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Synthesis and Characterization of an Orthometalated Aminoalane, $[MeAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$: Molecular Structures of $[MeAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ and $[Me_2AlN(CH_2Ph)_2]_2$

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The chemical reactivity of organoaluminum,[1−7] -gallium,[2−5] and -indium[2,4] compounds toward amines and the properties of the resulting adducts and condensation products are of current interest due to their possible use as precursors for the synthesis of electronic and ceramic materials. We have been interested in these systems and have reported the synthesis and characterization of three series of Me_3M·secondary amine adducts (M = Al, Ga, In)[8,9] and two series of aminoalane[9] and aminogallane[10] dimers, obtained from adduct thermolysis. Reaction of Me_3Ga with $HN(CH_2Ph)_2$ in toluene solution at 120 °C leads to initial aminogallane dimer formation, but before conversion of the adduct to the dimer is complete, additional CH_4 elimination occurs.[10,11] Subsequent heating of the reaction mixture at 150 °C leads to the formation of the novel aminogallane orthometalated dimer $[MeGaN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$.[11] Therefore, the analogous reaction of Me_3Al with $HN(CH_2Ph)_2$ in 1:1 mol ratio in toluene solution was followed as a function of temperature and time by ^1H and ^{13}C NMR spectroscopy in order to monitor the ease of 1,2-CH_4 elimination and possible orthometalated aminoalane dimer formation.

Addition of Me_3Al to $HN(CH_2Ph)_2$ in 1:1 mol ratio at −70 °C leads to the formation of the $Me_3Al·HN(CH_2Ph)_2$ adduct (**3**), whose synthesis,[9] characterization,[9] and molecular structure[12] have been reported. Careful thermolysis of **3** at 120 °C in toluene solution yields the aminoalane dimer, $[Me_2AlN(CH_2Ph)_2]_2$, **2**, via CH_4 elimination.[9] The $Me_3Al/HN(CH_2Ph)_2$ reaction mixture was then heated gradually from 120 to 150 °C, and the composition of the reaction mixture was monitored over this temperature range by ^1H NMR for three weeks. The ^1H NMR spectral data suggest that the thermolysis of **2**, which ultimately leads at 150 °C to the formation of **1**, follows a reaction scheme similar to that for the thermolysis of $[Me_2GaN(CH_2Ph)_2]_2$, where there is a stepwise elimination of 2 equiv of CH_4 from the dimer, which results in the orthometalation of one benzyl moiety on each nitrogen.[11]

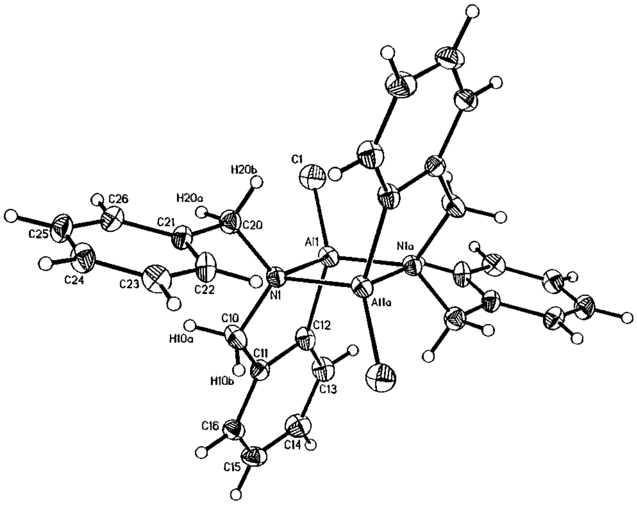

Figure 1. Molecular structure of **1** showing the atom-labeling scheme.

