Synthesis, NMR Characterization, and Molecular Structural Studies of a Series of Ortho-Metalated Aluminum−Nitrogen Dimers

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Summary: The thermolysis of 1:1 mole ratio reaction mixtures of $R_3Al/HN(CH_2Ph)_2$, where R = Me, Et, Pr^n, Bu^n, Bu^i and of a 1:2 reaction mixture of Me_3Al with $HN(CH_2Ph)_2$ yield ortho-metalated aminoalane dimers as products. These dimers were characterized by elemental analysis, ^{13}C and ^1H NMR, FT-IR, and single-crystal X-ray determination. The results obtained are discussed in terms of the influence of R on the ease of ortho metalation, structural parameters of the Al_2N_2 ring, and the nature of the alkyl chain conformations in solution and the solid state.

Introduction

Our research group has investigated the synthesis, characterization, spectral properties, and molecular structures of several series of group 13/15 Lewis acid−base complexes and their correspondence to thermolysis products.[1−9] We recently reported[1] that the thermolysis of 1:1 mole ratio reaction mixtures of Me_3Al with $HN(CH_2Ph)_2$ at 120 °C led to the formation of the expected aminoalane dimer $[Me_2AlN(CH_2Ph)_2]_2$. However, thermolysis of the analogous $Me_3Ga/HN(CH_2Ph)_2$ reaction mixture at 120 °C led initially to the formation of the aminogallane dimer, $[Me_2GaN(CH_2Ph)_2]_2$,[6] but before there was total conversion to the dimer, additional alkane elimination occurred. Careful monitoring of the reaction as a function of temperature and time by ^1H NMR spectroscopy established reaction conditions at 155 °C for obtaining the unique GaN-ortho-metalated species $[MeGaN(CH_2Ph)$-μ-$(CH_2C_6H_4)]_2$.[5] The NMR data support a stepwise elimination of 2 equiv of methane from $[Me_2GaN(CH_2Ph)_2]_2$, which results in the ortho-metalation of one benzyl moiety on each nitrogen. Subsequently, thermolysis of the $Me_3Al/HN(CH_2Ph)_2$ reaction mixture at 155 °C led to the formation of the analogous AlN-ortho-metalated dimer and $[MeAlN(CH_2$-$Ph)$-μ-$(CH_2C_6H_4)]_2$ (**1**) was isolated and characterized.[7] To our knowledge, only two other molecular structures of ortho-metalated aminoalane dimers have been reported.[10,11] Thus, we investigated the thermolysis of $R_3Al/HN(CH_2Ph)_2$ reaction systems to study the requirements for orthometalation as a function of the steric bulk of the R group and to establish the generality of this reaction.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were employed for the synthesis and manipulation of all compounds. Hexane and toluene were distilled under nitrogen over calcium hydride. Dibenzylamine, toluene-d_8, and benzene-d_6 (Aldrich) were stored over molecular sieves. Trialkylaluminum reagents (Texas Alkyls) were used as obtained. ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 NMR spectrometer operating at 400.132 and 100.625 MHz, respectively. All ^1H and ^{13}C NMR chemical shifts were referenced to the solvent at 300 K. IR spectra were obtained using split mull samples in Nujol and Kel-F (halocarbon) on KBr plates. EI-MS data were obtained with an electron energy of 70 eV. The samples were introduced using a direct-insertion probe under inert-atmosphere conditions. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Parsippany, NJ. Melting points were obtained using sealed capillaries under nitrogen and are uncorrected.

