

Aluminum Derivatives of a New Chiral Binucleating Ligand

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A new chiral bis(β -amino alcohol) ligand, LH₂, has been prepared in 40% yield by the Cu-catalyzed coupling of 4,6-diiododibenzofuran with diphenylpyrrolidin-2-yl-methanol, the latter of which is prepared from L-proline. The protonolysis reaction of LH₂ with 2 equiv of AlⁱBu₃ forms LAl₂ⁱBu₄ (**1**), which was isolated in 40% yield. In the solid state, compound **1** adopts a conformation that gives the molecule approximate C₂ symmetry. Each half of the molecule features a distorted tetrahedral Al center that interacts with a chelating β -amino alcoholate and two ⁱBu anions. The reaction of LH₂ with 2 equiv of AlMe₃ failed to yield isolable product, but the use of excess AlMe₃ formed LAl₄Me₁₀ (**2**) in 79% isolated yield. Compound **2** has a structure that is similar to that of **1** except that the alcoholate oxygen of each deprotonated ligand is also coordinated to an AlMe₃ group. ¹H NMR spectroscopic data of **1** in C₆D₆ solution are consistent with overall C₂ symmetry. Thus the two ⁱBu groups on each Al center are inequivalent, and four resonances are observed for the diastereotopic α -CH₂ protons of these ⁱBu ligands. The addition of 4 equiv of pyrimidine to the solution results in rapid exchange of the two inequivalent ⁱBu groups. A different process occurs in the presence of a large excess of D₆-methyl sulfoxide (D₆-DMSO). Under these conditions, the ⁱBu groups no longer possess diastereotopic α -methylenes. This indicates that the ⁱBu groups are being removed from the chiral environment, at least temporarily.

Introduction

Bimetallic complexes play important roles in numerous areas of chemistry including metalloprotein modeling, supramolecular chemistry, and catalysis.¹ To control the physical properties and chemical reactivities of this class of compounds, it is necessary that a broad range of well-defined binucleating ligands be developed.² Generally these ligands feature multiple donor groups that are linked together with some sort of unreactive spacer. When properly designed, these ligands can prevent unwanted processes such as fragmentation and oligomerization. Their design is also useful for tailoring reactivity. In this context, we and others³ have been developing new preorganized binucleating ligands that are suitable for the preparation of main-group metal bimetallics. Earlier reports have included dialuminum and dizinc organometallics supported by bis(amidinate) and bis(amidoamine) supporting ligands.⁴ Here we present the preparation and characterization of a new chiral ligand prepared in several steps from L-proline and 4,6-diiododibenzofuran. Also reported are two struc-

turally characterized Al-containing derivatives that display fluxional structural behavior in the presence of Lewis bases.

Results and Discussion

Multigram quantities of the enantiopure ligand LH₂ were conveniently prepared by the Cu-catalyzed coupling of 4,6-diiododibenzofuran with 1 equiv of diphenylpyrrolidin-2-yl-methanol using the general method developed by Buchwald⁵ (Scheme 1). The bis(β -amino

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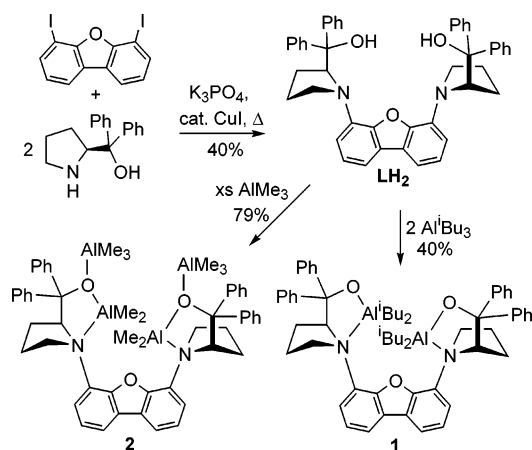
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Table 1. Crystallographic Data and Collection Parameters

