe) in the ¹³C NMR spectrum. At higher temperature (70 °C; toluene d_8 , 500 MHz instrument) the CH₂ and the NMe groups each give only one singlet in the ¹H NMR spectrum, while at -80 °C these groups result in four doublets (CH₂) and four singlets (NMe). The related compounds **2a** and $[2-(Me_2NCH_2)C_6H_4]_2$ AlMe were investigated in detail by variable-temperature ¹H 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 C2-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

Table 3. ²⁷Al NMR Shifts (ppm)

а	b	
118	109	
96 ^a	87	
158	145	
145	134	
	a 118 96 ^a 158 145	

^a Taken from ref 11.

2b fully resemble those of the chloride **2a**. Therefore, we assume the same dynamic processes in solution.

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 CH₂ groups, with separation trends similar to those found for the alanes of type **1**, plus two singlets for the NMe₂ and one for the *t*Bu group in the ¹H NMR spectra. A respective pattern can be seen in the ¹³C NMR spectra.

²⁷Al 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 ²⁷Al NMR chemical shifts.¹⁶ The δ (²⁷Al) 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 ²⁷Al 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). NaN₃ was dried at 110 °C under high vacuum for 12 h. The reagents [2-(Me₂-NCH₂)C₆H₄]₂AlCl (**2a**),¹¹ [2-(Me₂NCH₂)C₆H₄]Al*t*BuCl (**4a**),¹¹ Li(CH₂)₃NMe₂,¹⁷ and [Me₂N(CH₂)₃]AlCl₂^{10b} were prepared according to the literature methods.

NMR spectra were obtained on a Varian Unity 500 at ambient temperature (¹H, 499.843 MHz; ²⁷Al, 130.195 MHz; ¹³C, 125.639 MHz) and calibrated against residual protons of the deuterated solvents. ¹H and ¹³C chemical shifts are reported relative to TMS and ²⁷Al values relative to the external standard [Al(acac)₃] in C₆D₆. As a result of the electric quadrupole moment of the ²⁷Al nucleus, not all of the carbon atoms bound to aluminum could be detected in ¹³C NMR experiments. The assignments of the ¹H and ¹³C NMR signals were made either with the aid of ¹H/¹³C-HMQC experiments

⁽¹⁶⁾ Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A. J. Organomet. Chem. 1987, 333, 155.

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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 N₂ and are uncorrected.

Chlorobis[3-(dimethylamino)propyl]aluminum (1a). A suspension, prepared with Li(CH₂)₃NMe₂¹⁷ (9.31 g, 100.0 mmol) in 200 mL of Et₂O, was added dropwise to a solution of AlCl₃ (6.66 g, 49.9 mmol) in 200 mL of Et₂O 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 C10H24AlClN2 (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 C10H24Al35ClN2 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-d₈, 293 K): δ 0.13 (m, 4H, AlCH₂), 1.46 (m, 2H, -CHH-), 1.72 (m, 4H, NCHH, -CHH-), 1.95 (s, broad, 12H, NCH₃), 2.71 (m, 2H, NCH*H*). ${}^{13}C{}^{1}H$ NMR (toluene- d_8): δ 1.69 (broad, AlCH₂), 20.85 (AlCH₂CH₂), 44.98 (broad, NCH₃), 60.92 (NCH₂). ²⁷Al 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 NaN₃ (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 C₁₀H₂₄AlN₅ (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 C₁₀H₂₄AlN₅ 241.1847, found 241,1848. MS: *m*/*z* 241 $(M^+, 7)$, 199 $(M^+ - N_3, 32)$, 155 $(M^+ - C_5H_{12}N, 100)$, 113 $(C_5H_{12}- C_5H_{12}N, 100)$ AlN⁺, 9). ¹H NMR (C₆D₆): δ -0.15 (m, 2H, AlC*H*H), -0.05 (m, 2H, AlCHH), 1.38 (m, 2H, AlCH2CHH), 1.60 (s, broad, 6H, N(CH₃)(CH₃)), 1.67 (m, 2H, NCHH), 1.73 (m, 2H, AlCH₂CHH), 2.05 (s, broad, 6H, N(CH₃)(CH₃)), 2.38 (m, 2H, NCHH). ¹³C-{¹H} NMR (C₆D₆): δ 0.25 (broad, AlCH₂), 20.99 (AlCH₂CH₂), 43.46 (broad, N(CH₃)(CH₃)), 45.51 (broad, N(CH₃)(CH₃)), 61.73 (NCH₂). ²⁷Al NMR (C₆D₆): δ 109 ($h_{1/2}$ = 1550 Hz). IR (toluene; $\nu_{\rm as}(N_3)$, cm⁻¹): 2113.

Bromobis[3-(dimethylamino)propyl]aluminum (1c). Li-(CH₂)₃NMe₂ (2.48 g, 26.6 mmol) was added to a solution of AlBr₃ (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 C₁₀H₂₄AlBrN₂ 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 $^+$ – C₅H₁₂N, 100), 87 (C₅H₁₃N $^+$, 16), 86 (C₅H₁₂N $^+$, 17). ¹H NMR (C₆D₆): δ 0.09 (m, 2H, AlCHH), 0.20 (m, 2H, AlCHH), 1.45 (m, 2H, AlCH2CHH), 1.65 (m, 2H, NCHH), 1.77 (m, 2H, AlCH₂CHH), 1.95 (s, broad, 12H, NCH₃), 2.88 (m, 2H, NCHH). ${}^{13}C{}^{1}H$ NMR (C₆D₆): δ 1.89 (broad, AlCH₂), 20.56 (AlCH₂CH₂), 44.99 (broad, NCH₃), 60.47 (NCH₂). ²⁷Al NMR (C₆D₆): δ 118 ($h_{1/2}$ = 1750 Hz).