The molecular structure of **1** is shown in Figure 1. Details of the X-ray data collection are given in Table 1, and selected interatomic distances and angles are listed in Table 2. The structure of **1** exhibits a center of symmetry, indicating that the four-membered Al_2N_2 core is planar. The Al_2N_2 ring has slightly distorted square geometry, with internal angles of 88.8(1)° and 91.2(1)°. The Al−N bond distances of 1.984(4) and 1.945(3) Å are typical of those found in dimeric aminoalanes.[7,13,14] The Al(1)···Al(1a) and N(1)···N(1a) cross-ring distances of 2.748 and 2.808 Å, respectively, suggest no bonding interactions. Significant distortions from tetrahedral geometry about the aluminum atoms are observed, probably due to the formation of the five-membered orthometalated ring, with, for example, C(1)−Al(1)−C(12) = 126.2(2)° and N(1)−Al(1)−C(12) = 89.9(2)°. The structure of **1** is isomorphous with its

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Table 1. Summary of Crystallographic Data for 1 and 2

	1	2
formula	$C_{30}H_{32}Al_2N_2$	$C_{32}H_{40}Al_2N_2$
formula weight	474.5	506.6
space group	$P2_1/c$	$Cmc2_1$
crystal system	monoclinic	orthorhombic
temperature(K)	297	296
a (Å)	9.1208(9)	15.8358(25)
b (Å)	19.4907(24)	11.8798(19)
c (Å)	7.5259(14)	15.6772(25)
β (deg)	100.104(12)	
V (Å^3)	1317.1(7)	2949.1(15)
Z	2	4
D_{calc} (g/cm^3)	1.196	1.141
crystal size (mm)	0.20 × 0.20 × 0.10	0.30 × 0.25 × 0.20
absorption coefficent (mm^{-1})	0.131	0.121
F(000)	504	1088
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range (deg)	5.0−45.0	5.0−45.0
scan type	$2\theta-\omega$	$2\theta-\omega$
index ranges	$-9 \leq h \leq 0, -20 \leq k \leq 0, -8 \leq l \leq 8$	$-16 \leq h \leq 16, -12 \leq k \leq 12, 0 \leq l \leq 16$
no. of reflections collected	2452	3053
no. of independent reflections	1236 (R_{merge} = 2.50%)	1050 (R_{merge} = 2.62%)
no. of observed reflections	690 ($F > 6.0\sigma$)	829 ($F > 6.0\sigma$)
R, R_w	3.58, 3.84 (6σ data)	3.59, 3.98 (6σ data)
R, R_w (all data)	9.19, 5.63	4.96, 5.15
largest diff peak/hole (e Å^{-3})	0.29/−0.31	0.22/−0.21

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

Al(1)−N(1)	1.984 (4)	Al(1)−C(1)	1.911 (5)
Al(1)−C(12)	1.965 (5)	Al(1)⋯Al(1a)	2.748 (3)
Al(1)−N(1a)	1.945 (3)	N(1)−C(10)	1.497 (5)
N(1)−C(20)	1.496 (6)	N(1)−Al(1a)	1.945 (3)
C(10)−C(11)	1.516 (8)	C(11)−C(12)	1.400 (6)
C(11)−C(16)	1.394 (6)	C(12)−C(13)	1.405 (8)
N(1)−Al(1)−C(1)	116.0 (2)	N(1)−Al(1)−C(12)	89.9 (2)
C(1)−Al(1)−C(12)	126.2 (2)	C(1)−Al(1)−N(1a)	116.3 (2)
N(1)−Al(1)−N(1a)	91.2 (1)	Al(1)−N(1)−C(20)	114.8 (3)
C(12)−Al(1)−N(1a)	108.7 (2)	Al(1)−N(1)−Al(1a)	88.8 (1)
Al(1)−N(1)−C(10)	107.6 (3)	C(20)−N(1)−Al(1a)	115.5 (3)
C(10)−N(1)−C(20)	109.3 (3)	C(10)−C(11)−C(12)	119.3 (4)
C(10)−N(1)−Al(1a)	119.2 (3)	C(12)−C(11)−C(16)	121.7 (5)
N(1)−C(10)−C(11)	112.7 (3)	Al(1)−C(12)−C(13)	134.3 (3)
Al(1)−C(12)−C(11)	108.7 (4)	C(11)−C(12)−C(13)	117.0 (4)