	LH ₂ ·Et ₂ O	Al ⁱ Bu ₃ (1)	AlMe ₃ (2)
formula	C ₅₀ H ₅₂ N ₂ O ₄	C ₆₂ H ₇₆ Al ₂ N ₂ O ₃	C ₅₆ H ₇₀ Al ₄ N ₂ O ₃
fw	744.94	915.21	927.06
space group	P2 ₁ 2 ₁ 2 ₁ (#19)	P2 ₁ (#4)	C222 ₁ (#20)
temp (°C)	-134	-136	-133
a (Å)	7.9529(6)	10.2369(9)	13.1193(6)
b (Å)	16.6653(11)	12.5527(11)	17.4889(7)
c (Å)	30.830(2)	21.4906(19)	22.9015(10)
α (deg)	90	90	90
β (deg)	90	100.301(2)	90
γ (deg)	90	90	90
Z	4	2	4
V (Å ³)	4086.1(5)	2717.0(4)	5254.6(4)
d _{calc} (g/cm ³)	1.211	1.163	1.172
θ range (deg)	1.80–27.48	1.89–27.48	1.78–27.48
μ (mm ⁻¹)	0.076	0.100	0.132
cryst size (mm)	0.5 × 0.1 × 0.1	0.4 × 0.35 × 0.3	0.25 × 0.15 × 0.10
no. of reflns collected	32 593	21 274	20 987
no. of data/restraints/params	9363/0/507	12 378/1/630	6020/0/299
R1 (for F _o > 4σF _o)	0.0704	0.0857	0.0711
R1, wR2 (all data)	0.1307, 0.1645	0.1622, 0.2241	0.1505, 0.1604
GOF	0.955	0.974	0.967
largest peak, hole (e/Å ³)	0.22, -0.27	0.73, -0.38	0.30, -0.25

Scheme 1

alcohol)⁶ was isolated in 40% yield as colorless crystals from Et₂O at -40 °C. ¹H NMR spectroscopic data of C₆D₆ solutions of LH₂ are consistent with overall C₂ symmetry with the axis of symmetry passing through the dibenzofuran oxygen atom. In contrast, the conformation of the ligand in the solid state (Figure 1) features the two β-amino alcohol groups oriented in a parallel fashion.

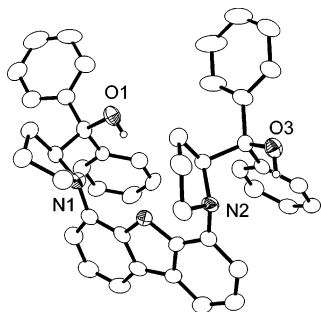


Figure 1. Structure of LH₂ drawn with 50% thermal ellipsoids. Cocrystallized Et₂O molecule and hydrogens are omitted except for the hydroxy groups.

Reaction of LH₂ with 2 equiv of AlⁱBu₃ in benzene formed dialuminum 1 with the elimination of 2 equiv of isobutane. 1 was isolated as colorless crystals in 40%

yield following the addition of hexanes and cooling to 6 °C. The related reaction using AlMe₃ in place of AlⁱBu₃ failed to yield any isolable product. The use of excess AlMe₃, however, formed the tetraaluminum 2, which was isolated in 79% yield. The structures of both 1 and 2 have been determined by single-crystal X-ray diffraction (Tables 1 and 2). As shown in Figure 2, complex 1 adopts a conformation that gives the overall molecule approximate (noncrystallographic) C₂ symmetry. Each half of the molecule features a four-coordinate Al center that interacts with a chelating β-amino alcoholate and two ⁱBu anions. Geometry at Al can be described as distorted trigonal pyramidal, with the apical position being occupied by the weak 3° amine donor. Bond lengths are typical⁷ and reflect the oxophilicity of the Al centers. The Al–O distances are 1.745(3) and 1.754(3) Å at Al1 and Al2, respectively. The bonds to the amine donors are much longer (Al1–N1, 2.104(4) Å; Al2–N2, 2.093(4) Å). The four Al–ⁱBu bonds are all identical within statistical error and have an average value of 1.98 Å. Compound 2 rests on a crystallographic C₂ axis of symmetry (Figure 3). Overall it has a structure that is similar to that of 1 except that the oxygen atom of each deprotonated β-amino alcoholate is also coordinated to an AlMe₃ group. This additional donor interaction is reflected in the Al1–O1 bond length of 1.848(3) Å, which is ca. 0.1 Å longer than the Al–O bonds in 1. The interaction between the AlMe₃ and the alcoholate oxygen is weaker, with an Al2–O1 distance of 1.925(3) Å.