General Synthesis of Ortho-Metalated Compounds, $[RAlN(CH_2Ph)$-μ-$(CH_2C_6H_4)]_2$. Dibenzylamine (1.00 g, 5.07 mmol) and the respective trialkylaluminum, R_3Al (R = Et, Pr^n, Bu^n, Bu^i) were mixed in a 1:1 mole ratio in 15 mL of toluene at room temperature. A high-pressure reaction tube containing each mixture was placed in an oil bath at 155 ± 5 °C. The progress of each reaction was monitored by ^1H NMR. $[(PhCH_2)_2$-$NAlN(CH_2Ph)$-μ-$(CH_2C_6H_4)]_2$ was synthesized by mixing 2.00 g of dibenzylamine (10.14 mmol) with 0.365 g (5.06 mmol) of Me_3Al in 15 mL of toluene and heating at 155 °C. The time required for conversion to the ortho-metalated product was approximately the same for all five compounds and varied between 21 and 25 days. The solvent was removed in vacuo

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(1) Thomas, C. J.; Krannich, L. K.; Watkins, C. L. *Polyhedron* **1993**, *12*, 389.
(2) Thomas, C. J.; Krannich, L. K.; Watkins, C. L. *Polyhedron* **1993**, *12*, 89.
(3) Schauer, S. J.; Watkins, C. L.; Krannich, L. K.; Gala, R. B.; Gundy, E. M.; Lagrone, C. B. *Polyhedron* **1995**, *14*, 3505.
(4) Lagrone, C. B.; Schauer, S. J.; Thomas, C. J.; Gray, G. M.; Watkins, C. L.; Krannich, L. K. *Organometallics* **1996**, *15*, 2458.
(5) Schauer, S. J.; Lake, C. H.; Watkins, C. L.; Krannich, L. K. *Organometallics* **1996**, *15*, 5641.
(6) Schauer, S. J.; Lake, C. H.; Watkins, C. L.; Krannich, L. K.; Powell, D. H. *J. Organomet. Chem.* **1997**, *549*, 31.
(7) Styron, E. K.; Lake, C. H.; Watkins, C. L.; Krannich, L. K. *Organometallics* **1998**, *17*, 4319.
(8) Lake, C. H.; Schauer, S. J.; Krannich, L. K.; Watkins, C. L. *Polyhedron* **1999**, *18*, 879.
(9) Styron, E. K.; Lake, C. H.; Schauer, S. J.; Watkins, C. L.; Krannich, L. K. *Polyhedron* **1999**, *18*, 1599.
(10) Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257.
(11) Lee, B.; Pennington, W. T.; Robinson, G. H. *Inorg. Chim. Acta* **1991**, *190*, 173.

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to obtain a yellow solid, which was washed with hexane to leave a white solid. Recrystallization from toluene at −15 °C gave X-ray-quality crystals of each compound. All compound yields are reported in terms of recrystallized product. IR and elemental analysis data are given in the Supporting Information.

Synthesis of [AlN-μ-$(CH_2C_6H_4)_2]_x$. Dibenzylamine (1.00 g, 5.07 mmol) and Me_3Al (0.372 g, 5.16 mmol) were mixed neat in a high-pressure reaction tube and placed in a sand bath at 270 °C. The reaction appeared to be complete after heating for 36 h. The light green product was washed with hexanes and dried under vacuum. The product was only sparingly soluble in common organic solvents. X-ray-quality crystals could not be obtained.

Characterization of [EtAlN(CH_2Ph)-μ-$(CH_2C_6H_4)]_2$ (2). Yield: 45%. Mp: 193−197 °C. ^{1}H NMR (C_6D_6): δ_H 0.39 (qd, 2H, H1B); 0.25 (qd, 2H, H1A); 1.30 (t, 6H, H2); 3.76 (d, 2H, H10A); 4.44 (d, 2H, H10B); 7.65 (d, 2H, H13); 7.08 (dd, 2H, H14); 7.16 (dd, 2H, H15); 6.90 (d, 2H, H16); 3.49 (d, 2H, H20A); 4.11 (d, 2H, H20B); 7.26 (m, 4H, H22, H26); 7.25 (m, 4H, H23, H25); 7.13 (m, 2H, H24). ^{13}C NMR (C_6D_6): δ_C −1.8 (C1); 9.44 (C2); 58.72 (C10); 149.98 (C11); 143.5 (C12); 136.81 (C13); 126.49 (C14); 128.92 (C15); 123.98 (C16); 56.10 (C20); 139.53 (C21); 127.76 (C22, C26); 128.97 (C23, C25); 127.56 (C24).

