Synthesis and Spectroscopic Studies of Alkylaluminum Alkoxides Derived from Optically Active Alcohols. Crystal and Molecular Structure of Monomeric Dimethylaluminum (2*S*,3*R*)-(+)-4-(Dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide

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The reaction of trialkylaluminum derivatives, R_3Al (R = Me, Et, *i*-Bu), with optically active alcohols quantitatively yields R_2AlOR' (R = Me (**1a**), Et (**1b**), OR′ = (*S*)-(−)-1-methyl-2-pyrrolidinemethanolate; R = Me (**2a**), Et (**2b**), OR′ = (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanolate; R = Me (**3a**), Et (**3b**), OR′ = (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alkoxide; R = Me (**4a**); Et (**4b**), *i*-Bu (**4c**), OR′ = (2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide; R = Me, OR′ = cinchonine, **5**; R = Me, OR′ = quinidine, **6**, R = Me, OR′ = quinine, **7**) and the corresponding alkane RH. The resulting compounds **1a**,**b**, **2a**,**b**, **3a**,**b**, **4a**–**c**, and **5**–**7**, have been characterized by ^1H and ^{13}C NMR spectroscopy. Compounds **1a**, **2a**, **3a**, **5**–**7** undergo a dynamic process with respect to the dissociation of the Al–N dative bond. This is consistent with equilibria between four- and five-coordinate aluminum species with Arrhenius activation energies of 12.5 ± 0.6, 13.9 ± 0.6, 25.0 ± 1.2, 19.3 ± 0.9, 17.3 ± 0.7, and 22.5 ± 1.6 kcal mol^{-1}, respectively. The structure of **4a** was determined by single crystal X-ray diffraction techniques and found to be in the monoclinic crystal system space group $P2_1$ (No. 4) with cell constants $a = 7.368(1)$ Å, $b = 15.859(3)$ Å, $c = 17.589(5)$ Å, $\beta = 92.81(2)°$, and $Z = 4$ (monomers); $R = 4.61\%$ ($R_w = 4.03\%$) based on 2228 observed reflections with $I_o \geq 3.0\sigma(I)$. The molecule exists as a monomer with an Al–O bond distance of 1.73 Å and an Al–N bond distance of 2.03 Å.

Introduction

During the past several years a number of organoaluminum derivatives have been used in regio- and stereospecific organic syntheses.[1] Among the derivatives studied, the modified aluminum hydride "ate" complexes (e.g., $LiAlH_2(OR)_2$, $LiAlH_2(O_2R)$, R = optically-active group) have been found to be very attractive intermediates in enantio- and stereoselective organic syntheses.[2,3] These chiral reducing agents also have been used in the synthesis of optically active triorganotin hydrides.[4] A few optically-active organoaluminum compounds such as EtAl(Cl)OR* [5] (OR* = *l*-mentholate) have been used as reaction intermediates in the enantioselective *ortho*-hydroxyalkylation of phenols[6] and in asymmetric Diels–Alder reactions.[7] However few of these derivatives have been studied by either NMR spectroscopy or by X-ray diffraction to provide details concerning their structures. Recently we reported the synthesis, X-ray structural characterization, and detailed spectroscopic investigations of optically-active organoaluminum derivatives of *l*-menthol and *l*-borneol.[8] We also reported preliminary results on the structure and properties of bis[dimethylaluminum (1*R*,2*S*)-(−)-α-(1-methylaminoethyl)benzyl alkoxide], **3a**.[9] In this paper we provide additional details on the synthesis of this type of complex utilizing bifunctional protic substrates including (*S*)-(−)-1-methyl-2-pyrrolidinemethanol, **1a**,**b**, (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanol (*l*-isolucinol), **2a**,**b**, (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alcohol (*l*-ephedrine), **3a**,**b**, (2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanol (Chirald), **4a**–**c**, cinchonine, **5**, quinidine, **6**, and quinine, **7** (**a**, R = Me; **b**, R = Et; **c**, R = *i*-Bu) in order to gain insights into the steric and electronic effects influencing the formation of the five-coordinate versus the four-coordinate aluminum center. The chemistry of organoaluminum complexes containing bidentate ligands has received considerable attention due to the wealth of information which can be obtained from aluminum centers with uncommon coordination numbers.[10,11] The geometry around aluminum in these complexes can be viewed as the intermediate stage of an S_N2-like process in which the fifth, neutral, ligand attacks the aluminum center forming the five-coordinate species. When an optically active bidentate ligand is utilized, one observes

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100% induction of optical activity upon the formation of the five-coordinate aluminum complex from its optical rotation and structure.[8]

Experimental Section

General Data. All solvents were purified and dried by standard techniques.[12] Argon gas was purified by passing through a series of columns containing Deox catalyst, phosphorus pentoxide, and calcium sulfate. Aluminum alkyls (Aldrich: 2.0 M Me_3Al solution in toluene, 1.9 M Et_3Al solution in toluene, 1.0 M i-Bu_3Al solution in toluene), (*S*)-(−)-1-methyl-2-pyrrolidinemethanol (Aldrich), (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanol (Aldrich), (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alcohol, (2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol (Aldrich), (*S*)-(+)-isoleucinol (Aldrich), cinchonine (Aldrich), quinidine (Aldrich), and quinine (Aldrich) were used as received. All glassware used in the synthetic work was oven or flame dried. The compounds are both extremely oxygen and water sensitive so standard Schlenk line and drybox techniques were employed. ^{1}H and ^{13}C NMR spectra were routinely recorded on a General Electric QE 300 or GN 300 or Varian Unity 500 spectrometers at room temperature. The chemical shifts were referenced to residual protic benzene-d_6 peaks (^{1}H, $\delta = 7.15$ ppm; ^{13}C, $\delta = 128.0$ ppm). Variable-temperature ^{1}H NMR spectra were recorded on a General Electric GN 300 spectrometer equipped with the standard computer-controlled variable-temperature unit in toluene-d_8 (^{1}H, $\delta = 2.09$ ppm). Elemental analyses on selected compound were performed by Galbraith Laboratories, Knoxville, TN. It should be noted that substantial problems in carbon analysis of organoaluminum derivatives, especially amides, have been observed by a number of groups.[13-15] This has been attributed to incomplete combustion with formation of carbides. Samples with no detectable impurities based on NMR analysis were sealed in glass ampules and sent for analysis. The hydrogen and nitrogen analyses were within reasonable limits; the carbon analysis was always less than calculated.

Preparation of Bis[dimethylaluminum (*S*)-(−)-1-methyl-2-pyrrolidinemethanolate], 1a. Into 1.19 mL of (*S*)-(−)-1-methyl-2-pyrrolidinemethanol (1.15 g, 0.01 mol) dissolved in Et_2O (50 mL) was syringed Me_3Al (5.0 mL, 0.01 mol) as quickly as permitted by the evolution of methane gas (ca. 5 min). The resulting reaction was vigorous, bringing the Et_2O to reflux. The reaction was allowed to stir for 2 h following the addition of the Me_3Al. The solvent was removed under vacuum to leave a white solid. The product was recrystallized by dissolving it in 15 mL of Et_2O and cooling this solution to −20 °C for a period of 12 h. The white crystalline solid was collected, washed with 10−15 mL of very cold pentane, and dried under vacuum. This solid was identified as $[Me_2Al(OCH_2\text{-}2\text{-}(S)\text{-}C_4H_7(NCH_3)]_2$: Yield 94%, mp 118−119 °C. Anal. Calcd for $C_8H_{18}AlNO$: C 56.12; H, 10.60; N, 8.18. Found: C, 55.41; H, 10.55; N, 8.33. ^{1}H NMR (C_6D_6, δ, ppm): δ 3.51 (dd, $^2J = 10$ Hz, $^3J = 6$ Hz, 1H), 3.12 (dd, $^2J = 10$ Hz, $^3J = 8$ Hz, 1H) (CH_2), 2.88 (m, 1H), 2.26 (m, 1H), 2.00 (m, 1H), 1.35 (m overlapping m, 4H) (pyrrolidine ring), 1.88 (s, 3H, NMe), −0.59 (s, 6H, AlMe). ^{13}C NMR (C_6D_6, δ, ppm): 67.5 (OC), 59.5 (NCH), 54.5 (NCH_2), 42.8 (NMe), 25.7, 20.9, −9.4 (AlMe).