¹H NMR spectroscopic data of 1 in C₆D₆ solution are consistent with overall C₂ symmetry, with the rotation

(6) A closely related bis(β-amino alcohol) ligand has been developed and used as a catalyst for aldol reactions mediated by organozinc intermediates: Ito, H.; Trost, B. M. *J. Am. Chem. Soc.* **2000**, *122*, 12003.

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Table 2. Selected Bond Distances (Å) and Angles (deg)

		LH ₂ ·Et ₂ O			
O1–C21	1.433(4)	O3–C22	1.422(4)	N1–C1	1.420(4)
N1–C13	1.495(5)	N1–C16	1.464(4)	N2–C12	1.434(4)
N2–C17	1.484(5)	N2–C20	1.491(5)		
		LAl ₂ ⁱ Bu ₄ (1)			
Al1–O1	1.745(3)	Al1–N1	2.104(4)	Al1–C47	1.997(5)
Al1–C51	1.970(5)	Al2–O3	1.754(4)	Al2–N2	2.093(4)
Al2–C55	1.980(6)	Al2–C59	1.988(5)	O1–Al1–N1	85.4(2)
O1–Al1–C47	118.5(2)	O1–Al1–C51	112.8(2)	N1–Al1–C47	107.8(2)
N1–Al1–C51	115.4(2)	C47–Al1–C51	113.7(2)	O3–Al2–N2	85.9(2)
O3–Al2–C55	114.7(2)	O3–Al2–C59	117.9(2)	N2–Al2–C55	113.9(2)
N2–Al2–C59	106.7(2)	C55–Al2–C59	114.2(3)		
		LAl ₄ Me ₁₀ (2)			
Al1–O1	1.848(3)	Al1–N1	2.076(3)	Al1–C24	1.956(5)
Al1–C25	1.942(5)	Al2–O1	1.925(3)	Al2–C26	1.960(5)
Al2–C27	1.961(5)	Al2–C28	1.970(5)	O1–Al1–N1	87.0(1)
O1–Al1–C24	112.8(2)	O1–Al1–C25	117.3(2)	N1–Al1–C24	106.5(2)
N1–Al1–C25	107.5(2)	C24–Al1–C25	119.6(2)	Al1–O1–Al2	115.9(2)

axis bisecting the dibenzofuran backbone. Thus at each Al center the two ⁱBu groups are inequivalent and the α-CH₂ protons are diastereotopic. Four distinct resonances are expected for these α-CH₂ protons. These are observed upfield at δ 0.55, 0.42, –0.57, and –0.70 as broad and featureless resonances. At 0 °C these resonances become doublets of doublets with coupling constants of 14 and 7 Hz for the two-bond (geminal) and

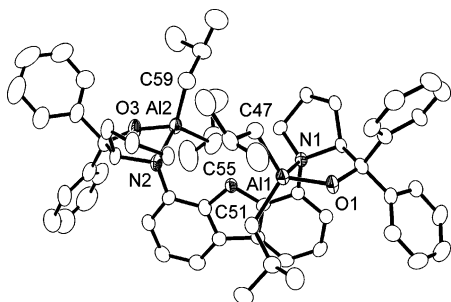


Figure 2. Structure of **1** drawn with 50% thermal ellipsoids. Hydrogens are omitted.

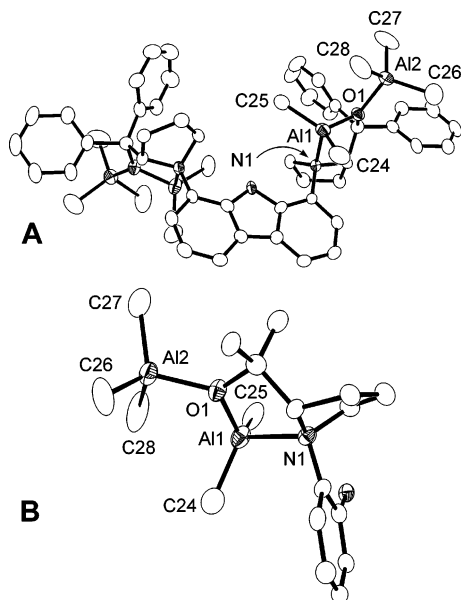
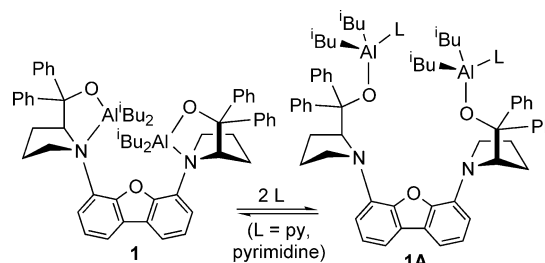


Figure 3. (A) Structure of **2** drawn with 50% thermal ellipsoids. Hydrogens are omitted. (B) Structure of the asymmetric unit of **2** with the H atoms and non-*ipso* C atoms of the Ph groups omitted. Drawn with 50% thermal ellipsoids.

