# Synthesis and Molecular Structural Studies of a Series of Orthometalated Dimers [RAlN(*t*-Bu)-$\mu$-($CH_2C_6H_4$)]$_2$, where R = Me, Et, *n*-Pr, *n*-Bu, *i*-Bu

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

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

Arnold L. Rheingold and Louise M. Liable-Sands

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

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*Summary: The orthometalated aluminum−nitrogen dimer series [RAlN(t-Bu)-$\mu$-($CH_2C_6H_4$)]$_2$ (R = Me,* ***1****; Et,* ***2****; n-Pr,* ***3****; n-Bu,* ***4****; i-Bu,* ***5****) was synthesized by thermolysis of 1:1 mixtures of $R_3Al$ with HN(t-Bu)$CH_2Ph$. The reaction times and temperatures required for orthometalation, the molecular structural data, and the $^1H$ and $^{13}C$ NMR spectral parameters of the dimers are compared with the reported data for the series [RAlN($CH_2Ph$)-$\mu$-($CH_2C_6H_4$)]$_2$.*

## Introduction

The reactivity of palladium compounds with benzylamine and other aromatic amine derivatives to yield cyclometalated complexes has been reviewed extensively.[1] Initially, tertiary benzylamine derivatives were found to be better ligands for the formation of cyclometalated products than secondary or primary benzylamine derivatives.[2] However, recent reports have suggested that the introduction of bulky substituents into the secondary or primary benzylamine framework increases significantly the reactivity in terms of the formation of orthometalated palladium complexes.[3] In contrast, only a few studies have been reported on the synthesis and structural characterization of orthometalated dimers of group 13 metals employing dibenzylamine or similar aromatic amine derivatives.[4−8] Recently, we reported the first systematic study on possible steric effects in such systems by synthesizing and characterizing a series of five orthometalated aluminum−nitrogen dimers, [RAlN($CH_2Ph$)-$\mu$-($CH_2C_6H_4$)]$_2$, resulting from the 1:1 reaction of $R_3Al$ with dibenzylamine at 155 °C, where R = Me, Et, *n*-Pr, *n*-Bu, and *i*-Bu.[8] Varying the R group on the Al within this series did not appreciably change the time required for reaction completion nor alter significantly the molecular structures of the dimers. In this study, an analogous series of reactions involving $R_3Al$ and the asymmetric amine HN(*t*-Bu)$CH_2Ph$ were investigated to determine the effect on the reactivity of substituting the sterically demanding *tert*-butyl group for a benzyl group on the N atom and to relate any structural changes in the resulting orthometalated dimer products to the incorporation of the *tert*-butyl group into the Al−N orthometalated dimer framework. The reaction times and thermolysis temperatures for orthometalated dimer formation were significantly lower than for the analogous thermolyses in the $R_3Al$/dibenzylamine system. The $^1H$ and $^{13}C$ NMR data and the molecular structure data obtained from single-crystal X-ray diffraction studies for the five orthometalated Al−N dimers are reported for comparison with the data for those corresponding dimers from the previous $R_3Al$/dibenzylamine reactions.

## Experimental Section

**General Procedures.** Standard inert atmosphere and vacuum line techniques were used for the synthesis and purification of all compounds. Toluene was refluxed over sodium and distilled under nitrogen. *tert*-Butylbenzylamine (Aldrich) was stored over molecular sieves. The trialkylaluminum reagents (Ethyl Corporation) were used as received. $^1H$ and $^{13}C$ NMR spectra were recorded 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 $Me_4Si$ as internal standard. $^1H$ and $^{13}C$

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* 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. Tel: (205) 934-8137. Fax: (205) 934-2543.

