Notes

Synthesis and Molecular Structure Studies of $[Me_2AlN(i\text{-}Pr)CH_2Ph]_2$ and the Related Orthometalated Dimers $[RAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$, where R = Me, *n*-Pr, *n*-Bu, *i*-Bu

Omar M. Kekia, Larry K. Krannich,* and Charles L. Watkins*

Department of Chemistry, University of Alabama at Birmingham,
Birmingham, Alabama 35294

Christopher D. Incarvito and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received September 16, 2002

Summary: $[Me_2AlN(i\text{-}Pr)CH_2Ph]_2$ (**1**) *and the related dimer series* $[RAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$, *R* = *Me* (**2**), *n-Pr* (**3**), *n-Bu* (**4**), *and i-Bu* (**5**), *were synthesized by thermolysis of 1:1 mixtures of* R_3Al *and* $HN(i\text{-}Pr)CH_2Ph$. *The reaction times and temperatures required and the molecular structure and NMR data for* **1**−**5** *are compared with reported data for* $[Me_2AlN(CH_2Ph)_2]_2$ *and the series* $[RAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ *and* $[RAlN(t\text{-}Bu)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$.

Introduction

Recently, there have been several reports discussing the influence that bulky substituents have on the formation of orthometalated palladium complexes.[1] Also, we have reported the synthesis and characterization of two series of orthometalated aluminum−nitrogen dimers from the thermolysis of R_3Al (R = Me, Et, *n*-Pr, *n*-Bu, *i*-Bu) with dibenzylamine and with *tert*-butylbenzylamine.[1−3] Therein, the effects of the steric bulk of the organic substituents on the nitrogen and aluminum atoms were investigated in terms of the ease of the formation of the orthometalated dimers and their spectral and structural properties. The reactions of R_3Al and $HN(CH_2Ph)_2$ lead to the formation of $[R_2AlN(CH_2Ph)_2]_2$ at 120 °C,[3−6] but the orthometalated dimers are obtained only after heating at 150 °C for three weeks. The thermolysis reactions of mixtures of R_3Al and $HN(t\text{-}Bu)CH_2Ph$ proceed more readily,[1] and the orthometalated dimers $[RAlN(t\text{-}Bu)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ are obtained at lower temperatures, with much shorter reaction times, and in higher yields. In fact, the orthometalation reactions are so facile that they proceed before the initial reactants are consumed and dimer formation, $[R_2AlN(t\text{-}Bu)CH_2Ph]_2$, is complete; as a consequence, no dimers were isolated for the *tert*-butylbenzylamine reaction system. To our knowledge, the synthesis and characterization of only two similar aluminum−nitrogen orthometalated dimers have been reported.[7,8] Therefore, to understand more fully the requirements for orthometalation in these systems, we have chosen the amine $HN(i\text{-}Pr)CH_2Ph$, with the less bulky isopropyl group, for reaction with R_3Al in an attempt to optimize both dimer and orthometalated dimer formation and to investigate in more detail the influence of the groups attached to the aluminum and nitrogen atoms. In this paper, we report the study of the thermolysis reactions of $HN(i\text{-}Pr)CH_2Ph$ with R_3Al. The ease of synthesis and spectral and molecular structure properties of the three orthometalated dimer series $[RAlN(R')\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ (R′ = benzyl, *i*-Pr, *t*-Bu) are compared in terms of R and R′.

Results and Discussion

Synthesis. Equimolar mixtures of R_3Al and $HN(i\text{-}Pr)CH_2Ph$ in toluene (R = Me, Et, *n*-Pr, *n*-Bu, *i*-Bu) were heated from 80 to 120 °C and monitored by ^1H NMR to establish experimental conditions for dimer formation. The aminoalane dimers, $[R_2AlN(i\text{-}Pr)CH_2Ph]_2$ (R = Me, Et, *n*-Pr, *n*-Bu), were formed under moderate conditions (80−100 °C, 12−36 h) and isolated in almost quantitative yields (90−98%),[9] but crystals suitable for X-ray diffraction studies were obtained only

---

* Corresponding authors. (L.K.K.) E-mail: krannich@uab.edu. Tel: (205) 934-8017. Fax: (205) 934-2543. (C.L.W.) E-mail: watkins@uab.edu.

[1] Kekia, O. M.; Watkins, C. L.; Krannich, L. K.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **2001**, *20*, 582.

