Synthesis and Structural Characterization of Chiral Amine Alcohol Complexes of Aluminum

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The syntheses and full characterization of chiral amine alcohol complexes of aluminum are reported. These complexes are of two general formulae, those resulting from the reaction of 1 equiv of an aluminum reagent with an amine alcohol, $[AA-AlR_2]_2$ (where AA = phenylglycinol (PGly), R = Me (**1**), Et (**2**), $SiMe_3$ (**3**); phenylalaninol (PAla), R = Me (**4**), Et (**5**), $SiMe_3$ (**6**); and diphenylalaninol (DPAla), R = Me (**7**), Et (**8**), $SiMe_3$ (**9**), and the series resulting from the reaction of 2 equiv of $AlMe_3$ with an amine alcohol, $AA(AlMe_2)-AlMe_3$ (where AA = PGly (**10**), PAla (**11**), and DPAla (**12**)). These compounds significantly increase the number of chiral group 13 complexes that have been reported in the literature. Additionally, the crystal structures of **5**, **6**, and **11** have been obtained.

Introduction

Organoaluminum reagents are widely employed in such reactions as the reduction of aldehydes and ketones[1] and have been used in molecular recognition[2] and as living polymerization catalysts.[3] In many of these reactions chiral aluminum complexes would be particularly useful, being able to support stereospecific transformations. However, fully characterized chiral aluminum complexes are very rare and few have been structurally characterized. Some recent structurally characterized examples include aluminum complexes with optically active alcohols,[4] mixed oxygen−nitrogen systems,[5] and a diazaaluminolidine.[6] Considering the biological origin of many of the ligands in these systems, these types of compounds may also be used in studies concerning the toxic effects of aluminum compounds,[7,8] as models for heavier group 13 imaging agents,[9] and as catalysts for biological reactions.[10] An understanding of structure is crucial since there will be a direct correlation between structure and the behavior of these complexes in both catalytic and biological environments.

For these reasons we have begun a fundamental study of the synthesis and characterization of such group 13 complexes, focusing on those incorporating aluminum. In the present manuscript are reported aluminum complexes derived from three chiral amine alcohols, (Figure 1a−c). On the basis of the stoichiometry of the aluminum reagent, the resulting complexes are either dimeric (Figure 1d) or monomeric (Figure 1e). They have been characterized by physical and spectroscopic techniques and, in three instances, by X-ray crystallography. Compounds **3**, **6**, and **9** incorporate the relatively underutilized $SiMe_3$ group on aluminum and may be viewed as potential precursors to biologically active Al−O−Si compounds.

Results and Discussion

The amine alcohols (Figure 1a−c) are soluble in solvents such as H_2O and alcohols, solvents that are generally reactive toward group 13 reagents. Thus, compounds **1**−**9** are prepared by the addition of the group 13 reagent to a slurry of the amine alcohol (AA) in toluene (eq 1). The exothermic reaction quickly

$$AA + AlR_3 \xrightarrow{-RH} [AA\text{-}AlR_2]_2 \qquad \text{(Eq 1)}$$

AA = PGly; R = Me (**1**), Et (**2**), TMS (**3**)
= PAla; R = Me (**4**), Et (**5**), TMS (**6**)
= DPAla; R = Me (**7**), Et (**8**), TMS (**9**)

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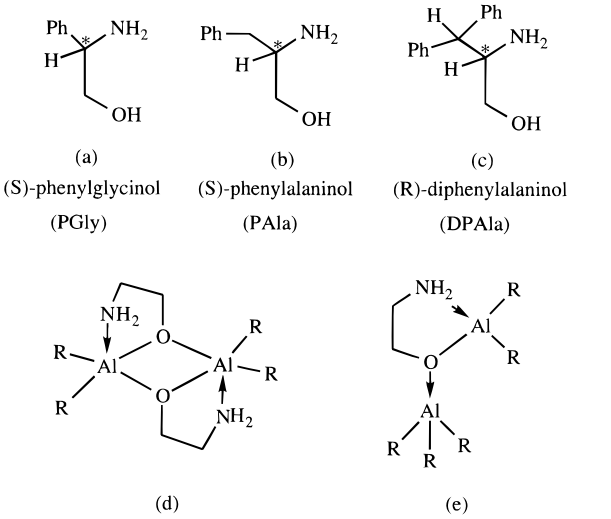

Figure 1. Chiral amine alcohols (a−c) and the structural formulae for the group 13 compounds reported in this study (d and e).

produces a pale yellow solution and is allowed to stir for several hours. Following this, the solution is concentrated under vacuum and cooled to −30 °C to yield the compounds as pale yellow or white solids in moderate to high yield.

A listing of selected ^{1}H NMR data and the ν_{NH} IR shift for compounds **1**−**12** is shown in Table 1. The ^{1}H NMR data for these compounds demonstrated complex patterns of coupling due to the chirality of the ligands. Primarily, this involves the coupling of diastereotopic protons on the same carbon atom. For example, the spectrum of **4** (Figure 2) demonstrates that the proton on the chiral carbon (c) is coupled to four separate protons ($H_{a,b,d,e}$) producing a complex multiplet. Hydrogens a, b are coupled to one another as well as c, producing two doublet of doublets. The same situation is observed for d and e. The unassigned singlets at δ 2.1 and 0.28 are due to toluene and silicon grease, respectively.

A significant feature of this spectrum and, indeed, the spectra for the other 1:1 complexes is the fact that only one sharp Al−R resonance is detected at 25 °C. In similar systems reported by Oliver (R_2Al complexes with optically active alcohols)[4] the room-temperature NMR data indicated that rapid dissociation of the amine portion of the ligand produced a singlet for the AlR protons. Upon cooling, however, this resonance split, indicating a slowing of the dynamic behavior and consequent inequivalence of the AlR groups. On the basis of the ligand chirality, a similar situation is expected for **1**−**9**.