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chemical shift assignments were based on both coupled and decoupled 1D NMR, $^{13}$DEPT, and $^1$H{$^1$H} COSY, $^{13}$C{$^1$H} HETCOR, and $^1$H{$^1$H} NOESY 2D NMR data. The numbering system used for NMR spectral assignments is consistent with that reported for the [RAlN($CH_2Ph$)-$\mu$-($CH_2C_6H_4$)]$_2$ dimers.[8] Elemental analyses were performed by E & R Microanalytical Laboratory, Inc., Parsippany, NJ. The FT-IR spectra were recorded using split mull samples in Nujol and Kel-F (halocarbon) on KBr plates.

**General Synthesis of [RAlN(*t*-Bu)-*μ*-($CH_2C_6H_4$)]$_2$.** *tert*-Butylbenzylamine (10 mmol in 5 mL of toluene) and the corresponding trialkylaluminum compound, $R_3Al$ (10 mmol in 5 mL of toluene), R = Me (**1**), Et (**2**), *n*-Pr (**3**), *n*-Bu (**4**), *i*-Bu (**5**), were mixed in a high-pressure glass reaction tube at room temperature, and the reaction tube was then heated in an oil bath to the desired temperature. At selected time intervals, the reaction tube was removed from the oil bath and allowed to cool to room temperature. After transferring the reaction tube to the drybox, a small aliquot was removed for NMR sample preparation. The progress of each reaction was monitored by $^1$H NMR. Once the spectra indicated conversion of the reactants to the orthometalated product, the reaction tube was slowly cooled to −15 °C to give good yields of colorless X-ray grade crystals. The reaction times and temperature involved in each reaction are as follows: **1**, 3 days at 100 °C followed by 4 days at 120 °C; **2**, 2 days at 100 °C followed by 2 days at 120 °C; **3**, 2 days at 120 °C; **4**, 1 day at 120 °C; **5**, 1 day at 120 °C. The compounds were characterized by $^1$H and $^{13}$C NMR; FT-IR; C, H, N elemental analyses; and single-crystal X-ray crystallography.

**Characterization of [MeAlN(*t*-Bu)-*μ*-($CH_2C_6H_4$)]$_2$ (1).** Mp: 242−244 °C. Yield: 72%. $^1$H NMR: $\delta_H$ −0.11 (s, 6H, H1), 0.97 (s, 18H, H21), 4.06 (d, 2H, H10a), 4.58 (d, 2H, H10b), 7.07 (2H, H16), 7.25 (2H, H15), 7.25 (2H, H14), 7.82 (2H, H13). $^{13}$C NMR: $\delta_C$ −6.26 (C1), 29.77 (C21), 54.10 (C10), 56.83 (C20), 123.12 (C16), 126.59 (C14), 128.51 (C15), 135.79 (C13), 149.18 (C12), 151.02 (C11). Anal. Calcd (found) for $C_{24}H_{36}Al_2N_2$: C, 70.93 (70.73); H, 8.87 (9.19); N, 6.90 (6.89).

**Characterization of [EtAlN(*t*-Bu)-*μ*-($CH_2C_6H_4$)]$_2$ (2).** Mp: 195−197 °C. Yield: 71%. $^1$H NMR: $\delta_H$ 0.40, 0.48 (m, 4H, H1), 0.96 (s, 18H, H21), 1.41 (t, 6H, H2), 4.05 (d, 2H, H10a), 4.50 (d, 2H, H10b), 7.06 (2H, H16), 7.24 (2H, H14), 7.25 (2H, H15), 7.88 (2H, H13). $^{13}$C NMR: $\delta_C$ 4.39 (C1), 9.71 (C2), 29.93 (C21), 53.77 (C10), 56.46 (C20), 123.24 (C16), 126.48 (C14), 128.50 (C15), 136.27 (C13), 148.46 (C12), 151.29 (C11). Anal. Calcd (found) for $C_{26}H_{40}Al_2N_2$: C, 71.86 (71.67); H, 9.28 (9.39); N, 6.45 (6.51).

