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Reactions of AlR_3 (R = Me, Et) with $H_2NCH_2CH_2NMe_2$: Synthesis and Characterization of Amido- and Imidoalanes

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The reactions of R_3Al (R = Me, Et) with *N,N*-dimethylethylenediamine (DMEDA) in a 1:1 molar ratio produce adducts, $R_3Al{\cdot}NH_2C_2H_4NMe_2$ (**1a**, R = Me; **1b**, R = Et), which upon heating in refluxing toluene result in alkane elimination to afford the chelated monomers $R_2AlNHC_2H_4NMe_2$ (**2a**, R = Me; **2b**, R = Et), respectively. Compounds **2a**,**b** form adducts with 1 equiv of R_3Al through the 3-coordinate nitrogen atom to produce $R_3AlN(H)C_2H_4NMe_2AlR_2$ (**3a**, R = Me; **3b**, R = Et), which can be alternatively prepared by the reaction of R_3Al with DMEDA in a 2:1 molar ratio by alkane elimination at room temperature. Thermolysis of **3a**,**b** at 140 °C in sealed ampules produces a mixture of cis and trans isomers of tetrametallic imidoalanes, $[R_2Al(\mu\text{-}NC_2H_4NMe_2AlR_2)]_2$ (**4a**, R = Me; **4b**, R = Et). Slow recrystallization of the isomeric mixture affords crystals of only the cis isomer for both **4a** and **4b**, but in solution *cis*-**4a** and *cis*-**4b** equilibrate with the respective trans isomers. The cis → trans isomerization of **4a** has been studied by ^1H NMR spectroscopy. The equilibrium has been observed to follow reversible first-order kinetics with $\Delta H° = 1.67 \pm 0.60$ kJ mol^{-1} and $\Delta S° = 9.07 \pm 2.80$ J mol^{-1} K^{-1}. The activation parameters for the cis → trans conversion are $\Delta H_1 = 125.8 \pm 9.3$ kJ mol^{-1} and $\Delta S_1 = 89.7 \pm 1.2$ J mol^{-1} K^{-1}, and those for the reverse process are $\Delta H_{-1} = 124.2 \pm 9.3$ kJ mol^{-1} and $\Delta S_{-1} = 80.7 \pm 1.2$ J mol^{-1} K^{-1}. Pyrolysis of **4a**,**b** in the presence of 2 equiv of DMEDA at 190 °C in sealed ampules gives hexameric imidoalanes, $(RAlNC_2H_4NMe_2)_6$ (**5a**, R = Me; **5b**, R = Et), by alkane elimination. Compounds **5a**,**b** can be also prepared by pyrolysis of **2a**,**b** under similar conditions, but in lower yields. The molecular structures of *cis*-**4b** and **5b** have been determined by single-crystal X-ray diffraction. The molecular geometry of *cis*-**4b** involves one four-membered Al_2N_2 ring and two five-membered AlN_2C_2 rings of cis conformation, and it has approximate C_2 symmetry with the C_2 axis going through the center of the Al_2N_2 ring. The hexameric imidoalane **5b** consists of a hexagonal prism of the $(AlN)_6$ cage formed by two flat six-membered $(AlN)_3$ rings linked together by six transverse Al−N bonds.

Introduction

The synthesis and characterization of amido- and imidoalane complexes[1−3] has been of current interest due to their rich structural and bonding features and potential applications as single-source precursors for the preparation of aluminum nitride thin films. The original work of Davidson et al.[4] and subsequent studies by other groups[2,3] have shown that the initial reaction of organoaluminum species (R_3Al) with various primary amines (H_2NR') results in the formation of adducts of the formula $R_3Al{\cdot}NH_2R'$. Subsequent thermolysis of the adducts generally yielded the mono-, di-, or trimeric amidoalanes and, in turn, the oligomeric imidoalanes

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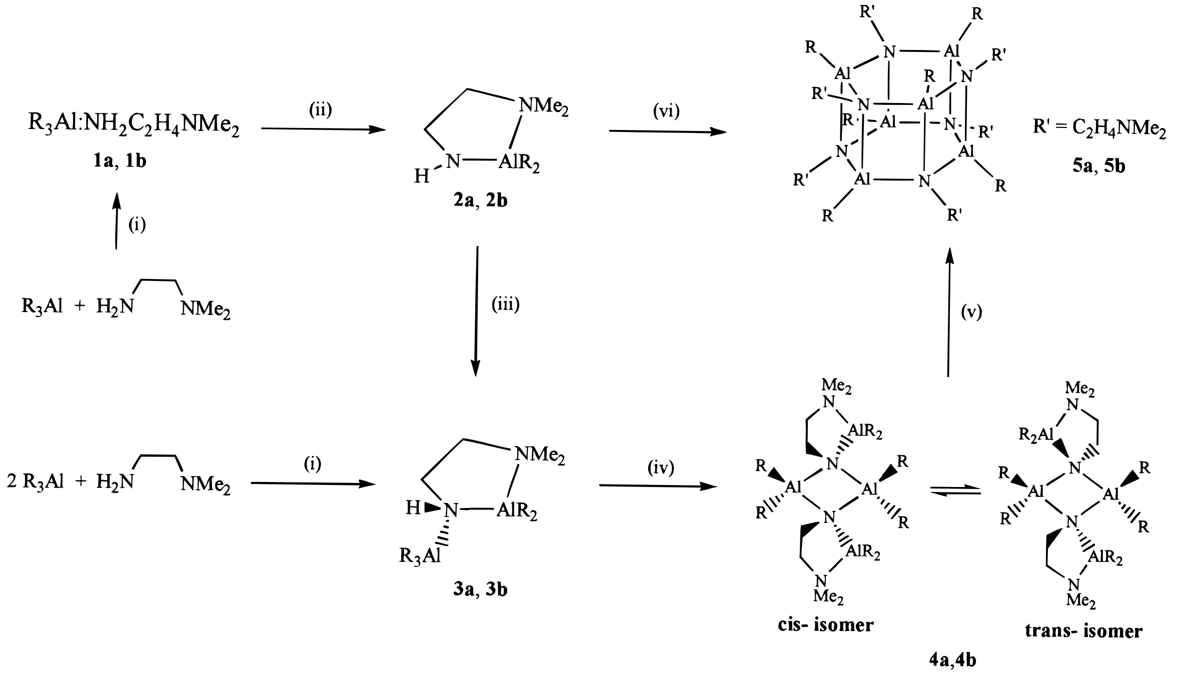
Scheme 1[a]



[a] Reagents and conditions: (i) CH_2Cl_2, room temperature, 3 h; (ii) toluene reflux, 2 h; (iii) R_3Al (1 equiv), CH_2Cl_2, room temperature, 2 h; (iv) sealed ampule, 140 °C, 2 h; (v) DMEDA (2 equiv), sealed ampule, 190 °C, 2 h; (vi) sealed ampule, 190 °C, 2 h.

by successive elimination of alkanes as shown in eq 1.

$$R_3Al + NH_2R' \rightarrow R_3Al\cdot NH_2R' \xrightarrow{-RH} \underset{n = 1-3}{(R_2AlNHR')_n} \xrightarrow{-RH} \underset{m = 2-8}{(RAlNR')_m} \quad (1)$$

Recent reports on the reactions of R_3Al with chelating bi- or polydentate amines have further extended the range of cluster formation and the diversity of novel structural features of the amido- and imidoalanes, involving chelating and/or bridging ligands and 4-, 5-, and 6-coordinated Al atoms. Chelating ligands such as ethylenediamine,[1b,3a,b] various *N*-substituted ethylenediamines,[3c−e] 8-quinolylamine,[3f] 2-pyridylmethylamine,[3g] 1,2-diaminobenzene (bidentates),[3h] tetraethyldiethylenetriamine (tridentate),[3i] *N*,*N*′-bis(3-aminopropyl)ethylenediamine,[3j] and 1,4,8,11-tetraazacyclotetradecane (tetradentates)[3k−m] have been successfully employed to stabilize electrophilic alkylaluminum compounds, producing a number of interesting amido- and imidoalane complexes.