Azidobis{2-[(dimethylamino)methyl]phenyl}aluminum (2b). A mixture of NaN₃ (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 C₁₈H₂₄AlN₅ (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⁺ - CH₃, 13), 295 (M⁺ - N₃, 27), $203 \; (M^+ - C_9 H_{12} N, \, 21), \, 135 \; (C_9 H_{13} N^+, \, 57), \, 134 \; (C_9 H_{12} N^+, \, 47),$ 91 ($C_7H_7^+$, 69), 58 ($C_3H_8N^+$, 100). ¹H NMR (C_6D_6): δ 2.04 (s, broad, 6H, N(CH₃)(CH₃)), 2.23 (s, broad, 6H, N(CH₃)(CH₃)), 3.26 (s, broad, 2H, CHH), 3.65 (s, broad, 2H, CHH), 6.91 (m, 2H, 3-H), 7.20 (m, 4H, 4,5-H), 7.63 (m, 2H, 6-H). $~^{13}\mathrm{C}\{^{1}\mathrm{H}\}~\mathrm{NMR}$ (C₆D₆): δ 45.18 (broad, NCH₃), 46.05 (broad, NCH₃), 66.63 (CH₂), 125.90 (CH), 126.05 (CH), 127.65 (CH), 138.31 (C-6), 147.07 (C-2), 147.4 (broad, C-ipso). ²⁷Al NMR (C₆D₆): δ 87 (h_{1/2} = 4400 Hz). IR (toluene; $v_{as}(N_3)$, 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 [Me₂N(CH₂)₃]AlCl₂ (4.06 g, 22.1 mmol) dissolved in 120 mL of Et₂O 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 shortpath distillation (60 mm Vigreux, bp 42-45 °C, 10⁻³ Torr) (3.11 g, 66%). HRMS: *m*/*z* calcd for C₉H₂₁AlClN 205.1178, found 205.1179. MS: m/z 205 (M⁺, 1), 170 (M⁺ - Cl, 5), 148 (M⁺ -C₄H₉, 100), 58 (C₃H₈N⁺, 92). ¹H NMR (C₆D₆): δ 0.21 (m, 2H, AlCH₂), 1.14 (s, 9H, C(CH₃)₃), 1.30 (m, 1H, AlCH₂CHH), 1.53 (m, 1H, NCHH), 1.70 (s, 3H, NCH₃), 1.73 (m, 1H, AlCH₂CHH), 1.99 (s, 3H, NCH₃), 2.18 (m, 1H, NCH*H*). ¹³C{¹H} NMR (C₆D₆): δ 0.40 (broad, AlCH₂), 20.66 (AlCH₂CH₂), 29.63 (C(CH₃)₃), 43.43 (NCH₃), 46.43 (NCH₃), 63.70 (NCH₂). ²⁷Al NMR (C₆D₆): δ 158 ($h_{1/2} = 1700$ Hz).

Azido-tert-butyl[3-(dimethylamino)propyl]aluminum (3b). A mixture of NaN₃ (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 C₉H₂₁AlN₄ (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 C₉H₂₁AlN₄ 212.1582, found 212.1583. MS: *m*/*z* 212 $(M^+, 1)$, 170 $(M^+ - N_3, 3)$, 155 $(M^+ - C_4H_9, 100)$, 58 $(C_3H_8N^+, 100)$ 22). ¹H NMR (C₆D₆): δ 0.02 (m, 1H, AlCHH), 0.10 (m, 1H, AlCHH), 1.09 (s, 9H, C(CH₃)₃), 1.19 (m, 1H, AlCH₂CHH), 1.43 (m, 1H, NCHH), 1.53 (s, broad, 3H, NCH₃), 1.58 (m, 1H, AlCH₂-CHH), 1.79 (s, broad, 3H, NCH₃), 1.93 (m, 1H, NCHH). ¹³C- ${^{1}H}$ NMR (C₆D₆): δ -1.89 (broad, AlCH₂), 20.77 (AlCH₂CH₂), 29.49 (C(CH₃)₃), 43.14 (NCH₃), 45.50 (NCH₃), 63.92 (NCH₂). ²⁷Al NMR (C₆D₆): 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 NaN₃ (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 C₁₃H₂₁AlN₄ (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⁺ – C₄H₉ (C₉H₁₂AlN₄) 203.0877, found 203.0879. MS: m/z 203 (M⁺ – C₄H₉, 33), 135 (C₉H₁₃N⁺, 98), 134 (C₉H₁₂N⁺, 76), 91 (C₇H₇⁺, 91), 58 (C₃H₈N⁺, 100). ¹H NMR (C₆D₆): δ 1.15 (s, 9H, C(CH₃)₃), 1.57 (s, 3H, NCH₃), 1.84 (s, 3H, NCH₃), 2.73 (d, J = 14.0 Hz, 1H, CH₂), 3.28 (d, J = 14.0 Hz, 1H, CH₂), 6.74 (m, 1H, 3-H), 7.15 (m, 2H, 4,5-H), 7.70 (m, 1H, 6-H). ¹³C{¹H} NMR (C₆D₆): δ 29.36 (C(*C*H₃)₃), 44.27 (NCH₃), 45.47 (NCH₃), 67.05 (CH₂), 124.36 (CH), 127.39 (CH), 128.57 (CH), 137.66 (C-6), 143.82 (C-2). ²⁷Al NMR (C₆D₆): 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 K α radiation at -70 °C on a Siemens Stoe AED2 diffractometer equipped with a graphite monochromator ($\lambda = 0.710$ 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 C₁₈H₂₄AlN₅ (1b). See reference 3.

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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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