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Inorganic Chemistry Article

Steric Stabilization of a Monomeric Proalumatrane: Experimental and Theoretical Studies

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Treatment of tripodal tris(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)amine (L) with 1 equiv of trimethylaluminum in toluene gave the stable proalumatrane (AlL) (**1**) [wherein L = tris(3-*tert*-butyl-5-methyl-2-oxidobenzyl)amine] featuring a distorted trigonal monopyramidal four-coordinate aluminum geometry. An analogous reaction uses the less sterically congested isomer of L, namely, tris(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)amine provided dimeric $(\mathrm{AlL'})_2$ (**2**) [wherein L′ = tris(5-*tert*-butyl-3-methyl-2-oxidobenzyl)amine], which contains two bridging alumatrane moieties possessing five-coordinate TBP aluminum geometries. Reaction of AlL with water provided the adduct $\mathrm{H_2O{\cdot}AlL}$ (**3**), a species that is representative of a coordinatively stabilized intermediate in the hydrolysis of an aluminum alkoxide. Theoretical calculations revealed that considerable stabilization energy is obtained by the coordination of a water molecule to the tetracoordinate aluminum in AlL and that this result is consistent with the postulate that the Lewis acidity of AlL exceeds that of boron trifluoride, despite the presence of the transannular N→Al bond in AlL.

Introduction

Prometallatranes and proazametallatranes are C_3-symmetric four-coordinate tricyclic metal complexes that possess a framework of the type $\mathrm{M[OC_x]_3N}$ or $\mathrm{M[NC_x]_3N}$, respectively, in which a bridgehead−bridgehead N→M bond is present and wherein x is 2 or 3.[1] Such species in which M is a transition metal possess an exocyclic fifth coordination site for activating substrate molecules[2] and for forming ligand−metal multiple bonds involving 3d metal orbitals.[2a,3,4] Schrock and co-workers have synthesized several prometallatranes of this type and have demonstrated that a trigonal monopyramidal (TMP) provanadatrane can readily bind to a variety of ligands to form, for example, five-coordinate trigonal bipyramidal imido and chalcogenido metallatranes of C_3 symmetry.[5] Meyer and co-workers have established that a Co(I) prometallatrane bearing a nitrogen-anchored tripodal carbene ligand was able to form a corresponding cobaltatrane by binding to a dioxygen ligand in a side-on manner[2f] or an imido ligand via a Co−N multiple bond.[3a] Borovik and co-workers have described a TMP Fe(II) proferratrane supported by the tripodal tris(*N*′-*tert*-butylureaylato)-*N*-ethylaminato ligand, which functioned as a precursor to a monomeric Fe(III) ferratrane in which an oxo group in the fifth coordination site was stabilized inside a hydrogen-bonding cavity formed by the three arms of the ligand.[2e,f] In contrast to TMP transition-metal prometallatranes, the only previous examples of main-group analogues

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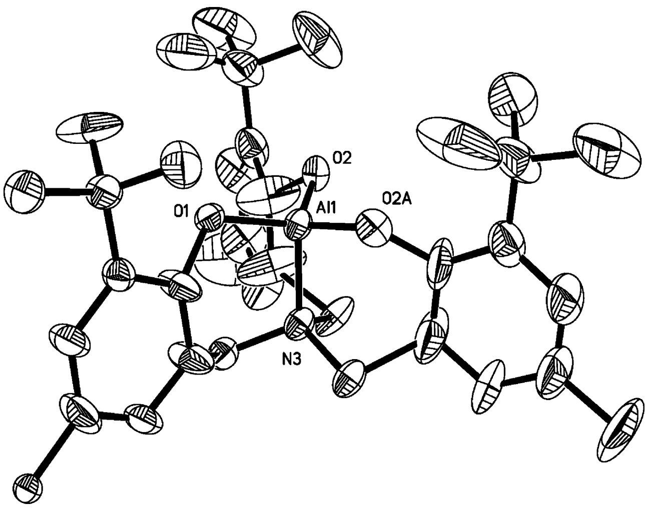


Figure 1. ORTEP of compound **1** at the 30% probability level with hydrogen atoms omitted for clarity. A set of disordered oxygen and carbon atoms were also omitted for clarity.

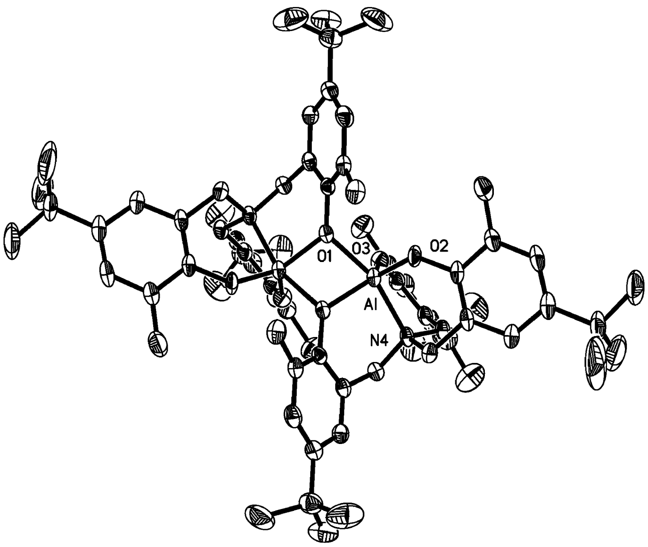
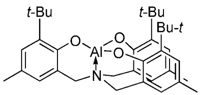


Figure 2. ORTEP of compound **2** at the 50% probability level with hydrogen atoms omitted for clarity.

that have been reported are N→B transannulated proboratrane $B(OCH_2CH_2)_3N$;[6] three examples of group 13 proazatranes reported from our laboratories,[7] namely, $[B(RNCH_2CH_2)_3N]$ ($R = Me$, $SiMe_3$) and $[Al(Me_3SiNCH_2CH_2)_3N]$; and many examples of proazaphosphatranes of the type $P(RNCH_2CH_2)_3N$.[8] Five-coordinate main-group atranes, including some examples of phosphatranes,[1,9] alumatranes,[7,10] azaphosphatranes,[8] silatranes,[1,11−13] and azasilatranes,[14] have received intensive synthetic and structural scrutiny. Notably absent from the main-group proatrane/atrane class, however, is an example of a proalumatrane.