**Characterization of [*n*-PrAlN(*t*-Bu)-*μ*-($CH_2C_6H_4$)]$_2$ (3).** Mp: 209−211 °C. Yield: 80%. $^1$H NMR: $\delta_H$ 0.43, 0.52 (m, 4H, H1), 0.98 (s, 18H, H21), 1.21 (t, 6H, H3), 1.78 (m, 4H, H2), 4.07(d, 2H, H10a), 4.53 (d, 2H, H10b), 7.07 (2H, H16), 7.24 (2H, H14), 7.25 (2H, H15), 7.87 (2H, H13). $^{13}$C NMR: $\delta_C$ 14.22 (C1), 19.93 (C2), 21.40 (C3), 29.94 (C21), 53.88 (C10), 56.51 (C20), 123.16 (C16), 126.47 (C14), 128.48 (C15), 136.23 (C13), 148.65 (C12), 151.23 (C11). Anal. Calcd (found) for $C_{28}H_{44}Al_2N_2$: C, 72.69 (72.54); H, 9.59 (9.69); N, 6.06 (6.04).

**Characterization of [*n*-BuAlN(*t*-Bu)-*μ*-($CH_2C_6H_4$)]$_2$ (4).** Mp: 194−196 °C. Yield: 93%. $^1$H NMR: $\delta_H$ 0.44, 0.53 (m, 4H, H1), 1.00 (s,18H, H21), 1.76 (m, 4H, H2),1.56 (m, 4H, H3), 1.04 (t, 6H, H4) 4.08 (d, 2H, H10a), 4.55 (d, 2H, H10b), 7.09 (2H, H16), 7.25 (2H, H14), 7.26 (2H, H15), 7.92 (2H, H13). $^{13}$C NMR: $\delta_C$ 13.44 (C1), 14.06 (C4), 28.65 (C2), 29.49 (C3), 29.97 (C21), 53.90 (C10), 56.51 (C20), 123.18 (C16), 126.49 (C14), 128.51 (C5), 136.23 (C13), 148.61 (C12), 151.24 (C11). Anal. Calcd (found) for $C_{30}H_{48}Al_2N_2$: C, 73.43 (73.54); H, 9.86 (9.81); N, 5.71 (5.66).

**Characterization of [*i*-BuAlN(*t*-Bu)-*μ*-($CH_2C_6H_4$)]$_2$ (5).** Mp: 167−169 °C. Yield: 86%. $^1$H NMR: $\delta_H$ 0.43, 0.56 (m, 4H, H1), 1.01 (s, 18H, H21), 1.15 (d, 6H, H3 or H4), 1.24 (d, 6H, H3 or H4), 2.22 (m, 2H, H2), 4.09 (d, 2H, H10a), 4.51 (d, 2H, H10b), 7.07 (2H, H16), 7.24 (2H, H15), 7.24 (2H, H14), 7.94 (2H, H13). $^{13}$C NMR: $\delta_C$ 25.37 (C1), 26.69 (C2), 28.63, 28.92 (C3, C4), 30.06 (C21), 54.27 (C10), 56.77 (C20), 123.12 (C16), 126.50 (C14), 128.50 (C15), 136.54 (C13), 148.71 (C12), 151.20 (C11). Anal. Calcd (found) for $C_{30}H_{48}Al_2N_2$: C, 73.43 (73.57); H, 9.86 (9.85); N, 5.71 (5.63).