An interesting trend can be seen in the chemical shifts attributed to the NH groups. They progressively become more deshielded as the size of the R group grows. For example, in **1**−**3** the values are δ 1.38, 1.59, and 1.95 ppm, respectively. This may be interpreted in terms of a lengthening of the Al−N bond due to the increasing steric bulk. This bond change would lead to slight change in hybridization on the Al atom (the lengthened bond would possess more p character) and, consequently, on N as well. This would lead to an N−H bond which would possess more s character and show a more acidic, downfield shift, as the steric bulk on Al grows. This is partially borne out by the increasing average Al−N bond distances for **5** and **6** of 2.18(1) and 2.26(1) Å, respectively. Moreover, this explanation is supported by work on the Me_3Al-PR_3 systems where the increasing bulk of the alkyl group leads to more downfield ^{1}H and ^{13}C NMR resonances of the Me_3Al fragment.[11]

The addition of 2 equiv of $AlMe_3$ to the amine alcohol leads to monomeric 2:1 complexes (eq 2) in reasonable

$$AA + 2\ AlR_3 \xrightarrow{-RH} AA(AlR_2)\text{-}AlR_3 \quad \text{(Eq 2)}$$

R = Me; AA = PGly (**10**), PAla (**11**), DPAla (**12**)

yields. However, attempts to conduct this reaction with $AlEt_3$ and Al^iBu_3 lead to complex mixtures of products as evidenced by the ^{1}H NMR data. However, in the case of $Al(SiMe_3)_3$, the mixture could be separated to produce high yields of **3**, **6**, **9**, and unreacted $Al(SiMe_3)_3$. From these results it is clear that a steric effect inhibits the formation of the 2:1 complexes in cases where the alkyl is more sterically encumbered than methyl. This scenario is also supported by the crystal structure data for **11** (vide infra). These compounds are highly air sensitive, with reactivity approaching that of free $AlMe_3$. For instance, after isolation these compounds will show signs of decomposition even while being handled under dry nitrogen. This reactivity also led to problems getting accurate elemental analyses; in all cases, after repeated runs, the values were found to be low. A low value is what would be expected if some of the Al−Me groups were being converted into Al−OH groups.

The ^{1}H NMR spectra for **10**−**12** are similar to that seen for **1**−**9** with one exception. There are now three types of Al−Me groups, which is manifested as three singlets in the NMR spectrum. On the basis of the integrations, there is one resonance for the $AlMe_3$ group and one resonance each for the remaining two Al−Me groups. Compared to the 1:1 complexes this implies that the adduct formation between the second $AlMe_3$ group and ligand oxygen prevents dissociation of the *amine* portion of the ligand. In the subsequent absence of dynamic behavior the inequivalence of the Al−Me resonances is observed.

Crystals suitable for X-ray diffraction for **5**, **6**, and **11** were grown from a toluene solution cooled to −30 °C for at least 24 h. In keeping with the chirality of the starting materials, each of these compounds adopt noncentrosymmetric space groups ($P2_1$, $P1$, and $P2_12_12_1$, respectively). A summary of crystallographic data is shown in Table 2. Molecular structures and atom numbering schemes for **5**, **6**, and **11** are shown in Figures 3−5, respectively. Atomic coordinates are given in the Supporting Information. Selected bond distances and angles are given in Table 3.

The 1:1 complexes (**5** and **6**) form oxygen-bridged dimers wherein the aluminum atom is five-coordinate and in a distorted trigonal bipyramidal geometry. Thus, for **5** the axial atoms (O(1) and N(2)) form an O−Al−N angle of 152.4(7)°. The atoms C(1), O(2), and C(3), form equatorial angles that fall in the range 125.2(10)°−

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Table 1. Selected Spectroscopic Data for Compounds 1−12

compd	δ (ppm) NH	NCH	OCH	PhCH	ν_{NH} (cm^{-1})
[PGly(AlMe$_2$)]$_2$ (**1**)	1.38 (d)	3.59 (m)	3.32 (m) 3.85 (dd)		3349
[PGly(AlEt$_2$)]$_2$ (**2**)	1.59 (d)	3.69 (m)	3.34 (m) 3.91 (dd)		3249
[PGly(Al(SiMe$_3$)$_2$)]$_2$ (**3**)	1.95 (d)	3.87 (m)	3.53 (m) 3.95 (dd)		3524
[PAla(AlMe$_2$)]$_2$ (**4**)	1.05 (d)	2.70 (m)	3.13 (dd) 3.57 (dd)	1.94 (dd) 2.18 (dd)	3349
[PAla(AlEt$_2$)]$_2$ (**5**)	1.35 (d)	2.78 (m)	3.15 (dd) 3.65 (dd)	1.95 (dd) 2.20 (dd)	3349
[PAla(Al(SiMe$_3$)$_2$)]$_2$ (**6**)	1.69 (d)	2.97 (m)	3.12 (m) 3.73 (dd)	1.96 (dd) 2.15 (dd)	3348
[DPAla(AlMe$_2$)]$_2$ (**7**)	1.46 (d)	3.51 (m)	3.37 (m) 3.72 (m)	3.36 (m)	3343
[DPAla(AlEt$_2$)]$_2$ (**8**)	1.55 (d)	3.55 (m)	3.24 (m) 3.73 (dd)	3.24 (m)	3354
[DPAla(Al(SiMe$_3$)$_2$)]$_2$ (**9**)	2.03 (d)	3.80 (m)	3.26 (m)	3.26 (m) 3.80 (m)	3283
PGly(AlMe$_2$)−AlMe$_3$ (**10**)	1.31 (m)	3.92 (m)	3.32 (m)		3302
PAla(AlMe$_2$)−AlMe$_3$ (**11**)	1.17 (dd) 1.34 (dd)	2.58 (m)	3.28 (dd) 3.60 (dd)		3304
DPAla(AlMe$_2$)−AlMe$_3$ (**12**)	1.33 (m)	3.14 (m)	3.36 (dd) 3.50 (dd)	3.34 (d)	3273