Characterization of [Pr^{n}AlN(CH_2Ph)-μ-$(CH_2C_6H_4)]_2$ (3). Yield: 46%. Mp: 161−165 °C. ^{1}H NMR (C_6D_6): δ_H 0.29 (ddd, 2H, H1A); 0.42 (ddd, 2H, H1B); 1.70 (m, 4H, H2); 1.12 (t, 6H, H3); 3.78 (d, 2H, H10A); 4.45 (d, 2H, H10B); 7.66 (d, 2H, H13); 7.08 (dd, 2H, H14); 7.14 (dd, 2H, H15); 6.90 (d, 2H, H16); 3.50 (d, 2H, H20A); 4.13 (d, 2H, H20B); 7.26 (m 4H, H22, H26); 7.25 (m, 4H, H23, H25); 7.13 (m, 2H, H24). ^{13}C NMR (C_6D_6): δ_C 10.15 (C1); 19.49 (C2); 20.59 (C3); 58.77 (C10); 149.90 (C11); 143.92 (C12); 136.76 (C13); 126.54 (C14); 128.91 (C15); 123.94 (C16); 56.32 (C20); 139.52 (C21); 127.87 (C22, C26); 128.95 (C23, C25); 127.57 (C24).

Characterization of [Bu^{n}AlN(CH_2Ph)-μ-$(CH_2C_6H_4)]_2$ (4). Yield: 31%. Mp: 138−141 °C. ^{1}H NMR (C_6D_6): δ_H 0.29 (ddd, 2H, H1A); 0.42 (ddd, 2H, H1B); 1.66 (m, 4H, H2); 1.46 (h, 4H, H3); 0.97 (t, 6H, H4); 3.80 (d, 2H, H10A); 4.46 (d, 2H, H10B); 7.68 (d, 2H, H13); 7.09 (dd, 2H, H14); 7.16 (dd, 2H, H15); 6.92 (d, 2H, H16); 3.53 (d, 2H, H20A); 4.14 (d, 2H, H20B); 7.28 (m, 4H, H22, H26); 7.26 (m, 4H, H23, H25); 7.13 (m, 2H, H24). ^{13}C NMR (C_6D_6): δ_C 7.06 (C1); 28.35 (C2); 28.01 (C3); 14.17 (C4); 58.75 (C10); 149.93 (C11); 143.97 (C12); 136.76 (C13); 126.55 (C14); 128.92 (C15); 123.97 (C16); 56.28 (C20); 139.51 (C21); 127.92 (C22, C26); 128.94 (C23, C25); 127.60 (C24).

Characterization of [Bu^{i}AlN(CH_2Ph)-μ-$(CH_2C_6H_4)]_2$ (5). Yield: 35%. Mp: 178−181 °C. ^{1}H NMR (C_6D_6): δ_H 0.27 (dd, 2H, H1A); 0.46 (dd, 2H, H1B); 2.11 (n, 2H, H2); 1.09 (d, 6H, H3); 1.13 (d, 6H, H4); 3.81 (d, 2H, H10A); 4.43 (d, 2H, H10B); 7.69 (d, 2H, H13); 7.08 (dd, 2H, H14); 7.15 (dd, 2H, H15); 6.91 (d, 2H, H16); 3.55 (d, 2H, H20A); 4.14 (d, 2H, H20B); 7.31 (m, 4H, H22, H26); 7.27 (m, 4H, H23, H25); 7.15 (m, 2H, H24). ^{13}C NMR (C_6D_6): δ_C 19.22 (C1); 26.51 (C2); 28.26 (C3); 28.03 (C4); 58.82 (C10); 149.69 (C11); 144.40 (C12); 136.78 (C13); 126.63 (C14); 128.85 (C15); 123.93 (C16); 56.74 (C20); 139.48 (C21); 128.07 (C22, C26); 128.89 (C23, C25); 127.61 (C24).

