4094 *Inorg. Chem.* **1997,** *36,* 4094−4098

Synthesis and Structure of Alkoxy- and (Aryloxy)alanes. Observation of a Ring-Opening Reaction Involving Tetrahydrofuran

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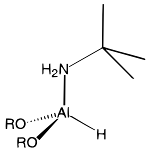
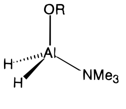
Dihydrogen elimination from aluminum hydrides and alcohols was used to produce new alkoxide and aryloxide complexes. Dimethylethylamine−alane (DMEAA) reacted with 2 equiv of 2,6-diisopropylphenol (DIPH) in THF at −78 °C to give $(DIP)_2AlH\cdot 2THF$ (**1**) in 94% yield. It was characterized by NMR, IR, MS, and X-ray crystallography and found to be trigonal bipyramidal with both axial sites occupied by THF. Crystal data for **1**: $C_{32}H_{51}AlO_4$, monoclinic, $C2/c$, $a = 21.37(1)$ Å, $b = 9.324(3)$ Å, $c = 15.30(1)$ Å, $\beta = 94.16(5)°$, $V = 3040(5)$ Å^3, $Z = 4$. DMEAA reacted with 2 equiv of triphenylcarbinol, Ph_3COH, in THF at −78 °C to give $(Ph_3CO)_2AlH\cdot THF$ (**2**) in 42% yield. The lower coordination number was attributed to the larger cone angle of the ligand. Crystal data for **2**: $C_{42}H_{39}AlO_3$, triclinic, $P\bar{1}$, $a = 8.482(1)$ Å, $b = 9.067(1)$ Å, $c = 23.59(1)$ Å, $\alpha = 90.919(1)°$, $\beta = 92.624(1)°$, $\gamma = 116.093(1)°$, $V = 1626.2(2)$ Å^3, $Z = 2$. Three equivalents of DIPH in THF reacted with DMEAA at −78 °C to form the unexpected compound $(DIP)_3(THF)(NMe_2Et)Al$ (**3**) in 89% yield. Both solution spectroscopic and X-ray crystallographic data established that THF underwent a ring-opening reaction. Crystal data for **3**: $C_{44}H_{70}AlNO_4$, monoclinic, Cc, $a = 23.50(1)$ Å, $b = 10.81(1)$ Å, $c = 19.37(1)$ Å, $\beta = 122.25(3)°$, $V = 4162(2)$ Å^3, $Z = 4$.

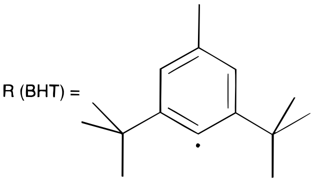
Introduction

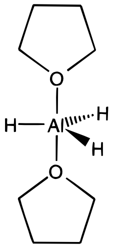
Aluminum hydrides have attracted recent interest as precursors to solid state materials.[1] Two of the molecules that are under serious consideration for use in the chemical vapor deposition of aluminum, dimethylethylamine−alane (DMEAA) and dimethylaluminum hydride (DMAH), contain hydride ligands.[1,2] Much effort is underway to determine the formula and structure of the surface-bound species on silica, silicon, metals, and semiconductors. On silica or oxidized silicon surfaces, free and/or hydrogen-bonded hydroxyl groups are available to react with incoming molecules of DMEAA[3] or DMAH. This paper summarizes our use of alcohols to prepare structural and spectroscopic models of the species formed upon reaction of DMEAA with surface O−H groups.

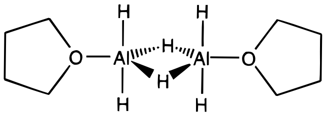
Structurally characterized alkoxy- and (aryloxy)aluminum hydrides are rare. A significant obstacle to structural characterization of these compounds is the difficulty in obtaining an isolable product. Alkoxyalanes tend to form polymeric aggregates of uncertain stoichiometry or intractable solid masses. Bulky ligands, such as 2,6-di-*tert*-butyl-4-methylphenoxo (BHT), have been used effectively to mitigate this problem.[4] Another strategy involves using ether solvents to saturate the remaining coordination sites and prevent the formation of rings, and clusters or polymers.[5,6] An impressive example of this involves the isolation and structural characterization of $AlH_3\cdot 2THF$ and $[AlH_3\cdot THF]_2$, shown below.[7]