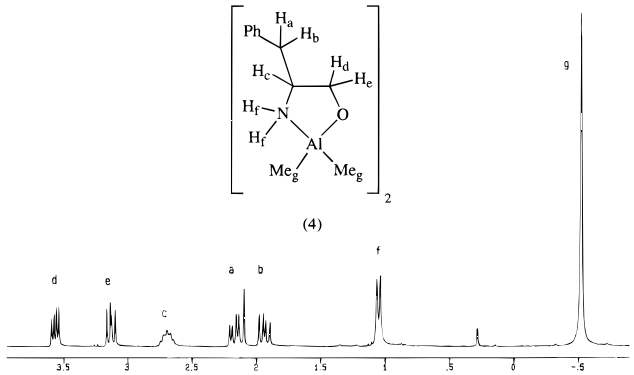

Figure 2. Representative ^{1}H NMR spectrum of [PAla(AlMe$_2$)]$_2$ (**4**).

116.9(11)°. Similarly, for **6**, the axial atoms (O(2) and N(1)) form an angle of 153.3(4)° with the atoms O(1), Si(1), and Si(2) forming equatorial angles in the range 124.2(2)°−115.6(2)°. The presence of distorted trigonal bipyramidal geometries in these systems is in keeping with the general trend seen for other five-coordinate aluminum complexes incorporating open-chain ligands.[12]

The structures of **5** and **6** are of the same morphology as other ligand systems possessing both NH and OH functionalities. For example, the reaction of alkylaluminum reagents, such as AlMe$_3$, with l-ephedrine leads to a dimeric complex having this general structure (Figure 1d).[5a] The Al atom in this complex also adopts a trigonal bipyramidal geometry with a long Al−N axial bond (2.193 (8) Å). This bond in **5** is roughly of the same value (Al(1)−N(2) = 2.190(14) Å) while that for **6** is somewhat longer (2.241(8) Å). The central Al$_2$O$_2$ four-membered rings in **5** and **6** are planar with the ligands adopting a trans orientation.

There are relatively few compounds reported which possess the AlSiMe$_3$ moiety.[14] In compounds **3**, **6**, and **9** this group apparently behaves in a manner analogous to traditional alkyl groups (such as Me and Et) and has the steric requirements similar to a *tert*-butyl group. The Al−Si bond distances in **6** average 2.48(1) Å. This compares closely to [(SiMe$_3$)$_2$AlNH$_2$]$_2$ where the average distance is 2.48(1) Å.[14a] As stated previously, the primary importance of an Al−S linkage in these molecules lies in their use as precursors to aluminosilicates bound by the amine alcohols.

When 2 equiv of R$_3$Al are added to the amine alcohols (eq 2), the dimerization seen for the 1:1 complexes is

Table 2. Crystal Data for [PAla(AlEt$_2$)]$_2$ (5), [PAla(AlSiMe$_3$)$_2$)]$_2$ (6), and PAla(AlMe$_2$)−AlMe$_3$ (11)

	compound 5	6	11
formula	$C_{26}H_{44}Al_2N_2O_2$	$C_{30}H_{60}Al_2N_2O_2Si_4$	$C_{14}H_{27}Al_2NO$
fw	470.6	647.1	279.3
cryst system	monoclinic	triclinic	orthorhombic
space group	$P2_1$	$P1$	$P2_12_12_1$
a (Å)	6.717(4)	9.009(1)	8.266(1)
b (Å)	17.153(2)	9.624(1)	10.519(1)
c (Å)	12.687(3)	12.873(1)	20.910(2)
α (deg)		71.21(1)	
β (deg)	103.55(3)	77.31(1)	
γ (deg)		84.45(1)	
V (Å^3)	1424.7(9)	1030.4(2)	1809.3(3)
Z	2	1	4
D_{calc} (g/cm^3)	1.97	1.043	1.025
cryst size (mm)	(0.4)^3	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.3
temp (K)	298	298	298
2θ range (deg)	3.5−45	3.5−45	3.5−45
scan type	2θ−θ	2θ−θ	2θ−θ
scan speed (deg/min)	8−60	8−60	8−60
scan range (deg)	0.40	0.30	0.31
reflcns collcd	2697	3263	1907
indp reflcns	2062	3255	1738
obsd reflcns	851 ($F > 6.0\sigma(F)$)	2331 ($F > 4.0\sigma(F)$)	915 ($F > 4.0\sigma(F)$)
no. of params	288	358	163
R	0.0556	0.0423	0.0571
R_w	0.0591	0.0426	0.0585
GOF	1.58	0.78	1.46
lar diff peak (e/Å^3)	0.22	0.29	0.26

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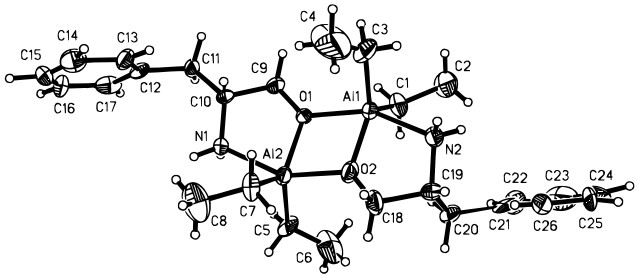

Figure 3. Molecular structure and atom-numbering scheme for $[PAla(AlEt_2)]_2$ (**5**).