We have previously reported that the reaction of Me_3Al with H_2NNMe_2 (1,1-dimethylhydrazine) affords the dimeric amidoalane $[Me_2Al\text{-}\mu\text{-}N(H)NMe_2]_2$ as a mixture of trans and cis isomers.[5] As an extension of this work on bidentate diamine ligands containing two acidic hydrogens on the same nitrogen atom, we have investigated the reactions of R_3Al (R = Me, Et) with 1 or 2 equiv of $H_2NCH_2CH_2NMe_2$ (*N*,*N*-dimethylethylenediamine, DMEDA). These reactions have resulted in the formation of adducts (**1a**, R = Me; **1b**, R = Et) and chelated monomers (**2a**,**b** and **3a**,**b**), which, upon pyrolysis, are converted to a mixture of cis and trans tetrametallic imidoalanes (**4a**,**b**) and hexameric imidoalanes (**5a**,**b**) by alkane elimination. Herein we report full details of the chemistry shown in Scheme 1, together with structural characterization of the tetrametallic imidoalane *cis*-**4b** and the hexameric imidoalane **5b**.

Results and Discussion

Synthesis and Characterization of 1−5. The reactions of R_3Al with DMEDA in a 1:1 ratio at ambient temperature produce the respective adducts $R_3Al\cdot NH_2C_2H_4NMe_2$ (**1a**, R = Me; **1b**, R = Et) as colorless liquids in almost quantitative yields. Both **1a** and **1b** have been characterized by ^{1}H, ^{13}C, and ^{27}Al NMR and IR spectroscopic methods. The ^{27}Al NMR spectra of **1a**,**b** show a single broad resonance at δ 165.4 ppm for **1a** and at δ 157.6 ppm for **1b**, respectively, which is characteristic of 4-coordinated Al atoms.[6] The NH_2 hydrogen resonances of **1a** (δ 1.85) and **1b** (δ 2.02) are shifted to lower field by ca. 1 ppm compared to those of

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free DMEDA ligand (δ 0.81). This would be expected if the less sterically hindered NH_2 end of the DMEDA ligand is bound to the Al centers in adducts **1a**,**b**, as shown in Scheme 1. Two bands due to symmetric and asymmetric N−H stretches are observed in the IR spectra of **1a**,**b**, respectively.

Heating of **1a**,**b** in refluxing toluene results in alkane elimination (RH), affording the chelated monomers $R_2\overline{AlNHC_2H_4N}Me_2$ (**2a**, R = Me; **2b**, R = Et), as colorless liquids in ca. 80% yields after purification by vacuum distillation. The ^{27}Al NMR spectra of **2a**,**b** reveal resonances due to characteristic 4-coordinate Al atoms at δ 150.4 for **2a** and at δ 148.2 for **2b**. The NMe_2 methyl hydrogen resonance (δ 1.88 for **2a** and δ 1.93 for **2b**) of the chelated monomer is observed at lower field than that in **1a** (δ 1.74) or **1b** (δ 1.74), which supports the idea that the NMe_2 moiety is coordinated to the aluminum in **2a**,**b**. IR spectra of both compounds show a single N−H stretch, at 3282 cm^{-1} for **2a** and 3260 cm^{-1} for **2b**. The monomeric nature of **2a**,**b** has been confirmed by cryoscopic molecular weight data of both compounds in benzene (see Experimental Section). The proton and carbon resonances of methyl groups on the aluminum atom of **2a** appear as two distinct singlets in a 1:1 ratio (δ_H, − 1.10 and − 1.12; δ_C, − 8.94 and − 11.28) at −60 °C in dichloromethane-d_2. As the temperature increases, these ^1H and ^{13}C resonances of **2a** become broad and coalesce into a single peak. Other resonances remain unaffected in the variable-temperature ^1H and ^{13}C NMR spectra of **2a**. This observation could be explained by inversion about nitrogen,[7] which averages the chemical environment of both sides of the ring. Beachley and Racette[3c,d] reported the first example of a 4-coordinate chelated monomer, $Me_2\overline{AlN(Et)C_2H_4N}Me_2$ (**6**), prepared by the reaction of Me_3Al and $H(Et)NC_2H_4NMe_2$ with methane elimination at 100 °C. The monomeric nature of **6** was further supported by subsequent structural characterization of $Cl_2\overline{AlN(Et)C_2H_4N}Me_2$[8] and $Me_2\overline{AlN(Ph)C_2H_4N}H_2$[3e] compounds, in which both imido nitrogens are virtually in a planar conformation.

Compounds **2a**,**b** form adducts with 1 equiv of R_3Al through the 3-coordinate N atom to give $R_3Al\overline{N(H)C_2H_4NMe_2Al}R_2$ (R = Me (**3a**), as a colorless solid; R = Et (**3b**), as a colorless oil). Compound **3a** could be purified by sublimation at 45 °C, whereas oily **3b** could not be obtained as a pure material. However, **3b** was pure enough to be used for the preparation of **4b**. A cryoscopic molecular weight measurement revealed the monomeric nature of **3a**. The NMe_2 (δ 2.51 and 2.54) and $AlMe_2$ (δ −0.70 and −0.79) hydrogens of **3a** appear as two singlets, respectively, which is consistent with the unsymmetrical environment of the two methyl groups on the nitrogen or aluminum atom of the chelated ring. A singlet at δ −1.04 of the highest intensity is assigned to the $AlMe_3$ hydrogens. The ^1H NMR spectrum of **3b** shows features similar to those of **3a**. Beachley[3c] and Interrante[1b] previously proposed the formation of complexes similar to **3a**,**b**, $Et_3Al\overline{N(H)C_2H_4NH_2Al}Et_2$ and $Me_3Al\overline{N(Et)C_2H_4NMe_2Al}Me_2$, as reaction intermediates. These compounds were too unstable to permit their isolation and thus were not fully characterized. Compounds **3a**,**b** can be alternatively prepared by the reaction of R_3Al with DMEDA in a 2:1 ratio even at room temperature. The likely reaction pathway of the latter reaction involves the formation of a 2:1 adduct $R_3AlNH_2C_2H_4NMe_2AlR_3$, in which aluminum coordination to both ends of DMEDA enhances not only the acidity of the NH_2 end but also the nucleophilicity of the R group bound to the NMe_2 end,[9] and thus alkane (RH) elimination is facilitated to afford **3a**,**b**, in contrast to the 1:1 adduct.

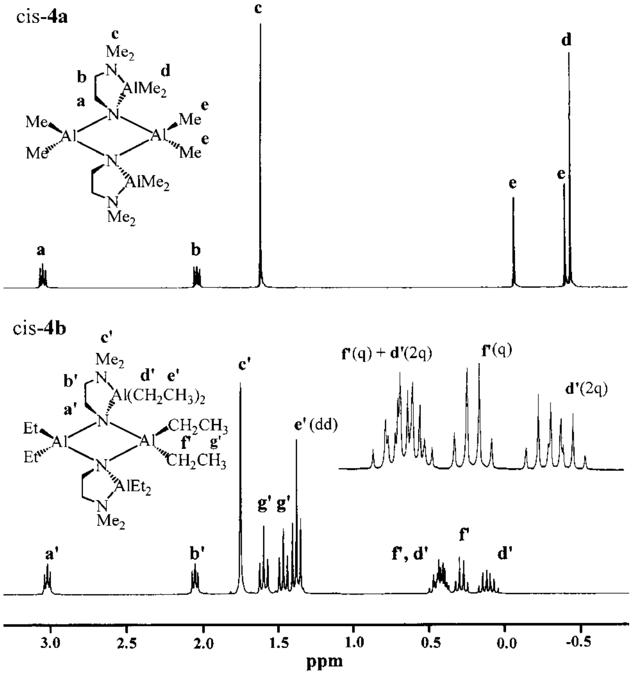

Figure 1. ^1H NMR spectra (300 MHz, benzene-d_6) of *cis*-**4a** (top) and *cis*-**4b** (bottom).