Scheme 2



three-bond couplings, respectively. In addition to being dependent on temperature, the observed ¹H NMR data are also affected by the presence of Lewis bases. For example, the ¹H NMR spectrum of **1** (C₆D₆) in the presence of 4 equiv of pyrimidine leads to dramatic changes in the resonances associated with the supporting ligand and the ⁱBu groups. Most notably, the ¹H NMR spectrum features only two upfield doublets (*J* = 14, 7 Hz) at δ –0.01 and –0.10 for the diastereotopic methylenes of the Al-ⁱBu groups. These data are consistent with the formation of adduct **1A**, which under the reaction conditions undergoes fast exchange of free and coordinated pyrimidine (Scheme 2). This process allows for inversion at Al and thus exchange of the inequivalent ⁱBu groups.

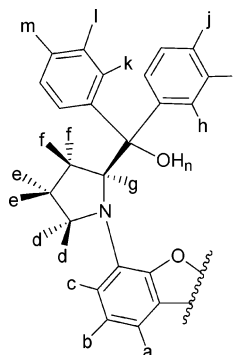
The addition of a large excess of methyl sulfoxide (DMSO) to **1** revealed a different process. The ¹H NMR spectrum of **1** dissolved in 30% D₆-DMSO (in C₆D₆) shows only one upfield doublet at δ –0.13 (³*J* = 6.5 Hz) for all of the α-CH₂ protons. All the other resonances are significantly shifted from the dmsu-free spectrum, and they do not correspond to LH₂ in the same solvent mixture. Since the α-CH₂ protons are not diastereotopic, it must be concluded that they are removed from the chiral environment, at least temporarily. Our data do not indicate the mechanism for this process, but one possibility (among many) is a base-induced disproportionation of **1** to form AlⁱBu₃(D₆-DMSO)_n and L₃Al₂(D₆-DMSO)_x.

In conclusion, a new chiral bis(β-amino alcoholate) ligand has been prepared and used for the preparation of two structurally characterized Al derivatives. These complexes and related ones are of potential use in a range of organic transformations mediated by Lewis acids.

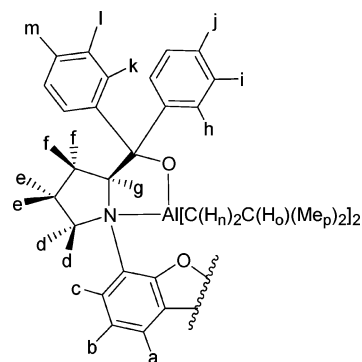
Experimental Section

General Considerations. Standard Schlenk-line and glove-box techniques were used unless stated otherwise. Hexanes, Et₂O, and toluene were passed through columns of activated alumina and sparged with N₂ prior to use. C₆D₆ and D₈-toluene were vacuum transferred from Na-benzophenone ketyl. 2-Propanol and methanol were distilled from CaH₂ under N₂. 4,6-Diiododibenzofuran⁸ was prepared following a published procedure. Diphenylpyrrolidin-2-yl-methanol⁶ was prepared from L-proline using a modified literature procedure. All other chemical reactants were obtained from commercial sources and used as received. Chemical shifts (δ) for ¹H NMR spectra are given relative to residual protium in the deuterated solvents at 7.16 and 2.10 ppm for C₆D₆ and D₈-toluene, respectively. Infrared spectroscopic data were acquired on mineral oil mulls between KBr plates, unless stated otherwise. Elemental analyses were determined by Desert Analytics and at the University of Michigan. All NMR spectroscopic data were acquired on Varian 400 and 500 MHz spectrophotometers. The ¹H NMR spectroscopic data were assigned on the basis of coupling data.