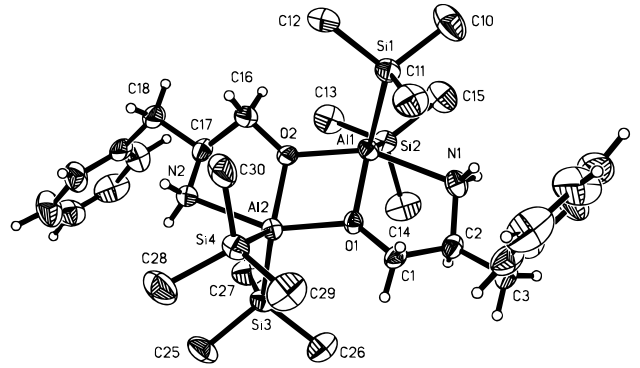

Figure 4. Molecular structure and atom numbering scheme for $[PAla(AlSiMe_3)_2)]_2$ (**6**).

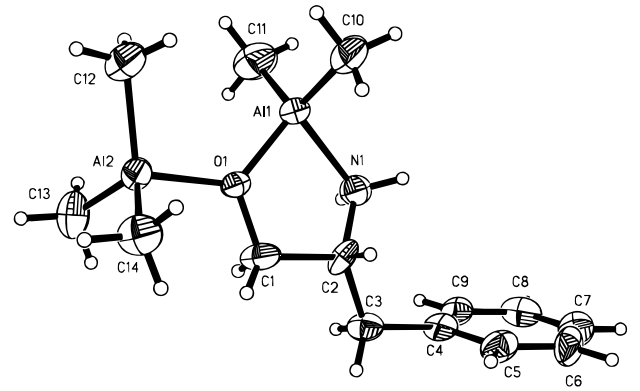

Figure 5. Molecular structure and atom-numbering scheme for $PAla(AlMe_2)-AlMe_3$ (**11**).

prevented, and monomeric 2:1 complexes (Scheme 1e) are obtained. For the $AlMe_3$ reaction, an X-ray crystallographic study confirmed that the second AlR_3 group forms an adduct with the oxygen of the ligand (Figure 5). The methyl groups adopt a staggered conformation to reduce the steric repulsions. The closest approach of two of the methyl groups in this conformation is 3.85 Å, with the hydrogens at 2.56 Å. With groups other than methyl these interactions would be even more pronounced and prevent the 2:1 complex from forming.

Both Al atoms in **11** adopt T_d geometries. For Al(2) this geometry is nearly ideal. For Al(1) the geometry is somewhat distorted due to the chelation of the ligand with the maximum deviation occurring in the C−Al−C angle (119.8(6)°). The five-membered ring formed by the ligand chelation is planar. The five-membered ring made up of the chelating ligand and Al(1) takes a nonplanar conformation where the O(1) atoms is projected 0.59 Å above the plane defined by Al(1), N(1), C(1), and C(2). By comparison, **11** is of the same overall morphology as $Me_2Al(^tBu)N{=}CHC(Me)_2OAlMe_3$.[5b]

Conclusion

The present work represents an expansion of the number of chiral aluminum complexes that have been reported in the literature along with structural characterization of three representative examples. Further work will be focused on applying the information gained on compounds **1**−**9** to applications in catalysis and the activity of aluminum in the biosphere.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glovebox. All solvents were rigorously dried prior to use. The ligands (*S*)-phenylglycinol (PGly),[15] (*S*)-phenylalaninol (PAla),[16] and (*R*)-diphenylalaninol (DPAla)[17] were synthesized as previously described. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 (^{1}H) and 62.5 (^{13}C) MHz. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 Analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

Synthesis of $[PGly(AlMe_2)]_2$ (1). To a rapidly stirring solution of (*S*)-phenylglycinol (0.510 g, 3.72 mmol) in 20 mL of toluene was added trimethylaluminum (0.270 g, 3.75 mmol) neat at 25 °C. The exothermic reaction was allowed to stir for 48 h at 25 °C. The toluene was removed in vacuo, and the remaining white solid was washed with diethyl ether and then filtered. The residual ether was removed in vacuo yielding the title compound as a white solid (yield 0.54g, 75%): Mp 153−157 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.41 (s, 6H, AlC*H*$_3$), 1.38 (d, 2H, N*H*$_2$), 3.32 (app t, 1H, OC*H*$_2$), 3.54−3.66 (m, 1H, NC*H*), 3.85 (dd, 1H, OC*H*$_2$), 6.38 (d, 2H, Ph*H*), 6.91−7.11 (m, 3H, Ph*H*); IR (KBr) 3349 s, 2965 s. 2918 s, 1262 vs, 1092 vs, 1024 vs, 802 vs, 696 vs. Anal. Calcd: C, 62.16; H, 8.35. Found: C, 62.01; H, 8.28.

Synthesis of $[PGly(AlEt_2)]_2$ (2). To a rapidly stirring solution of (*S*)-phenylglycinol (0.500 g, 3.64 mmol), in 20 mL of toluene, was added triethylaluminum (1.0 *M* in hexane, 0.692 g/mL, 2.519 g, 3.64 mmol) in 15 mL of toluene at 25 °C. The exothermic reaction was allowed to stir at 25 °C for 4 h. The resulting solution was filtered and the solvent removed in vacuo. The white solid was washed with hexane and the hexane removed via cannula, the residual hexane removed in vacuo leaving the title compound as a white solid (0.580 g, 72%): Mp 125−127 °C;

^{1}H NMR (270 MHz, C_6D_6) δ −0.17 (q, 4H, AlC*H*$_2$CH$_3$), 1.45 (t, 6H, AlCH$_2$C*H*$_3$), 1.59 (d, 2H, N*H*$_2$), 3.34 (app t, 1H, OC*H*$_2$), 3.59−3.79 (m, 1H, NC*H*), 3.91 (dd, 1H, OC*H*$_2$), 6.47 (d, 2H, Ph*H*), 6.95−7.10 (m, 3H, Ph*H*); ^{13}C NMR (62.5 MHz, C_6D_6) δ 1.37 (AlCH$_2$*C*H$_3$), 11.50 (Al*C*H$_2$CH$_3$), 57.08 (O*C*H$_2$), 127.75 (Ph), 127.87 (Ph), 128.10 (Ph), 128.23 (Ph), 128.82 (Ph); IR (KBr) 3249 s, 3285 s, 2953 vs, 2855 vs, 1588 s, 1262 vs, 1088 vs, 1022 vs, 802 vs. Anal. Calcd: C, 65.14; H, 9.11. Found: C, 64.82; H, 8.96.