Thermolysis of **3a**,**b** at 140 °C in sealed ampules produces a mixture of cis and trans isomers of tetrametallic imidoalane, $[R_2Al(\mu\text{-}\overline{NC_2H_4NMe_2Al}R_2)]_2$ (**4a**, R = Me, cis:trans = 1:0.8; **4b**, R = Et, cis:trans = 1:0.2), in ca. 70% yields. The dimeric formulations of **4a**,**b** are indicated by the observation of the ($M^+ - R$) ion in the EI mass spectra of **4a**,**b**. Slow recrystallization of the isomer mixture affords crystals of only the cis isomer for both **4a** and **4b**, but in solution *cis*-**4a** and *cis*-**4b** equilibrate with the respective trans isomers. The cis isomer involves the two five-membered AlN_2C_2 rings in a cis conformation with respect to the four-membered Al_2N_2 ring, as shown in Scheme 1 (vide infra). The ^1H NMR spectra of *cis*-**4a** and *cis*-**4b** are compared in Figure 1. The ^1H NMR spectrum of *cis*-**4a** (the top spectrum of Figure 1) exhibits two distinct resonances (δ −0.07 and −0.40, labeled as **e**) due to inequivalent methyl groups on each aluminum atom of the Al_2N_2 ring, whereas that of *trans*-**4a** shows a singlet peak (δ

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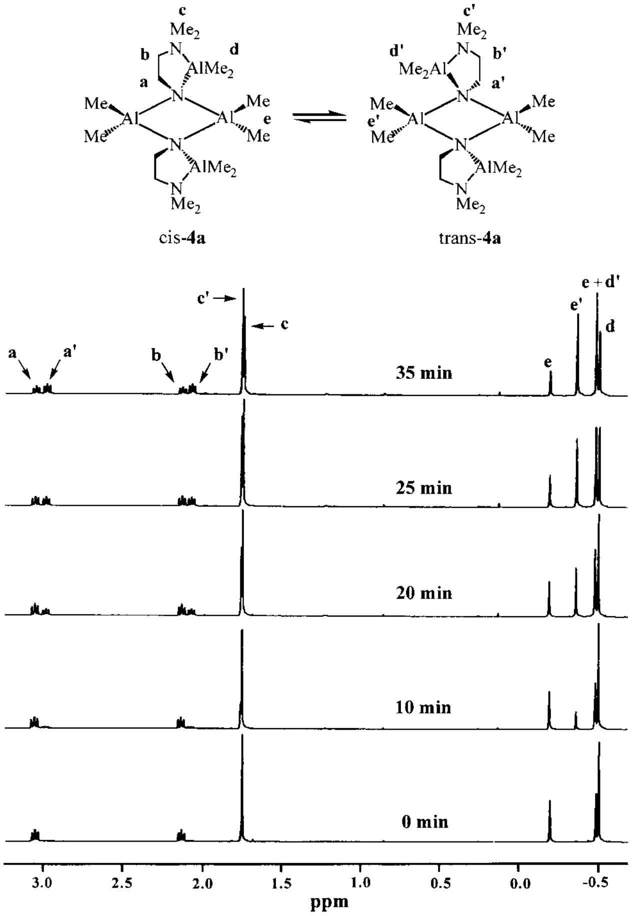

Figure 2. Time-resolved ^1H NMR spectra (300 MHz, benzene-d_6) for the cis−trans isomerization of **4a** at 70 °C.

−0.25, labeled as **e′**; see Figure 2) for the four equivalent $Al-CH_3$ groups of the Al_2N_2 ring. The methyl groups on the Al atom of the five-membered AlN_2C_2 ring appear as a single peak at δ −0.43 (**d**) for *cis*-**4a** and δ −0.39 (**d′** in Figure 2) for *trans*-**4a**, since all four methyl groups of each isomer are equivalent. This observation and the rest of the proton resonances are consistent with the symmetry properties of *cis*-**4a** (C_{2v}) and *trans*-**4a** (C_{2h}) isomers in solution. The general features of the ^1H NMR spectra of *cis*-**4b** and *trans*-**4b** are quite similar to those of *cis*-**4a** and *trans*-**4a**, although the former spectra are much more complicated due to the presence of inequivalent and diastereotopic hydrogens of the ethyl groups. Each pair (**g′** and **f′**) of the triplet−quartet pattern of *cis*-**4b** at δ 1.60−0.43 and 1.47−0.28 is assigned to the two inequivalent ethyl groups on the Al atom of the four-membered ring (see the bottom spectrum of Figure 1). The two CH_2 hydrogens (H_a and H_b) of all four equivalent ethyl groups on the Al atom of the five-membered ring are diastereotopic and thus appear as two doublets of quartets (labeled as **d′**: H_a, δ 0.46 (q) and 0.13 (q); H_b, δ 0.41 (q) and 0.08 (q); $^2J_{HH} = 99$ Hz). The pseudo-triplet pattern at δ 1.38 (**e′**) is an overlap of the dd pattern due to couplings of methyl groups to H_a and H_b. Three quartets (**f′** + **d′**) and two quartets (**d′**) are superimposed in the regions δ 0.50−0.37 and 0.17−0.03, respectively (see the inset of Figure 1). The peak assignments and coupling patterns of *cis*-**4b** have been confirmed by a decoupling experiment and the 2D $^1H-^1H$ correlated NMR spectrum. The ^1H NMR spectrum of *trans*-**4b** reveals four equivalent ethyl groups on the Al atoms of the four-membered ring as well as those of the five-membered ring. Nevertheless, the CH_2 hydrogens of all the ethyl moieties are diastereotopic and thus show complex patterns of resonances (total of eight quartets) moreover with overlap of the corresponding *cis*-**4b** resonances, which precluded detailed assignments of *trans*-**4b** resonances. Compounds **4a**,**b** are likely to be formed from **3a**,**b** by alkane elimination upon thermolysis to afford $R_2\overline{Al{\cdots}NC_2H_4}\text{-}\overline{NMe_2Al}R_2$ as an intermediate followed by dimerization of this species. If the dimerization reaction is a cycloaddition reaction between two molecules of this intermediate with partial $Al{\cdots}N$ π-bonding,[7,11] the orthogonal approach of the π-bonds of two intermediates in the least hindered orientation followed by a cycloaddition could result in the cis isomer as a preferred kinetic product, as was proposed by Beachley.[10] This proposal is consistent with our observation that ethyl derivative **4b** with the bulkier substituents has a larger cis to trans ratio (1:0.2) than does the methyl derivative **4a** (1:0.8). We confirmed that no cis−trans isomerization of **4a**,**b** occurs in the solid state at high temperatures, similar to synthetic conditions for **4a**,**b**. The most closely related example to **4a**,**b** is $Al_4(\mu_3\text{-8-quinolimide})_2Me_8$, which was reported by Wang[3f] to exist only as the trans isomer of C_{2h} symmetry both in solution and in the solid state.

Pyrolysis of **4a** and **4b** in the presence of 2 equiv of DMEDA at 190 °C in sealed ampules gave hexameric imidoalanes, $(RAlNC_2H_4NMe_2)_6$ (**5a**, R = Me; **5b**, R = Et), in ca. 85% yield by alkane elimination. Compounds **5a**,**b** can be also prepared by pyrolysis of **2a**,**b** under similar conditions, but in lower (ca. 45%) yield. X-ray structure determination of **5b** reveals a hexagonal prism of the $(AlN)_6$ framework as shown in Scheme 1 (vide infra). The ^1H NMR spectra of **5a**,**b** indicate that six substituents on the cage aluminum and nitrogen atoms are equivalent, respectively, due to the S_6-symmetric nature of these compounds in solution. Imidoalanes tend to exist as oligomeric species $(RAlNR')_n$ (n = 4−8; R and R′ = a variety of alkyl, aryl, and hydrogen substituents) due to the weak Al−N π-interaction.[11] The first structurally characterized imidoalane, $(PhAlNPh)_4$, was reported in 1972 and found to contain a regular Al_4N_4 cubane framework.[12] Since then, structurally characterized imidoalanes have been reported for tetrameric,[2d,13] pentameric,[14] hexameric,[13c,15] heptameric,[16] and octa-

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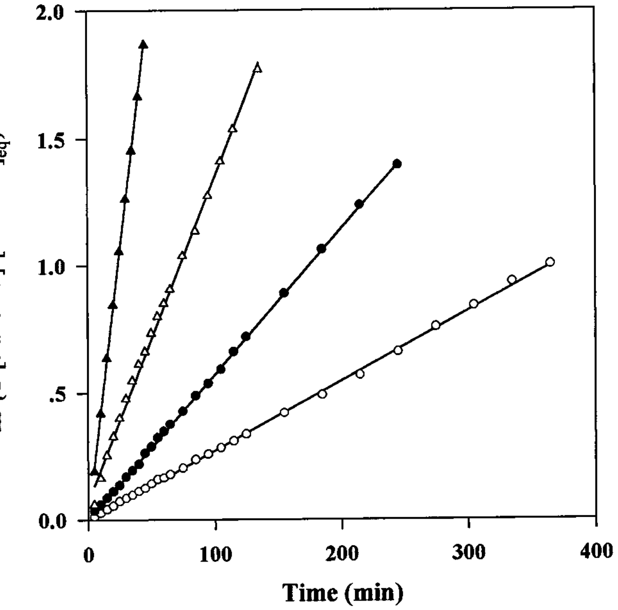

Figure 3. Kinetics plots for the cis−trans isomerization of **4a** in benzene-d_6 at 50 °C (○), 55 °C (●), 60° C (△), and 70 °C (▲).