[2] Styron, E. K.; Lake, C. H.; Watkins, C. L.; Krannich, L. K.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2000**, *19*, 3253.

[3] Styron, E. K.; Lake, C. H.; Watkins, C. L.; Krannich, L. K. *Organometallics* **1998**, *17*, 4319.

[4] Thomas, C. J.; Krannich, L. K.; Watkins, C. L. *Polyhedron* **1993**, *12*, 389.

[5] Styron, E. K.; Lake, C. H.; Schauer, S. J.; Watkins, C. L.; Krannich, L. K. *Polyhedron* **1999**, *18*, 1595.

[6] Styron, E. K.; Lake, C. H.; Powell, D. H.; Watkins, C. L.; Krannich, L. K. *Polyhedron* **2002**, *21*, 1747.

[7] Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257.

[8] Lee, B.; Pennington, W. T.; Robinson, G. H. *Inorg. Chim. Acta* **1991**, *190*, 173.

[9] The synthesis and characterization of $[R_2AlN(i\text{-}Pr)CH_2Ph]_2$, where R = Et, *n*-Pr, *n*-Bu, is given in the Supporting Information.

10.1021/om020768n CCC: $22.00

from the methyl derivative, **1**. Reaction of $(i\text{-Bu})_3Al$ with $HN(i\text{-Pr})CH_2Ph$ leads initially to dimer formation, $[(i\text{-Bu})_2AlN(i\text{-Pr})CH_2Ph]_2$, but its decomposition occurs before the reactants are consumed. The reaction conditions for formation of $[R_2AlN(i\text{-Pr})CH_2Ph]_2$ are similar to those for the series $[R_2AlN(CH_2Ph)_2]_2$, but for the latter all five dimers were isolated and characterized.[3-6] However, the thermolysis reactions of 1:1 mixtures of R_3Al with $HN(t\text{-Bu})CH_2Ph$ at 100 °C are similar to the reaction of $(i\text{-Bu})_3Al$ with $HN(i\text{-Pr})CH_2Ph$ in that the reactions are facile and the dimers formed are subject to further alkane elimination.[1] The role of R and R′ in influencing the reaction sequence $2R_3Al + HNR'_2 \rightarrow 2R_3Al{\cdot}HNR'_2 \rightarrow [R_2AlNR'_2]_2 + 2RH$ has been discussed in terms of the steric and electronic effects of the R and R′ groups.[10] Our results are in agreement with those of Bradley[10] in that the influence of R′ is more important than that of R and that the effect is primarily steric in nature. Mass spectral studies on the related series $[Me_2InNR'_2]_2$[11] and on $[Me_2AlN(CH_2Ph)_2]_2$ and $[Me_2AlN(H)CH_2Ph]_2$[12,13] suggest that the dimers become less stable in the vapor phase with increasing steric bulk of the R′ group.

Thermolysis of the $R_3Al/HN(i\text{-Pr})CH_2Ph$ mixtures at higher temperatures results in additional alkane elimination. Orthometalated dimer formation is complete for **2** after heating for 6 days at 150 °C followed by 4 days at 175 °C, whereas compounds **3**−**5** require less heating (6 days at 155 °C).[14] The synthesis of $[RAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ requires heating of the $R_3Al/HN(CH_2Ph)_2$ mixtures at 150−155 °C for three weeks, independent of R; however, the reaction conditions for the formation of $[RAlN(t\text{-Bu})\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ from thermolysis of $R_3Al/HN(t\text{-Bu})CH_2Ph$ are more moderate (120 °C, 1−4 days, with R = Me requiring heating for the longest time).[1] Substitution of an isopropyl or *tert*-butyl group for a benzyl group in the secondary amine facilitates the orthometalation reaction, and as the steric bulk of the R′ group increases, the reaction conditions depend more on the nature of the R alkyl group. Also, $[R_2AlN(Me)CH_2Ph]_2$ is readily formed from the thermolysis of $R_3Al/HN(Me)CH_2Ph$ mixtures, but the corresponding orthometalated dimers are obtained from these reaction mixtures only at high temperatures and very long heating times.[15] The thermolysis reaction of Me_3Al with the primary amine H_2NCH_2Ph, where R′ = H instead of benzyl, at 135 °C results in the formation of the hexameric cage compound $[MeAlNCH_2Ph]_6$,[12] rather than the orthometalated dimer.