Characterization of [$(PhCH_2)_2$NAlN(CH_2Ph)-μ-$(CH_2C_6H_4)]_2$ (6). Yield: 25.1%. Mp: 285 °C dec. ^{1}H NMR (C_6D_6): δ_H 3.85 (d, 2H, H10); 4.59 (d, 2H, H10); 7.73 (d, 2H, H13); 6.99 (m, 2H, H14); 6.99 (m, 2H, H15); 6.56 (d, 2H, H16); 3.49 (d, 2H, H20); 4.30 (d, 2H, H20); 7.64 (d, 4H, H22, H26); 7.37 (dd, 4H, H23, H25); 7.24 (m, 2H, H24); 3.94, 4.11 (dd, 8H, H30, H37); 7.17 (m, 8H, H32, H36, H39, H43); 7.08−7.10 (m, 8H, H33, H35, H40, H42); 7.08−7.10 (m, 4H, H34, H41).

Characterization of [AlN-μ-$(CH_2C_6H_4)_2]_x$ (7). Yield: 26%. Mp: >300 °C dec. ^{1}H NMR (C_6D_6): δ_H 3.59 (d, 2H, H10); 4.02 (d, 2H, H10); 7.42 (d, 2H, H13); 7.07 (dd, 2H, H14); 7.09 (dd, 2H, H15); 6.62 (d, 2H, H16). ^{13}C NMR (C_6D_6): δ_C 60.54 (C10); 149.2 (C11); 142.0 (C12); 137.2 (C13); 126.6 (C14); 128.9 (C15); 124.2 (C16).

Data Collection, Solution, and Refinement of X-ray Crystallographic Studies. For each of the structural studies, an X-ray-quality crystal was sealed into a thin-walled glass capillary under anaerobic conditions. The crystals of compounds **2**−**5** were mounted and aligned upon an Enraf-Nonius CAD4 single-crystal diffractometer. Intensity data (Mo Kα, λ = 0.710 73 Å) were collected at room temperature using graphite-monochromated radiation. All data were corrected for Lorentz and polarization effects as well as for absorption. The crystallographic calculations for **2**−**5** were carried out on an IBM-PC using the Siemens SHELXTL-PC program package.[12] The analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[13] Each structure was solved by the use of direct methods. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were not located directly but were input in calculated positions with d(C−H) = 0.96 Å and with the appropriate staggered-tetrahedral geometry.[14] The isotropic thermal parameter of each hydrogen atom was defined as equal to the U_{eq} value of that carbon atom to which it was bonded. Refinement continued until convergence was reached with $\Delta/\sigma < 0.001$; the structural solution was then verified by means of a final difference Fourier synthesis in which no chemically meaningful residuals were found.

The crystal structure data for **6** (Mo Kα, λ = 0.710 73 Å) were collected using a Siemens P4 diffractometer equipped with a SMART/CCD detector at 203(2) K. The structure was solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix, least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogens were treated as idealized contributions. There are two independent, but chemically equivalent, half-molecules in the asymmetric unit, both of which lie on crystallographic inversion centers. Because the structural data for the two molecules are very similar (within 3σ), data are reported in Table 3 for molecule 1 and in the Supporting Information for molecule 2. All software and sources of the scattering factors are contained in the SHELTXL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Selected bond distances and angles for structures **1**−**5** are listed in Tables 1 and 2 and for **6** in Table 3.

Results and Discussion

Thermolysis of 1:1 mole ratio mixtures of R_3Al with $HN(CH_2Ph)_2$ at 100−120 °C led to the formation of the expected aluminum−nitrogen dimer, $[R_2AlN(CH_2Ph)_2]_2$, where R = Me,[1] Et,[9] Pr^n,[15] Bu^n,[15] and Bu^i.[15] Additional heating of these mixtures at 155 °C in toluene solution over a period of 3 weeks resulted in the formation of $[RAlN(CH_2Ph)$-μ-$(CH_2C_6H_4)]_2$, as reported for the R = Me derivative.[7] Monitoring each of the reactions by ^{1}H NMR, as a function of time, suggests that the reactions for R = Et, Pr^n, Bu^n, and Bu^i follow generally the same pathway as that of the R = Me reaction.[7] While the time required for reaction completion does not depend on the nature of the R group on aluminum, the percent yield of recovered product, which ranges from 57% for R = Me[7] (**1**) to 31% for R = Bu^n (**4**), decreases with increasing steric bulk of R.