Table 1. Kinetic and Thermodynamic Data in Benzene-d_6

t, °C	K_{eq}	10^3k_{obs}, min^{-1}	10^3k_1, min^{-1}	10^3k_{-1}, min^{-1}
50	1.59 ± 0.11	2.73 ± 0.13	1.68 ± 0.07	1.05 ± 0.06
55	1.61 ± 0.13	5.19 ± 0.16	3.20 ± 0.10	1.99 ± 0.06
60	1.63 ± 0.12	12.8 ± 0.3	7.92 ± 0.17	4.86 ± 0.13
70	1.65 ± 0.14	41.7 ± 0.6	26.0 ± 0.3	15.7 ± 0.3

meric[15b] compounds. All of these imidoalanes constitute a very interesting class of cage structures in which both Al and N atoms are 4-coordinate. The lower imidoalanes (n = 2, 3) have been recently reported for dimeric $[(2,4,6\text{-}^tBu_3C_6H_2)AlNPh]_2$[17] and trimeric $[MeAlN\text{-}(2,6\text{-}^iPr_2C_6H_3)]_3$[18] complexes with 3-coordinate Al and N atoms and bulky substituents.

Cis−Trans Isomerization of 4a. The cis → trans isomerization of **4a** reaction was studied by ^1H NMR spectroscopy. Typical time-resolved ^1H NMR spectra of **4a** in benzene-d_6 at 70 °C are shown in Figure 2. As the intensities of the resonances of *cis*-**4a** decrease, those corresponding to *trans*-**4a** increase in intensity. Relative concentrations of the two isomers were measured by integration of the peaks due to Al−CH$_3$ at δ −0.07 (**e**, half of the total concentration) for *cis*-**4a** and at δ −0.25 (**e′**) for *trans*-**4a**. Analyses according to reversible first-order kinetics give excellent fits of experimental data at various temperatures, as shown in Figure 3. The kinetic and thermodynamic data are listed in Table 1. The equilibrium constants, K_{eq}, measured for the isomerization range from 1.59 to 1.65, indicating that the trans isomer is favored in this equilibrium. The plot of ln K_{eq} vs $1/T$ (correlation coefficient, 0.9781) yields $\Delta H° = 1.67 \pm 0.60$ kJ mol^{-1} and $\Delta S° = 9.07 \pm 2.8$ J mol^{-1} K^{-1} for the process. The cis isomer is thermodynamically more stable, but the positive entropy change favors the trans isomer. Activation parameters derived from the Eyring plots of $\ln(k/T)$ vs $1/T$ and $\ln(k_{-1}/T)$ vs $1/T$ (correlation coefficients 0.9944 and, 0.9944, respectively) are $\Delta H_1 = 125.8 \pm 9.3$ kJ mol^{-1} and $\Delta S_1 = 89.7 \pm 1.2$ J mol^{-1} K^{-1} for the forward isomerization and $\Delta H_{-1} = 124.2 \pm 9.3$ kJ mol^{-1} and $\Delta S_{-1} = 80.7 \pm 1.2$ J mol^{-1} K^{-1} for the reverse process. The net enthalpy and entropy changes for *cis*-**4a** to *trans*-**4a** from the thermodynamic data are in good agreement with those obtained from the kinetic data, $\Delta H_1 - \Delta H_{-1} = \Delta H°$ and $\Delta S_1 - \Delta S_{-1} = \Delta S°$, within experimental error. The relatively large positive values of ΔS_1 and ΔS_{-1} reflect that the symmetry of the transition state for the reversible isomerization is considerably reduced from that of both isomers.

Most of the known amidoalane dimers of the formula $[R_2Al(\mu\text{-}NHR')]_2$ crystallize as either the trans or cis isomer and undergo cis−trans isomerization in solution, although use of sterically demanding aluminum alkyls results in the exclusive formation of the cis isomer.[19] We previously reported kinetic studies of the cis−trans isomerization of dimeric amidoalanes and amidogallanes, $[Me_2M\text{-}\mu\text{-}N(H)^tBu]_2$ (M = Al (**7**),[20] Ga (**8**)[21]) and $[Me_2M\text{-}\mu\text{-}N(H)NMe_2]_2$ (M = Al (**9**), Ga (**10**)),[5] in which the isomerization pathway is proposed to be an initial breaking of the M−N bond, followed by rotation about the nonbridged M−N bond and rebridging. The rate of isomerization, therefore, has been markedly accelerated by Lewis bases due to the facile cleavage of the M−N bond by an attack of Lewis bases on the M atom, as was well documented in $[Me_2M(\mu\text{-}NMePh)]_2$ (M = Al,[22] Ga[10b]), **7**,[20] and **8**.[21] The isomerization of **4a**, however, is not affected in the presence of ca. 1 equiv of pyridine or 4-methylpyridine. This observation may be attributed to the role of the NMe$_2$ end of DMEDA as an internal Lewis base in facilitating the Al−N bond scission of the four-membered ring in **4a**. Similar results have been also observed with **9** and **10**, which have free NMe$_2$ ends within the molecular framework.[5] The ΔH_1 and ΔH_{-1} values obtained for **4a** may reflect the bond strength of the dissociating Al−N bonds in *cis*-**4a** and *trans*-**4a**, respectively. For comparison, we note that enthalpies (in kcal mol^{-1}) of formation of Me$_3$Al adducts with amines have been reported as NMe$_3$ (−29.96 ± 0.19), HNMe$_2$ (−30.84 ± 0.26), and H$_2$NMe (−30.02 ± 0.31).[23]

Crystal Structure of *cis*-4b. The overall molecular geometry of *cis*-**4b** with the atomic labeling scheme is shown in Figure 4. Selected bond distances and angles are listed in Table 2.

The tetrametallic molecule **4b** has one four-membered Al$_2$N$_2$ ring and two five-membered AlN$_2$C$_2$ rings of cis conformation and possesses approximate C_2 symmetry with the C_2 axis going through the center of the Al$_2$N$_2$ ring. Significant distortion from an ideal tetrahedral geometry is observed for all the atoms in the four-membered Al$_2$N$_2$ ring with the ring angles of 89.7(4)° (average) at aluminum and 85.5(4)° (average) at nitro-

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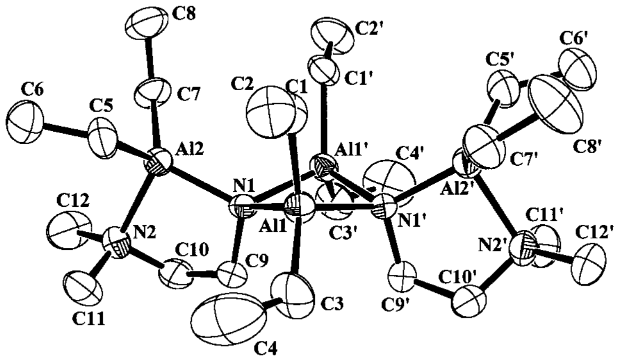