Experimental Section

General Procedures. All reactions were performed under an inert atmosphere of Ar or nitrogen using standard Schlenk line techniques, or in a nitrogen-filled glovebox. Infrared spectra were obtained using a Mattson Polaris Mod 8 FTIR spectrometer, and NMR spectra were taken on a Bruker A200 200 MHz spectrometer. A Sciex API III mass spectrometer (Sciex, Thornhill, Ontario, Canada) was used to obtain electrospray mass spectra. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Melting points (uncorrected) were performed in capillaries loaded in the glovebox under nitrogen, and sealed with silicone grease. Solvents were freshly distilled from sodium benzophenone ketyl under nitrogen immediately before use. 2,6-Diisopropylphenol, triphenylcarbinol, and dimethylethylamine were obtained from Aldrich and used as received. Dimethylethylamine−alane, DMEAA, was synthesized by one of the two literature procedures.[2,8]

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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Bis(2,6-diisopropylphenolato)aluminum Hydride−Bis(tetrahydrofuran) ((DIP)$_2$AlH·2THF (1)). A 50 mL three-neck round bottom flask was fitted with a rubber septum, a gas adapter, and a 30 mL pressure-equalizing dropping funnel and was connected to the Schlenk line. The setup was carefully flame-dried under a purge of Ar and allowed to cool. The reaction flask was charged with 15 mL of freshly distilled THF and 0.71 mL (5.36 mmol) of DMEAA. The addition funnel was filled with 10 mL of freshly distilled THF and 2.0 mL (10.8 mmol) of 2,6-diisopropylphenol. The reaction flask was cooled using a dry ice/acetone bath, and the phenol was added dropwise, over 30 min. The cold bath was allowed to warm to room temperature. The reaction mixture was stirred under Ar for 3 days, after which the solvent was removed under vacuum, yielding 2.65 g (5.03 mmol, 94%) of white powdered crystalline (DIP)$_2$AlH·2THF, melting point 194 °C (dec.). Anal. Calcd for $C_{32}H_{51}AlO_4$: C, 72.97; H, 9.76. Found: C, 72.8; H, 9.63.

IR (THF): $\upsilon_{Al-H} = 1803$ cm^{-1}. ^{1}H NMR (δ ppm, C_6D_6): 1.313,1.344 (C*H*$_3$, d, 12H), 3.58 (OC*H*$_2$, broad triplet, 4H), 3.73 ((CH$_3$)$_2$C*H*, multiplet, 2H), 7.15 (C*H* aromatic, m, 3H). Ion spray MS (*m*/*z*, negative ion): 388.3 (100, (DIP)$_2$AlH·2THF + Li), 355.2 (92.4, (THF)$_2$Al + Li), 210.2 (40.0, (DIP)Al + Li).

Bis(triphenylcarbinolato)aluminum Hydride−Tetrahydrofuran ((Ph$_3$CO)$_2$AlH·THF (2)). A 50 mL three-neck round bottom flask was fitted with a rubber septum, a gas adapter, and a 30 mL pressure-equalizing dropping funnel and was connected to the Schlenk line. The setup was carefully flame-dried under a purge of Ar and allowed to cool. The reaction flask was charged with 20 mL of freshly distilled THF and 1.0 mL (7.56 mmol) of DMEAA. The addition funnel was filled with 10 mL of freshly distilled THF and 1.96 g (7.53 mmol) of triphenylcarbinol. The reaction flask was cooled in a dry ice/acetone bath, and the solution was added dropwise, over 30 min. The cold bath was allowed to warm to room temperature and removed. A white precipitate formed overnight. The reaction mixture was allowed to stir under Ar for 3 days, and the solvent was removed under vacuum. The remaining white residue was washed with three 20 mL portions of toluene, then redissolved in THF, and filtered on a 10−20 μ frit. The solvent was removed under vacuum to yield 0.98 g (1.58 mmol, 42%) of a white solid, (Ph$_3$CO)$_2$AlH·THF, melting point 155 °C. A satisfactory elemental analysis could not be obtained.

IR (THF): $\upsilon_{Al-H} = 1850$ cm^{-1}. ^{1}H NMR (δ, C_6D_6): 0.85 (OC*H*$_2$, 4H, broad triplet), 3.27 (C*H*$_2$, 4H, broad triplet), 7.15 (*m*- and *p-H*, 18H, multiplet), 7.63 (o-*H*, d, $J = 6$ Hz, 12H). No MS could be obtained.