Synthesis of $[PGlyAlTMS_2]_2$ (3). (*S*)-Phenylglycinol (0.465 g, 3.39 mmol) was suspended in 25 mL of toluene, and $Al(SiMe_3)_3$·THF (1.08 g, 3.39 mmol) was added at room temperature. The reaction was stirred at room temperature for 8 h, during which time the amino alcohol gradually dissolved. The reaction was concentrated to $^1/_2$ volume and stored at −30 °C, and colorless crystals grew after 2 days (0.543 g, 52%). A second batch of crystals was isolated from the filtrate after 1 week at −30 °C (combined yield, 0.797 g, 76%): Mp 184−186 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 0.31 (s, 18H, SiC*H*$_3$), 1.95 (d, J = 8 Hz, 2H, N*H*$_2$), 3.53 (t, J = 10 Hz, 1H, OC*H*$_2$), 3.84−3.90 (m, 1H, NC*H*), 3.95 (dd, J = 5, 10 Hz, 1H, OC*H*$_2$), 6.82−7.01, m, 5H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 3.0 (Si*C*H$_3$), 58.1 (O*C*H$_2$), 64.4 (N*C*H), 126.5 (Ph), 128.7, 129.5, 139.9; IR (neat) 3524, 3346, 3298, 2942, 2886, 1578, 1456, 1231, 1071, 1013,

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds 5, 6, and 11

[PAla(AlEt$_2$)]$_2$ (**5**)		[PAla(Al(SiMe$_3$)$_2$]$_2$ (**6**)		PAla(AlMe$_2$)−AlMe$_3$ (**11**)	
Al(2)−O(1)	1.850(13)	Al(1)−Si(1)	2.485(5)	Al(1)−O(1)	1.807(8)
Al(2)−O(2)	1.947(13)	Al(1)−Si(2)	2.474(4)	Al(1)−N(1)	2.005(9)
Al(2)−N(1)	2.181(13)	Al(1)−O(1)	1.850(8)	Al(1)−C(10)	1.930(10)
Al(2)−C(5)	1.973(26)	Al(1)−O(2)	1.935(6)	Al(1)−C(11)	1.934(12)
Al(2)−C(7)	1.967(23)	Al(1)−N(1)	2.241(8)	Al(2)−O(1)	1.895(8)
Al(1)−O(1)	1.960(13)	Al(2)−Si(3)	2.493(6)	Al(2)−C(12)	1.950(12)
Al(1)−O(2)	1.852(15)	Al(2)−Si(4)	2.466(5)	Al(2)−C(13)	1.963(11)
Al(1)−N(2)	2.190(14)	Al(2)−O(1)	1.922(7)	Al(2)−C(14)	1.963(12)
Al(1)−C(1)	1.954(25)	Al(2)−O(2)	1.843(9)	O(1)−C(1)	1.409(12)
Al(1)−C(3)	1.967(28)	Al(2)−N(2)	2.274(8)	N(1)−C(2)	1.488(14)
O(1)−C(9)	1.393(20)	O(1)−C(1)	1.405(12)		
O(2)−C(18)	1.410(22)	O(2)−C(16)	1.427(14)		
N(1)−C(10)	1.462(26)	N(1)−C(2)	1.496(15)		
N(2)−C(19)	1.489(28)	N(2)−C(17)	1.469(14)		
O(1)−Al(1)−O(2)	75.2(6)	Si(1)−Al(1)−Si(2)	124.2(2)	O(1)−Al(1)−N(1)	85.6(3)
O(1)−Al(1)−N(2)	152.4(7)	Si(1)−Al(1)−O(1)	119.2(2)	O(1)−Al(1)−C(10)	113.0(4)
O(2)−Al(1)−N(2)	77.6(6)	Si(2)−Al(1)−O(1)	115.6(2)	N(1)−Al(1)−C(10)	111.2(5)
O(1)−Al(1)−C(1)	97.3(8)	Si(1)−Al(1)−O(2)	102.5(3)	O(1)−Al(1)−C(11)	114.6(5)
O(2)−Al(1)−C(1)	117.8(8)	Si(2)−Al(1)−O(2)	100.6(2)	N(1)−Al(1)−C(11)	107.1(5)
N(2)−Al(1)−C(1)	98.9(7)	O(1)−Al(1)−O(2)	75.1(3)	C(10)−Al(1)−C(11)	119.8(6)
O(1)−Al(1)−C(3)	100.4(8)	Si(1)−Al(1)−N(1)	90.3(3)	O(1)−Al(2)−C(12)	103.2(5)
O(2)−Al(1)−C(3)	125.2(10)	Si(2)−Al(1)−N(1)	90.9(2)	O(1)−Al(2)−C(13)	103.6(4)
N(2)−Al(1)−C(3)	92.0(8)	O(1)−Al(1)−N(1)	78.2(3)	C(12)−Al(2)−C(13)	113.3(5)
C(1)−Al(1)−C(3)	116.9(11)	O(2)−Al(1)−N(1)	153.3(4)	O(1)−Al(2)−C(14)	103.6(4)
O(1)−Al(2)−O(2)	75.5(5)	Si(3)−Al(2)−Si(4)	120.6(2)	C(12)−Al(2)−C(14)	114.4(5)
O(1)−Al(2)−N(1)	78.1(6)	Si(3)−Al(2)−O(1)	103.6(3)	C(13)−Al(2)−C(14)	116.4(5)
O(2)−Al(2)−N(1)	153.5(6)	Si(4)−Al(2)−O(1)	103.4(2)	Al(1)−O(1)−Al(2)	126.4(3)
O(1)−Al(2)−C(5)	118.5(10)	Si(3)−Al(2)−O(2)	123.2(3)	Al(1)−O(1)−C(1)	115.5(7)
O(2)−Al(2)−C(5)	101.5(8)	Si(4)−Al(2)−O(2)	114.4(3)	Al(2)−O(1)−C(1)	117.8(7)
N(1)−Al(2)−C(5)	93.4(7)	O(1)−Al(2)−O(2)	75.6(3)	Al(1)−N(1)−C(2)	105.9(6)
O(1)−Al(2)−C(7)	121.2(8)	Si(3)−Al(2)−N(2)	87.4(3)		
O(2)−Al(2)−C(7)	96.2(7)	Si(4)−Al(2)−N(2)	92.1(3)		
N(1)−Al(2)−C(7)	95.0(7)	O(1)−Al(2)−N(2)	152.3(4)		
C(5)−Al(2)−C(7)	120.2(10)	O(2)−Al(2)−N(2)	77.1(3)		
Al(2)−O(1)−Al(1)	104.4(6)	Al(1)−O(1)−Al(2)	104.6(3)		
Al(2)−O(1)−C(9)	122.8(13)	Al(1)−O(1)−C(1)	121.8(6)		
Al(1)−O(1)−C(9)	132.6(13)	Al(2)−O(1)−C(1)	132.0(7)		
Al(2)−O(2)−Al(1)	104.9(6)	Al(1)−O(2)−Al(2)	104.4(4)		
Al(2)−O(2)−C(18)	128.5(13)	Al(1)−O(2)−C(16)	131.1(7)		
Al(1)−O(2)−C(18)	124.0(13)	Al(2)−O(2)−C(16)	124.2(6)		
Al(2)−N(1)−C(10)	105.3(10)	Al(1)−N(1)−C(2)	108.4(5)		
Al(1)−N(2)−C(19)	111.2(12)	Al(2)−N(2)−C(17)	103.9(5)		
Al(1)−C(1)−C(2)	120.5(16)				
Al(1)−C(3)−C(4)	123.6(23)				