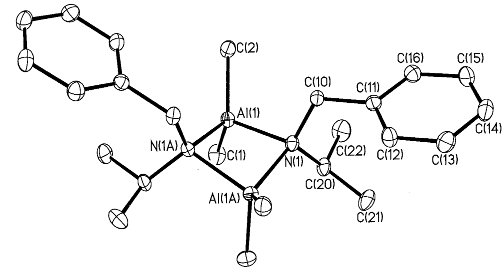

Figure 1. ORTEP diagram of $[Me_2AlN(i\text{-Pr})CH_2Ph]_2$ (**1a**). Hydrogen atoms omitted for clarity and thermal ellipsoids at 30% probability.

Therefore, our systematic study of the formation of the aluminum−nitrogen dimers $[R_2AlN(R')CH_2Ph]_2$ (where R′ = Me; benzyl, isopropyl, *tert*-butyl) and the requirements for formation of their respective orthometalated dimers $[RAlN(R')\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ have established that aluminum−nitrogen dimer stability and the subsequent ease of orthometalation depend to a significant degree on the steric nature of the group on the nitrogen atom of the amine, R′, and are affected only slightly by the alkyl group R. These findings are in agreement with reactivity studies involving the formation of orthometalated palladium complexes from dibenzylamine or similar aromatic amines.[1]

^{1}H and ^{13}C NMR Data. The ^{1}H and ^{13}C NMR chemical shift assignments for **1**−**5** were made using a combination of 1D and 2D NMR techniques and the procedures established for the NMR chemical shift assignments of $[Me_2AlN(H)CH_2Ph]_2$,[12] $[R_2AlN(CH_2Ph)_2]_2$,[3,6] $[RAlN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$,[2] and $[RAlN(t\text{-Bu})\text{-}\mu\text{-}(CH_2C_6H_4)]_2$.[1] The ^{1}H and ^{13}C NMR spectra of $[Me_2AlN(i\text{-Pr})CH_2Ph]_2$ (**1**) indicate the presence of both cis (**1a**) and trans (**1b**) isomers with respect to the Al_2N_2 ring in benzene-d_6 solution at RT in a 60:40 cis/trans isomer ratio. The ^{1}H NMR chemical shift assignments for the individual isomers were made from the 1D and the 2D $^1H\{^1H\}$ COSY and NOESY NMR spectra. The two ^{1}H NMR cis isomer methyl chemical shifts H(1) and H(2) (Figure 1), were assigned from the NOESY NMR spectra. Substitution of the more sterically demanding isopropyl group for a benzyl group in $[Me_2AlN(CH_2Ph)_2]_2$[3] causes significant downfield NMR chemical shifts for the ortho protons (H(12), H(16); $\Delta\delta_H = 0.41$ ppm) and the ipso (C(11); $\Delta\delta_C = 3.4$ ppm), ortho (C(12), C(16); $\Delta\delta_C = 0.94$), and methyl (C(1), $\Delta\delta_C = 1.2$; C(2), $\Delta\delta_C = 3.1$; trans-CH_3, $\Delta\delta_C = 2.6$ ppm) carbons. ^{13}C NMR chemical shifts are known to be sensitive to steric effects in related aluminum−nitrogen[4-6,10,16] and aluminum−phosphorus[17] systems.

Restricted conformational averaging is observed in portions of the ^{1}H NMR spectra for compounds **2**−**5** (Figure 2). There is chemical shift nonequivalence for the C(1) methylene group protons in **3**−**5**, the C(10) methylene group protons, the C(21) and C(22) methyl group protons in the isopropyl group, and the methyl group protons for the isobutyl group in **5**. The C(21) and C(22) methyl group protons were assigned from the 2D NOESY spectra, where the C(22) methyl group protons correlate with one of the C(10) methylene protons and the C(21) methyl group protons correlate with the C(13) aromatic ring proton. Interestingly, the C(22) methyl group protons are, on average, 0.30 ppm to higher field and the C(21) methyl group protons are 0.14 ppm to

---

[10] Bradley, D. C.; Harding, I. S.; Maia, I. A.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2969.

[11] Aitchison, K. A.; Backer-Dirks, J. D. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Short, R. L. *J. Organomet. Chem.* **1989**, *366*, 11.