Figure 4. Molecular geometry and atomic labeling scheme for *cis*-**4b**. Hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Esd's for *cis*-4b[a]

Bond Lengths			
Al(1)−N(1)	1.987(5)	Al(1)−N(1′)	1.957(5)
Al(1)−C(1)	1.976(8)	Al(1)−C(3)	1.978(7)
Al(2)−N(1)	1.889(5)	Al(2)−N(2)	2.026(6)
Al(2)−C(5)	1.982(8)	Al(2)−C(7)	2.008(7)
Al(1′)−N(1)	1.957(5)	Al(1′)−N(1′)	1.977(5)
Al(1′)−C(1′)	1.940(8)	Al(1′)−C(3′)	1.978(7)
Al(2′)−N(1′)	1.894(5)	Al(2′)−N(2′)	2.032(6)
Al(2′)-C(5′)	1.986(8)	Al(2′)−C(7′)	1.994(8)
N(1)−C(9)	1.494(8)	N(1′)−C(9′)	1.495(8)
Al(1)···Al(1′)	2.674(3)		
Bond Angles			
N(1)−Al(1)−N(1′)	89.5(2)	C(1)−Al(1)−C(3)	116.3(3)
N(1)−Al(2)−N(2)	91.0(2)	C(5)−Al(2)−C(7)	113.0(4)
N(1)−Al(1′)−N(1′)	89.8(2)	C(1′)−Al(1′)−C(3′)	117.1(4)
N(1′)−Al(2′)−N(2′)	91.0(2)	C(5′)−Al(2′)−C(7′)	114.4(4)
Al(1)−N(1)−Al(1′)	85.4(2)	Al(2)−N(1)−C(9)	106.6(4)
Al(1)−N(1′)−Al(1′)	85.6(2)	Al(1)−N(1′)−C(9′)	110.1(4)
Al(1′)−N(1′)−C(9′)	110.4(4)	Al(2′)−N(1′)−C(9′)	106.9(4)
Al(2)−N(2)−C(10)	100.8(4)	C(11)−N(2)−C(12)	108.1(7)
Al(2′)−N(2′)−C(10′)	99.8(4)	C(11′)−N(2′)−C(12′)	107.4(6)

[a] Atoms related by the pseudo-C_2 symmetry operation are labeled with a prime.

gen. The four-membered ring is puckered with an Al_2N plane fold angle of 32.6(7)°, presumably to relieve the steric congestion among ethyl groups on the aluminum atoms of the four- and five-membered rings. Similar distortion of the Al_2N_2 ring has been previously observed, affording a fold angle of 32.7° for *cis*-$[(Me_3CCH_2)_2Al\text{-}\mu\text{-}N(H)Ada]_2$ (Ada = adamantane),[19a] 28.9° for *cis*-$[(Me_3CCH_2)_2Al\text{-}\mu\text{-}N(H)^tBu]_2$,[19a] and 15.5° for *cis*-$[Me_2Al\text{-}\mu\text{-}N(H)^iPr]_2$.[24] Bradley and co-workers[19b] recently proposed that the Al_2N_2 ring of amidoalane dimers becomes more folded along the N···N line as the substituent on the nitrogen atom becomes bulkier, on the basis of their systematic studies on these dimers. The average bond distance of the Al_2N_2 ring is 1.970(7) Å, which is close to that observed in other dimers.[2,3] The imido nitrogen N(1) bridges three aluminum atoms (Al(1), Al(1′), and Al(2)) with a short N(1)−Al(2) bond distance of 1.889(5) Å. The coordination environment of the aluminum atom of the five-membered ring is also distorted tetrahedral. The Al(2)−N(2) distance (2.029(6) Å) is the longest among Al−N bonds in *cis*-**4b**, as expected for a dative bond, and comparable to those observed in adducts such as $H_3Al{\cdot}NMe_3$ (2.063 Å)[25] and $Me_3Al{\cdot}NMe_3$ (2.099 Å).[26] The methyl carbon atoms (C(8) and C(8′)) on the aluminum atoms of the five-membered rings are disordered, and those with higher occupancies (0.66 and 0.89) are shown in Figure 4. All other features of the molecular geometry are within the expected range.

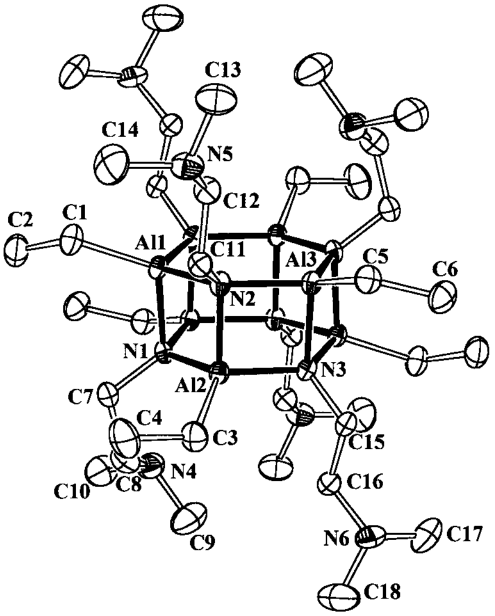

Figure 5. Molecular geometry and atomic labeling scheme for **5b**. Atoms related by the *i* symmetry operation are not labeled (see Table 3), and hydrogen atoms were omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) with Esd's for 5b[a]

Bond Lengths			
Al(1)−N(1)	1.966(3)	Al(1)−N(2)	1.896(3)
Al(1)−N(3′)	1.892(3)	Al(1)−C(1)	1.974(4)
Al(2)−N(1)	1.910(3)	Al(2)−N(2)	1.954(3)
Al(2)−N(3)	1.893(3)	Al(2)−C(3)	1.970(4)
Al(3)−N(1′)	1.898(3)	Al(3)−N(2)	1.899(3)
Al(3)−N(3)	1.994(3)	Al(3)−C(5)	1.954(4)
N(1)−C(7)	1.493(4)	N(2)−C(11)	1.507(4)
N(3)−C(15)	1.500(5)	Al(1)···Al(2)	2.688(2)
Al(1)···Al(3′)	2.710(2)	Al(2)···Al(3)	2.700(2)
Bond Angles			
N(1)−Al(1)−N(2)	91.58(14)	N(1)−Al(1)−N(3′)	91.52(13)
N(2)−Al(1)−N(3′)	113.29(14)	N(3′)−Al(1)−C(1)	120.9(2)
N(1)−Al(2)−N(2)	91.52(13)	N(1)−Al(2)−N(3)	114.01(13)
N(2)−Al(2)−N(3)	91.93(14)	N(1)−Al(2)−C(3)	121.3(2)
N(1′)−Al(3)−N(2)	114.30(14)	N(1′)−Al(3)−N(3)	90.46(13)
N(2)−Al(3)−N(3)	90.50(14)	N(1′)−Al(3)−C(5)	124.8(2)
Al(1)−N(1)−Al(2)	87.81(13)	Al(1)−N(1)−Al(3′)	89.07(13)
Al(2)−N(1)−Al(3′)	124.6(2)	Al(1)−N(1)−C(7)	123.4(2)
Al(1)−N(2)−Al(2)	88.56(13)	Al(1)−N(2)−Al(3)	125.9(2)
Al(2)−N(2)−Al(3)	88.95(13)	Al(1)−N(2)−C(11)	114.1(2)
Al(1′)−N(3)−Al(2)	126.1(2)	Al(1′)−N(3)−Al(3)	88.40(13)
Al(2)−N(3)−Al(3)	87.95(13)	Al(1′)−N(3)−C(15)	113.3(2)

[a] Atoms related by the *i* symmetry operation are labeled with a prime.

Crystal Structure of 5b. The overall molecular geometry of **5b** with the atomic labeling is presented in Figure 5. Selected bond distances and angles are listed in Table 3.