Tris(2,6-diisopropylphenolato)(4-(dimethylethylammonium)butanato)aluminum ((DIP)$_3$(O(CH$_2$)$_4$NMe$_2$Et)Al (3)). A 50 mL three-neck round bottom flask was fitted with a rubber septum, a gas adapter, and a 30 mL pressure-equalizing dropping funnel and was connected to the Schlenk line. The setup was carefully flame-dried under a purge of Ar and allowed to cool. The reaction flask was charged with 20 mL of freshly distilled THF and 0.95 mL (7.18 mmol) of DMEAA. The addition funnel was filled with 10 mL of freshly distilled THF and 4 mL (21.6 mmol) of 2,6-diisopropylphenol. The reaction flask was cooled in a dry ice/acetone bath, and the phenol was added dropwise over 30 min. The cold bath was allowed to warm to room temperature and removed, and the reaction mixture was allowed to stir under Ar for 5 days. The solvent was then removed in vacuum, yielding 4.51 g (6.41 mmol, 89%) of an off-white solid, (DIP)$_3$(O(CH$_2$)$_4$NMe$_2$Et)Al, mp 150−160 °C. Anal. Calcd for $C_{44}H_{70}AlNO_4$: C, 75.07; H, 10.02; N, 1.99. Found: C, 76.05; H, 10.38; N, 1.97.

^{1}H NMR (δ, C_6D_6): 1.015 (C*H*$_3$, DIP, 36H), 1.20 (NCH$_2$C*H*$_3$, 6H), 1.546 (CH$_2$C*H*$_2$CH$_2$, 4H), 2.474 (NC*H*$_3$, 6H), 2.770 (NC*H*$_2$CH$_3$, 6H), 3.146 (NC*H*$_2$CH$_2$, 2H), 3.601 ((CH$_3$)$_2$C*H*, 6H), 3.998 (OC*H*$_2$, THF, 2H), 6.589 (*p*-C*H*, 3H), 6.802 (*m*-C**H**, 6H).

MS (FABMS, 10 V, *m*-nitrobenzyl alcohol): $m/z = 710.4$ ((DIP)$_3$(O(CH$_2$)$_4$NMe$_2$Et)Al + Li).

Table 1. Crystallographic Parameters for **1**−**3**

	1	**2**	**3**
formula	$C_{32}H_{51}AlO_4$	$C_{42}H_{39}AlO_3$	$C_{44}H_{70}AlNO_4$
formula wt	526.73	618.71	703.99
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	*Cc* (No. 9)
a (Å)	21.37(1)	8.482(1)	23.50(1)
b (Å)	9.324(3)	9.067(1)	10.81(1)
c (Å)	15.30(1)	23.59(1)	19.37(1)
α (deg)		90.919(1)	
β (deg)	94.16(5)	92.624(1)	122.25(3)
γ (deg)		116.093(1)	
vol (Å^3)	3040(5)	1626.2(2)	4162(2)
Z	4	2	4
ρ_{obs} (g/cm^3)	n/a	n/a	n/a
ρ_{calc} (g/cm^3)	1.151	1.264	1.123
λ (Å)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
μ_α(Mo Kα) (cm^{-1})	0.95	1.03	0.89
diffractometer	CAD-4	SMART	SMART
T (°C)	−100(2)	−100(2)	−150(2)
R_1 ($I > 2\sigma(I)$)	0.061[a]	0.0913[a]	0.0645[a]
R_2	0.061[b]	0.2295[c]	0.1801[c]

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. [c] $R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

X-ray Crystallography. Crystals of (DIP)$_2$AlH·2THF were grown from THF at −15 °C, giving colorless blocks. A suitable crystal (0.57 × 0.52 × 0.52 mm) was removed from a Schlenk flask and quickly covered with oil, transferred to the tip of a glass fiber, and mounted on the goniometer of the Enraf-Nonius CAD-4 (graphite-monochromatized Mo Kα radiation with $\lambda = 0.710\,73$ Å). It was cooled to −100 °C with an Enraf-Nonius FR558SH low-temperature device. The search routine collected 25 reflections at low angles, which provided an initial cell. A search out the axes provided higher angle reflections between 20° and 52° in 2θ, which were carefully centered and refined to give the final cell constants and orientation matrix. At this time, a check was performed for a higher symmetry unit cell; none was found. ω scans were collected in one shell to 24° using a prescan speed of 16.48°/min, and from 24 to 26° at 4.1°/min. Three strong reflections were chosen as intensity checks and monitored every hour during data collection. No decay was observed. Six reflections between 19° and 52° in 2θ were chosen as orientation and reorientation checks, and monitored every 400 reflections during data collection. Crystallographic parameters are given in Table 1.

The data were processed and the structure solved and refined using the TEXSAN 5.0 series of programs. Systematic absences and statistics revealed the space group to be *C*2/*c* (No. 11). The aluminum atom was located by the direct methods program MITHRIL, and the other non-hydrogen atoms were found by Fourier techniques and the direct methods program DIRDIF. The hydride was located in the difference map and refined isotropically. After a full isotropic refinement, the nonhydridic hydrogens were placed in idealized positions with $d_{CH} = 0.95$ Å and *B* values 20% greater than the B_{eq} of the carbon to which they were bonded. Their positions were updated every cycle of least squares using a riding model; they were not refined but were included in the structure factor calculation. After isotropic refinement of this model, redundant data were averaged. Anisotropic refinement, performed using full-matrix least squares on *F* of all non-hydrogen atoms, converged to a final $R = 0.061$ (2σ). An empirical absorption correction was applied after isotropic refinement using the program DIFABS. Scattering factors were taken from the usual sources, and the effects of anomalous dispersion were included for the nonhydrogen atoms.[9,10] Table 2 lists selected atomic coordinates.