Preparation of Bis[diethylaluminum (*S*)-(−)-1-methyl-2-pyrrolidinemethanolate], 1b. The procedure for this reaction is the same as described for **1a**, using 1.13 mL of (*S*)-(−)-1-methyl-2-pyrrolidinemethanol (1.09 g, 9.50 mmol) and Et_3Al (5.0 mL, 9.50 mmol), yielding a white solid product. This was recrystallized from 16 mL of pentane/Et_2O (15:1). The white crystalline solid was collected, washed with 10−15 mL of very cold pentane, and dried under vacuum. This solid was identified as $[Et_2Al(OCH_2\text{-}2\text{-}(S)\text{-}C_4H_7(NCH_3)]_2$: Yield 88%, mp 64−65 °C. ^{1}H NMR (C_6D_6, δ, ppm): 3.58 (dd, $^2J = 10$ Hz, $^3J = 6$ Hz, 1H), 3.13 (dd, $^2J = 10$ Hz, $^3J = 8$ Hz, 1H) (CH_2), 2.88 (m, 1H), 2.45 (m, 1H), 2.13 (m, 1H), 1.31 (overlapping m, 4H), 0.83 (d, 3H), 0.77 (d, 5H) (pyrrolidine ring), 1.94 (s, 3H, NMe), 1.43 (t, $^3J = 8$ Hz, 6H, $AlCH_2CH_3$), 0.11 (m, 4H, Al-CH_2CH_3). ^{13}C NMR (C_6D_6, δ, ppm): 67.3 (OC), 60.7 (NCH), 53.9 (NCH_2), 42.5 (NCH_3), 24.9, 20.6, 11.2 ($AlCH_2CH_3$), 1.1 ($AlCH_2CH_3$).

Preparation of Bis[dimethylaluminum (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanolate], 2a. The procedure for this reaction is the same as described for **1a**, using (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanol (*l*-isolucenol) (0.50 g, 4.27 mmol) and Me_3Al (2.14 mL, 4.27 mmol), yielding a white solid product. This was recrystallized by dissolving in 11 mL of pentane/Et_2O (10:1) and cooling to −20 °C over 12 h. The solid was collected, washed with 10−15 mL of cold pentane, and dried under vacuum. The solid was identified as $[Me_2Al(OCH_2\text{-}(S)\text{-}CH(NH_2)\text{-}(S)\text{-}CH(CH_3)CH_2CH_3)]_2$: Yield 85%, mp 122−124 °C. Anal. Calcd for $C_8H_{20}AlNO$: C, 55.47; H, 11.64; N, 8.09. Found: C, 52.72; H, 11.27; N, 7.93. ^{1}H NMR (C_6D_6, δ, ppm): 3.76 (dd, $^2J = 10$ Hz, $^3J = 5$ Hz, 1H), 3.09 (apparent t, $^2J = {}^3J = 10$ Hz, 1H), 2.34 (m, 1H), 1.16 (d, $^3J = 5$ Hz, 2H), 0.81 (m, 1H), 0.53 (overlapping m, 5H), 0.35 (d, $^3J = 6$ Hz, 3H), −0.46 (s, 6H, AlMe). ^{13}C NMR (C_6D_6, δ, ppm): 61.3 (OC), 56.8 (NCH), 37.7 (MeCH), 25.3 ($MeCH_2$), 14.3 (CH*Me*), 10.7 (CH_2*Me*), −8.3 (AlMe).

Preparation of Bis[diethylaluminum (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanolate], 2b. The procedure for this reaction is the same as described for **1a**, using (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanol (0.34 g, 2.90 mmol) and Et_3Al (1.53 mL, 2.90 mmol), yielding a white solid product. This was recrystallized by dissolving in pentane (ca. 15 mL) and cooling to −20 °C over 12 h. The solid was collected, washed with 10−15 mL of cold pentane, and dried under vacuum. The solid was identified as $[Et_2Al(OCH_2\text{-}(S)\text{-}CH(NH_2)\text{-}(S)\text{-}CH(CH_3)CH_2CH_3)]_2$: Yield 80%, mp 65−66 °C. Anal. Calcd for $C_{10}H_{24}AlNO$: C, 59.67; H, 12.02; N, 6.96. Found: C, 57.14; H, 11.67; N, 6.82. ^{1}H NMR (C_6D_6, δ, ppm): 3.82 (dd, $^2J = 10$ Hz, $^3J = 5$ Hz, 1H), 3.14 (apparent t, $^2J = {}^3J = 10$ Hz, 1H), 2.43 (m, 1H), 1.34 (d, $^3J = 9$ Hz, 2H), 0.87 (m, 1H), 0.57 (overlapping m, 5H), 1.47 (t, $^3J = 8$ Hz, 6H, $AlCH_2CH_3$), 0.19 (q, $^3J = 8$ Hz, 4H, $AlCH_2CH_3$). ^{13}C NMR (C_6D_6, δ, ppm): 62.2 (OC), 57.2 (NCH), 37.8 (MeCH), 25.4 ($MeCH_2$), 14.3 (CH*Me*), 10.8 (CH_2-*Me*), 11.5 ($AlCH_2CH_3$), 2.1 ($AlCH_2CH_3$).

Preparation of Bis[dimethylaluminum (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alkoxide], 3a. The procedure for this reaction is the same as described for **1a**, using (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alcohol (*l*-ephedrine) (1.03 g, 6.23 mmol) in Et_2O (60 mL) and Me_3Al (3.12 mL, 6.23 mmol). A white precipitate formed as the solution was stirred for 5 h. The solution was decanted, leaving a white solid. The product was washed with 10−15 mL of very cold pentane and dried under vacuum. This solid was identified as $[Me_2Al(O\text{-}(R)\text{-}CHC_6H_5(S)\text{-}CH(S)\text{-}NHCH_3)CH_3)]_2$ and recrystallized from hot toluene: Yield > 95%, mp 215−216 °C. Anal. Calcd for $C_{12}H_{20}AlNO$: C, 65.15; H, 9.11; N, 6.33. Found: C, 64.67; H, 9.24; N, 6.21. ^{1}H NMR (C_6D_6, δ, ppm): 7.27−7.02 (m, 5H, Ph), 4.90 (d, $^3J = 5.8$ Hz, 1H, PhC(*H*)O), 2.81 (m, 1H, NH), 1.62 (d, $^3J = 6.3$ Hz, 3H, NMe), 0.90 (m, 1H, *CH*Me), 0.24 (d, $^3J = 6.6$ Hz, 3H, CH*Me*), −0.51 (s, 3H), −0.85 (s, 3H) (AlMe). ^{13}C NMR (C_6D_6, δ, ppm): 140.5, 128.3, 127.7, 127.5, (Ph), 74.6 (O*CH*), 57.5 (NCH), 30.4 (NMe), 14.4 (CH*Me*), −7.7, −11.5 (AlMe).

Preparation of Bis[diethylaluminum (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alkoxide], 3b. The procedure for this reaction is the same as described for **1a**, using (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alcohol (1.02 g, 6.17 mmol) and Et_3Al (3.25 mL, 6.17 mmol). The volume of the solution was slowly reduced under vacuum leaving a white solid. The

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product was washed with 10−15 mL of very cold pentane, dried under vacuum, and identified as [Et_2Al(O-(*R*)-CHC_6H_5((*S*)-CH((*S*)-$NHCH_3$)CH_3)]$_2$: Yield 84%, mp 122−124 °C. Anal. Calcd for $C_{14}H_{24}AlNO$: C, 67.44; H, 9.70; N, 5.62. Found: C, 65.06; H, 9.49; N, 5.57. ^{1}H NMR (C_6D_6, δ, ppm): 7.27−7.03 (m, 5H, Ph), 4.95 (d, ^3J = 5.6 Hz, 1H, Ph*C*(*H*)O), 2.93 (m, 1H, NH), 1.77 (d, ^3J = 6.0 Hz, 3H, NMe), 1.56 (vb, 3H), 1.15 (m, 1H), 1.05 (vb, 3H), 0.25 (d overlapping m, ^3J = 6.4 Hz, 5H), −0.31 (vb, 2H). ^{13}C NMR (C_6D_6, δ, ppm): 140.4, 128.3, 127.7, 127.4, 127.5 (Ph), 75.7 (OCH), 58.0 (NCH), 31.1 (NMe), 14.5 (CH*Me*), 11.6, 9.8 ($AlCH_2\mathit{CH}_3$), 3.5, 0.5 ($Al\mathit{CH}_2CH_3$).

Preparation of Dimethylaluminum (2*S*,3*R*)-(+)-4-(Dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide, 4a. (2*S*,3*R*)-(+)-4-(Dimethylamino)-1,2-diphenyl-3-methyl-2-butanol (Chirald) (1.00 g, 3.52 mmol) was dissolved in pentane (50 mL), and Me_3Al (1.76 mL, 3.52 mmol) was added over a period of 5 min. During the addition a white precipitate formed. The reaction mixture was stirred for 2 h following the addition to ensure complete reaction. The solid was crystallized from hot pentane/toluene (10:1 ratio). The product was collected, washed with 10−15 mL of pentane, and dried under vacuum. This solid was identified as Me_2Al((2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide): Yield 90%, mp 164−166 °C. ^{1}H NMR (C_6D_6, δ, ppm): 7.00−7.67 (m, 10H, $\mathit{Ph}CH_2$), 3.15 (s, 2H, PhCH_2), 2.30 (dd, ^2J = 13 Hz, ^3J = 11 Hz, 1H), 0.90 (d, ^2J = 13 Hz, 1H, MeC(H)CH_2), 1.93 (m, 1H, Me*C*(*H*)CH_2), 1.46, 1.37 (6H, Me_2NCH_2), 0.61 (d, ^3J = 8 Hz, 3H, *Me*C(H)CH_2), −0.67, −0.42 (6H, AlMe). ^{13}C NMR (C_6D_6, δ, ppm): 146.8, 139.5, 132.1, 128.7, 128.6, 127.8, 126.7, 126.4 (Ph), 79.8 ($PhCH_2$(Ph)*C*), 64.5 (PhCH_2), 48.6, 48.5 (Me_2N), 45.4 (MeC(H)CH_2), 38.1 (Me*C*(*H*)CH_2), 18.1 (*Me*C(H)CH_2), −8.2, −8.1 (AlMe).