gallium analogue, $[MeGaN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$.[11] As expected, the Al−N distances in **1** are shorter than the Ga−N distances, 2.045(3) and 2.018(3) Å, in the gallium orthometalated dimer. To our knowledge, structural data have been reported for only two other Al−N orthometalated dimers, $[\{Me(\mu\text{-}NPh_2)Al\}_2NPh(\mu\text{-}C_6H_4)]\cdot 0.5PhMe$[15] (**4**) and [Bu^{i}Al−iminodibenzyl][16] (**5**). The structure of **4** consists of a central $\{Me(\mu\text{-}NPh_2)\text{-}Al\}_2$ core with the Al atoms also being bonded to a bridging $-NPh(\mu\text{-}C_6H_4)$ group through the nitrogen for one aluminum and the *ortho* position of the phenyl ring for the other. The structure of **5** is more appropriately compared to that of **1**. In **5**, the two Al−N distances are 2.040(7) and 1.949(7) Å and the Al−N−Al and N−Al−N angles are 89.4(2)° and 90.6(2)°, respectively, for the planar Al_2N_2 core.

The molecular structure of **2** was determined for comparison with that of **1** and the related aminogallane dimer $[Me_2GaN(CH_2Ph)_2]_2$[10] and is given in Figure 2. A summary of the X-ray data collection is given in Table 1, and selected interatomic distances and angles are listed in Table 3. Interestingly, the four-membered Al_2N_2 core is not planar, but slightly puckered, with an angle of fold about the N(1)⋯N(1a) axis of 4.0° as defined by the intercept of the planes N(1)−Al(1)−N(1a) and N(1)−Al(2)−N(1a). The internal angles of the Al_2N_2 ring are N(1)−Al(1)−N(1a) = 90.9(2)°, N(1)−Al(2)−N(1a) = 90.7(3)°, and Al(1)−N(1)−Al(2) = Al(1)−N(1a)−Al(2) = 89.1(1)°. These data indicate that the Al_2N_2 core in **2** adopts a slightly folded square geometry in contrast to the planar geometry in **1**. The structure of **2** is isomorphous with that of $[Me_2GaN(CH_2Ph)_2]_2$.[10] The

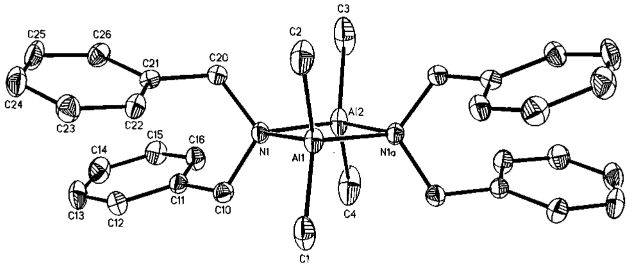

Figure 2. Molecular structure of **2** showing the atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Al(1)⋯Al(2)	2.783 (3)	Al(1)−N(1)	1.982 (4)
Al(1)−C(1)	1.962 (7)	Al(1)−C(2)	1.981 (10)
Al(1)−N(1a)	1.982 (4)	Al(2)−N(1)	1.984 (4)
Al(2)−C(3)	1.977 (9)	Al(2)−C(4)	1.951 (11)
Al(2)−N(1a)	1.984 (4)	N(1)−C(10)	1.512 (7)
N(1)−C(20)	1.498 (7)		
N(1)−Al(1)−C(1)	111.4 (2)	C(1)−Al(1)−C(2)	118.0 (4)
N(1)−Al(1)−C(2)	111.0 (3)	N(1)−Al(1)−N(1a)	90.9 (2)
C(1)−Al(1)−N(1a)	111.4 (2)	C(2)−Al(1)−N(1a)	111.0 (3)
N(1)−Al(2)−C(3)	109.2 (3)	C(3)−Al(2)−C(4)	118.5 (5)
N(1)−Al(2)−C(4)	112.9 (3)	N(1)−Al(2)−N(1a)	90.7 (3)
C(3)−Al(2)−N(1a)	109.2 (3)	C(4)−Al(2)−N(1a)	112.9 (3)
Al(1)−N(1)−Al(2)	89.1 (1)	Al(1)−N(1)−C(10)	113.7 (3)
Al(2)−N(1)−C(10)	114.2 (4)	Al(1)−N(1)−C(20)	114.5 (4)
Al(2)−N(1)−C(20)	113.0 (3)	C(10)−N(1)−C(20)	110.8 (3)
N(1)−C(10)−C(11)	115.2 (4)	N(1)−C(20)−C(21)	116.8 (4)