Crystals of (Ph$_3$CO)$_2$AlH·THF were grown by layering a 0.050 g portion of pure product in 1.55 mL of THF with 20 mL of pentane. Colorless prisms formed within 4 days; however, the quality of these were poor. After preliminary examination of three crystals a data set was collected for two of these (one using the CAD-4 and one using the SMART system). Only the data set collected on the SMART system (graphite-monochromatized Mo Kα radiation with $\lambda = 0.710\,73$ Å) was suitable for refinement. This crystal (0.50 × 0.45 × 0.37 mm) had been mounted on the tip of a glass fiber with STP oil. It was transferred to the goniometer of a Siemens SMART CCD system and cooled to −100 °C with a Siemens LT-2 low-temperature device.

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[9] Cromer, D. T.; W., J. T. In *International Tables for X-Ray Crystallography*, The Kynoch Press: Birmingham, England, 1974; Vol. IV; Table 2.

[10] Cromer, D. T. In *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV; Table 2.

Table 2. Selected Atomic Coordinates ($\times 10^4$) for compounds **1**, **2**, and **3**

	$(DIP)_2AlH{\cdot}2THF$ (**1**)		
Al1	5000	3113(1)	2500
O1	4542(1)	4089(2)	3195(1)
O2	5678(1)	3171(2)	3503(1)
C1A	3925(1)	4378(3)	3260(2)
H1	5000	142(4)	2500
	$(Ph_3CO)_2AlH{\cdot}THF$ (**2**)		
Al(1)	6252(2)	3932(2)	2480(1)
O(1)	7295(5)	3440(4)	1970(1)
O(2)	6308(5)	2966(4)	3087(1)
O(3)	3840(5)	2758(5)	2269(2)
C(1)	7683(6)	3332(6)	1403(2)
C(2)	7034(7)	2979(6)	3632(2)
H(1)	6398(53)	5673(50)	2524(17)
	$(DIP)_3[Me_2EtN(CH_2)_4O]Al$ (**3**)		
Al(1)	−4335(1)	5459(1)	−1041(1)
O(1)	−4705(2)	6898(3)	−1171(2)
O(2)	−3782(2)	5523(3)	−1383(2)
O(3)	−4971(2)	4377(3)	−1608(2)
O(4)	−3884(2)	4962(3)	−31(2)
N(1)	−1954(3)	4596(4)	2278(5)
C(1A)	−4697(2)	8135(5)	−1290(4)
C(1B)	−3116(3)	5347(4)	−1061(3)
C(1C)	−5634(2)	4354(4)	−2195(3)
C(1D)	−4095(4)	4901(7)	537(4)
C(2D)	−3838(3)	3752(6)	1047(4)
C(3D)	−3060(4)	3527(8)	1486(6)
C(4D)	−2672(4)	4529(9)	2032(6)

Crystal quality and centering were confirmed by taking a 60 s rotation frame. A search was performed by taking a series of frames in three orthogonally related regions of reciprocal space. Each region investigated was composed of 20 10 s frames, separated by 0.3° in ω. These were harvested to yield a total of about 100 reflections with intensities greater than 10σ. An initial unit cell was obtained and checked for centering and higher symmetry. None was found. The initial cell constants were refined, and an initial orientation matrix was found. Data were collected by examining a randomly oriented region of reciprocal space in three segments; the frames collected in a given segment were 0.3° apart in ω. The highest resolution data collected was 0.87 Å. Two 30 s frames were collected, and the data were summed, thus doubling the dynamic range of the detector. The default gain on the detector signal was 4×, which was automatically dropped to 1× when the detector range was exceeded. Final cell constants were determined during integration of the data using 8192 intense, well-centered reflections. Crystallographic parameters are given in Table 1.

The structure was solved and refined using the SHELXTL-Plus 5.0 series of programs. The space group was determined to be $P\bar{1}$ (No. 2) based on systematic extinctions and intensity statistics. The structure was solved using the direct methods program xs. The hydride was located in the difference map and refined isotropically. The remaining hydrogens were placed in calculated positions and refined with a riding model with B values 20% larger than those on the attached carbon atoms. Full anisotropic refinement of all non-hydrogen atoms was performed using full-matrix least squares on F^2 using the program xl and converged to a final $R_1 = 0.0913$ (2σ). Both the poor quality of the crystals and some disorder in the coordinated THF contributed to the high R-factor. A semiempirical ψ-scan correction was applied to the data prior to solution and refinement. The effects of anomalous dispersion were included for the non-hydrogen atoms.