Preparation of Diethylaluminum (2*S*,3*R*)-(+)-4-(Dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide, 4b. The procedure for this reaction is the same as described for **4a**, using (2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanol (1.00 g, 3.52 mmol) and Et_3Al (1.85 mL, 3.52 mmol). The solid was isolated and purified as described for **4a**. This solid was identified as Et_2Al((2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide): Yield 80%, mp 124−125 °C. Anal. Calcd for $C_{22}H_{34}AlNO$: C, 75.17; H, 9.33; N, 3.81. Found: C, 72.74; H, 9.26; N, 3.34. ^{1}H NMR (C_6D_6, δ, ppm): 7.00−7.63 (m, 10H, $\mathit{Ph}CH_2$), $\delta_A = 3.13$, $\delta_B = 3.19$, $^2J_{AB}$ = 13.5 Hz, $\Delta\delta = 0.055$, (2H, PhCH_2), 2.30 (dd, ^2J = 13 Hz, ^3J = 11 Hz, 1H), 0.89 (d, ^2J = 13 Hz, 1H, MeC(H)CH_2), 1.91 (m, 1H, Me*C*(*H*)CH_2), 1.53, 1.44 (6H, Me_2NCH_2), 0.61 (d, ^3J = 7 Hz, 3H, *Me*C(H)CH_2), 1.48 (t, ^2J = 8 Hz), 1.40 (t, ^3J = 8 Hz) ($AlCH_2\mathit{Me}$), 0.31 (m, 1H, ^3J = 8 Hz, ^2J = 14 Hz), 0.20 (m, 1H, ^3J = 8 Hz, ^2J = 14 Hz), −0.03 (m, 1H, ^3J = 8 Hz, ^2J = 14 Hz), −0.08 (m, 1H, ^3J = 8 Hz, ^2J = 14 Hz, $Al\mathit{CH}_2Me$). ^{13}C NMR (C_6D_6, δ, ppm): 146.2, 139.2, 131.7, 128.3, 127.6, 127.3, 126.3, 126.0 (Ph), 79.2 ($PhCH_2$(Ph)*C*), 64.3 (PhCH_2), 48.1, (Me_2N), 44.8 (MeC(H)CH_2), 39.0 (Me*C*(*H*)CH_2), 18.0 (*Me*C(H)CH_2), 10.1, 10.0 ($AlCH_2\mathit{Me}$), 1.1, 0.7 ($Al\mathit{CH}_2Me$).

Preparation of Diisobutylaluminum (2*S*,3*R*)-(+)-4-(Dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide, 4c. The reaction was carried out using the same procedure as described for **4a**, using (2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanol (1.00 g, 3.52 mmol) and (*i*-Bu)$_3$Al (3.52 mL, 3.52 mmol). The resulting solution deposited colorless crystals over a period of 24 h at −20 °C. This solid was identified as (*i*-Bu)$_2$Al((2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide): Yield 96%, mp 134−135 °C. Anal. Calcd for $C_{26}H_{42}AlNO$: C, 76.55; H, 9.99; N, 3.31. Found: C, 75.03; H, 9.97; N, 3.19. ^{1}H NMR (C_6D_6, δ, ppm): 6.94−7.58 (m, 10H, $\mathit{Ph}CH_2$), $\delta_A = 3.105$, $\delta_B = 3.295$, J_{AB} = 14.0 Hz, $\Delta\delta = 0.188$ (2H, PhCH_2), 2.41 (dd, ^2J = 13 Hz, ^3J = 11 Hz, 1H), 0.92 (d, ^2J = 13 Hz, 1H, MeC(H)CH_2), 1.89 (m, 1H, Me*C*(*H*)CH_2), 1.57, 1.54 (6H, Me_2NCH_2), 0.59 (d, ^3J = 7 Hz, 3H, *Me*C(H)CH_2), 2.29 (septet, 1H, ^3J = 7 Hz), 2.04 (septet, 1H, ^3J = 7 Hz) ($AlCH_2\mathit{CH}Me_2$), 1.34 (d, ^3J = 7 Hz), 1.31 (d, ^3J = 6 Hz) 1.25 (d, ^3J = 7 Hz), 1.17 (d, ^3J = 6 Hz), ($AlCH_2CH\mathit{Me}_2$), 0.24 (dd, 1H, ^3J = 7 Hz, ^2J = 14 Hz), 0.16 (dd, 2H, ^3J = 7 Hz, ^2J = 14 Hz), −0.29 (dd, 1H, ^3J = 7 Hz, ^2J = 14 Hz, $Al\mathit{CH}_2CHMe_2$). ^{13}C NMR (C_6D_6, δ, ppm): 145.4, 139.2, 131.5, 128.6, 127.5, 127.2, 126.2, 125.8 (Ph), 79.5 ($PhCH_2$(Ph)*C*), 65.0 (PhCH_2), 48.7, 48.0 (Me_2N), 45.9 (MeC(H)CH_2), 40.6 (Me*C*(*H*)CH_2), 18.1 (*Me*C(H)CH_2), 23.0, 24.4 ($Al\mathit{CH}_2CHMe_2$), 29.2, 26.2 ($AlCH_2\mathit{CH}Me_2$), 28.9, 28.8 ($AlCH_2CH\mathit{Me}_2$).

Preparation of Bis(dimethylaluminum alkoxide) Derived from Cinchonine, 5. The procedure for this reaction is the same as described for **1a**, using cinchonine (1.06 g, 3.60 mmol) in Et_2O (100 mL) with Me_3Al (1.80 mL, 3.60 mmol), with the exception that it was stirred for 12 h following the addition of the reactants, during which time a white precipitate formed. The solution was decanted from the product, which was washed with 10−15 mL of very cold Et_2O and dried under vacuum. The product was recrystallized from 10 mL of toluene at 25 °C for a period of 2 days. This solid was identified as the Me_2Al(alkoxide) derived from cinchonine: Yield 74%, dec 257 °C. Anal. Calcd for $C_{21}H_{27}AlN_2O$: C, 71.98; H, 7.77; N, 7.99. Found: C, 70.35; H, 7.63; N, 7.81. ^{1}H NMR: δ 8.96−7.12 (m, 6H), 6.06 (d, 1H), 4.43 (m, 1H), 4.27 (d, 1H), 4.15 (d, 1H), 3.28 (m, 1H), 2.96 (m, 1H), 2.66 (m, 1H), 2.52 (m, 1H), 2.07 (m, 1H), 2.39 (m, 1H), 1.07 (m, 1H), 0.97 (overlapping m, 4H), −0.28 (2, 3H, AlMe), −1.03 (s, 3H, AlMe). ^{13}C NMR: δ 150.3, 150.1, 148.9, 148.0, 138.0, 131.6, 128.7, 126.3, 123.7, 121.9, 115.1, 68.7, 59.3, 49.5, 49.3, 39.0, 27.7, 25.3, 23.9, −6.8 (Al−Me), −8.0 (Al−Me).

Preparation of Bis(dimethylaluminum alkoxide) Derived from Quinidine, 6. The procedure for this reaction is the same as described for **5**, using quinidine (0.91 g, 2.81 mmol) and Me_3Al (1.41 mL, 2.81 mmol). The solution was decanted, and the white solid was washed with 10−15 mL of very cold Et_2O and dried under vacuum. The product was recrystallized from 10 mL of toluene at 25 °C for a period of 8 days. This solid was identified as the Me_2Al(alkoxide) derived from quinidine: Yield 79%, dec 260 °C. Anal. Calcd for $C_{22}H_{30}AlN_2O_2$: C, 69.27; H, 7.93; N, 7.34. Found: C, 65.60; H, 7.47; N, 6.97. ^{1}H NMR: δ 8.98−7.12 (m, 5H), 6.08 (d, 1H), 4.55 (m, 1H), 4.39 (d, 1H), 4.23 (d, 1H), 3.33 (s overlapping m, 4H), 2.97 (m, 1H), 2.76 (m, 1H), 2.60 (m, 1H), 2.07 (m, 1H), 1.44 (m, 1H), 1.08 (m, 5H), 0.92 (m, 1H), −0.26 (s, 3H, AlMe), −0.97 (s, 3H, AlMe). ^{13}C NMR: δ 157.9, 157.1, 147.8, 147.1, 144.5, 138.0, 132.7, 122.3, 120.8, 115.2, 103.0, 68.9, 59.5, 49.5, 49.3, 39.0, 27.7, 25.3, 24.1, −6.8 (Al−Me), −8.1 (Al−Me).