[12] Styron, E. K.; Lake, C. H.; Powell, D. H.; Krannich, L. K.; Watkins, C. L. *J. Organomet. Chem.* **2002**, *649*, 78.

[13] Beachley, O. T., Jr. *Inorg. Chem.* **1981**, *20*, 2825.

[14] The synthesis and characterization of $[EtAlN(i\text{-Pr})\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ is given in the Supporting Information. No crystals suitable for X-ray analysis could be obtained.

[15] Kekia, O. M.; Lake, C. H.; Krannich, L. K.; Watkins, C. L. Presented at the 216th National Meeting of the American Chemical Society, Boston, MA, August 1998, INORG 255.

[16] Schauer, S. J.; Watkins, C. L.; Krannich, L. K.; Gala, R. B.; Gundy, E. M.; Lagrone, C. B. *Polyhedron* **1995**, *14*, 3505.

[17] Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047.

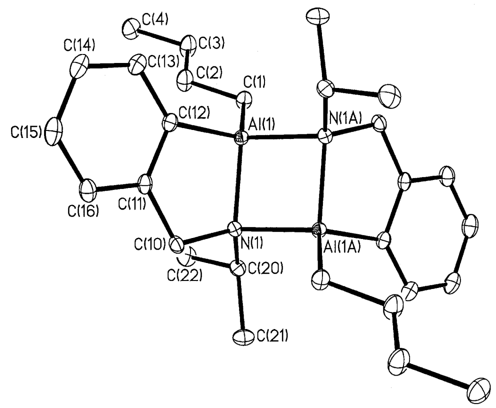

Figure 2. ORTEP diagram of [n-BuAlN(i-Pr)-μ-($CH_2C_6H_4$)]$_2$ (**4**). Hydrogen atoms omitted for clarity and thermal ellipsoids at 30% probability.

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

Al(1)−N(1A)	1.977 (2)	Al(1)−N(1)	2.031(2)
Al(1)−C(1)	1.990 (3)	Al(1)−C(2)	1.979 (3)
Al(1)····Al(1A)	2.7948 (15)	N(1)−C(10)	1.515 (3)
N(1)−C(20)	1.524 (3)	N(1)−Al(1A)	1.977 (2)
N(1A)−Al(1)−C(2)	120.10 (11)	N(1A)−Al(1)−C(1)	110.64 (11)
C(2)−Al(1)−C(1)	112.40 (13)	N(1A)−Al(1)−N(1)	88.42 (9)
C(2)−Al(1)−N(1)	112.05 (11)	C(1)−Al(1)−N(1)	110.84 (12)
C(10)−N(1)−C(20)	113.9 (2)	C(10)−N(1)−Al(1A)	119.02 (15)
C(20)−N(1)−Al(1A)	114.27 (16)	C(10)−N(1)−Al(1)	107.30 (15)
C(20)−N(1)−Al(1)	110.43 (16)	Al(1A)−N(1)−Al(1)	88.40 (9)
N(1)−C(10)−C(11)	119.4 (2)	N(1)−C(20)−C(21)	113.2 (2)

lower field in **2**−**5**, compared to **1a** and **1b**. In contrast, the ^{1}H NMR spectra show that the C(21) and C(22) methyl group protons are chemically equivalent in **1a** and in **1b**, as are the C(10) methylene group protons; also, the *tert*-butyl methyl group protons are equivalent in [RAlN(t-Bu)-μ-($CH_2C_6H_4$)]$_2$.[1] The NOESY data suggest a trans conformation for **2**−**5** in solution with respect to the Al_2N_2 ring, consistent with the X-ray data, and the ^{1}H NMR solution and X-ray data for [RAlN-(t-Bu)-μ-($CH_2C_6H_4$)]$_2$.[1] Substitution of a *tert*-butyl for a benzyl group in the othometalated dimer series [RAlN-(CH_2Ph)-μ-($CH_2C_6H_4$)]$_2$[2] results in significant ^{13}C NMR chemical shift changes at the C(1) ($\Delta\delta_C$(av) = 5.9 ppm), C(10) (−4.8 ppm), and C(12) (4.8 ppm) carbons. Substitution of an isopropyl group for a benzyl group leads to a large ^{13}C chemical shift change only at the C(10) carbon ($\Delta\delta_C$(av) = −9.1 ppm). This ^{13}C NMR chemical shift change, larger than any observed for the substitution of a *tert*-butyl group for a benzyl group, may arise due to a significant interaction with the C(22) methyl group, as evidenced by the restricted rotation of isopropyl group in **2**−**5**.