Because thermolysis of 1:1 mixtures of R_3Al and dibenzylamine led to elimination of one R group at 120 °C and to two R groups at 155 °C from the Al atom,

(12) Siemens SHELXTL-PC Manual, Release 4.1; Siemens Analytical Instruments, Madison, WI, 1990.
(13) . *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99−101, 149−150.
(14) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.
(15) Styron, E. K. Ph.D. Dissertation, University of Alabama at Birmingham, March 1999.

experimental conditions were sought which would lead to the removal of all three R groups. Two approaches were taken. First, thermolysis of 1:1 mixtures of Me_3Al and dibenzylamine was attempted at higher temperatures. Heating the reactants neat in a high-pressure tube inserted into a 270 °C sand bath led to the formation of a light green solid. Elemental analysis and ^1H and ^{13}C NMR data indicate that all three methyl groups were eliminated from the Al moiety upon heating at 270 °C and that the resulting Al−N compound is fully ortho-metalated, $[AlN\text{-}\mu\text{-}(CH_2C_6H_4)_2]_x$. Unfortunately, all attempts at growing X-ray-quality crystals failed. The presence of a parent ion peak with *m*/*z* 572.18 in the EI mass spectrum suggests the existence of a trimer, $C_{35}H_{29}Al_3N_3$, in the gas phase. This ion could arise from the loss of a benzyl group (*m*/*z* 91) from the trimer, $C_{42}H_{36}Al_3N_3$. The ion peaks at *m*/*z* 91 and 572 are the most prominent peaks in the mass spectrum and are of almost equal intensity. Typically, EI mass spectra of aminoalanes exhibit $[M-R]^+$ as the molecular ion.[1,2,4,16,17] The formation of a trimer in the gas phase is not unexpected, as Waggoner and Power[18] have shown that the reactions of trimethylaluminum with bulky primary amines upon heating lead to compounds of the type $[MeAlNR]_x$, where *x* depends on the steric nature of R.

The second approach involved performing a thermolysis reaction between Me_3Al and dibenzylamine in a 1:2 mole ratio at 155 °C. This reaction led to an ortho-metalated species, **6**, wherein a dibenzylamino moiety has replaced the methyl group on the Al. An independent reaction of a 1:1 mole reaction mixture of **1** and dibenzylamine at 155 °C also led to the formation of **6**.

^{13}C and ^1H NMR Studies. The ^1H and ^{13}C NMR chemical shift assignment procedure for the benzyl groups in compounds **2**−**5** was similar to that for **1**.[7] (See Figure 1 for atom numbering.) The ^1H NMR assignments were determined from ^1H NMR 2-D COSY spectra and by comparing the results of the ^1H NMR 2-D NOESY spectra with calculated H−H distances from the X-ray data for the compounds.[5,7] The ^{13}C NMR chemical shift assignments were obtained by a combination of ^{13}C decoupled and ^{13}C DEPT-45 NMR spectra, 2-D $^{13}C\{^1H\}$ heteronuclear $^1J(C,H)$ correlations (HETCOR), and 2-D $^1H\{^{13}C\}$ heteronuclear $^3J(C,H)$ correlations (HMBC).[5,7] The ^1H and ^{13}C NMR chemical shifts for the ortho-metalated and normal benzyl groups in compounds **1**−**5** are similar to each other and show no significant variation with the nature of the attached alkyl group.