**Table 1. Selected Bond Lengths (Å)**

| bond | **1A** | **2A** | **3A** | **4** | **5** |
|---|---|---|---|---|---|
| Al(1)−N(1) | 1.976(3) | 1.991(2) | 1.981(6) | 1.982(2) | 1.993(2) |
| Al(1)−C(1) | 1.976(4) | 2.001(3) | 1.961(8) | 1.989(3) | 1.995(2) |
| Al(1)−C(12) | 1.958(3) | 1.990(3) | 1.950(6) | 1.977(3) | 1.974(2) |
| Al(1)−N(1A) | 2.004(3) | 2.018(2) | 1.994(5) | 2.007(2) | 2.0054(18) |
| N(1)−C(10) | 1.532(4) | 1.536(4) | 1.517(8) | 1.522(4) | 1.522(3) |
| N(1)−C(20) | 1.527(4) | 1.545(3) | 1.506(10) | 1.545(4) | 1.532(3) |
| C(10)−C(11) | 1.527(5) | 1.529(4) | 1.518(9) | 1.535(4) | 1.507(3) |
| C(11)−C(12) | 1.408(5) | 1.414(4) | 1.408(10) | 1.389(4) | 1.411(3) |
| C(11)−C(16) | 1.398(4) | 1.411(4) | 1.354(9) | 1.404(4) | 1.399(3) |
| C(12)−C(13) | 1.395(4) | 1.418(4) | 1.401(9) | 1.419(4) | 1.409(3) |

**X-ray Crystallographic Structural Determinations.** Crystals suitable for single-crystal X-ray diffraction were selected and mounted in nitrogen-flushed, thin-walled capillaries. The data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. The systematic absences in the diffraction data are uniquely consistent with the reported space groups for **1**, **4**, and **5**, and no evidence of symmetry higher than triclinic was observed in the diffraction data of **2** and **3**. *E*-statistics suggested the centrosymmetric space group option, *P*, for **2** and **3**. Solution in the respective space groups yielded chemically reasonable and computationally stable results of refinement. 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 parameters, and all hydrogen atoms were treated as idealized contributions. There are two independent, but chemically equivalent half-molecules (labeled **A** and **B**), each on an inversion center in the asymmetric unit for **1**, **2**, and **3**. Several attempts were made to recrystallize **3**; however, each crystal diffracted weakly and diffusely. 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 **1**−**5** are given in the Supporting Information. Selected bond distances and angles are given in Tables1 and 2 for **1A**−**3A**, **4**, and **5**.

## Results and Discussion

**Synthesis.** The reactivity of an unsymmetric benzylamine, containing a sterically demanding substituent, HN(*t*-Bu)($CH_2Ph$), with the trialkyl aluminum compounds $R_3Al$ (R = Me, Et, *n*-Pr, *n*-Bu, and *i*-Bu), was investigated to determine the effect that alkyl substituent steric bulk at the nitrogen site has on the ease of orthometalated dimer formation. The results of the study are compared to the reported synthesis and properties of the orthometalated dimers [RAlN($CH_2Ph$)-$\mu$-($CH_2C_6H_4$)]$_2$, obtained from the thermolysis of $R_3Al$ with dibenzylamine.[8] The initial room-temperature $^1$H NMR spectra of the $R_3Al$/HN(*t*-Bu)($CH_2Ph$) reaction mixtures showed resonance peaks assignable to $R_3Al$·NH(*t*-Bu)($CH_2Ph$) 1:1 adducts, except for the *i*-$Bu_3Al$ reaction, where gas evolution occurred immediately upon mixing. Upon heating the mixtures at 100 °C for 12−48 h, new $^1$H NMR resonance peaks were observed that suggested initially the formation of [$R_2$AlN(*t*-Bu)-($CH_2Ph$)]$_2$ and then partial dimer decomposition before reactant consumption was complete. Further thermolysis at 120 °C led to reaction completion with [RAlN(*t*-