Preparation of Bis(dimethylaluminum alkoxide) Derived from Quinine, 7. The procedure for this reaction is the same as described for **5**, using quinine (0.92 g, 2.84 mmol) and Me_3Al (1.41 mL, 2.84 mmol). The solution was decanted, and the white solid was washed with 10−15 mL of very cold Et_2O and dried under vacuum. The product was recrystallized from 10 mL of toluene at 25 °C for a period of 3 days. This solid was identified as Me_2Al(alkoxide) derived from quinine: Yield 76%, dec 270 °C. Anal. Calcd for $C_{22}H_{30}AlN_2O_2$: C, 69.27; H, 7.93; N, 7.34. Found: C, 66.50; H, 7.52; N, 6.75. ^{1}H NMR: δ 9.04−7.16 (m, 5H), 6.19 (d, 1H), 5.47 (m, 1H), 4.86 (m, 2H), 3.67 (m, 1H), 3.28 (s overlapping m, 4H), 3.07 (m, 1H), 2.78 (m, 1H), 2.45 (m, 1H), 2.17 (m, 1H), 1.66 (m, 2H), 1.08 (overlapping m, 2H), 0.86 (m, 1H), 0.53 (m, 1H), −0.23 (s, 3H, AlMe), −0.96 (s, 3H, AlMe). ^{13}C NMR: δ 157.9, 151.4, 147.9, 145.6, 145.2, 141.1, 133.3, 121.9, 120.8, 114.8, 102.9, 69.2, 59.9, 56.5, 54.9, 44.0, 38.5, 27.3, 26.1, 24.5, −6.1 (Al−Me), −7.5 (Al−Me).

Thermolysis of 3a To Yield [MeAl(O-(*R*)-CHC_6H_5-(*S*)-CH-(*S*)-(NCH_3)CH_3)]$_2$, 8. [Me_2Al(O-(*R*)-CHC_6H_5-(*S*)-CH-(*S*)-($NHCH_3$)CH_3)]$_2$ (1.03 g, 2.33 mmol) was dissolved in toluene (60 mL), and the solution was refluxed for a period of 10 days. The reaction mixture was allowed to cool to room temperature and the solvent removed under vacuum. The product was washed with 10−15 mL of very cold pentane and dried under vacuum. This solid was identified as [MeAl(O-(*R*)-CHC_6H_5-(S)-CH-(S)-(NCH_3)CH_3)]$_2$: Yield >98%, mp 114−115 °C. Anal.

Table 1. Experimental Parameters for the X-ray Diffraction Study of Monomeric [Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], 4a

compd	[Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], **4a**
formula	$C_{21}H_{30}ONAl$
mol weight	339.42
cryst habit	needles (0.35 × 0.62 × 0.35 mm^3)
cryst color	colorless
cryst system	monoclinic
space group	$P2_1$ (No. 4)
Z	4 (monomers)
a	7.369(1) Å
b	15.865(3) Å
c	17.583(5) Å
β	92.81(2)°
V	2053.1 (0.8) Å^3
d(calc)	1.098 g cm^{-3}
F(000)	736 electrons
radiation type (λ)	Cu K$\bar{\alpha}$ (1.541 84 Å, Ni Filtered)
temp	20 °C
type of data collcn	$\theta/2\theta$ scan
2θ scan range	6−110°
octants used	$h,k,\pm l$
scan rate	3−8 deg/min
scan width	1.0° below Kα_1 to 1.1° above Kα_2
bkgd/scan ratio	0.5
std reflcns	3 measd per every 100 reflcns
dev from std	3%
no. of data collcd	2926 (R_{ing} = 0.0180)
no. of unique reflcns	2678
no. of obsd reflcns with $I_o \geq 3.0\sigma(I)$	2228
linear abs coeff (μ)	4.48 cm^{-1}
abs corr	none applied
no. of params refined	432 (215 in block 1; 217 in block 2)
obsd/param ratio	5:1
R	4.61% (4.75%)^a
R_w ($w^{-1} = \sigma^2(F_o) + g(F_o)^2$)	4.03% (4.20%)^a
overall shift/esd	0.000
resid electron density	0.17 e/Å^3; 1.77 Å^3 from O1

^{a} Values in parentheses are for the enantiomer, [Me_2Al(2*R*,3*S*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide].

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in [Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], 4a

atom	x	y	z	U_{eq}^{a}
		Molecule 1		
Al1	−0.2788(3)	−0.24847	−0.65515(9)	0.0563(6)
O1	−0.4040(4)	−0.1625(2)	−0.6282(2)	0.051(1)
N1	−0.0727(6)	−0.1858(3)	−0.7034(2)	0.060(2)
C1	−0.4155(9)	−0.3136(4)	−0.7325(4)	0.107(3)
C2	−0.173(1)	−0.3180(4)	−0.5714(4)	0.093(3)
C3	−0.3754(8)	−0.0833(3)	−0.5121(3)	0.054(2)
C4	−0.5564(9)	−0.1111(4)	−0.4858(3)	0.056(2)
C5	−0.5944(9)	−0.1971(4)	−0.4763(3)	0.064(3)
C6	−0.755(1)	−0.2234(4)	−0.4470(3)	0.077(3)
C7	−0.8819(9)	−0.1652(5)	−0.4253(3)	0.080(3)
C8	−0.848(1)	−0.0820(5)	−0.4352(3)	0.077(3)
C9	−0.690(1)	−0.0551(4)	−0.4648(3)	0.069(3)
C10	−0.4753(7)	−0.0170(3)	−0.6409(3)	0.049(2)
C11	−0.5023(8)	−0.0638(4)	−0.6108(3)	0.061(2)
C12	−0.6121(9)	0.1219(3)	−0.6512(4)	0.070(3)
C13	−0.6983(8)	0.10016(4)	−0.7197(3)	0.067(3)
C14	−0.6689(8)	0.0221(4)	−0.7492(3)	0.061(2)
C15	−0.5611(8)	−0.0359(3)	−0.7107(3)	0.053(2)
C16	−0.3547(7)	−0.0829(3)	−0.5995(3)	0.049(2)
C17	−0.1484(8)	−0.0680(3)	−0.6135(3)	0.053(2)
C18	−0.1032(8)	−0.0927(4)	−0.6937(3)	0.059(2)
C19	−0.0791(8)	0.0221(4)	−0.5969(3)	0.070(2)
C20	−0.069(1)	−0.2026(4)	−0.7861(4)	0.107(3)
C21	0.1091(9)	−0.2086(4)	−0.6685(4)	0.095(3)
		Molecule 2		
Al2	−0.8115(2)	0.4802(1)	−0.83020(9)	0.0522(6)
O2	−0.9364(4)	0.3979(2)	−0.8705(2)	0.050(1)
N2	−0.5900(6)	0.4135(3)	−0.7927(2)	0.061(2)
C1A	−0.930(1)	0.5242(5)	−0.7428(4)	0.117(4)
C2A	−0.735(1)	0.5646(4)	−0.9021(4)	0.101(3)
C3A	−0.9359(8)	0.3330(3)	−0.9935(3)	0.057(2)
C4A	−1.1242(8)	0.3611(4)	−1.0180(3)	0.052(2)
C5A	−1.171(1)	0.4458(4)	−1.0167(3)	0.071(3)
C6A	−1.340(1)	0.4740(4)	−1.0425(4)	0.086(3)
C7A	−1.4649(9)	0.4177(6)	−1.0715(4)	0.082(3)
C8A	−1.424(1)	0.3346(5)	−1.0738(3)	0.080(3)
C9A	−1.256(1)	0.3063(4)	−1.0474(3)	0.071(3)
C10A	−1.0049(7)	0.2513(3)	−0.8721(3)	0.047(3)
C11A	−1.0771(8)	0.2630(3)	−0.8006(3)	0.053(2)
C12A	−1.1773(8)	0.1999(4)	−0.7668(3)	0.063(2)
C13A	−1.2029(9)	0.1244(4)	−0.8039(4)	0.071(3)
C14A	−1.1328(9)	0.1116(4)	−0.8737(4)	0.073(3)
C15A	−1.0339(8)	0.1747(4)	−0.9068(3)	0.064(2)
C16A	−0.8939(7)	0.3220(3)	−0.9063(3)	0.046(2)
C17A	−0.6860(8)	0.3065(3)	−0.8946(3)	0.052(2)
C18A	−0.6191(8)	0.3222(3)	−0.8115(3)	0.060(2)
C19A	−0.6175(8)	0.2194(3)	−0.9184(3)	0.067(2)
C20A	−0.422(1)	0.4421(4)	−0.8285(4)	0.103(3)
C21A	−0.555(1)	0.4199(4)	−0.7099(3)	0.109(3)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^{*}\cdot a_j^{*}\bar{a}_i\cdot\bar{a}_j$.