824, 663, 590, 542, 472 cm^{-1}. Anal. Calcd for $C_{28}H_{56}N_2O_2Al_2Si_4$: C, 54.34; H, 9.14; N, 4.52. Found: C, 54.10; H, 8.23; N, 4.32.

Synthesis of [PAla(AlMe$_2$)]$_2$ (4). Trimethylaluminum (0.240 g, 3.31 mmol), in 10 mL of toluene, was added to a rapidly stirring solution of (*S*)-phenylalaninol (0.500 g, 3.31 mmol) in 35 mL of toulene at 25 °C. The exothermic reaction was stirred at 25 °C for 3 h. The toluene was removed in vacuo leaving the title compound as a white solid (0.597 g, 87%): Mp 137−139 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.52 (s, 6H, AlCH_3), 1.05 (d, J = 7 Hz, 2H, NH_2), 1.94 (dd, J = 9, 14 Hz, 1H, CH_2-Ph), 2.18 (dd, J = 6, 14 Hz, 1H CH_2Ph), 2.67−2.73, (m, 1H, NCH), 3.13 (dd, J = 8, 10 Hz, 1H, CH_2O), 3.57 (dd, J = 5, 10 Hz, 1H, CH_2O), 6.75 (d, J = 7 Hz, 2H, PhH), 6.98−7.15 (m, 3H, PhH); ^{13}C NMR (62.5 MHz, C_6D_6) δ −7.92 (AlCH_3), 39.5 (PhCH_2), 53.7 (NCH), 62.7 (OCH_2), 126.9 (Ph), 128.9 (Ph), 129.1 (Ph), 129.3 (Ph), 137.8 (Ph); IR (KBr) 3349 s, 3279 s, 2909 vs, 1591 s, 1497 s, 1454 s, 1179 vs, 1045 vs, 700 vs cm^{-1}; MS (DIP/MS) *m/e* 399 (D^+ − Me), 384 (D^+ − 2Me), 367, (D^+ − 3Me − 2H), 323 (D^+ − PhCH$_2$), 207 (M^+), 192 (M^+ − Me), 175 (M^+ − 2Me − 2H), 91 (PhCH$_2^+$), 57 (AlCH$_2^+$). Anal. Calcd: C, 63.77; H, 8.70. Found: C, 63.66; H, 8.62.

Synthesis of [PAla(AlEt$_2$)]$_2$ (5). To a rapidly stirring solution of (*S*)-phenylalaninol (0.500 g, 3.31 mmol) in 35 mL of toluene was syringed triethylaluminum (1.0 *M* in hexane, 3.31 mL) at 25 °C. The exothermic reaction was allowed to stir at 25 °C for 3 h. The toluene was removed in vacuo leaving the title compound as a white solid. Crystals suitable for X-ray analysis were grown by redissolving the white solid in toluene and cooling to −30 °C (0.597 g, 77%): Mp 100−103 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ 0.90 (q, 4H, AlCH_2CH$_3$), 1.29 (t, 6H, AlCH$_2$CH_3), 1.35 (d, 2H, NH_2), 1.95 (dd, 1H, PhCH_2), 2.20 (dd, 1H, PhCH_2), 2.71−2.85 (m, 1H, NCH_2), 3.15 (dd, 1H, OCH_2), 3.65 (dd, 1H, OCH_2), 6.75 (d, 2H, PhH), 6.98−7.15 (m, 3H, PhH); IR (KBr) 3349 s, 3291 s, 2924 s, 2859 vs, 2787 vs, 1586 s, 1495 s, 1453 s, 1082 vs, 1028 vs, 650 vs. Anal. Calcd: C, 66.36; H, 9.42. Found: C, 66.14; H, 9.25.