The ^1H NMR chemical shifts for the alkyl groups in compounds **2**−**5** were determined from the 1-D ^1H NMR and 2-D ^1H COSY NMR spectra. These spectra are interesting in that restricted conformational averaging is observed on the NMR time scale, leading to chemical shift nonequivalence for most of the methylene protons, as well as for the methyl protons in the Bu^i group of **5**. The C(1) CH_2 protons are nonequivalent and appear as AB quartets with further $^3J(H,H)$ coupling; their ^1H NMR chemical shift difference, $\Delta\delta_H$ (ppm), ranges from 0.14 to 0.19 ppm. Assignments for the chemically nonequivalent C(1) methylene protons in **2**−**5** and for the two methyl groups in **5** were made by comparison of the ^1H 2-D NMR NOESY data with calculated H−H distances from the X-ray data. Analysis of the $^3J(H,H)$ coupling data suggests that the Pr^n group is in a trans conformation in solution with regard to the C(1)−C(2) bond, similar to that demonstrated in the solid-state molecular structure (Figure 1). The ^1H NMR spectrum for the *n*-butyl group in **4** is similar to that of **3** for the C(1) and C(2) methylene protons; however, the C(3) CH_2 protons demonstrate rapid conformational averaging in solution. Variable-temperature ^1H NMR studies of compounds **2**−**5** conducted in toluene-d_8 solution from 30 to 90 °C detected no additional conformational averaging with increased temperature. The ^{13}C NMR chemical shifts for the alkyl groups in **1**−**5** were determined by comparison of the ^{13}C 2-D NMR heteronuclear-correlated spectra with the known ^1H NMR chemical shifts. The δ_C data for **1**−**5** are comparable to those reported for $[R_2AlN(CH_2Ph)_2]_2$,[1,9,15] except that the C(1) δ_C signal is to higher field by about 4 ppm in the ortho-metalated dimers.

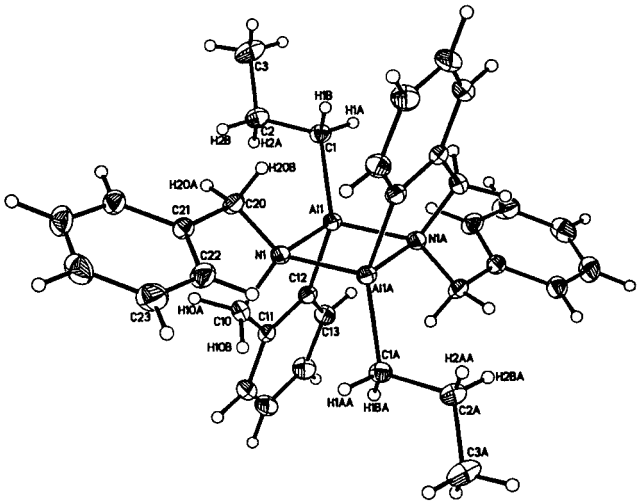

Figure 1. ORTEP diagram of $[Pr^nAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2\text{-}C_6H_4)]_2$ (**3**). Thermal ellipsoids at 20% probability.

Almost complete ^1H NMR chemical shift assignments were made for $[(PhCH_2)_2NAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ (**6**). The ^1H NMR chemical shift assignments for that portion of **6** common with **1**−**5** are consistent with, but slightly different from, those of compounds **1**−**5**. The ^1H and ^{13}C NMR spectra of **7** showed only one set of resonances each for all of the ortho-metalated benzyl groups in the molecule, suggesting an oligomeric form where all the benzyl groups are chemically equivalent. The ^1H and ^{13}C NMR chemical shift assignments and values for **7** are similar to those of the orthometalated benzyl groups in **1**−**5**.

X-ray Crystallographic Data. X-ray structures of the five ortho-metalated aminoalane dimers were determined in order to identify any structural differences in the compounds due to the nature of the alkyl group bound to the aluminum atoms and for comparison with the structure of **1**,[7] where R = Me. The ORTEP drawing of the molecular structure of compound **3** is given in Figure 1. Selected structural data for **1**−**6** are given in Tables 1−3.All the ortho-metalated dimers crystallized

(16) Cesari, M.; Cucinella, S. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic: London, 1987; Vol. 1, Chapter 6.
(17) Bradley, D. C.; Harding, I. S.; Maia, I. A.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2969.
(18) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