X-ray Crystallography Data. The ORTEP drawing of the molecular structure and the atom labeling scheme for *cis*-[Me_2AlN(i-Pr)CH_2Ph]$_2$ (**1a**) are shown in Figure 1, with selected bond lengths (Å) and angles (deg) summarized in Table 1. The molecular structure of **1a** has a nonplanar Al_2N_2 core with a fold angle about the Al···Al axis of 26.9°. These data are consistent with those reported for *cis*-[Me_2AlN(H)i-Pr]$_2$,[18] *cis*-[Me_2AlN-(Me)CH_2Ph]$_2$,[15] and [$Me_2AlN(C_6H_{11})_2$]$_2$,[19] with fold angles of 15.5°, 20.4°, and 27.4°, respectively. The molecular structure data for **1a** are in agreement with published data and correlations of the steric properties of functional groups attached to the amine nitrogen with the corresponding dimer geometries.[3,6,10−12,18−22]

Table 2. Selected Bond Lengths (Å) for 2−5

bond	**2**	**3**	**4**	**5**
Al(1)−N(1)	1.968 (3)	1.977 (3)	1.9629 (15)	1.9705 (17)
Al(1)−N(1A)	1.984 (3)	1.978 (2)	1.9707 (16)	1.9793 (16)
Al(1A)−N(1)	1.989 (3)	1.978 (2)	1.9707 (16)	1.9793 (16)
Al(1A)−N(1A)	1.973 (3)	1.977 (3)	1.9629 (15)	1.9705 (17)
Al(1)−C(1)	1.972 (4)	1.972 (3)	1.9645 (18)	1.970 (2)
Al(1)−C(12)	1.974 (4)	1.978 (3)	1.962 (2)	1.970 (2)
N(1)−C(10)	1.511 (5)	1.505 (3)	1.499 (2)	1.501 (2)
N(1)−C(20)	1.525 (5)	1.514 (4)	1.507 (2)	1.502 (3)
Al(1)···Al(1A)	2.7782 (17)	2.7711 (15)	2.7605 (10)	2.7712 (11)
C(10)−C(11)	1.531 (6)	1.521 (4)	1.514 (3)	1.511 (3)
C(11)−C(12)	1.419 (6)	1.397 (5)	1.411 (2)	1.405 (3)

Table 3. Selected Bond Angles (deg) for 2−5

angle	**2**	**3**	**4**	**5**
N(1)−Al(1)−C(1)	120.04 (18)	123.60 (14)	123.74 (8)	122.87 (9)
N(1)−Al(1)−C(12)	90.75 (16)	90.13 (12)	90.36 (7)	89.86 (8)
C(1)−Al(1)−C(12)	125.43 (19)	123.65 (13)	123.00 (8)	129.40 (9)
C(1)−Al(1)−N(1A)	113.68 (17)	112.90 (12)	113.55 (8)	109.18 (8)
N(1)−Al(1)−N(1A)	90.94 (14)	91.03 (10)	90.86 (6)	90.89 (6)
Al(1)−N(1)−C(20)	119.5 (2)	120.04 (18)	119.78 (11)	119.69 (13)
C(12)−Al(1)−N(1A)	109.09 (15)	109.53 (11)	109.38 (7)	107.40 (8)
Al(1)−N(1)−Al(1A)	89.21 (13)	88.97 (10)	89.14 (6)	89.11 (6)
Al(1)−N(1)−C(10)	108.7 (2)	108.20 (17)	108.66 (11)	108.43 (12)
C(20)−N(1)−Al(1A)	110.5 (2)	111.05 (17)	110.76 (12)	111.81 (12)
C(10)−N(1)−C(20)	111.9 (3)	111.7 (2)	111.54 (14)	111.29 (14)
C(10)−C(11)−C(12)	119.2 (3)	119.4 (2)	119.14 (16)	119.01 (19)
C(10)−N(1)−Al(1A)	115.5 (2)	115.35 (18)	115.45 (12)	115.02 (13)
N(1)−C(10)−C(11)	112.4 (3)	112.8 (2)	112.51 (14)	112.20 (16)
Al(1)−C(12)−C(13)	135.2 (3)	134.4 (2)	134.43 (14)	134.38 (17)
Al(1)−C(12)−C(11)	108.3 (3)	108.8 (2)	108.57 (14)	108.75 (14)