LH₂. 4,6-Diiododibenzofuran (4.98 g 11.9 mmol), K₃PO₄ (10.1 g, 47.6 mmol), CuI (0.228 g, 1.20 mmol), and diphenylpyrrolidin-2-yl-methanol (6.02 g, 23.7 mmol) were combined in a 200 mL round-bottomed flask. 2-Propanol (50 mL) and ethylene glycol (2.7 mL) were added to the solids to form a white suspension. The reaction mixture was heated to reflux for 4 days, after which the 4,6-diiododibenzofuran had been completely consumed (¹H NMR). The reaction mixture was cooled to ambient temperature, and the volatile components were removed under reduced pressure. The resulting solid was extracted with CHCl₃ (3 × 100 mL) and filtered. The CHCl₃ extract was washed with H₂O (2 × 100 mL) and dried over MgSO₄. Filtration of the solution and evaporation yielded the crude product as a pale green-brown solid. This solid was crystallized from Et₂O (50 mL) at -40 °C to yield colorless crystals of the product (3.2 g, 40%). ¹H NMR (C₆D₆, 500 MHz): δ 7.82 (d, 4H, *J* = 8.5 Hz, H_h), 7.48 (d, 4H, *J* = 8.5 Hz, H_k), 7.25 (t, 4H, *J* = 7.5 Hz, H_i), 7.24 (d, 2H, *J* = 7.5 Hz, H_c), 7.07 (t, 2H, *J* = 7.0 Hz, H_j), 6.86 (t, 2H, *J* = 7.5 Hz, H_b), 6.73 (t, 4H, *J* = 8.0 Hz, H_l), 6.68 (d, 2H, *J* = 8.5, 1.0 Hz, H_a), 6.65 (m, 2H, H_m), 5.34 (dd, 2H, *J* = 8.0, 5.0 Hz, H_g), 4.35 (s, 2H, H_n), 3.67 (m, 2H, H_d), 3.21 (q, 2H, *J* = 5.5 Hz, H_e), 2.09–2.18 (m, 4H, H_f), 1.74 (m, 2H, H_e), 1.65 (m, 2H, H_e) ppm. ¹³C{¹H} NMR (CDCl₃): δ 149.6, 146.5, 145.9, 135.9, 128.2, 127.4, 126.7, 126.2, 126.2, 125.9, 125.4, 123.0, 121.7, 115.2, 79.4, 67.6, 57.7, 29.8, 25.5 ppm. IR: 3317 (m, ν_{OH}), 2926 (s), 2725 (m), 2369 (w), 1628 (w), 1599 (w), 1491 (m), 1463 (s), 1413 (m), 1377 (s), 1309 (m), 1272 (w), 1241 (w), 1195 (m), 1110 (w), 1050 (w), 1034 (w), 967 (w), 890 (w), 869 (w), 847 (w), 781 (m), 739 (m), 702 (m), 653 (w), 427 (s) cm⁻¹. Anal. Calcd (Found) for LH₂, C₄₆H₄₂O₃N₂: C, 82.36 (81.74); H, 6.31 (6.30); N, 4.18 (3.91).