Crystals of $(DIP)_3[O(CH_2)_4NMe_2Et]Al$ were grown by layering a 0.33 g portion of pure product in 2.0 mL of THF with 15 mL of pentane. Colorless prisms formed within 2 days, and one having dimensions 0.5 × 0.3 × 0.2 mm was chosen for study. The data collection and structure solution followed the procedure described for $(Ph_3CO)_2AlH{\cdot}THF$. Crystallographic parameters are given in Table 1.

Results and Discussion

Synthesis. All of the reactions described in this paper were conducted in THF. Based on the IR spectral evidence, most of the DMEAA dissolved in THF is converted into $AlH_3{\cdot}2THF$. Pure DMEAA in the gas phase exhibits an Al−H stretching vibration at 1790 cm^{-1}.[2] The THF solutions of DMEAA exhibit a ν_{Al-H} at 1734 cm^{-1}, similar to the value of 1727 cm^{-1} reported for THF solutions of $AlH_3{\cdot}2THF$.[7] Reactions of DIPH with THF solutions of DMEAA (eq 1) result in either **1** or **3**, depending upon the stoichiometry. 1:1 DIPH/DMEAA gives the compound $(DIP)_2AlH{\cdot}2THF$ in low yield (40%), whereas a 2:1 ratio improves this to 94%. Compound **1** is air and moisture sensitive. The ^1H NMR spectrum in C_6D_6 shows a shift of the methyl doublet downfield to 1.21 ppm from 1.14 ppm in the free ligand. The methine protons are shifted from 2.91 ppm in the free ligand to 3.57 ppm in the product. The hydride signal could not be observed due to the quadrupolar broadening by the Al nucleus. The α-methylene protons of the coordinated THF are shifted to 3.58 ppm from the 3.68 ppm observed in the free molecule. A unique resonance due to the the β-protons of the coordinated THF is not observed, but the integration establishes that it appears at the same chemical shift as the methyl groups of the isopropyl substituents. No evidence is found for $(DIP)AlH_2{\cdot}THF$, the expected inital product in eq 3, suggesting that the second H_2 elimination is faster than the first. The trend of increasing reactivity of the Al−H groups with increasing substitution is broken once two hydrides are replaced, possibly due to the steric bulk of the phenol.

$$Me_2EtN{\cdot}AlH_3 + 2DIPH \xrightarrow[THF]{-78\ °C} \underset{\mathbf{1}}{(DIP)_2AlH{\cdot}2THF} + Me_2EtN + 2H_2 \quad (1)$$

Reaction of 3:1 DIPH/DMEAA yields (eq 2) **3** in 89% yield. The zwitterionic compound **3** is not especially air sensitive, but does hydrolyze slowly in the presence of moisture, forming an intractable mass. This product contains a THF molecule that has undergone ring-opening. The oxygen remains coordinated to the aluminum, whereas the amine is attached to the δ-carbon. The ^1H NMR (C_6D_6) of $(DIP)_3(Me_2EtN(CH_2)_4O)Al$ shows a shift of the DIP ligand methyl protons to 1.01 ppm, as opposed to 1.2 ppm. The methine protons still exhibit the characteristic downfield shift to 3.60 ppm. Signals attributable to the (dimethylethylammonium)butanato ligand are clearly visible in the ^1H NMR spectrum.

$$Me_2EtN{\cdot}AlH_3 + 3DIPH \xrightarrow[THF]{-78\ °C} \underset{\mathbf{2}}{(DIP)_3[Me_2EtN(CH_2)_4O]Al} + 3H_2 \quad (2)$$

Ring-opening of THF by a hydride has been discussed by Wiberg, who postulated a mechanism involving hydride transfer to reduce the C−O single bond of a coordinated THF.[5] Nucleophilic attack involving a second THF on $Cl_3Al{\cdot}THF$ has been proposed as a mechanism of polymerization of THF by $AlCl_3$.[11] As stated above, dissolution of DMEAA in THF leads to free amine and THF-solvated alane with no evidence of ring-opening. Considering that solutions of **1** also contain free amine, yet do not exhibit this reaction, we conclude that the ring-opening occurs by attack of Me_2EtN on $(DIP)_3Al{\cdot}THF$. Apparently the cumulative effect of three electronegative ligands on aluminum is necessary to activate THF at room temperature.