Calcd for $C_{11}H_{16}AlNO$: C, 64.38; H, 7.86; N, 6.82. Found: C, 64.40; H, 7.68; N, 6.71. ^1H NMR (C_6D_6, δ, ppm): 7.27−6.98 (m, 5H, Ph), 4.82 (d, ^3J = 6 Hz, 1H), 3.45 (m, 1H), 1.98 (s, 3H), 0.85 (d, ^3J = 7 Hz, 3H), −0.57 (s, 3H, AlMe), −0.61 (s, 3H, AlMe). ^{13}C NMR (C_6D_6, δ, ppm): 139.6, 128.3, 127.9, 126.7, 77.7 (OCH), 58.1 (NCH), 31.2 (NMe), 14.0 (CH*Me*), −10.0, −12.6 (AlMe).

X-ray Structure Determination of [Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], 4a. Crystals of **4a** were grown from a pentane/toluene (20:1 ratio) solution at 20 °C. A crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube in a drybox, plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed on a P2$_1$ Nicolet diffractometer for data collection. Parameters from the crystal structure determination are presented in Table 1.

The crystal was found to be in the monoclinic crystal system. Lattice constants were verified by axial photographs, and the crystal was assigned to the space group $P2_1$ (No. 4) or $P2/m$ (No. 11) on the basis of the systematic absences with $P2_1$ required by the optically active center in **4a**. Data reduction was carried out using the SHELXTL program.[16] The direct methods routine produced an acceptable solution for the structure, placing all of the non-hydrogen atoms. Full-matrix least-squares refinement was carried out using SHELX-76.[17] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, nitrogen, oxygen, and aluminum atoms were used.[18] Each hydrogen atom was placed in a calculated position with a C−H bond distance of 0.95 Å. The X-ray data collection and refinement parameters are given in Table 1. The structure was determined for both enantiomers, (2*S*,3*R*) and (2*R*,3*S*), and refined slightly better for the expected (2*S*,3*R*) form with R = 4.61% vs 4.75% and R_w = 4.03% vs 4.20%. The atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms are given in Table 2 with selected bond distances and angles listed in Table 3.

Results and Discussion

Synthesis. The organoaluminum alkoxides R_2AlOR^* were prepared from the reaction of the optically active alcohol with the trialkylaluminum R_3Al (R = Me, Et,

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(16) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, Federal Republic of Germany, 1978.

(17) Sheldrick, G. M. *SHELX-76*; University Chemical Laboratory: Cambridge, England, 1976.

(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor, D. Reidel, Dordrecht, The Netherlands).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Dimeric [Me_2Al(1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alkoxide)]$_2$, 3a, and Monomeric [Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], 4a

3a		4a			
		molecule 1		molecule 2	
atoms	dist	atoms	dist	atoms	dist
Al1−Al1′	3.000(4)	Al1−O1	1.726(3)	Al2−O2	1.730(4)
Al1−O1	1.864(6)	Al1−N1	2.035(5)	Al2−N2	2.028(5)
Al1−O1′	1.946(7)	Al1−C1	1.948(7)	Al2−C1A	1.933(7)
Al1−N1	2.193(8)	Al1−C2	1.970(6)	Al2−C2A	1.943(6)
Al1−C1	1.999(8)				

3a		4			
		molecule 1		molecule 2	
atoms	angle	atoms	angle	atoms	angle
Al1−O1−Al1′	104.0(3)	Al1−O1−C16	132.7(3)	Al2−O2−C16A	135.0(3)
O1−Al1−O1′	74.8(3)	Al1−N1−C18	108.3(3)	Al2−N2−C18A	109.2(3)
O1−Al1−N1	78.5(3)	Al1−N1−C20	111.9(4)	Al2−N2−C20A	112.1(4)
O1−Al1−C1	127.7(3)	Al1−N1−C21	112.6(4)	Al2−N2−C21A	112.6(4)
O1−Al1−C2	113.7(3)	O1−Al1−N1	98.5(2)	O2−Al2−N2	98.2(2)
O1′−Al1−N1	151.6(3)	O1−Al1−C1	110.2(2)	O2−Al2−C1A	110.3(3)
O1′−Al1−C1	98.0(3)	O1−Al1−C2	115.8(2)	O2−Al2−C2A	114.8(2)
O1′−Al1−C2	100.0(3)	N1−Al1−C1	109.8(2)	N2−Al2−C1A	108.5(4)
N1−Al1−C1	90.7(3)	N1−Al1−C2	108.0(3)	N2−Al2−C2A	108.5(3)
N1−Al1−C2	99.3(3)	C1−Al1−C2	113.4(3)	C1A−Al2−C2A	115.1(3)
C1−Al1−C2	118.5(4)				

i-Bu) in a 1:1 stoichiometry to afford the alkoxide complexes, **1a**,**b**, **2a**,**b**, **3a**,**b**, **4a**−**c**, and **5**−**7**, and the corresponding alkane, RH, in quantitative yields (eq 1).

$$R_3Al + R^*OH \rightarrow [R_2AlOR^*]_n + RH \qquad (1)$$

R = Me (**1a**), Et (**1b**); OR* = (*S*)-(−)-1-methyl-2-pyrrolidinemethanolate; $n = 2$

R = Me (**2a**), Et (**2b**); OR* = (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanolate; $n = 2$

R = Me (**3a**), Et (**3b**); OR* = (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alkoxide; $n = 2$

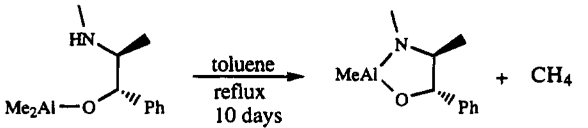
R = Me (**4a**), Et (**4b**), *i*-Bu (**4c**); OR* = (2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide; $n = 1$

R = Me (**5**), OR* = cinchoninate, $n = 2$

R = Me (**6**), OR* = quinidinate, $n = 2$

R = Me (**7**), OR* = quininate, $n = 2$

The dimethylaluminum alkoxide derivatives of (1*R*,2*S*)-(−)-α-(1-(methylamino)ethyl)benzyl alcohol (**3a**) and (2*S*,3*S*)-(+)-2-amino-3-methyl-1-pentanol (**2a**,**b**) formed by the reaction described in eq 1 contain a 2° and 1° amino substituent, respectively. The N−H bonds in these derivatives do not react readily with the Al−C bond at room temperature, but the amide complex, **8**, was formed from **3a** after refluxing in toluene for 10 days (eq 2).



3a **8** (>98 %) (2)

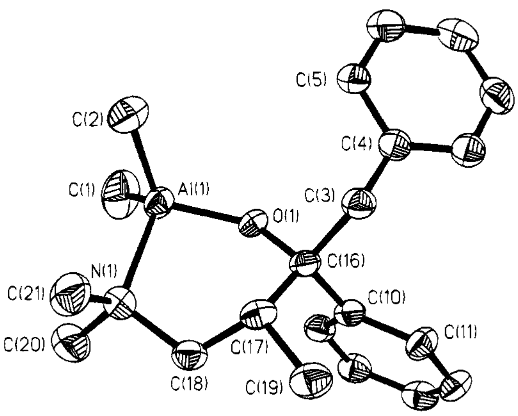
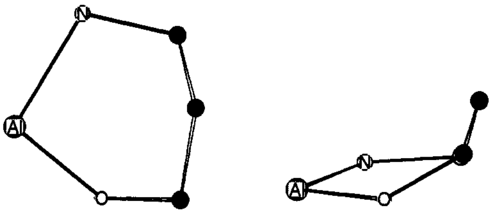


Figure 1. ORTEP diagram (50% thermal ellipsoids) of [Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], **4a**, showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

The compounds have been isolated as colorless, transparent crystals and are both air and moisture sensitive, decomposing over a period of seconds in the solid state after exposure to air. All the compounds are very soluble in aromatic (i.e. benzene and toluene) and ether solvents. Donor solvents do not appear to form stable isolable addition complexes due to the presence of an internal nucleophile and/or the formation of stable Al−O−Al bridge bonds.

Structure and Bonding in [Me_2Al(2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanoxide], 4a. An ORTEP diagram for **4a** is shown in Figure 1. The aluminum center in **4a** is in a four-coordinate environment bonded to two methyl groups, a nitrogen atom, and an oxygen atom of the alkoxide ligand and is contained in a six-membered heterocyclic ring. The ring is in a skew-boat conformation as shown in I. Selected bond distances and angles are given in Table 3, and those from **3a** are listed for comparison.