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Al−N bond distances of 1.982(4) and 1.984(4) Å in **2** are slightly shorter than the respective Ga−N distances of 2.042(6) and 2.045(6) Å for the gallium analogue. The fold angle about the N(1)···N(1a) axis in the gallium analogue is 2.7°. The bond angles and distances for the Al_2N_2 core are well within the range of values reported for other aminoalane dimers derived from secondary amines.[7,13,14] The Al−N distance in **3**, which is formally a dative bond, has been reported as 2.058 Å.[12]

Complete ^1H and ^{13}C NMR chemical shift assignments for **1** in C_6D_6 solution were made using a combination of 1-D and 2-D NMR experiments. The aliphatic region of the ^1H NMR spectrum for **1** consists of a single resonance for the Me-Al protons and four doublets for the CH_2 benzyl protons. Each CH_2 proton in the monomer unit has a different δ_H value. These protons are labeled 10a, 10b, 20a, and 20b in Figure 1. The aromatic region of the ^1H NMR spectrum consists of two distinct subspectra, one for the phenyl group (three distinct resonances) and one for the four protons in the metalated benzyl group (four distinct resonances). ^1H homonuclear-decoupled and 2-D COSY spectra were used to establish the following connectivities: H(13)−H(14)−H(15)−H(16); H(22)−H(23)−H(24); H(20a)−H(20b); and H(10a)−H(10b). Assignments for H(20a), H(20b), H(10a), H(10b), H(13), and H(16) were accomplished using a combination of ^1H 2-D NOESY data and distances calculated from the molecular structure of **1**. For example, the NOESY spectrum shows cross-peaks from the protons on the two methyl groups to only three of the four CH_2 protons. Examination of the relative distances from the molecular structure data indicates that protons 10b, 20a, and 20b have at least one contact less than a distance 3 Å to the methyl group protons, but that the closest contact for proton 10a is 3.88 Å. H(16) and H(13) can be differentiated by NOESY contacts of H(16) to H(10a) (2.56 Å) and H(10b) (2.59 Å). Likewise, H(20b) is identified by its contact to H(13) (3.21 Å), whereas there is no contact for H(20a). The three quaternary carbon ^{13}C resonances were identified by comparison of the $^{13}C\text{-}\{^1H\}$ decoupled and DEPT-45 spectra. The δ_C for C(12) is easily determined due to its very broad resonance, resulting from the quadrupolar relaxation of the directly attached aluminum. All the remaining ^{13}C NMR resonance assignments were made using ^1J(C,H) correlations obtained from the $^{13}C-\{^1H\}$ 2-D HETCOR experiment. Assignments for C(11) and C(21) were made based on ^3J(C,H) correlations obtained from the $^1H-\{^{13}C\}$ 2-D HMBC experiment. The HMBC and NOESY correlations, as well as comparison to previously reported assignments for the gallium analogue,[11] were used as a final check on the ^1H and ^{13}C NMR chemical shift values.

Other novel molecular architectures from these interesting group 13/15 systems are under investigation in our laboratory.