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**Table 2. Selected Bond Angles (deg)**

| angle | **1A** | **2A** | **3A** | **4** | **5** |
|---|---|---|---|---|---|
| N(1)−Al(1)−C(1) | 114.96(15) | 113.23(12) | 116.3(3) | 116.90(13) | 110.23(9) |
| N(1)−Al(1)−C(12) | 119.57(11) | 121.48(11) | 118.9(3) | 118.38(11) | 119.36(8) |
| C(1)−Al(1)−C(12) | 112.25(15) | 112.65(13) | 112.1(3) | 113.96(13) | 115.60(10)) |
| C(1)−Al(1)−N(1A) | 127.23(15) | 127.95(12) | 125.6(3) | 123.23(12) | 130.15(9) |
| N(1)−Al(1)−N(1A) | 88.37(12) | 88.23(10) | 89.7(2) | 88.43(10) | 87.95(7) |
| Al(1)−N(1)−C(20) | 120.23(18) | 118.55(18) | 120.1(4) | 119.61(16) | 116.73(15) |
| C(12)−Al(1)−N(1A) | 91.70(13) | 90.94(11) | 91.0(3) | 91.39(11) | 91.19(9) |
| Al(1)−N(1)−Al(1A) | 91.63(12) | 91.77(10) | 90.3(2) | 91.57(10) | 92.05(7) |
| Al(1)−N(1)−C(10) | 107.55(19) | 108.06(17) | 108.0(5) | 108.53(17) | 107.22(13) |
| C(20)−N(1)−Al(1A) | 118.7(2) | 120.69(17) | 119.4(5) | 119.41(19) | 123.08(13) |
| C(10)−N(1)−C(20) | 111.1(3) | 111.0(2) | 111.3(5) | 110.4(2) | 110.94(17) |
| C(10)−C(11)−C(12) | 119.3(3) | 117.4(2) | 116.8(6) | 119.0(2) | 117.9(2) |
| C(10)−N(1)−Al(1A) | 105.3(2) | 104.58(16) | 105.3(4) | 105.23(16) | 104.51(14) |
| C(12)−C(11)−C(16) | 121.4(3) | 121.7(3) | 122.0(6) | 121.6(3) | 121.4(2) |
| N(1)−C(10)−C(11) | 113.2(3) | 113.1(2) | 114.5(6) | 113.3(2) | 114.23(17) |
| Al(1)−C(12)−C(13) | 134.4(3) | 133.4(2) | 134.2(6) | 134.3(3) | 134.58(17) |
| Al(1)−C(12)−C(11) | 108.4(2) | 108.3(2) | 109.8(4) | 108.16(19) | 108.18(17) |
| C(11)−C(12)−C(13) | 116.9(3) | 117.2(3) | 115.6(7) | 117.2(3) | 116.8(2) |

Bu)-$\mu$-$(CH_2C_6H_4)]_2$ as product. The formation of the isobutyl orthometalated dimer was complete within 24 h at 120 °C, with longer times required for the less bulky R groups ($n$-Bu = 36 h, $n$-Pr = 48 h, Et = 48 h, Me = 96 h).

Thermolysis of 1:1 $R_3Al/HN(CH_2Ph)_2$ reaction mixtures at 120 °C led only to the formation and isolation of the expected Al−N dimers $[R_2AlN(CH_2Ph)_2]_2$.[9−11] Formation of the corresponding orthometalated dimers required heating for three weeks at 150−155 °C.[8] Thus, the substitution of the bulky *tert*-butyl group for a benzyl group on the amine nitrogen significantly enhanced reactivity and the formation of the orthometalated dimers with much lower heating times and temperatures required, similar to that reported for the synthesis of cyclopalladated complexes of secondary benzylamines with sterically bulky substituents.[3] The isolated product yields (71−93%) were significantly greater than in the $R_3Al$/dibenzylamine reaction system (31−57%). Because of the substitution of the *tert*-butyl group, the steric bulk of the R group on the aluminum atom now becomes important in terms of determining the time required for reaction completion.