Table 1. Selected Bond Lengths (Å)

bond	1[a]	2	3	4	5
Al(1)−N(1)	1.984(4)	1.977(2)	1.982(2)	1.979(3)	1.978(2)
Al(1)−C(1)	1.911(5)	1.951(2)	1.949(3)	1.962(4)	1.969(3)
Al(1)−C(12)	1.965(5)	1.970(3)	1.959(3)	1.957(4)	1.966(3)
Al(1)−N(1A)	1.945(3)	1.947(2)	1.947(2)	1.955(3)	1.960(3)
N(1)−C(10)	1.497(5)	1.496(3)	1.493(3)	1.504(5)	1.491(3)
N(1)−C(20)	1.496(6)	1.498(3)	1.501(4)	1.477(5)	1.497(3)
C(10)−C(11)	1.516(8)	1.516(5)	1.514(4)	1.522(5)	1.514(3)
C(11)−C(12)	1.400(6)	1.393(3)	1.400(4)	1.391(5)	1.402(3)
C(11)−C(16)	1.394(6)	1.392(3)	1.385(4)	1.389(5)	1.387(3)
C(12)−C(13)	1.405(8)	1.407(5)	1.396(4)	1.399(5)	1.401(4)

[a] Data taken from ref 7.

Table 2. Selected Bond Angles (deg)

angle	1[a]	2	3	4	5
N(1)−Al(1)−C(1)	116.0(2)	115.7(1)	115.6(1)	115.0(1)	116.6(1)
N(1)−Al(1)−C(12)	89.9(2)	89.8(1)	89.9(1)	89.9(1)	89.5(1)
C(1)−Al(1)−C(12)	126.2(2)	129.3(1)	129.2(1)	124.7(2)	131.1(1)
C(1)−Al(1)−N(1A)	116.3(2)	114.0(1)	113.7(1)	117.0(1)	113.6(1)
N(1)−Al(1)−N(1A)	91.2(1)	91.4(1)	91.5(1)	90.7(1)	91.3(1)
Al(1)−N(1)−C(20)	114.8(3)	115.8(1)	114.5(2)	113.9(2)	117.2(1)
C(12)−Al(1)−N(1A)	107.7(2)	107.9(1)	108.3(1)	110.7(1)	105.7(1)
Al(1)−N(1)−Al(1A)	88.8(1)	88.6(1)	88.5(1)	89.3(1)	88.7(1)
Al(1)−N(1)−C(10)	107.6(3)	108.0(2)	107.8(2)	108.2(2)	107.5(1)
C(20)−N(1)−Al(1A)	115.5(3)	116.0(2)	116.6(2)	113.7(2)	115.2(2)
C(10)−N(1)−C(20)	109.3(3)	109.6(2)	110.1(2)	111.2(3)	108.5(2)
C(10)−C(11)−C(12)	119.3(4)	119.2(2)	119.0(2)	119.5(3)	118.3(2)
C(10)−N(1)−Al(1A)	119.2(3)	117.3(1)	117.3(2)	118.5(2)	118.7(2)
C(12)−C(11)−C(16)	121.7(5)	122.2(3)	121.4(3)	121.5(4)	121.9(2)
N(1)−C(10)−C(11)	112.7(3)	112.1(2)	112.2(2)	112.1(3)	111.9(2)
Al(1)−C(12)−C(13)	134.3(3)	134.9(2)	134.0(2)	133.1(3)	134.9(2)
Al(1)−C(12)−C(11)	108.7(4)	108.7(2)	108.8(2)	109.3(2)	108.8(2)
C(11)−C(12)−C(13)	117.0(4)	116.2(2)	117.0(3)	117.5(3)	116.1(2)

[a] Data taken from ref 7.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 6 (Molecule 1)

Al(1A)−N(1A)	1.971(4)	C(10A)−C(11A)	1.514(7)
Al(1A)−N(2A)	1.776(4)	C(11A)−C(12A)	1.395(6)
Al(1A)−C(12A)	1.938(5)	C(11A)−C(16A)	1.407(6)
Al(1A)−N(1AA)	1.944(4)	C(12A)−C(13A)	1.387(7)
N(1A)−C(10A)	1.494(6)	N(2A)−C(30A)	1.444(6)
N(1A)−C(20A)	1.481(6)	N(2A)−C(37A)	1.480(6)