The hexameric imidoalane has crystallographically required *i* symmetry and consists of a hexagonal prism

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of the $(AlN)_6$ cage formed by two flat six-membered $(AlN)_3$ rings linked together by six transverse Al−N bonds. The Al−N bonds in the six-membered rings (1.897(7) Å (average)) are significantly shorter than the transverse bonds (1.971(5) Å (average)). Each aluminum atom is tetrahedrally bonded to three nitrogen atoms and vice versa. Six $CH_2CH_2NMe_2$ moieties on nitrogen atoms and six ethyl groups on aluminum atoms are disposed away from the cage, whereas the two $CH_2CH_2NMe_2$ substituents on N(1) and N(1′) are folded back toward the cage through C(8)−N(4) and C(8′)−N(4′) bonds. The N−Al−N bond angles (113.9(2)° (average)) in six-membered rings are systematically smaller than the corresponding Al−N−Al bond angles (125.5(3)° (average)). The trend is opposite for the same angles in the four-membered rings. The mean values are 88.5(3)° for N−Al−N angles and 91.3(3)° for Al−N−Al angles. The general structural features of **5b** are similar to those observed for other hexameric imidoalanes such as $(HAlN^iPr)_6$,[15a] $(HAlN^nPr)_6$,[15b] $(ClAlN^iPr)_6$,[15c] and $(MeAlNPh)_6$.[15d] There are no unusual intermolecular contacts in **5b**. The NMe_2 ends of the DMEDA ligand remain uncoordinated. All other features of the molecular geometry are within the expected range.

Experimental Section

General Comments. All experiments were performed under an atmosphere of argon either in a Vacuum Atmospheres drybox or with standard Schlenk techniques. Trimethylaluminum (97%), triethylaluminum (93%), and DMEDA (95%) were purchased from Aldrich and used without further purification. Dichloromethane was refluxed over CaH_2 and then distilled under an argon atmosphere. *n*-Hexane, benzene, and toluene were distilled over sodium benzophenone under an argon atmosphere.

Infrared spectra were obtained as KBr pellets on a Bomem MB-100 FT-IR spectrophotometer. ^1H (300 MHz), ^{13}C (75 MHz), and ^{27}Al (78 MHz) NMR spectra were recorded on a Bruker AM-300 spectrometer. ^{27}Al NMR spectra were referenced to external $[Al(H_2O)_6]^{3+}$ and subtracted by the ^{27}Al background signal.[6] Melting points were obtained in sealed capillaries under argon (1 atm) and were uncorrected. Mass spectra were obtained by the staff of the Korea Basic Science Institute using a JEOL JMS-SX-102A mass spectrometer. Elemental analyses were performed either by Oneida Research Services, USA or by the analytical laboratory of Agency for Defense Development, Korea.

Preparation of $Me_3Al·NH_2C_2H_4NMe_2$ (1a). To a dichloromethane solution (10 mL) of Me_3Al (1.220 g, 13.73 mmol) cooled to 0 °C was added a dichloromethane solution (10 mL) of DMEDA (0.990 g, 13.84 mmol). The resulting colorless mixture was stirred at room temperature for 3 h. Evaporation of the solvent in vacuo afforded **1a** (2.112 g, 13.18 mmol, 96%) as a colorless oil: ^1H NMR (C_6D_6, 298 K) δ −0.46 (9H, s, $Al(CH_3)_3$), 1.61 (2H, t, $CH_2N(CH_3)_2$), 1.74 (6H, s, $N(CH_3)_2$), 1.85 (2H, br, NH_2), 2.06 (2H, tt, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −8.68 ($Al(CH_3)_3$), 37.79 ($CH_2N(CH_3)_2$), 44.51 ($N(CH_3)_2$), 58.14 (NH_2CH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 165.4; IR ν(NH) 3310, 3382 cm^{-1}. Anal. Calcd for $C_7H_{21}AlN_2$: C, 52.45; H, 13.22; N, 17.49. Found: C, 52.41; H, 13.13; N, 17.76.

Preparation of $Et_3Al·NH_2C_2H_4NMe_2$ (1b). The reaction of Et_3Al (1.020 g, 8.93 mmol) and DMEDA (0.780 g, 8.85 mmol) were carried out by following a procedure similar to that for **1a**. Evaporation of the solvent gave **1b** (1.690 g, 8.39 mmol, 94%) as a colorless oil: ^1H NMR (C_6D_6, 298 K) δ 0.13 (6H, q, $Al(CH_2CH_3)_3$), 1.42 (9H, t, $Al(CH_2CH_3)_3$), 1.58 (2H, t, $CH_2N(CH_3)_2$), 1.74 (6H, s, $N(CH_3)_2$), 2.02 (2H, br, NH_2), 2.02 (2H, t, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −0.96 ($Al(CH_2CH_3)_3$), 10.49 ($Al(CH_2CH_3)_3$), 37.84 ($CH_2N(CH_3)_2$), 44.53 ($N(CH_3)_2$), 58.16 (NH_2CH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 157.6; IR ν(NH) 3315, 3378 cm^{-1}. Anal. Calcd for $C_{10}H_{27}AlN_2$: C, 59.35; H, 13.46; N, 13.85. Found: C, 59.07; H, 13.19; N, 14.16.

Preparation of $Me_2AlNHC_2H_4NMe_2$ (2a). A toluene solution (10 mL) of compound **1a** (0.880 g, 5.47 mmol) was heated at reflux for 2 h. The volatile material was removed under reduced pressure. Purification by vacuum distillation (10^{-3} mmHg, 45 °C) gave **2a** (0.650 g, 4.48 mmol, 82%) as a colorless oil: ^1H NMR (C_6D_6, 298 K) δ −0.48 (6H, s, $Al(CH_3)_2$), 0.92 (1H, br, NH), 1.88 (6H, s, $N(CH_3)_2$), 1.91 (2H, t, $CH_2N(CH_3)_2$), 2.47 (2H, td, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −9.97 ($Al(CH_3)_2$), 39.65 ($CH_2N(CH_3)_2$), 45.37 ($N(CH_3)_2$), 61.49 ($NHCH_2$); ^1H NMR (CD_2Cl_2, 298 K) δ −0.88 (6H, s, $Al(CH_3)_2$), 1.05 (1H, br, NH), 2.17 (6H, s, $N(CH_3)_2$), 2.28 (2H, t, $CH_2N(CH_3)_2$), 2.67 (2H, td, NH_2CH_2); ^{13}C NMR (CD_2Cl_2, 298 K) δ −10.70 ($Al(CH_3)_2$), 39.99 ($CH_2N(CH_3)_2$), 45.76 ($N(CH_3)_2$), 62.02 ($NHCH_2$); ^{27}Al NMR (C_6D_6, 298 K) δ 150.4; IR ν(NH) 3282 cm^{-1}. Anal. Calcd for $C_6H_{17}AlN_2$: C, 49.96; H, 11.89; N, 19.43. Found: C, 49.67; H, 11.69; N, 19.46.

Preparation of $Et_2AlNHC_2H_4NMe_2$ (2b). The same procedure was followed as for the preparation of **2a**. A colorless oil of **2b** (0.390 g, 2.25 mmol, 81%) was obtained from **1b** (0.560 g, 2.77 mmol) after purification by vacuum distillation (10^{-3} mmHg, 50 °C): ^1H NMR (C_6D_6, 298 K) δ 0.19 (4H, q, $Al(CH_2CH_3)_2$), 1.36 (6H, t, $Al(CH_2CH_3)_2$), 2.01 (1H, br, NH), 1.93 (6H, s, $N(CH_3)_2$), 2.01(2H, t, $CH_2N(CH_3)_2$), 2.57 (2H, td, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −1.17 ($Al(CH_2CH_3)_2$), 9.59 ($Al(CH_2CH_3)_2$), 39.90 ($CH_2N(CH_3)_2$), 44.87 ($N(CH_3)_2$), 61.49 ($NHCH_2$); ^{27}Al NMR (C_6D_6, 298 K) δ 148.2; IR ν(NH) 3260 cm^{-1}. Anal. Calcd for $C_8H_{21}AlN_2$: C, 55.76; H, 12.29; N, 16.27. Found: C, 55.27; H, 12.13; N, 16.78.