I

The Al−C bond distances of 1.950 and 1.972 Å are comparable to those found in related organoaluminum compounds.[10,11] The structural features which are worthy of comment are the Al−O and the Al−N distances. In **4a**, the Al−O and Al−N bond distances are 1.73 and 2.03 Å, which are substantially shorter than those observed in **3a** and related dimeric organoaluminum alkoxides[10,11] but comparable to those observed in monomeric four-coordinate species such as Me_2Al(2,6-di-*tert*-butyl-4-methylphenoxide)·Py.[19] The presence of a relatively short Al−O bond distance together with a large Al−O−C angle in **4a**, where neither a vacant p orbital nor an energetically accessible aluminum d orbital is available for π-bonding, is consistent with the proposal that π-donation from the oxygen lone pair

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[19] Healy, M. D.; Ziller, J. W.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2949.

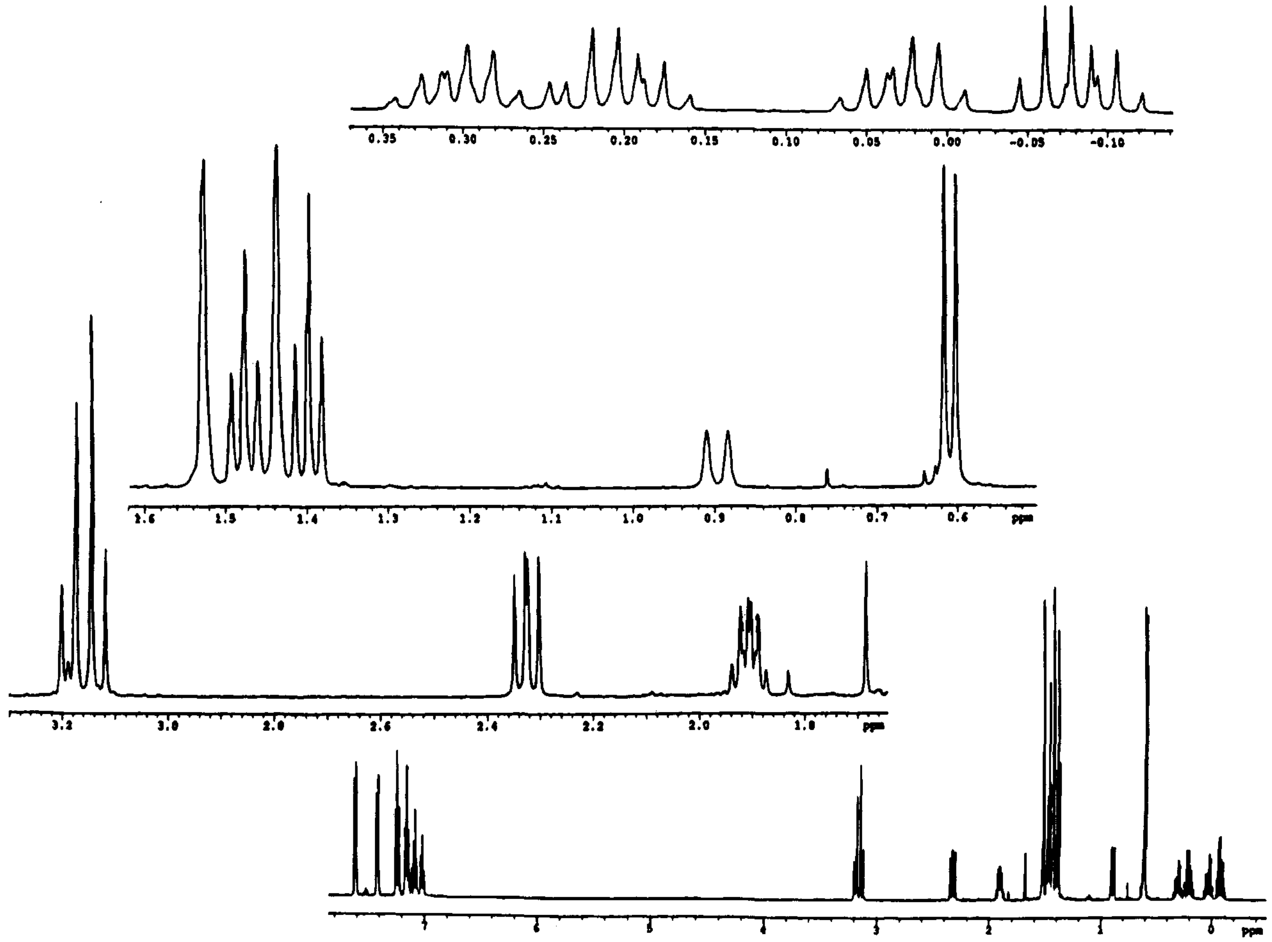

Figure 2. 500 MHz proton NMR spectrum of **4b**. The upper inserts are expansions of the upfield portion of the spectrum.

orbitals to the Al−C and Al−E σ antibonding orbitals exists.[19−21] An alternative explanation for this bond shortening has been discussed by others who suggest that the large variation observed in the Al−O distance is due to mixing of "normal" and "dative" bonds.[22]

NMR Studies. In the ^{1}H NMR spectrum of R_2AlOR^*, the absence of the −OH resonance of bifunctional amino alcohols, and the presence of a sharp upfield resonance for the alkyl group attached to aluminum in the $-AlR_2$ moiety of R_2AlOR^*, in the appropriate integration provide good evidence for the $-AlR_2$ coordination at the alkoxy oxygen. However, the positions of ^{1}H resonances associated with the alkyl groups attached to aluminum are virtually the same as those for the corresponding protons in the parent trialkylaluminums. Similar observations in chemical shifts have been reported in other organoaluminum alkoxides.[8,23] The ^{13}C spectra of the R_2AlOR^* compounds also show the presence of appropriate resonances which are slightly shifted from the corresponding resonances in the parent alcohols and alkylaluminums and thus support the formation of complexes.

The NMR spectra of the organoaluminum alkoxides **4a-c** display a number of interesting patterns. The methylene protons of the $PhCH_2$ group are diastereotopic and show a substantial dependence on the metal substituent. In **4a** the AB pattern collapsed with apparent equivalent chemical shifts for A and B, in the ethyl derivative, **4b**, $\Delta\delta = 0.055$ ppm and $J_{AB} = 13.5$ Hz, and a well-defined AB pattern is observed in **4c**, $\Delta\delta = 0.188$ and $J_{AB} = 14.0$ Hz. This $\Delta\nu/J$ effect may be attributed to the restricted rotation around the C−C bond and the increase in steric interaction on going from methyl to ethyl to isobutyl group. In the complex, the alkoxide ligand is fixed in a six-membered heterocyclic ring in the skew-boat or twist conformation. The C_2H_3 unit linked to the amine gives rise to an ABC pattern with a J_{AB} coupling of 13 Hz and a J_{AC} coupling of 11 Hz. The third coupling constant, J_{BC}, is equal to zero. The nonobservance of vicinal coupling is probably due to the fact that the two adjacent CH σ bonds are locked orthogonally (i.e., the dihedral angle $\alpha = 90°$) in the six-membered chelate ring. As a result, there should be little or no orbital overlap and thus no splitting of the absorption peaks. These results were confirmed by simulation of the spectrum for **4a** by using the GENSIM program.[24] The experimental values of chemical shifts and coupling constants used for simulation were as follows: $\delta_A = 2.30$ ppm, $\delta_B = 0.92$ ppm, $\delta_C = 1.93$ ppm, $J_{AB} = 13$ Hz, $J_{AC} = 11$ Hz, and $J_{BC} = 0$ Hz. The chemical shift nonequivalence of the methyl groups of both NMe_2 and $AlMe_2$ moieties is also observed because they are present close to a chiral center. In the case of

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(20) Lichtenberger, D. L.; Hogan, R. H.; Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 3369.

(21) Lichtenberger, D. L.; Hogan, R. H.; Healy, M. D.; Barron, A. R. *Organometallics* **1991**, *10*, 609.

(22) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; pp 1−51.

(23) Kumar, R.; Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 484.

(24) General Electric GN-300 NMR spectrometer software, version 8.