**$^1$H and $^{13}$C NMR Data.** Preliminary $^1$H NMR chemical shifts were assigned for compounds **1**−**5** using 1D $^1$H NMR coupled and single-frequency decoupled spectral data. Final assignments were determined from the $^1$H 2D COSY and NOESY NMR spectra (see Figure 1 for atom numbering). Only one set of $^1$H NMR resonances were observed for each compound, although both cis and trans structures would be expected because of the asymmetric amine reactant. However, the 2D $^1$H NOESY NMR correlations between the *tert*-butyl protons and H(13) and between the C(1) alkyl protons and H(10) strongly suggest a trans structure in solution. The $^{13}$C NMR chemical shifts were determined from 1D $^{13}$C decoupled and DEPT spectra and 2D $^{13}C\{^1H\}$ $^1J$(C,H) correlations (HETCOR). There are only small variations in the NMR chemical shift data for the individual $^1$H and $^{13}$C benzyl resonances in **1**−**5**, suggesting that the nature of the attached alkyl group has little influence in this case.

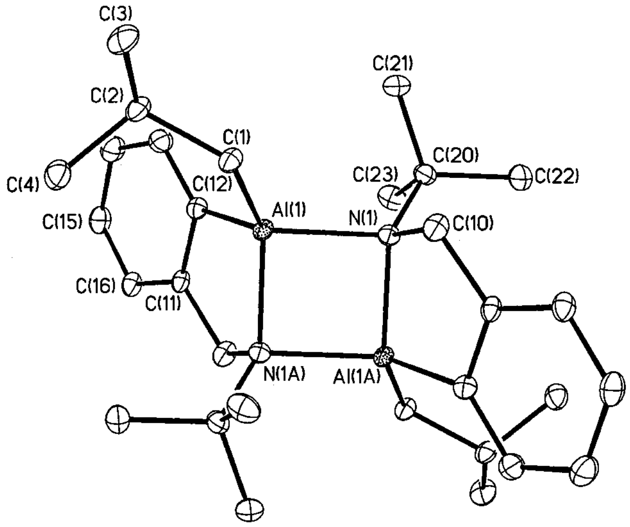

**Figure 1.** ORTEP diagram of [$i$-BuAlN($t$-Bu)-$\mu$-$(CH_2C_6H_4)]_2$ (**5**). Hydrogen atoms omitted for clarity and thermal ellipsoids at 30% probability.

The $^1$H and $^{13}$C chemical shift data for **1**−**5** are consistent with the alkyl and orthometalated benzyl data from [RAlN$(CH_2Ph)$-$\mu$-$(CH_2C_6H_4)]_2$.[8] Substitution of a *tert*-butyl for a benzyl group in the orthometalated dimer results in small $^1$H NMR downfield chemical shifts ($\Delta\delta_H = 0.10$ to 0.35 ppm). In contrast, changes in the $^{13}$C NMR chemical shifts are more significant, with the greatest changes occurring at the C(1) ($\Delta\delta_C$(av)) = 5.9 ppm), C(10) (−4.8 ppm), C(11) (1.3 ppm), and C(12) (4.8 ppm) positions. $^{13}$C NMR chemical shifts have been shown to be sensitive to steric effects in several similar group 13/15 and 13/16 systems.[9,12−15] For example, the observed progressive downfield C(1) $^{13}$C NMR chemical shift with increasing steric bulk on the ligand coordinated to a group 13 metal in $R_3M{\cdot}HNR'_2$ systems has been explained in terms of increasing p character of the M−C bond as the C−M−C bond angles decrease to accommodate larger amine ligands.[15] From single-crystal X-ray data discussed below, substitution of the

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*tert*-butyl group for the benzyl group into the orthometalated dimer framework causes an average C−Al−C angle decrease of 14.8°, which is consistent with the observed $^{13}C$ NMR chemical shift changes in the C(1) and C(12) resonances.