N(1A)−Al(1A)−N(2A)	118.60(19)
N(1A)−Al(1A)−C(12A)	90.70(18)
N(2A)-Al(1A)−C(12A)	121.9(2)
N(2A)−Al(1A)−N(1AA)	115.97(17)
N(1A)−Al(1A)−N(1AA)	90.60(17)
Al(1A)−N(1A)−C(20A)	113.7(3)
C(12A)−Al(1A)−N(1AA)	112.5(2)
Al(1A)−N(1A)−Al(1C)	89.40(17)
Al(1A)−N(1A)−C(10A)	107.7(3)
C(20A)−N(1A)−Al(1C)	113.3(3)
C(10A)−N(1A)−C(20A)	110.3(4)
C(10A)−C(11A)−C(12A)	119.8(4)
C(10A)−N(1A)−Al(1C)	120.6(3)
C(12A)−C(11A)−C(16A)	121.1(5)
N(1A)−C(10A)−C(11A)	111.8(4)
Al(1A)−C(12A)−C(13A)	134.6(4)
Al(1A)−C(12A)−C(11A)	108.4(4)
C(11A)−C(12A)−C(13A)	116.9(5)

with a planar Al_2N_2 core that possesses inversion symmetry. The asymmetric unit of **2**−**5** consists of half of the appropriate dimeric molecule, while that of **6** consists of two half-molecules. The structure of the Al_2N_2 ring is a slightly distorted square plane where the internal angles are very similar, ranging from 90.60(17)° for **6** to 91.4(1)° for **2** for the N−Al−N and from 88.5(1)° for **3** to 89.40(17)° for **6** for the Al−N−Al angles. The two Al−N bond distances associated with each four-membered core are slightly asymmetric. The Al−N distances (1.971(4) Å for **6** to 1.984(4) Å for **1**) included in the five-membered ortho-metalated ring are slightly longer than the Al−N distances (1.944(4) Å for **6** to 1.960(3) Å for **5**) in the four-membered core. Varying the steric bulk of the R group bound to the group 13 metal atom had only a minor impact on the Al−N bond distances. These geometries are representative of those found in dimeric aminoalanes of the type $[R_2AlNR'_2]_2$.[4,16,17,19] The Al−N distance associated with the $(PhCH_2)_2N$ ligand in **6** (Al(1A)−N(2A) bond distance is 1.776(4) Å) is significantly different. This distance is similar to that reported in systems containing a four-coordinate aluminum atom bonded to a three-coordinate nitrogen atom.[18,20,21] Haaland has suggested that when the aluminum and nitrogen are three-coordinate Al−N bonds contain a greater percentage of covalent character and therefore should be shorter than the four-coordinate case.[22] The angles about the aluminum atoms in all the compounds are highly distorted, as previously observed in the structure of **1**, due to the incorporation of the aluminum atom in the five-membered ring formed upon orthometalation. The internal angles and Al−N distances for the Al_2N_2 ring in **1**−**6** are comparable with those reported for the [Bu^{t}Al-iminodibenzyl] orthometalated dimer.[11] The *n*-propyl (**3**) and *n*-butyl (**4**) alkyl chains are in an extended trans conformation in the solid state. The H(1A)−C(1)−C(2)−H(2A) and H(1B)−C(1)−C(2)−H(2B) angles are 179.5 and 178.8°, respectively, in compound **3** (see Figure 1) with similar values for the dihedral angles about the C(1)−C(2) (174.7, 173.2°) and C(2)−C(3) (175.9, 175.9°) bonds in **4**, suggesting that the alkyl chain conformations are similar in solution and the solid state.

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Supporting Information Available: Tables of summary of crystallographic data, X-ray crystal data, structure solution and refinement, atomic coordinates, interatomic distances and angles, and hydrogen atom coordinates for compounds **2**−**6**, IR data and elemental analyses, ^{1}H NMR spectra of the alkyl regions of **2**−**5**, and COSY spectra of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Schauer, S. J.; Robinson, G. H. *J. Coord. Chem.* **1993**, *30*, 197.
(20) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1969**, 2279.
(21) Waggoner, K. M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.
(22) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 1.