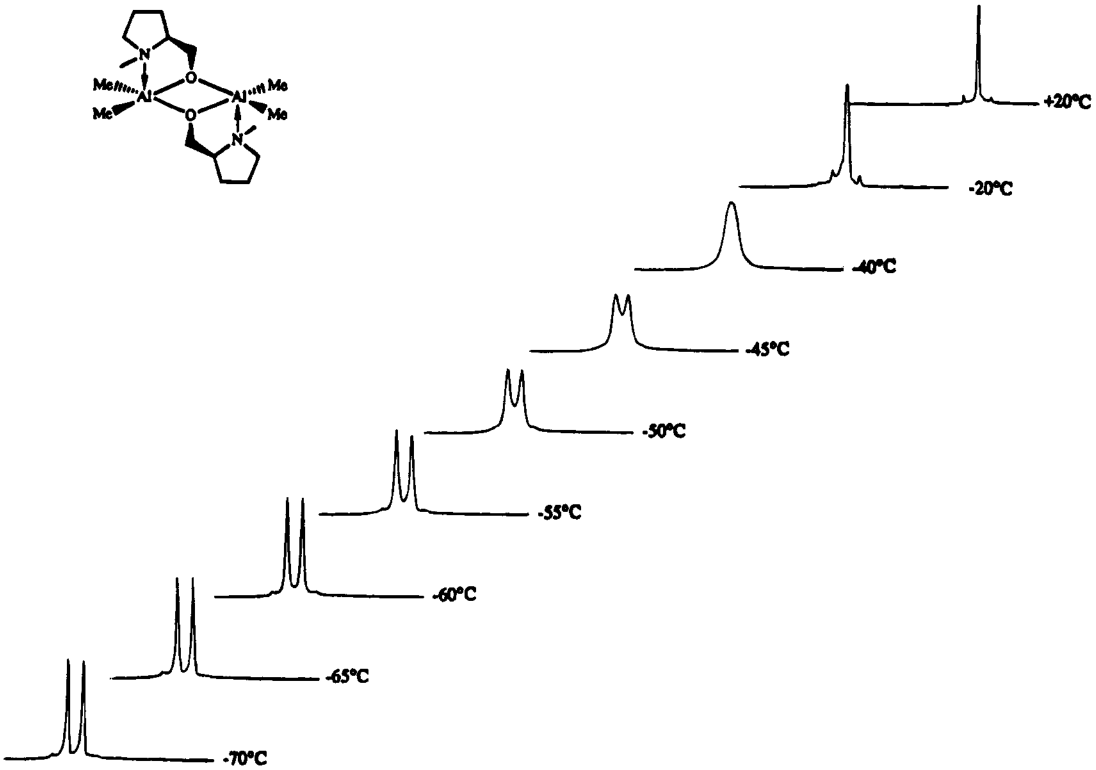
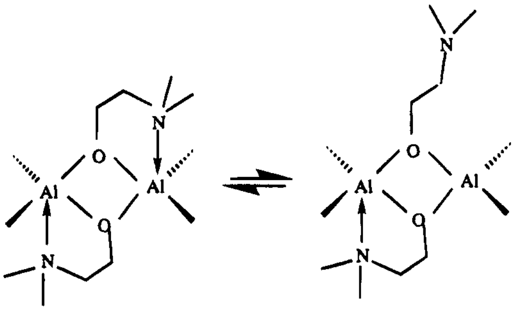


Figure 3. Variable-temperature ^1H NMR spectra of the $-AlMe_2$ region of $[Me_2Al(OCH_2-2-(S)-C_4H_7(NCH_3))]_2$, **1a**, in toluene-$d_8$.

ethyl and isobutyl derivatives, the spectra become much more complex in the alkylaluminum region and additional coupling information may be obtained. On the 300 MHz instrument, the methyl resonances of the ethyl groups in **4b** appear as two triplets ($^3J = 8$ Hz) and the methylene resonances are well separated and appear as two 15-line ABC patterns. At 500 MHz, the latter resonances are well resolved into four sets of 8-line patterns (Figure 2). In the isobutyl derivative, the methylene protons show two ABC patterns, the methine protons show two septets, and the methyl protons show two doublets and an apparent triplet. One of the ABC patterns of methylene protons is very well resolved with a J_{AB} coupling constant of 14 Hz and J_{AC} coupling constant of 8 Hz, while in the other ABC pattern $\Delta\nu/J$ is small. Finally, the nonequivalence of $-AlR_2$ and NMe_2 is also observed in the ^{13}C NMR spectra of these compounds. Variable-temperature NMR studies over the temperature range 25 to 70 °C showed no significant change in the spectra, indicating that compounds **4a-c** are nonfluxional in solution and that the Al$-$N adduct bond is stable under these experimental conditions.

Variable-Temperature NMR Studies. We reported in a communication that the organoaluminum complexes **3a-b** are dimeric, five-coordinate species in the solid state and this structure is retained in solution.[9] The room-temperature ^1H and ^{13}C NMR spectra of these complexes display nonequivalent alkyl groups attached to an aluminum center which is consistent with the structure observed in the solid state for **3a**. As the temperature is increased, the lines associated with these groups broaden and coalesce indicating that the magnetic environment is averaged on the NMR time scale. As an extension of this work to similar systems, we find that compounds **1a**,**b** **2a**,**b**, and **5**$-$**7** display similar behavior with nonequivalent alkyl groups, but that the temperature range for fluxtional behavior is dependent on the bridging ligand. The variable-temperature ^1H NMR spectra of **1a** and **2a** are shown in Figures 3 and 4. Each spectrum was analyzed thruogh the use of a deconvolution program and standard line shape analysis to determine the lifetimes of the five-coordinate aluminum species. The exchange rates as a function of temperature are listed in Table 4. The rate of exchange in these systems is concentration independent, and the process is reversible. These results can best be interpreted in terms of a dissociative process (shown in eq 3) in whch the Al$-$N bond breaks permitting the two alkyl groups to become equivalent on the NMR time scale. At the same time the Al_2O_2 ring remains intact preserving the nature of the complex.



(3)

The activation parameters can be determined by fitting the experimental data in Table 4 to either the Arrhenius equation

$$\text{rate} = A\exp(-\Delta E_a/RT) \qquad (4)$$

to determine the energy of activation or the Eyring equation

$$\ln(k/T) = [\ln(k_B/h) + (\Delta S^{\ddagger}/R)] - [(\Delta H^{\ddagger}/R)(1/T)] \qquad (5)$$

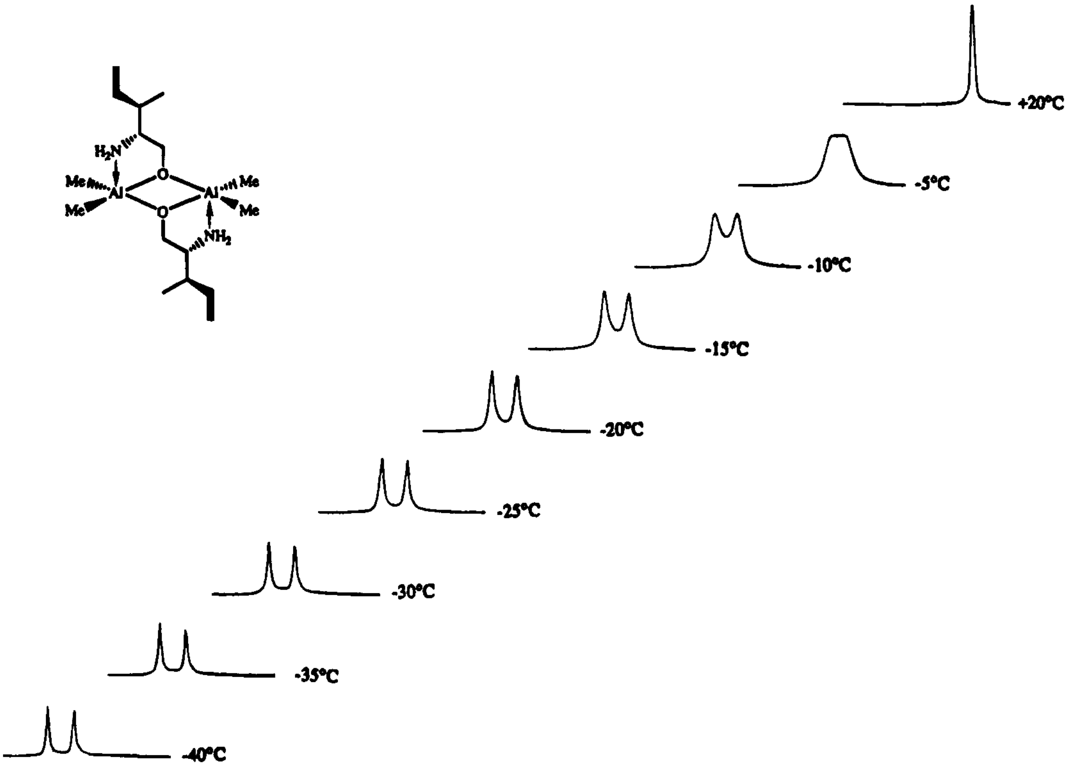


Figure 4. Variable-temperature ^{1}H NMR spectrum of the $-AlMe_2$ region of $[Me_2Al(OCH_2\text{-}(S)\text{-}CH(NH_2)\text{-}(S)\text{-}CH(CH_3)CH_2CH_3)]_2$, **2a**, in toluene-$d_8$.