The ORTEP drawing of the molecular structure of the orthometalated dimer [n-BuAlN(i-Pr)-μ-($CH_2C_6H_4$)]$_2$ (**5**) is shown in Figure 2, and representative bond lengths and bond angles for **2**−**5** are listed in Tables 2 and 3. The molecular structures of [RAlN(i-Pr)-μ-($CH_2C_6H_4$)]$_2$ each exhibit a planar Al_2N_2 core that possesses inversion symmetry. The Al_2N_2 ring is flanked on both sides by bridging $CH_2C_6H_4$ groups in a trans orientation relative to the core ring. The Al_2N_2 ring geometry is almost square planar; the N−Al−N angle varies from 90.80(14)° to 91.03(10)° and the Al−N−Al angle from 88.97(10)° to 89.20(13)° with R. The two Al−N distances are very similar, with the Al−N bond included in the five-membered orthometalated ring being slightly shorter (1.9629(15)−1.977(3) Å) than the other Al−N bond (1.9707(16)−1.986(3) Å). There are only minor variations in the Al_2N_2 ring geometry with R.

The Al_2N_2 ring geometries for the [RAlN(i-Pr)-μ-($CH_2C_6H_4$)]$_2$ and [RAlN(CH_2Ph)-μ-($CH_2C_6H_4$)]$_2$ dimers are very similar. Substitution of the isopropyl for a benzyl group results in small increases in the nonorthometalated Al−N bond distances (average, 0.027 Å) and slight changes in the N−Al−N and Al−N−Al bond angles, with the Al_2N_2 rings becoming more square. Modest changes occur in certain angles external to the ring, with the greatest change being 6.8° for the C(1)−

---

(18) Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377.

(19) Belgardt, T.; Storre, J.; Klemp. A.; Gornitzka, H.; Häming, L.; Schmidt, H.-G.; Roesky, H. W. *J. Chem. Soc., Dalton Trans.* **1995**, 3747.

(20) Schauer, S. J.; Robinson, G. H. *J. Coord. Chem.* **1993**, *30*, 197.

(21) Lagrone, C. B.; Schauer, S. J.; Thomas, C. J.; Gray, G. M.; Watkins, C. L.; Krannich, L. K. *Organometallics* **1996**, *15*, 2458.

(22) Dümichen, U.; Gelbrich, T.; Sieler, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 262.

Al(1)−N(1) angle. Substitution of the more sterically demanding *tert*-butyl group for a benzyl group causes a reversal in the relative magnitudes of the N−Al−N and Al−N−Al angles[1] with elongation of the Al_2N_2 ring now along the Al···Al line. For the dibenzylamine and isopropylbenzylamine orthometalated dimers, the N···N distances are longer. Also, four angles external to the Al_2N_2 ring change more than 10° upon *t*-Bu group substitution.

Experimental Section

Standard inert atmosphere and vacuum line techniques were employed for the synthesis and purification of the compounds. All solvents were dried by refluxing over sodium and were distilled under nitrogen. The trialkylaluminum compounds (Texas Alkyls) were used as received. Isopropylbenzylamine (Aldrich) was stored over molecular sieves. ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 FT-NMR spectrometer, operating at 400.132 and 100.625 MHz, respectively. Solutions for NMR analysis were prepared using benzene-d_6 with $(CH_3)_4Si$ as internal reference. Complete ^1H and ^{13}C NMR chemical shift assignments were made on the basis of both coupled and decoupled 1D NMR, ^{13}DEPT, and $^1H\{^1H\}$ COSY, $^{13}C\{^1H\}$ HETCOR, and $^1H\{^1H\}$ NOESY 2D NMR experiments. The FT-IR spectra were obtained using split mull samples in Nujol and Kel-F (halocarbon emulsions) on KBr disks. Elemental analyses were carried out by E & R Microanalytical Laboratory, Inc. Parsippany, NJ. All melting points reported are uncorrected and were obtained in sealed capillaries under nitrogen.