Preparation of $Me_3AlN(H)C_2H_4N(Me)_2AlMe_2$ (3a). To a dichloromethane solution (10 mL) of Me_3Al (0.960 g, 13.33 mmol) cooled to 0 °C was added a dichloromethane solution (10 mL) of DMEDA (0.587 g, 6.96 mmol). The resulting mixture was stirred at room temperature for 3 h. Gas evolution (presumably methane) was apparent from the observed frothing. The volatile material was removed under reduced pressure. Upon sublimation (10^{-3} mmHg, 45 °C), compound **3a** (1.106 g, 4.99 mmol, 75%) was obtained as a colorless solid. This material was not stable at room temperature for prolonged periods and thus was stored at −20 °C: mp 51 °C; ^1H NMR ($CDCl_3$, 298 K) δ −1.04 (9H, s, $Al(CH_3)_3$), −0.79 (3H, s, $AlCH_3$), −0.70 (3H, s, $AlCH_3$), 0.73 (1H, br t, NH), 2.51 (3H, s, NCH_3), 2.54 (3H, s, NCH_3), 2.79 (2H, m, $CH_2N(CH_3)_2$), 2.95 (2H, m, NH_2CH_2); ^{13}C NMR ($CDCl_3$, 298 K) δ −10.59 ($AlCH_3$), −8.77 ($AlCH_3$), 38.86 ($CH_2N(CH_3)_2$), 45.50 (NCH_3), 46.34 (NCH_3), 62.11 (NH_2CH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 170.1; IR ν(NH) 3428 cm^{-1}. Anal. Calcd for $C_9H_{26}Al_2N_2$: C, 49.96; H, 12.12; N, 12.96. Found: C, 49.75; H, 12.13; N, 12.76.

Preparation of $Et_3AlN(H)C_2H_4N(Me)_2AlEt_2$ (3b). Compound **3b** was prepared by a procedure similar to that used for **3a** with Et_3Al (1.320 g, 11.51 mmol) and DMEDA (0.510 g, 5.79 mmol). After removal of the solvent in vacuo, compound **3b** was obtained as a viscous oil. The crude product was not further purified and was subsequently used to prepare compound **4b**. This material was stored at −20 °C: ^1H NMR ($CDCl_3$, 298 K) δ −0.33 (6H, q, $Al(CH_2CH_3)_3$), −0.10 (4H, m, $Al(CH_2CH_3)_3$), 0.83 (1H, br t, NH), 0.98 (15H, m, $AlCH_2CH_3$), 2.52 (3H, s, NCH_3), 2.58 (3H, s, NCH_3), 2.73 (2H, m, $CH_2N(CH_3)_2$), 2.89 (2H, m, NH_2CH_2); ^{13}C NMR ($CDCl_3$, 298 K) δ −5.49 ($AlCH_2CH_3$), −2.98 ($AlCH_2CH_3$), 5.12 ($AlCH_2CH_3$), 6.28 ($AlCH_2CH_3$), 7.12 ($Al\ CH_2CH_3$), 39.56 ($CH_2N(CH_3)_2$), 45.36 (NCH_3), 46.65 (NCH_3), 63.96 (NH_2CH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 159.2; IR ν(NH) 3389 cm^{-1}.

Preparation of $[Me_2Al(\mu\text{-}NC_2H_4N(Me)_2AlMe_2)]_2$ (4a). Compound **3a** (0.690 g, 3.19 mmol) was heated at 140 °C for

2 h in a sealed ampule. The crude product was recrystallized in dichloromethane at −20 °C to produce **4a** (0.447 g, 1.12 mmol, 70%, cis:trans = 1:0.8) as colorless crystals. Pure *cis*-**4a** could be obtained by repeated recrystallization in dichloromethane−hexane.

cis-**4a**: mp 150 °C dec; ^{1}H NMR (C_6D_6, 298 K) δ −0.43 (12H, s, AlCH_3), −0.40 (6H, s, AlCH_3), −0.07 (6H, s, AlCH_3), 1.61 (12H, s, N$(CH_3)_2$), 2.04 (4H, t, $CH_2N(CH_3)_2$), 3.05 (4H, t, NCH_2); ^{13}C NMR (C_6D_6, 298 K) δ −10.10 (AlCH_3), −7.94 (AlCH_3), −3.52 (AlCH_3), 43.32 ($CH_2N(CH_3)_2$), 46.23 (N$(CH_3)_2$), 64.21 (NCH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 160.9; MS (70 eV) *m*/*z* 385 ($M^+ - CH_3$). Anal. Calcd for $C_{16}H_{44}Al_4N_4$: C, 47.97; H, 11.08; N, 13.99. Found: C, 47.53; H, 10.97; N, 13.78.

trans-**4a** (data obtained from an equilibrium mixture): ^{1}H NMR (C_6D_6, 298 K) δ −0.39 (12H, s, AlCH_3), −0.25 (12H, s, AlCH_3), 1.60 (12H, s, N$(CH_3)_2$), 1.95 (4H, t, $CH_2N(CH_3)_2$), 2.98 (4H, t, NCH_2); ^{13}C NMR (C_6D_6, 298 K) δ −8.20 (AlCH_3), −6.06 (AlCH_3), 42.54 ($CH_2N(CH_3)_2$), 47.02 (N$(CH_3)_2$), 65.36 (NCH_2).

Preparation of $[Et_2Al(\mu\text{-}\overline{NC_2H_4N(Me)_2Al}Et_2)]_2$ (4b). Compound **3b** (0.780 g, 2.71 mmol) was heated at 150 °C for 1.5 h in a sealed ampule. Recrystallization of the crude product in dichloromethane at −20 °C afforded **4b** (0.485 g, 0.95 mmol, 70%, cis:trans = 1:0.2) as colorless crystals. Pure *cis*-**4b** was obtained by recrystallization in toluene−dichloromethane.

cis-**4b**: mp 152 °C dec; ^{1}H NMR (C_6D_6, 298 K) δ 0.25 (4H, dq, $^2J_{HH}$ = 99 Hz, AlCH_2CH_3), 0.30 (4H, dq, $^2J_{HH}$ = 99 Hz, AlCH_2CH_3), 0.28 (4H, q, AlCH_2CH_3), 0.43 (4H, q, AlCH_2CH_3), 1.38 (12H, dd (pseudo t), AlCH_2CH_3), 1.47 (6H, t, AlCH_2CH_3), 1.61 (6H, t, AlCH_2CH_3), 1.75 (12H, s, N$(CH_3)_2$), 2.06 (4H, t, $CH_2N(CH_3)_2$), 3.04 (4H, t, NCH_2); ^{13}C NMR (C_6D_6, 298 K) δ −0.48 (AlCH_2CH_3), 1.34 (AlCH_2CH_3), 4.90 (AlCH_2CH_3), 10.26 (AlCH_2CH_3), 11.03 (AlCH_2CH_3), 11.06 (AlCH_2CH_3), 43.43 ($CH_2N(CH_3)_2$), 45.70 (N$(CH_3)_2$), 63.81 (NCH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 158.9; MS (70 eV) *m*/*z* 483 ($M^+ - CH_2CH_3$). Anal. Calcd for $C_{24}H_{60}Al_4N_4$: C, 56.21; H, 11.80; N, 10.93. Found: C, 55.74; H, 11.01; N, 10.17.

trans-**4b** (data obtained from an equilibrium mixture): ^{1}H NMR (C_6D_6, 298 K) two dq patterns of AlCH_2CH_3 (in the Al_2N_2 ring) and those of AlCH_2CH_3 (in the AlN_2C_2 ring) are superimposed in the region of δ 0.16−0.45, δ 1.36 (12H, dd (pseudo t), AlCH_2CH_3), 1.50 (12H, dd (pseudo t), AlCH_2CH_3), 1.75 (12H, s, N$(CH_3)_2$), 2.02 (4H, t, $CH_2N(CH_3)_2$), 3.02 (4H, t, NCH_2); ^{13}C NMR (C_6D_6, 298 K) δ −0.36 (AlCH_2CH_3), 1.45 (AlCH_2CH_3), 11.06 (AlCH_2CH_3), 11.96 (AlCH_2CH_3), 44.34 ($CH_2N(CH_3)_2$), 46.58 (N$(CH_3)_2$), 64.79 (NCH_2).