Synthesis of [PAlaAlTMS$_2$]$_2$ (6). (*S*)-Phenylalaninol (0.119 g, 0.79 mmol) was suspended in 10 mL of toluene and Al(SiMe$_3$)$_3$−THF (0.250 g, 0.79 mmol) was added at room temperature. The reaction was stirred at room temperature for 12 h during which time the amino alcohol gradually dissolved. The reaction was concentrated to $^1/_2$ volume and stored at −30 °C, and colorless crystals suitable for X-ray analysis grew after 1 day (0.211 g, 83%): Mp 145−146 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 0.24 (s, 18H, SiCH_3), 1.69 (d, J = 8 Hz, 2H, NH_2), 1.96 (dd, J = 14, 7 Hz, 1H, PhCH_2), 2.15 (dd, J = 14, 6 Hz, 1H, PhCH_2), 2.97 (m, 1H, NCH_2), 3.12 (dd, J = 10 Hz, 1H, OCH_2), 3.73 (dd, J = 10, 4 Hz, 1H, OCH_2), 6.73−7.10 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ 2.9 (SiCH_3), 39.5 (PhCH_2), 54.7 (NCH), 63.3 (OCH_2), 127.4 (Ph), 129.0, 129.1, 136.3; IR (neat) 3348, 3277, 2935, 3891, 1582, 1454, 1231, 1051, 847, 822, 671, 546 cm^{-1}. Anal. Calcd for $C_{30}H_{60}N_2O_2Al_2Si_4$: C, 55.73; H, 9.29. Found: C, 55.20; H, 9.18.

***S*ynthesis of [DPAla(AlMe$_2$)]$_2$ (7).** To a rapidly stirring solution of (*R*)-diphenylalaninol (0.400 g, 1.76 mmol) in 20 mL

of toluene was added trimethylaluminum (0.13 g, 1.80 mmol) neat at 25 °C. The exothermic reaction was allowed to stir for 12 h at 25 °C. The toluene was removed in vacuo, and the remaining solid was washed with hexane and then filtered. The residual hexane was removed in vacuo leaving the title compound as a white solid (0.36 g, 71%): Mp 174−178 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.42 (s, 6H, AlCH_3), 1.46 (d, 2H, NH_2), 3.34−3.40 (m, 2H, Ph_2CH and OCH_2), 3.48−3.55 (m, 1H, NCH), 3.70−3.74 (m, 1H, OCH_2), 7.08−7.28 (m, 10H, PhH); IR (KBr) 3343 vs, 3283 s, 3025 s, 2828 s, 1588 vs, 1493 vs, 1453 vs, 1181 vs, 1086 vs, 1011 vs, 750 s. Anal. Calcd: C, 72.06; H, 7.83. Found: C, 71.89; H, 7.71.

Synthesis of [DPAla(AlEt$_2$)]$_2$ (8). To a rapidly stirring solution of (*R*)-diphenylalaninol (1.137 g, 5.0 mmol) in 25 mL of toluene was added triethylaluminum (1.0 *M* in hexane, 0.692 g/mL, 3.460 g, 5.0 mmol) in 15 mL of toluene at 25 °C. The exothermic reaction was allowed to stir at 25 °C for 15 h. The toluene was removed in vacuo leaving the title compound as a white crystalline solid (1.23 g, 79%): mp 157−161 °C (dec); ^{1}H (270 MHz, C_6D_6) δ 0.07 (q, 4H, AlCH_2CH$_3$), 1.32 (t, 6H, AlCH$_2$CH_3), 1.55 (d, 2H, NH_2), 3.21−3.27 (m, 2H, PhCH and OCH_2), 3.51−3.59 (m, 1H, NCH), 3.73 (dd, 1H, OCH_2), 6.89−7.04 (m, 10H, PhH); IR (KBr) 3354 s, 3084 s, 3028 s, 2930 vs, 2851 vs, 1587 s, 1493 s, 1452 s, 1262 s, 1084 vs, 1010 vs, 802 s, 704 vs, 637 vs. Anal. Calcd: C, 73.28; H, 8.42. Found: C, 73.31; H, 8.45.

Synthesis of [DPAlaAlTMS$_2$]$_2$ (9). (*R*)-Diphenylalaninol (0.570 g, 2.51 mmol) was suspended in 25 mL of toluene, and Al(SiMe$_3$)$_3$·THF (0.825 g, 2.59 mmol) was added at room temperature. The reaction was stirred at room temperature for 8 h during which time the amino alcohol gradually dissolved. The reaction was concentrated to $^1/_2$ volume and stored at −30 °C, and a white powder precipitated (0.663 g, 66%). A second batch of colorless crystals grew from the filtrate after 2 weeks at −30 °C (combined yield, 0.946 g, 94%): Mp 193−194 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 0.24 (s, 18H, SiCH_3), 2.03 (d, J = 8 Hz, 2H, NH_2), 3.26 (m, 2H, Ph_2CH and OCH_2), 3.80 (m, 2H, NCH and OCH_2), 6.91−7.12 (m, 10H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ 3.0 (SiCH_3), 58.9 (Ph_2CH), 59.0 (NCH), 63.5 (OCH_2), 127.6 (Ph), 127.8, 129.2, 129.6, 140.4, 140.8; IR (neat) 3283, 3352, 3030, 2934, 2881, 1588, 1452, 1229, 1078, 993, 820, 702, 669 cm^{-1}. Anal. Calcd for $C_{42}H_{68}N_2O_2Al_2Si_4$: C, 63.12; H, 8.59. Found: C, 63.46; H, 8.53.