Compound **2** was synthesized by the route shown in eq 3 in 42% isolated yield. The compound is air sensitive, especially in solution. The lower yield is due to the similar solubilities

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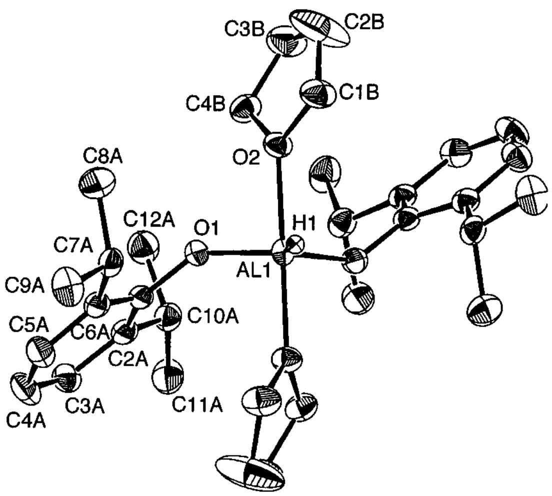

Figure 1. ORTEP thermal ellipsoid drawing of $(DIP)_2AlH\cdot 2THF$ (**1**). Hydrogen atoms are omitted for clarity. Only unique atoms are labeled. Ellipsoids shown are 50%.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(DIP)_2AlH\cdot 2THF$ (**1**)

Bond Lengths			
Al(1)−O(1)	1.752(2)	O(1)−C(1A)	1.354(3)
Al(1)−O(2)	2.034(2)	O(2)−C(1B)	1.448(3)
Al(1)−H(1)	1.58(4)	O(2)−C(4B)	1.453(4)
Angles			
O(1)−Al(1)−O(1)′	117.5(1)	O(2)−Al(1)−H(1)	91.53(7)
O(1)−Al(1)−O(2)	85.84(9)	Al(1)−O(1)−C(1A)	137.5(2)
O(1)−Al(1)−O(2)′	92.6(1)	Al(1)−O(2)−C(1B)	125.2(2)
O(1)−Al(1)−H(1)	121.27(7)	Al(1)−O(2)−C(4B)	125.0(2)
O(1)′−Al(1)−H(1)	121.27(7)	C(1B)−O(2)−C(4B)	108.7(2)
O(2)−Al(1)−O(2)′	176.9(1)		

$$Me_2EtN\cdot AlH_3 + 2Ph_3COH \xrightarrow[\text{THF}]{-78\ ^{\circ}\text{C}} \underset{\mathbf{3}}{(Ph_3CO)_2AlH\cdot 2THF} + Me_2EtN + 2H_2 \tag{3}$$

of the ligand and product, which renders isolation of the product difficult. Additionally, a 2-fold excess of DMEAA is required to ensure full consumption of the alcohol. Like the DIP compounds, the Ph_3COH does not stop at the monosubstituted product. Unlike the DIP ligand, however, Ph_3COH does not continue to react to form the trisubstituted product even when excess Ph_3COH is present. The Ph_3CO ligand may be too sterically bulky to form the trisubstituted product by this reaction.

The ^1H NMR spectrum (C_6D_6) of **2** shows the characteristic downfield shift of the ligand protons: complex multiplets are observed at 7.15 and 7.63 ppm, as opposed to a complex multiplet at 7.15 ppm in the starting alcohol. The coordinated THF is observed as triplets at 0.85 and 3.27 ppm. The IR spectrum of **1** in THF shows the characteristic Al−H stretch at 1803 cm^{-1}, while the Al−H stretch of **2** in THF is observed at 1850 cm^{-1}. The substitution of a hydride with an alkoxide is expected to shift the $\nu_{\mathrm{Al-H}}$ of any remaining hydride ligands to higher energy.[5] The drop in the $\nu_{\mathrm{Al-H}}$ value in going from **2** to **1** is due to the increase in coordination number from 4 to 5. A similar shift is found for $AlH_3\cdot NMe_3$ and $AlH_3\cdot 2NMe_3$.

Structures of 1, 2, and 3. A thermal ellipsoid drawing of $(DIP)_2AlH\cdot 2THF$ is shown in Figure 1; selected bond lengths and angles are given in Table 3. The compound crystallizes in space group *C*2/*c*, with the Al−H bond vector on the 2-fold axis. The molecule is trigonal pyramidal with the datively bonded THF molecules in the axial sites, and the equatorial sites occupied by the phenoxy groups and the hydride. This compound can be considered a derivative of $AlH_3\cdot 2THF$, which has long been known, but only recently structurally characterized.[5,7]