General Synthesis of $[Me_2AlN(i\text{-}Pr)CH_2Ph]_2$ and $[RAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$. $[Me_2AlN(i\text{-}Pr)CH_2Ph]_2$ (**1**) and $[RAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$, R = Me (**2**), *n*-Pr (**3**), *n*-Bu (**4**), *i*-Bu (**5**), were synthesized by mixing in the drybox at room temperature in a high-pressure thick-walled glass tube R_3Al (10 mmol) diluted in 5 mL of dry toluene with $HN(i\text{-}Pr)CH_2Ph$ (1.486 g, 10 mmol) also diluted in 5 mL of dry toluene. The total volume of the solution was then brought up to 15 mL with toluene. Each tube was then heated in an oil bath to the desired temperature. The progress of each reaction was monitored by ^1H NMR After the reaction was complete, the toluene was removed under reduced pressure, and the products were isolated as white solids. The products were purified by crystallization from pentane. X-ray grade crystals were obtained either by slowly cooling the toluene solution or from a saturated pentane solution of the isolated product. The reaction times for the completion of each reaction were as follows: **1**, 36 h at 80 °C; **2,** 6 days at 150 °C followed by 4 days at 175 °C; **3**, **4**, and **5**, 6 days at 155 °C.

Characterization of $[Me_2AlN(i\text{-}Pr)CH_2Ph]_2$ (1). Mp: 141−145 °C. Yield: 1.84 g, 90%. **1** exists as a cis−trans (**1a**, **1b**) mixture in solution in a 60:40 ratio. **1a**: ^1H NMR: δ_H −0.19 (s, 6H, H1), −0.11 (s, 6H, H2), 0.91 (d, 12H, H21, H22), 3.57 (m, 2H, H20), 4.03 (s, 4H, H10), 7.05 (2H, H14), 7.10 (4H, H13, H15), 7.39 (4H, H12, H16). ^{13}C NMR: δ_C −6.41 (C1), −4.49 (C2), 23.01 (C21, C22), 50.01 (C20), 52.48 (C10), 127.58 (C14), 128.30 (C13, C15), 130.43 (C12, C16), 140.12 (C11). **1b**: ^1H NMR: δ_H −0.13 (s, 12H, H1, H2), 0.94 (d, 12H, H21, H22), 3.46 (m, 2H, H20), 4.16 (s, 4H, H10), 7.06 (2H, H14), 7.10 (4H, H13, H15), 7.39 (4H, H12, H16). ^{13}C NMR: δ_C −5.0 (C1, C2), 23.15 (C21, C22), 48.39 (C20), 51.85 (C10), 127.33 (C14), 128.45 (C13, C15), 130.08 (C12, C16), 139.98 (C11). Anal. Calcd (found) for $C_{24}H_{40}Al_2N_2$: C, 70.21(70.17); H, 9.82 (9.75); N, 6.82 (6.76).

Characterization of $[MeAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ (2). Mp: 186−190 °C. Yield: 1.02 g, 54%. ^1H NMR: δ_H −0.41 (s, 6H, H1), 0.59 (d, 6H, H22), 1.03 (d, 6H, H21), 3.10 (m, 2H, H20), 3.95, 4.13 (dd, 4H, H10), 7.14 (2H, H16), 7.26 (2H, H14), 7.28 (2H, H15), 7.80 (2H, H13). ^{13}C NMR: δ_C −12.1 (C1), 19.88 (C22), 22.57 (C21), 48.85 (C20), 49.59 (C10), 123.86 (C16), 126.37 (C14), 128.68 (C15), 136.11 (C13), 145.2 (C12), 150.86 (C11). Anal. Calcd (found) for $C_{22}H_{32}Al_2N_2$: C, 69.82 (69.77); H, 8.52 (8.49); N, 7.40 (7.38).

Characterization of $[n\text{-}PrAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ (3). Mp: 156−160 °C. Yield: 1.20 g, 55%. ^1H NMR: δ_H 0.14, 0.29 (m, 4H, H1), 0.63 (d, 6H, H22), 1.07 (d, 6H, H21), 1.15 (t, 6H, H3), 1.64 (m, 4H, H2), 3.07 (m, 2H, H20), 3.96, 4.16 (dd, 4H, H10), 7.15 (2H, H16), 7.27 (2H, H14), 7.29 (2H, H15), 7.84 (2H, H13). ^{13}C NMR: δ_C 10.9 (C1), 19.39 (C2), 20.91 (C3), 20.11 (C22), 22.94 (C21), 48.86 (C20), 49.75 (C10), 123.83 (C16), 126.35 (C14), 128.64 (C15), 136.38 (C13), 145.1 (C12), 150.98 (C11). Anal. Calcd (found) for $C_{26}H_{40}Al_2N_2$: C, 71.86 (70.96); H, 9.28 (9.27); N, 6.45 (6.79).