Experimental Section

General Procedures. The synthesis, solution preparation, crystal mounting, and manipulations of all compounds in this study were performed using standard Schlenk, vacuum line, and drybox inert atmosphere techniques. Compounds **2**[9] and **3**[9] were synthesized as previously reported. $HN(CH_2Ph)_2$ was dried over KOH and distilled under vacuum prior to use. Toluene was distilled under an atmosphere of N_2 after being stored over calcium hydride. Benzene-d_6 (Aldrich) was stored over molecular sieves. Me_3Al (Texas Alkyls) was used as obtained. ^1H and ^{13}C NMR data for **1** were collected on a Bruker DRX-400 NMR spectrometer, using 0.1 M solutions in benzene-d_6, and referenced to the solvent. Standard Bruker programs were used for the 1-D and 2-D NMR experiments as described in the text. FT-IR data were collected on a Bruker Vector 22 FT spectrometer using samples prepared as Kel-F(halocarbon) and Nujol mulls on KBr plates. Elemental analysis of **1** was performed by E & R Microanalytical Laboratory, Parsippany, NJ.

Synthesis of $[MeAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$, 1. A 1.00 g sample of Me_3Al (13.9 mmol), 2.74 g of dibenzylamine (13.9 mmol), and 15 mL of toluene were mixed at RT, placed in a high-pressure tube, and heated to 150 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy over a three week period. A 1.88 g (3.96 mmol) sample of **1** was isolated from the reaction mixture by crystallization at −15 °C (57% yield). Mp: 189−93 °C. ^1H NMR: δ_H −0.26 (s, 6 H, H1); 3.41 (d, 2 H, H20a); 3.71 (d, 2 H, H10a); 4.10 (d, 2 H, H20b); 4.47 (d, 2H, H10b); 6.89 (d, 2H, H16); 7.06 (dd, 2H, H14); 7.11 (t, 2H, H24); 7.15 (dd, 2H, H15); 7.22(m, 4H, H23); 7.23 (m, 4H, H22); 7.57 (d, 2H, H13). ^{13}C NMR: δ_C −13.0 (C1); 56.47 (C20); 58.87 (C10); 123.85 (C16); 126.49 (C14); 127.42 (C24); 127.50 (C22); 128.96 (C15); 128.96 (C23); 136.46 (C13); 139.63 (C21); 143.9 (C12); 149.86 (C11). IR (cm^{-1}): 3083 (m), 3026 (w), 2924 (w), 2888 (w), 2866 (w), 2844 (w), 1251 (s), 1235 (w), 1195 (m), 1066 (s), 1051 (s), 969 (m), 929 (m), 744 (m), 731 (s), 696 (s), 660 (m), 630 (s). Anal. Calcd (found) for $C_{30}H_{32}Al_2N_2$: C, 75.93 (75.85); H, 6.80 (6.68); N, 5.90 (5.88).

Crystallographic Data. Crystals of **1** and **2** for X-ray structure determination were obtained by recrystallization at −15 °C from toluene and hexane solutions, respectively. In each case, crystals of **1** (0.20 × 0.20 × 0.10 mm) and **2** (0.30 × 0.25 × 0.20 mm) were sealed in thin-walled capillaries under anaerobic conditions. Data were collected on an Enraf-Nonius CAD4 single-crystal diffractometer with κ-geometry. The intensity data (Mo Kα, $\lambda = 0.71073$ Å) were corrected for Lorentz and polarization effects as well as for absorption. All calculations were carried out with the SHELXTL-PC program package.[17] The positional and anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with the appropriate staggered geometry. Further details of the data collection and structural refinement are given in Table 1 and the Supporting Information.

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Supporting Information Available: Tables listing X-ray data collection and refinement, positional, and thermal parameters and complete bond distances and angles for compounds **1** and **2**; ^1H and ^{13}C NMR 1-D and 2-D NMR spectra for **1** (15 pages). Ordering information is given on any current masthead page.

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[17] *Siemens SHELXTL-PC Manual*, Release 4.1; Siemens Analytical Instruments: Madison, WI, 1990.