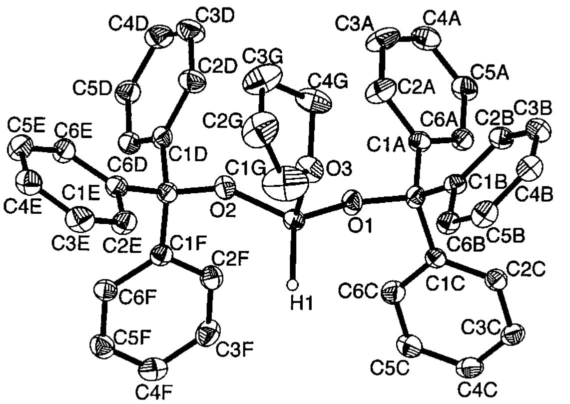

Figure 2. TELP thermal ellipsoid drawing of $(Ph_3CO)_2AlH\cdot THF$ (**2**). Hydrogen atoms are omitted for clarity. Ellipsoids shown are 30%.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $(Ph_3CO)_2AlH\cdot THF$ (**2**)

Bond Lengths			
Al(1)−H(1)	1.53(4)	O(3)−C(4G)	1.448(7)
Al(1)−O(1)	1.691(3)	C(1)−C(1B)	1.532(7)
Al(1)−O(2)	1.699(4)	C(1)−C(1C)	1.546(7)
Al(1)−O(3)	1.881(4)	C(1)−C(1A)	1.556(6)
O(1)−C(1)	1.404(5)	C(2)−C(1F)	1.529(7)
O(2)−C(2)	1.399(6)	C(2)−C(1E)	1.548(7)
O(3)−C(1G)	1.450(7)	C(2)−C(1D)	1.561(7)
Angles			
H(1)−Al(1)−O(1)	120(2)	O(2)−Al(1)−H(1)	119(2)
H(1)−Al(1)−O(2)	119(2)	O(3)−Al(1)−H(1)	100(2)
O(1)−Al(1)−O(2)	110.4(2)	C(1)−O(1)−Al(1)	152.6(3)
H(1)−Al(1)−O(3)	100(2)	C(2)−O(2)−Al(1)	150.7(3)
O(1)−Al(1)−O(3)	105.3(2)	C(1G)−O(3)−C(4G)	106.5(5)
O(2)−Al(1)−O(3)	98.8(2)	C(1G)−O(3)−Al(1)	122.9(4)
O(1)−Al(1)−H(1)	120(2)	C(4G)−O(3)−Al(1)	122.3(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(DIP)_3[Me_2EtN(CH_2)_4O]Al$ (**3**)

Bond Lengths			
Al(1)−O(1)	1.733(3)	O(1)−C(1A)	1.359(6)
Al(1)−O(4)	1.740(4)	O(2)−C(1B)	1.354(6)
Al(1)−O(2)	1.747(3)	O(3)−C(1C)	1.354(6)
Al(1)−O(3)	1.748(4)	O(4)−C(1D)	1.430(8)
Angles			
O(1)−Al(1)−O(4)	113.4(2)	O(2)−Al(1)−O(3)	110.3(2)
O(1)−Al(1)−O(2)	109.1(2)	C(1A)−O(1)−Al(1)	149.0(3)
O(4)−Al(1)−O(2)	108.0(2)	C(1B)−O(2)−Al(1)	137.0(3)
O(1)−Al(1)−O(3)	108.4(2)	C(1C)−O(3)−Al(1)	139.0(3)
O(4)−Al(1)−O(3)	107.6(2)	C(1D)−O(4)−Al(1)	128.8(4)

A thermal ellipsoid drawing of **2** is shown in Figure 2, and selected bond lengths and angles are given in Table 4. The aluminum is tetrahedrally coordinated, and at 1.53(4) Å the Al−H bond distance is shorter than found in **1**. The Al−O1 and Al−O2 distances are 1.691(3) and 1.699(4) Å, respectively, approximately 0.05 Å shorter than found in **1**. The Al−O1−C1 and Al−O2−C2 angles are 152.6(3)° and 150.7(3)°. The Al−O distance to the datively bonded THF is 1.881(4) Å, which is shorter than found in **1**, but comparable to those found in $(BHT)_2AlH\cdot OEt_2$, (1.907(2) Å).[4] Diethyl ether is slightly more bulky than THF, so one would expect it to be able to approach less closely to the metal center.