Characterization of $[n\text{-}BuAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ (4). Mp: 153−155 °C. Yield: 1.15. g, 50%. ^1H NMR: δ_H 0.14, 0.30 (m, 4H, H1), 0.66 (d, 6H, H22), 1.08 (d, 6H, H21), 0.99 (t, 6H, H4), 1.49 (m, 4H, H3), 1.60 (m, 4H, H2), 3.09 (m, 2H, H20), 3.98, 4.18 (dd, 4H, H10), 7.16 (2H, H16), 7.26 (2H, H14), 7.28 (2H, H15), 7.85 (2H, H13). ^{13}C NMR: δ_C 7.6 (C1), 14.08 (C4), 28.18 (C2), 29.21 (C3), 20.14 (C22), 22.96 (C21), 48.86 (C20), 49.75 (C10), 123.84 (C16), 126.36 (C14), 128.65 (C15), 136.36 (C13), 145.1 (C12), 151.00 (C11). Anal. Calcd (found) for $C_{28}H_{44}Al_2N_2$: C, 72.69 (72.19); H, 9.59 (9.74); N, 6.06 (6.16).

Characterization of $[i\text{-}BuAlN(i\text{-}Pr)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ (5). Mp: 159−162 °C. Yield: 1.37 g, 59%. ^1H NMR: δ_H 0.12, 0.27 (m, 4H, H1), 0.66 (d, 6H, H22), 1.10 (d, 6H, H21), 1.13 (d, 6H, H3 or H4), 1.16 (d, 6H, H3 or H4), 2.01 (m, 2H, H2), 3.07 (m, 2H, H20), 3.98, 4.16 (dd, 4H, H10), 7.14 (2H, H16), 7.26 (2H, H14), 7.27 (2H, H15), 7.89 (2H, H13). ^{13}C NMR: δ_C 20.1 (C1), 26.40 (C2), 28.43 (C3 or C4), 28.55 (C3 or C4), 20.18 (C22), 22.91 (C21), 48.85 (C20), 49.85 (C10), 123.83 (C16), 126.39 (C14), 128.62 (C15), 136.50 (C13), 145.3 (C12), 150.99 (C11). Anal. Calcd (found) for $C_{28}H_{44}Al_2N_2$: C, 72.69 (72.64); H, 9.59 (9.56); N, 6.06 (5.99).

X-ray Crystallography. Crystals suitable for single-crystal X-ray diffraction were selected and mounted in nitrogen-flushed capillaries. The data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. The systematic absences and diffraction symmetry are consistent for the space groups $C2/c$ and Cc for **1a** and $P1$ and $P\bar{1}$ for **2** and **4** and were uniquely consistent with the assigned space group options for **3** and **5**. The *E*-statistics suggested the centrosymmetric options for **1a**, **2**, and **4**, which yielded chemically reasonable and computationally stable results of refinement. Compound **1a** exists as 0.5 molecule per asymmetric unit lying on a 2-fold rotation axis, while compound **2** has 1.5 molecules per asymmetric unit with one molecule lying on a general position and 0.5 molecule lying on an inversion center. Compounds **3**, **4**, and **5** exist as 0.5 molecule per asymmetric unit lying on an inversion center. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI). X-ray crystal data collection and refinement parameters and structural data for **1a**−**5** are included in the Supporting Information. Selected bond distances and angles are given in Tables 1−3.

Supporting Information Available: Tables of X-ray crystallographic data, crystal data and structure refinement, atomic coordinates, interatomic distances and angles, and hydrogen atom coordinates for compounds **1a**−**5**. Synthesis and characterization data for $[R_2AlN(i\text{-}Pr)CH_2Ph]_2$, where R = Et (**6**), *n*-Pr (**7**), *n*-Bu (**8**), and $[EtAlN(i\text{-}Pr)\text{-}\mu\text{-}CH_2C_6H_4]_2$ (**9**). IR data for compounds **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020768N