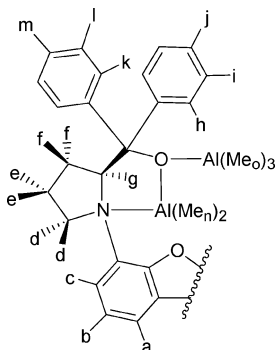


LAl₂ⁱBu₄ (1). C₆H₆ (10 mL) was added to LH₂ (0.516 g, 0.770 mmol) to form a clear colorless solution. AlⁱBu₃ (0.309 g, 1.56 mmol) was added, and the mixture was stirred overnight. The following day hexanes (10 mL) were added to the mixture, and it was cooled to 6 °C. The product was isolated the following day as colorless crystals (0.256 g, 40.3%). ¹H NMR (C₆D₆, 400 MHz): δ 7.94 (d, 4H, *J* = 7.0 Hz, H_k), 7.91 (d, 4H, *J* = 7.5 Hz, H_h), 7.25 (t, 4H, *J* = 7.5 Hz, H_i), 7.18–7.12 (m, 6H, H_i, H_c), 7.07 (t, 2H, *J* = 7.5 Hz, H_m), 7.05 (t, 2H, *J* = 8.5 Hz, H_j), 6.87 (d, 2H, *J* = 8.5 Hz, H_a), 5.88 (t, 2H, *J* = 8.0 Hz, H_b), 4.90 (dd, 2H, *J* = 7.0, 9.0 Hz, H_g), 4.83 (m, 2H, H_d), 3.68 (m, 2H, H_d), 2.31 (br, 2H, H_o), 2.09–1.97 (m, 4H, H_f), 1.82–1.62 (m, 6H, H_e, H_o), 1.44 (br, 12H, H_p), 0.93 (br, 12H, H_p), 0.56 (br, 2H, H_n), 0.45 (br, 2H, H_n), -0.56 (br, 2H, H_n), -0.68 (br, 2H, H_n) ppm. ¹H NMR (C₆D₆, 4 equiv pyrimidine, 500 MHz): δ 9.14 (br, 4H, pyrimidine), 8.09 (br, 8H, pyrimidine), 7.84 (d, 4H, *J* = 8.0 Hz, H_h), 7.65 (d, 4H, *J* = 8.0 Hz, H_k), 7.44 (d, 2H, *J* = 8.0 Hz, H_c), 7.33 (m, 8H, H_i, H_i), 7.23 (m, 4H, H_j, H_m), 7.11–7.00 (m, 4H, H_a, H_b), 6.15 (br, 4H, pyrimidine), 5.51 (m, 2H, H_g), 3.99 (m, 2H, H_d), 3.44 (m, 2H, H_d), 2.16–2.02 (m, 6H, H_f, H_o), 1.71–1.50 (m, 6H, H_e, H_o), 0.98–0.92 (m, 24H, H_p), -0.01 (dd, 4H, *J* = 7.0 Hz, 14.0 Hz, H_n), -0.10 (dd, 4H, *J* = 6.5 Hz, 14 Hz, H_n) ppm. ¹H NMR (C₆D₆, 30% D₆-DMSO, 400 MHz): δ 7.76 (d, 4H, *J* = 7.5 Hz, H_i), 7.59 (d, 4H, *J* = 7.5 Hz, H_i), 7.08 (d, 2H, *J* = 7.5 Hz, H_c), 6.95 (t, 4H, *J* = 7.5 Hz, H_m), 6.94 (t, 4H, *J* = 7.5 Hz, H_j), 6.88–6.81 (m, 8H, H_a, H_b, H_k, H_n), 4.90 (t, 2H, *J* = 7.0 Hz, H_g), 4.08 (q, 2H, *J* = 7.5 Hz, H_d), 3.33 (q, 2H, *J* = 7.5 Hz, H_d), 2.19 (m, 4H, H_f), 1.87 (nonet, 4H, *J* = 6.5 Hz, H_o), 1.54 (m, 2H, H_e), 1.42 (m, 2H, H_e), 0.96 (pseudo t, 24H, *J* = 6.5 Hz, H_p), -0.13 (d, 8H, *J* = 6.5 Hz, H_n) ppm. ¹³C{¹H} NMR (C₆D₆, 30% D₆-DMSO) δ 150.4, 149.1, 146.8, 138.2, 129.4, 129.3, 127.4, 126.9, 126.3, 126.2, 125.8, 122.9, 115.2, 110.1, 82.9, 68.2, 55.0, 29.5, 29.3, 29.3, 27.1, 24.9, 24.9 ppm. IR: 2923 (s), 2853 (s), 1598 (w), 1463 (s), 1377 (m), 1315 (w), 1171 (m), 1133 (m), 1072 (m), 1004 (w), 964 (w), 913 (w), 776 (m), 745 (m), 711 (m), 422 (s) cm⁻¹. Anal. Calcd (Found) for LAl₂ⁱBu₄, C₆₂H₇₆Al₂N₂O₃: C, 78.28 (78.22); H, 8.05 (8.08); N, 2.94 (2.75).