**X-ray Crystallographic Data.** The X-ray structures of compounds **1**−**5** were determined to identify any structural differences that could be related to the nature of the alkyl group R and for comparison with the analogous structures reported for $[RAlN(CH_2Ph)$-$\mu$-$(CH_2C_6H_4)]_2$.[8] The ORTEP drawing for the molecular structure of **5** is given in Figure 1. Selected structural data are summarized in Tables 1 and 2. The structures of **1**−**5** each exhibit a planar $Al_2N_2$ core that possesses inversion symmetry. Each asymmetric unit in **1**−**3** consists of two half-molecules, while those in **4** and **5** consists of one half of the respective dimer. The $Al_2N_2$ ring is flanked on both sides by bridging $CH_2C_6H_4$ groups that are in a trans-orientation to each other with respect to the core ring. The point of connection of the bridging groups to the $Al_2N_2$ ring is through the $CH_2$ to the nitrogen and the ortho-carbon of the phenyl group to the aluminum, forming a chairlike conformation. The *tert*-butyl groups on the nitrogen atoms are trans to each other, as are the alkyl groups on the aluminum atoms. The structure of the $Al_2N_2$ ring is a slightly distorted square plane, where the N−Al−N angle varies from 87.95(7)° for **5** to 89.7(2)° for **3A** and correspondingly for the Al−N−Al angle from 90.3(2)° for **3A** to 92.05(7)° for **5**. The two Al−N bond distances are slightly different, with the Al−N bond included in the five-membered orthometalated ring [Figure 1, Al(1)−N(1A)] being longer [1.994(5) Å for **3A** to 2.018(2) for **2A**] than the other Al−N bond [1.976(3) Å for **1A** to 1.993(2) Å for **5**]. Thus, there are only minor variations in the $Al_2N_2$ ring geometry with the nature of the R group attached to the aluminum atom. Comparison of the ring geometry with that of the $[RAlN(CH_2Ph)$-$\mu$-$(CH_2C_6H_4)]_2$ dimers[8] reveals some small changes in bond distances and angles for the $Al_2N_2$ ring, but more significant changes in four bond angles external to the ring, upon substitution of the more bulky *tert*-butyl group. Whereas for the *tert*-butylbenzylamine dimers the $Al_2N_2$ rings are slightly elongated along the Al····Al line, the dibenzylamine dimers have longer N···N distances because the N−Al−N bond angle is greater than 90° [average value = 91.2(1)°] and the Al−N−Al bond angle less than 90° [average value = 88.8(1)°] for each dimer. Relative magnitudes of the N−Al−N and Al−N−Al ring angles in aluminum−nitrogen dimers have been discussed in terms of the steric requirements of nitrogen atom substituents.[16] Substitution of a *tert*-butyl for a benzyl group results in a small expansion of the $Al_2N_2$ ring, with the Al−N bond distances increasing an average of 0.026 Å for the Al(1)−N(1A) and 0.034 Å for the Al(1)−N(1) bonds. Also, The Al−N distances and internal angles for the $Al_2N_2$ ring in **1**−**5** are comparable to those reported for the [*i*-BuAl−iminobenzyl] orthometalated dimer.[5] However, substitution of the *tert*-butyl for a benzyl group on the nitrogen atom results in large changes in certain angles external to the ring as the *tert*-butyl group is accommodated, with increases in the C(1)−Al(1)−N(1A) and the C(12)−Al(1)−N(1) angles of 11.0° and 11.5° and decreases in the C(1)−Al(1)−C(12) and C(10)−N(1)−Al(1) angles of 14.8° and 10.3°, respectively.

In conclusion, substitution of a *tert*-butyl group for a benzyl group in the $R_3Al$/dibenzylamine reaction system increased the reactivity substantially and reduced the time and temperature required for orthometalated dimer formation. A comparison of the single-crystal X-ray data revealed relatively large changes in four angles external to the $Al_2N_2$ ring upon incorporation of the *tert*-butyl group. Correspondingly, there were significant changes in the $^{13}C$ NMR chemical shifts for the carbon nuclei involved in these angle changes. Currently, we are investigating the effects of several substituent groups of differing steric requirements on the nitrogen atom in the $R_3Al$/dibenzylamine system in terms of overall reactivity, possible orthometalated dimer formation, and NMR spectral and structural features.

**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 **1**−**5**. IR data for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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