A thermal ellipsoid drawing of **3** is shown in Figure 3, and selected bond lengths and angles are given in Table 5. The compound crystallizes in the acentric space group *Cc*, and the geometry around the Al is approximately tetrahedral. The Al−O

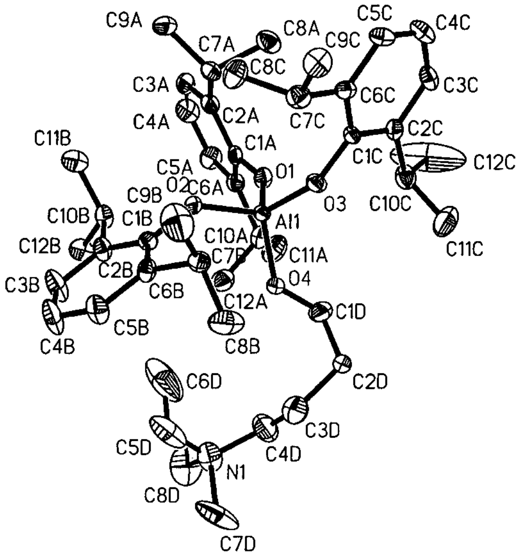

Figure 3. TELP thermal ellipsoid drawing of (DIP)$_3$(Me$_2$EtN(CH$_2$)$_4$O)-Al (**3**). Hydrogen atoms are omitted for clarity. Ellipsoids shown are 30%.

bond lengths range from 1.733(3) to 1.748(4) Å, with an average length of 1.742 Å. The Al−O bond to the ring-opened THF is 1.740(4) Å. The Al−O−C angles range from 128.8(4)° to 149.0(3)°, with an average of 138.5°. This average value is almost identical to the angles found in **1**, but narrower than observed in **2**. The intramolecular distance between the tethered Al and N of the zwitterion is 5.93(1) Å. Examination of intermolecular distances establish that this is only slightly shorter than the three closest intermolecular Al−N distances of 7.33(2), 7.46(2), and 7.55(2) Å. The distribution of the aluminate anions and the cationic ammonium groups in **3** represents a distorted zinc-blende lattice. The dipole moments of all of the zwitterions are aligned and point in the same direction.

The difficulty in accurately locating hydrogens has led to a large spread in the Al−H bond lengths. The Al−H distances range from 1.277 to 1.820 Å for terminal hydrides in the Cambridge Structural Database (CSD);[12,13] the average value is 1.53(9) Å. Both AlH_3·2THF (d_{Al-H} = 1.53(4) Å) and **1** (d_{Al-H} = 1.58(4) Å) have hydrides located in equatorial positions, and one might expect any major chemical differences in the Al−H bond to show up upon exchanging H^- for the electronegative DIP. The bond lengths, however, are indistinguishable to 2σ and fall on the average for all structurally characterized Al−H bonds.

The dative bond between THF and Al involves partial transfer of electron density to the aluminum without changing the formal oxidation state. Substitution of a hydride with a DIP withdraws electron density from the Al, which then compensates by more strongly binding the THF oxygen and shortening the Al−O bond. This can be seen by comparing the Al−THF bond in **1** with the corresponding bond in AlH_3·2THF. The bonds differ by 0.033 Å, a difference of 4σ using $\sigma = 0.007$ Å for the Al−O bond of AlH_3·2THF. Both of the five-coordinate complexes display notably longer Al−O(THF) bonds (by 0.15 Å) compared to the analogous distance in **2**.

Table 6. Summary of Structural Data

	1	AlH_3· 2THF[a]	**2**	(BHT)$_2$AlH· Et$_2$O[b]	**3**
Al−H (Å)	1.58(4)	1.51[c]	1.53(4)	1.47(3)	
Al−O(ether) (Å)	2.034[c]	2.067[c]	1.881(4)	1.907(2)	
Al−OR (Å)	1.752(2)		1.695[c]	1.708[c]	1.742[c]
Al−O−C (deg)	137.5(2)		152[c]	164[c]	138[c]
coordination no.	5	5	4	4	4

[a] Reference 7. [b] Reference 4. [c] Average value.

Consistent with several related four and five-coordinate Al compounds,[4,14] the Al−OR distances observed in **1**−**3** are unusually short, and the observed Al−O−C angles are notably wide for sp^3 oxygens (Table 6). Several explanations for this phenomenon have been advanced including π donation of electron density by oxygen to Al[4,14,15] and strong 1,3 "geminal" repulsion between the Al and C atoms attached to the oxygen.[16] While these factors may contribute to the short bond and the wide angles, it should be noted that other factors may also play a role. Formation of an aluminum−THF dative bond will transfer electron density to the aluminum, lengthening the bond. This is consistent with a steadily increasing Al−OR bond length in three-, four-, and five-coordinate complexes, with zero, one, and two dative bonds, respectively.[4,14] Additionally, the Al−O−C angle is expected to be soft[17,18] so that even relatively weak nonbonded repulsions[16] may distort the angle away from its ideal value.

These considerations suggest that no one interaction may control the metrics of these compounds, but that a combination of intermolecular steric interactions, bond polarity, and π-bonding may be balanced to control the bond lengths and angles.

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Supporting Information Available: Tables listing detailed crystallographic data, positional parameters, thermal parameters, bond distances, bond angles, and torsion angles (24 pages). Ordering information is given on any current masthead page.

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