Preparation of $(MeAlNC_2H_4NMe_2)_6$ (5a). Compound **4a** (0.360 g, 0.90 mmol) was dissolved in dichloromethane (10 mL), and DMEDA (0.158 g, 1.95 mmol) was added at 0 °C. The reaction mixture was warmed slowly to room temperature for 2 h. After evaporation of the solvent, the crude residue was heated at 190 °C for 2 h in a sealed ampule. Recrystallization of the crude product in dichloromethane at −20 °C produced **5a** (0.380 g, 0.50 mmol, 83%) as colorless crystals: mp 167 °C; ^{1}H NMR (C_6D_6, 298 K) δ −0.33 (18H, s, AlCH_3), 2.17 (36H, s, N$(CH_3)_2$), 2.39 (12H, t, $CH_2N(CH_3)_2$), 3.08 (12H, t, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −12.99 (AlCH_3), 43.82 ($CH_2N(CH_3)_2$), 46.78 (N$(CH_3)_2$), 66.25 (NCH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 139.4. Anal. Calcd for $C_{30}H_{78}Al_6N_{12}$: C, 46.84; H, 10.23; N, 21.86. Found: C, 46.52; H, 10.32; N, 21.67.

Preparation of $(EtAlNC_2H_4NMe_2)_6$ (5b). Compound **5b** was prepared by a procedure similar to that used for **5a** with **4b** (0.320 g, 0.80 mmol) and DMEDA (0.135 g, 1.53 mmol). Recrystallization of the crude product in dichloromethane at −20 °C afforded **5b** (0.397 g, 0.46 mmol, 86%) as colorless crystals: mp 179 °C; ^{1}H NMR (C_6D_6, 298 K) δ 0.51 (12H, q, AlCH_2CH_3), 1.49 (18H, t, AlCH_2CH_3), 2.23 (36H, s, N$(CH_3)_2$), 2.50 (12H, t, $CH_2N(CH_3)_2$), 3.28 (12H, t, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −1.05 (AlCH_2CH_3), 10.29 (AlCH_2CH_3), 43.70 ($CH_2N(CH_3)_2$), 46.51 (N$(CH_3)_2$), 66.92 (NCH_2); ^{27}Al NMR (C_6D_6, 298 K) δ 141.2. Anal. Calcd for $C_{36}H_{90}Al_6N_{12}$: C, 50.67; H, 10.64; N, 19.71. Found: C, 50.42; H, 10. 41; N, 20.01.

Table 4. Crystal and Structure Determination Data for *cis*-4b and 5b

	cis-**4b**	**5b**
formula	$C_{24}H_{60}Al_4N_4$	$C_{36}H_{90}Al_6N_{12}$
fw	512.68	426.55
temp, K	293(2)	293(2)
λ(Mo Kα), Å	0.716 09	0.710 69
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	10.695(6)	10.3314(10)
b, Å	21.066(4)	10.942(6)
c, Å	14.747(2)	13.486(3)
α, deg	90	112.95(2)
β, deg	97.89(2)	106.662(13)
γ, deg	90	98.77(2)
V, Å^3	3291(2)	1283.2(7)
Z	4	1
D_{calcd}, Mg m^{-3}	1.035	1.104
abs coeff, mm^{-1}	0.159	0.161
F(000)	1136	468
cryst dimens, mm	1.00 × 0.40 × 0.30	0.53 × 0.40 × 0.20
θ range for data collcn, deg	2.15−21.00	2.05−23.00
intensity variation (%)	<1.0	1.2
no. of rflns measd	3695	3749
no. of indep rflns	3527 (R_{int} = 0.0238)	3570 (R_{int} = 0.0151)
no. of data/restraints/params	3527/6/309	3570/0/244
goodness of fit on F^2	1.090	1.094
final *R* indices[a] ($I > 2\sigma(I)$)	$R = 0.0723$ $R_w = 0.1793$	$R = 0.0529$ $R_w = 0.1178$
R indices (all data)	$R = 0.1227$ $R_w = 0.2194$	$R = 0.0951$ $R_w = 0.1415$
D(*r*) and hole, e Å^{-3}	0.741 and −0.255	0.231 and −0.202

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

Conversion of 2a to 3a. Me_3Al (0.100 g, 1.39 mmol) was added to a dichloromethane solution (10 mL) of **2a** (0.200 g, 1.39 mmol) at 0 °C. The reaction mixture was warmed gradually to room temperature for 2 h. Solvent evaporation afforded **3a** in quantitative yield.

Conversion of 2b to 3b. Et_3Al (0.210 g, 1.84 mmol) was added to a dichloromethane solution (10 mL) of **2b** (0.370 g, 1.83 mmol) at 0 °C. The reaction mixture was warmed slowly to room temperature for 2 h. Solvent evaporation afforded **3b** in quantitative yield**.**

Conversion of 2a to 5a. Compound **2a** (0.210 g, 1.46 mmol) was heated at 190 °C for 2 h in a sealed ampule. Recrystallization of the crude product in dichloromethane at −20 °C afforded **5a** (0.084 g, 0.11 mmol, 45%) as colorless crystals.

Conversion of 2b to 5b. Compound **2b** (0.309 g, 1.53 mmol) was heated at 190 °C for 2 h in a sealed ampule. Recrystallization of the crude product in dichloromethane at −20 °C afforded **5b** (0.101 g, 0.13 mmol, 51%) as colorless crystals.

Molecular Weight Measurements. Molecular weight measurements were carried out cryoscopically under N_2 with benzene as the solvent using an apparatus similar to that described by Shriver.[27] The freezing point depressions of **2a**,**b** and **3a** were found to be 0.78 °C (molality (*m*) = 0.163), 0.90 °C (*m* = 0.193), and 0.77 °C (*m* = 0.159), resulting in calculated (found) molecular weights of 144 (153), 172 (187), and 216 (226), respectively.

^{1}H NMR Study of Isomerization of *cis*-4a to *trans*-4a. Crystals of *cis*-**4a** (ca. 5 mg) were transferred to four 5 mm NMR tubes, and benzene-d_6 (0.6 mL) was added to each NMR tube under an atmosphere of argon. The tubes were sealed and then heated in an NMR probe at 50, 55, 60, and 70 °C, respectively, while the resonances due to the methyl groups

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[27] Shriver, D. F.; Drezdzon, M. A. In *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986; p 38.

on the aluminum atoms, at δ −0.07 for *cis*-**4a** and δ −0.25 for *trans*-**4a**, were monitored periodically by ^{1}H NMR. The isomerization reactions followed reversible first-order kinetics and showed excellent fits of data to a common plot of $-\ln\{1 - [trans\text{-}\mathbf{4a}]/[trans\text{-}\mathbf{4a}]_{eq}\}$ vs time. Equilibrium constants at 50, 55, 60, and 70 °C were measured similarly by ^{1}H NMR after heating four NMR tubes in heated oil baths at controlled (±0.5 °C) temperatures, respectively. After equilibrium was reached, each NMR tube was quickly removed from the oil bath and placed into an ice bath to quench isomerization. The ^{1}H NMR spectrum of each sample was recorded at each equilibrium temperature.

X-ray Structure Determinations for *cis*-4b and 5b. Colorless crystals of *cis*-**4b** and **5b** suitable for X-ray structure determinations were obtained from a mixed solvent of toluene and dichloromethane at −20 °C. Both crystals were mounted in thin-walled glass capillaries under an argon atmosphere and then flame-sealed. Crystallographic details are presented in Table 4.

The determination of the unit cell parameters, the orientation matrix, and the collection of intensity data were made on an Enraf-Nonius CAD-4 diffractometer, employing graphite-monochromated Mo Kα radiation. The unit cell parameters, occurrences of equivalent reflections, and systematic absences in the diffraction data are uniquely consistent with the $P2_1/n$ space group for *cis*-**4b** and $P\bar{1}$ for **5b**. Lorentz and polarization corrections were applied to the intensity data, while no absorption correction was applied. All calculations were performed using the SHELXTL programs.[28] Both structures were solved using direct methods, completed by difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized, updated contributions.

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Supporting Information Available: A figure showing the disordered molecular geometry of *cis*-**4b**, and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and complete bond lengths and angles for *cis*-**4b** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM981032M

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[28] (a) Sheldrick, G. M. SHELXS86. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. SHELXS93: Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1993.