Table 4. Rate of Dissociation of the Al−N Dative Bond in the Five-Coordinate Aluminum Alkoxides vs Temperature

compd	T, °C	rate,[a] s^{-1}	compd	T, °C	rate,[a] s^{-1}
3a	25	9.6	**5**	35	12.6
	30	26.1		40	21.5
	33	41.7		45	43.7
	35	48.9		50	64.4
	38	69.4		55	75.9
	40	80.6		60	152.3
	43	117.9		65	257.8
	45	149.9		70	317.7
1a	−65	1.1	**6**	35	15.1
	−63	2.4		40	29.1
	−60	2.5		45	50.6
	−58	3.5		50	73.1
	−55	5.4		55	107.1
	−53	6.5		60	163.9
	−50	11.9		65	224.8
	−48	15.0		70	293.8
	−45	19.0			
	−43	21.1			
2a	−30	2.4	**7**	30	6.4
	−25	4.0		35	12.5
	−20	6.5		40	42.7
	−15	13.1		45	60.1
				50	115.4
	−10	20.2		55	186.4
	−5	35.2		60	217.9
				65	444.5
				70	504.2

[a] $\pi(\nu_{1/2} - \nu_0)$.

to determine the enthalpy and entropy of activation. The Eyring parameters were determined from the plots shown in Figure 5. The Gibbs free energy, $\Delta G^{\ddagger}$, can be calculated since k and T at coalescence are known. Assuming κ to be unity, the equation can be written as

$$\Delta G^{\ddagger} = aT[(10.319) + \log(T/k)] \qquad (6)$$

where $a = 4.575 \times 10^{-3}$ ($\Delta G^{\ddagger}$ in kcal mol^{-1}). The results of these calculations are listed in Table 5.

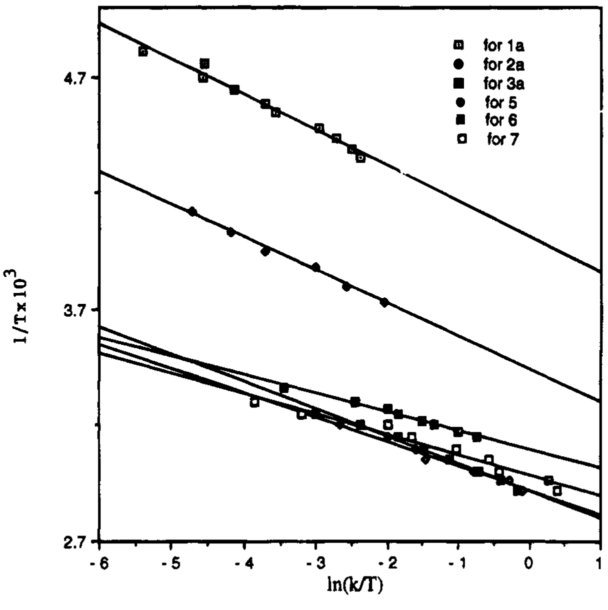


Figure 5. Plot of ln(k/T) vs 1/T for **1a**, **2a**, **3a**, and **5**−**7**. The slope of the line equals $\Delta H^{\ddagger}/R$; $R = 0.979$ for **1a**, 0.994 for **2a**, 0.983 for **3a**, 0.986 for **5**, 0.989 for **6**, and 0.963 for **7**. The parameters derived from these data are listed in Table 5.

In general, the activation parameters should be dependent on the substitution at the nitrogen center, on the stereochemistry at nitrogen, and on the substituents bound to aluminum. These factors will govern the basicity of the nitrogen, the flexibility of the pendent group, and the steric interactions between the various substituent groups. Examination of the data in Table 5 shows that there is no trend with the degree of substitution at the nitrogen center. The compound with the highest ΔE_a is **3a**, a secondary amine. Further study of this system shows that $\Delta H^{\ddagger}$ is only slightly

Table 5. Activation Parameters for the Dissociation of the Al−N Dative Bond in the Five−Coordinate Aluminum Alkoxides

compd	ΔE_a[a,b]	$\Delta H^{\ddagger}$ [b,c]	$\Delta S^{\ddagger}$ [c,d]	$\Delta G^{\ddagger}$ [b,c]
3a	25.0 ± 1.2	24.4 ± 1.3	28.3 ± 4	15.5 ± 3
7	22.5 ± 1.6	21.9 ± 1.6	17.9 ± 5	15.9 ± 3
5	19.3 ± 0.9	18.6 ± 0.9	7.2 ± 3	16.5 ± 2
6	17.3 ± 0.7	16.7 ± 0.7	1.5 ± 2	16.3 ± 1
2a	13.9 ± 0.6	13.9 ± 0.5	0.4 ± 2	13.7 ± 1
1a	12.5 ± 0.6	12.7 ± 0.7	3.4 ± 3	12.0 ± 1

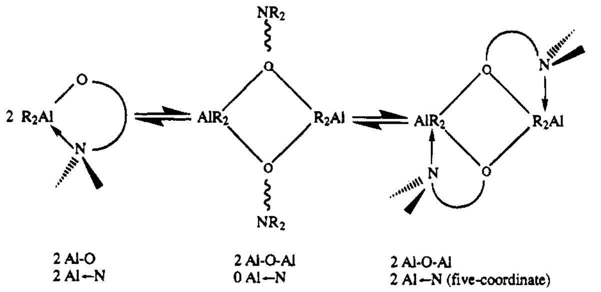
[a] Arrhenius activation energy. [b] Units are in kcal mol^{-1}. [c] Activation parameters determined from the Eyring equation. [d] Units are in cal K^{-1} mol^{-1}.

greater than for several of the other systems but that $\Delta S^{\ddagger}$ for this system is much greater. Reasonably large values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are also observed for **7**.

The remaining compounds have $\Delta S^{\ddagger}$ values near zero. Examination of the structures of **3a** and **7** does not provide any simple explanation for the difference of these two systems from the others. Comparison of **7** with **5** and **6** which have related structures shows an interesting result. The difference between **6** and **7** is in the stereochemistry at the carbon adjacent to the bridge head nitrogen involved in coordination. This change results in a substantial difference in both the enthalpy and the entropy of activation. The difference in the structures of **5** and **6** is in the substitution of a methoxy group for a hydrogen aromatic ring. This change leads to only a minor difference in the activation parameters and indicates that the methoxy group in this position has no significant impact on the aluminum coordination. Qualitative studies on the ethyl derivatives, **1b**, **2b**, and **3b**, showed that in each case they behaved in a manner similar to that described for the corresponding methyl derivatives, **1a**, **2a**, and **3a**, but line broadening and coalescence occurred at somewhat lower temperatures. This would be consistent with reduced stability of the Al←N coordinate bond.

Conclusions

The trialkylaluminums react with optically active amino alcohols to give organoaluminum alkoxides in excellent yield. The structures of these derivatives depend upon the nature of the moiety connecting the amine and alcohol functional groups. In **3a** the structure is a dimer with a five-coordinate aluminum center,[9] and in **2b** a partial structure was obtained in which the same general features were observed, an oxygen-bridged dimer with a fifth coordination site on aluminum occupied by the amine nitrogen. Unfortunately the structure for **2b** was severely disordered and a complete structure could not be obtained. The structure of **4a** revealed a monomer with a four-coordinate aluminum center. In the other systems described here, the data indicate formation of five-coordinate aluminum centers. The major difference between the dimeric systems with five-coordinate aluminum and the systems with monomeric units is that the nitrogen is separated by three atoms from aluminum instead of two as in **2b**, **3a**, and the other species which are five coordinate. These structural differences may be attributed to the formation of a stable six-membered chelate ring in **4a**. The relative stability of the four- vs five-coordinate species is determined by the differences in energy represented in the following equilibrium:



(7)

The conversion of two monomers to the dimer or dimer with five-coordinate aluminum alters the number of bonds and type of bonding present in the system as indicated in eq 7. The position of the equilibrium is determined by the change in enthalpy associated with bond formation and the entropy terms associated with the conversion of two monomers to a dimer.

There are three possible conditions depicted in the equilibrium. In these studies we have observed the shift from monomer to dimer and have observed the interaction of the pendent arm containing the base with the aluminum center. The shift from monomer to dimer is dependent to a large degree on the length and flexibility of the link between the oxygen and the secondary base site. The balance observed in the systems described here is dominated by the chain length with formation of a five-membered-ring system favoring the dimer with five-coordinate aluminum and the six-membered ring, yielding the monomeric four-coordinate derivative. Dimeric oxygen-bridged structures with five-coordinate aluminum centers are formed when five-membered heterocyclic rings can be formed. The one example with a six-membered heterocyclic ring gives a monomeric species with four-coordinate aluminum. The latter species is stable in solution, while the dimeric derivatives are involved in an equilibrium between four- and five-coordinate aluminum species. The energy of activation, ΔE_a, for the dissociation of the Al−N dative bond in these systems is dependent on the substitution of the nitrogen center and the steric interactions of the substituents bound to the aluminum center. The Lewis basicity of the nitrogen center is the predominating factor in determining the strength of the Al−N dative interaction when there are small steric interactions between the ligands. Research is continuing in this area to better understand the effects of electron-withdrawing and -donating substituents on the bidentate ligands which influence the formation of the five-coordinate aluminum species.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Tables of complete bond distances and bond angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (5 pages). Ordering information is given on any current masthead page.

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