LAl₄Me₁₀ (2). C₆H₆ (10 mL) was added to LH₂ (0.098 g, 0.15 mmol) to form a clear colorless solution. An excess of AlMe₃ (ca. 0.75 mL) was added, and the evolution of gas was observed. After 1.5 h, hexanes were slowly added by vapor diffusion. After 3 days the product was isolated from the reaction mixture as colorless crystals (0.030 g). The mother liquor was evaporated to yield a white residue, which was dissolved in C₆H₆. Vapor diffusion with hexanes yielded additional product (0.077 g) as colorless crystals (total yield: 79%). NMR spectroscopic data are reported for **2** in dmsO-C₆D₆ mixtures. Data acquired in the absence of dmsO were broad and complex, possibly due to the presence of multiple interconverting conformations in solution. ¹H NMR (C₆D₆, 30% D₆-DMSO, 400 MHz): δ 7.59 (d, 4H, *J* = 7.2 Hz, H_h), 7.58 (d, 4H, *J* = 7.2 Hz, H_k), 7.04–6.99 (m, 6H, H_i, H_m), 6.95 (t, 2H, *J* = 7.2 Hz, H_j), 6.84 (t, 2H, *J* = 7.6 Hz, H_b), 6.77 (t, 4H, *J* = 7.2 Hz, H_l), 6.70–6.67 (m, 4H, H_a, H_c), 5.47 (t, 2H, *J* = 5.2 Hz, H_g), 4.07 (q, 2H, *J* = 8.4 Hz, H_d), 3.36 (q, 2H, *J* = 8.4 Hz, H_d), 2.24 (q, 4H, *J* = 7.6 Hz, H_f), 1.58 (m, 4H, H_e), -0.79 (s, 18H,

H_o), -0.951 (s, 12H, H_n) ppm. ¹³C{¹H} NMR (C₆D₆, 30% D₆-DMSO): δ 150.6, 149.3, 146.1, 137.6, 129.1, 128.9, 127.6, 126.7, 126.3, 126.0, 125.7, 122.9, 114.8, 109.5, 83.5, 67.4, 54.0, 29.5, 24.6, -5.9, -6.6 ppm. IR: 2953 (s), 2923 (s), 2853 (s), 2727 (m), 1957 (w), 1907 (w), 1821 (w), 1626 (w), 1596 (m), 1494 (s), 1460 (s), 1415 (m), 1377 (s), 1348 (m), 1317 (m), 1283 (w), 1239 (m), 1191 (s), 1129 (m), 1076 (w), 1033 (m), 975 (m), 945 (m), 920 (m), 828 (m), 770 (m), 693 (s), 667 (s), 436 cm⁻¹. (s). Anal. Calcd (Found) for LAl₄Me₁₀, C₅₆H₇₀Al₄O₃N₂: C, 72.55 (72.73); H, 7.61 (7.51); N, 3.02 (3.08).



X-ray Crystallography. Table 1 lists a summary of crystal data and collection parameters for all crystallographically characterized compounds. Table 2 lists selected bond lengths and angles.

General Procedure. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo K α ; $\lambda = 0.71073$ Å; graphite monochromator), and cooled to -134(2) °C by a nitrogen-flow low-temperature apparatus. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A minimum of a hemisphere of data was collected using 0.3° ω scans. The raw data were integrated and the unit cell parameters refined using SAINT. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed on F^2 using the SHELXTL software package.⁹

Structure of LH₂·Et₂O. Crystals of LH₂ that were suitable for X-ray diffraction studies were grown from Et₂O at 0 °C. Preliminary data indicated a primitive orthorhombic cell. Analysis of the systematic absences of the full data set

suggested the space group $P2_12_12_1$ (#19). This choice was confirmed by the successful solution and refinement of the structure. Since LH₂ was prepared starting from enantiopure S-proline, the correct enantiomorph of the structure was chosen by inspection. Since LH₂ is a weak anomalous scatterer, the Flack parameter (-2.6(1.7)) did not refine to an acceptable value. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of 1. Crystals suitable for X-ray diffraction studies were grown at 25 °C by vapor diffusion of hexanes into a C₆H₆ solution. Preliminary data indicated a primitive monoclinic cell. Analysis of the systematic absences of the full data set suggested the space groups $P2_1$ (#4) and $P2_1/m$ (#11). The choice of the chiral group was expected for **1**, and this was confirmed by the successful solution and refinement of the structure. The Flack parameter refined to 0.115(5), suggesting that the correct absolute structure was chosen. The inverted structure gave unacceptable results. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of 2. Crystals suitable for X-ray diffraction studies were grown at 25 °C by vapor diffusion of hexanes into a C₆H₆ solution of **1**. Preliminary data indicated a C-centered orthorhombic cell. Analysis of the systematic absences of the full data set suggested the space group $C222_1$ (#20). This choice was confirmed by the successful solution and refinement of the structure. The Flack parameter refined to 0.074(4), indicating that the correct absolute structure was chosen. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

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Supporting Information Available: Crystallographic information files (CIF) are provided for LH₂, **1**, and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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