Synthesis of PGly(AlMe$_2$)−AlMe$_3$ (10). To a rapidly stirring solution of (*S*)-phenylglycinol (0.225 g, 1.64 mmol) in 10 mL of toluene at −10 °C was added trimethylaluminum (0.245 g, 3.40 mmol) in 10 mL of toluene at −10 °C. The exothermic reaction was allowed to warm to 25 °C and then stirred at 25 °C for 7 h. The solution was concentrated to $^1/_2$ volume and stored at −30 °C, which produced a white precipitate. After filtration, the title compound was collected as a colorless solid (0.342 g, 79%): Mp 134−138 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.44 (s, 3H, AlCH_3), −0.42 (s, 3H, AlCH_3), −0.22 (s, 9H, AlCH_3), 1.20−1.43 (m, 2H, NH), 3.22−3.42 (m, 2H, OCH_2), 3.85−3.99 (m, 1H, NCH), 6.18 (d, 2H, Ph-H), 6.88−7.08 (m, 3H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −9.1 (AlCH$_3$), −7.6 (AlCH_3), 56.8 (OCH_2), 66.0 (NCH), 126.3 (Ph), 129.1, 129.3, 134.8; IR (neat) 3302, 3246, 2926, 2890, 1578, 1198, 1148, 1030, 719, 673 cm^{-1}. Anal. Calcd for $C_{13}H_{25}$NOAl$_2$: C, 60.22; H, 9.68. Found: C, 57.30; H, 8.49.

Synthesis of PAla(AlMe$_2$)−AlMe$_3$ (11). To a rapidly stirring solution of (*S*)-phenylalaninol (0.471 g, 3.11 mmol) in 15 mL of toluene was added trimethylaluminum (0.471 g, 6.53 mmol) in 15 mL of toluene at −78 °C via cannula. The exothermic reaction was allowed to warm to 25 °C with stirring and then allowed to stir at this temperature for 4 h. The toluene was removed in vacuo to yield the title compound as an off-white crystalline solid (0.662 g, 76%): Mp 104−107 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.59 (s, 3H, AlCH_3), −0.45 (s, 3H, AlCH_3), −0.33 (s, 9H, AlCH_3), 1.17 (dd, J = 8, 13 Hz, 1H, NH), 1.34 (dd, J = 4, 13 Hz, 1H, NH), 1.93 (dd, J = 10, 14 Hz, 1H), 2.15 (dd, J = 5, 14 Hz, 1H), 2.55−2.60 (m, 1H, NCH), 3.28 (dd, J = 7, 11 Hz, 1H, OCH_2), 3.60 (dd, J = 4, 11 Hz, 1H, OCH_2), 6.70 (d, J = 7 Hz, 2H, Ph-H), 7.05−7.19 (m, 3H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −9.5 (AlCH_3), −8.6 (AlCH_3), −7.4 (AlCH_3), 37.3 (PhCH_2), 54.2 (NCH), 65.1 (OCH_2), 127.4 (Ph), 128.9, 129.5, 135.2; IR (neat) 3304, 3252, 2922, 1587, 1454, 1196, 1043, 723 cm^{-1}. Anal. Calcd for $C_{14}H_{27}$NOAl$_2$: C, 60.22; H, 9.68. Found: C, 57.30; H, 8.49.

Synthesis of DPAla(AlMe$_2$)−AlMe$_3$ (12). To a rapidly stirring solution of (*R*)-diphenylalaninol (0.500 g, 2.20 mmol) in 10 mL of toluene was added trimethylaluminum (0.350 g, 4.86 mmol) in 20 mL of toluene at −10 °C. The exothermic reaction was allowed to warm to 25 °C and then stirred at 25 °C for 1 h. The solution was concentrated to $^1/_5$ volume and stored at −30 °C, which produced a white precipitate. After filtration, the title compound was collected as a colorless solid (0.693 g, 89%): Mp 211−214 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.52 (s, 3H, AlCH_3), −0.42 (s, 3H, AlCH_3), −0.31 (s, 9H, AlCH_3), 1.23−1.43 (m, 2H, NH), 3.08−3.20 (m, 1H, NCH), 3.34 (d, J = 15 Hz, 1H, Ph_2CH), 3.36 (dd, J = 7, 9 Hz, 1H, OCH_2), 3.50 (dd, J = 4, 11 Hz, 1H, OCH_2), 6.77−7.14 (m, 10H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −9.3 (AlCH_3), −8.5 (AlCH_3), −7.7 (AlCH_3), 53.4 (Ph_2CH), 56.0 (NCH), 63.6 (OCH_2), 127.0 (Ph), 129.3, 129.8, 139.6; IR (neat) 3273, 3233, 3150, 2920, 1584, 1495, 1400, 1150, 1047, 702 cm^{-1}. Anal. Calcd for $C_{20}H_{31}$NOAl$_2$: C, 67.61; H, 8.73. Found: C, 65.13; H, 7.88.

X-ray Experimental Details. Details of the crystal data and a summary of data collection parameters for **5**, **6**, and **11** are given in Table 1. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα (0.710 73 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection, and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters. The data obtained for **5** and **11** were somewhat weak. This serves to explain the relatively large deviations observed for the positional parameters.

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Supporting Information Available: Tables of bond lengths and angles, positional and thermal parameters, and anisotropic thermal parameters and unit cell views (26 pages). Ordering information is given on any current masthead page.

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