By employing theoretical calculations on a model TMP prosilatrane, Kawashima and co-workers predicted that the silicon atom in this coordination environment would have strong Lewis acidity and would readily accept a fifth ligand to form a stable trigonal bipyramidal (TBP) silatrane structure.[13] Recently, Nelson and co-workers[15] have shown that a TMP aluminum complex readily accepts a Lewis-basic substrate to generate a pentacoordinate Lewis acid−base adduct that functions as an intermediate in an aluminum-catalyzed ketene−aldehyde cycloaddition reaction, whereas the parent tetrahedral aluminum complex is completely inactive in this process. We envisioned that by analogy, a TMP proalumatrane could function as a Lewis acid catalyst for facilitating the transformation of a substrate bound at its exocyclic fifth coordination site. Recently, we reported the syntheses of a series of five-coordinate alumatranes derived from a TBP alumatrane dimer supported by a tris(3,5-dimethyl-2-oxidobenzyl)amine ligand.[10b] Herein, we report for the first time the synthesis and molecular structure of monomeric proalumatrane **1**, which features a TMP coordination geometry (Figure 1), related dimeric alumatrane **2** (Figure 2), and isolable stable Lewis adduct **1**·H_2O (**3**).



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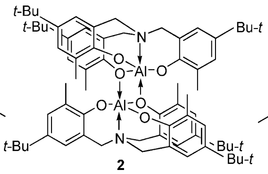

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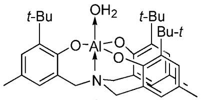

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Results and Discussion

In previous work, we found that the reaction of tris(2-hydroxy-3,5-dimethylbenzyl)amine with 1 equiv of trimethylamine gave a TBP alumatrane dimer consisting of two proalumatrane units bridged by two Al−O bonds, which was readily converted into TBP monomeric alumatranes via coordination to other ligands.[10b] These observations suggested to us that an appropriately bulky tripodal ligand could be expected to stabilize a coordinatively unsaturated aluminum center in the corresponding proalumatrane. This was accomplished by replacing the methyl groups at the 3-positions of tris(2-hydroxy-3,5-dimethylbenzyl)amine[2b] with *tert*-butyl groups. Accordingly, tris(3-*tert*-butyl-2-hydroxy-5-methyl-

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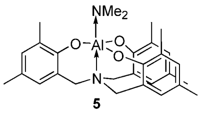
benzyl)amine **4**, initially reported by Holmes and coworkers,[11c] was synthesized for this purpose.

Treatment of **4** with 1 equiv of trimethylaluminum in toluene at room temperature for 3 h, followed by the removal of the solvent, afforded **1** as an off-white solid whose ^1H NMR and ^{13}C NMR spectra showed three equivalent benzene rings, reflecting the 3-fold symmetry of **1**. The very broad peak assigned to methylene protons observed in its ^1H NMR spectrum is attributed to the slow conformational inversion of the six-membered rings on the NMR time scale. Single crystals of **1** suitable for X-ray study were obtained by cooling a concentrated solution of this compound in toluene (2 mmol of **1** in 4 mL of toluene) for several days. The molecular structure of **1** depicted in Figure 1 reveals an aluminum atom coordinated by the three oxygen atoms and one nitrogen atom of ligand **4** in a TMP configuration. As a result of the flexibility of the six-membered rings in **1**, the three oxygen atoms and the carbon atoms of the three methylene groups are disordered. Although this disorder precludes a detailed discussion of the bond angles around the aluminum atom in **1**, the data do permit confirmation of the atom connectivities in the molecular structure. The average Al−O bond length [1.712(5) Å] in **1** is similar to that in the TBP alumatrane **5**.[10a] As expected, the N→Al transannular bond in **1** is significantly shorter than that in alumatrane **5** [1.921(5) Å vs 2.083(3) Å] owing to the absence of a ligand *trans* to the axial nitrogen atom in **1**. The Al−O bonds in **1** are shorter by about 0.2 Å than the Al−N bond.



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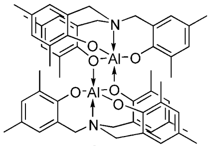

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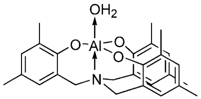

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Although it is conceivable that steric congestion in ligand **4** could result in the formation of ring-opened species or the coexistence of such species in equilibrium with **1** in solution at room temperature (as was reported for an analogous phosphatrane[9a]), the ^1H and ^{13}C NMR spectra of **1** were consistent with C_3 symmetry, and no ring-opened species were detected.

As we reported previously,[10b] alumatrane dimer **6** precipitated from the reaction medium and was poorly soluble in a range of organic solvents. By reacting the sterically less demanding isomer of **4** [namely tris(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)amine in which the bulky *tert*-butyl and methyl groups on each phenyl ring are interchanged] with 1 equiv of trimethylaluminum in toluene at room temperature, the *tert*-butyl groups at the 5-position of each phenyl ring provided good organic solvent solubility for **2**. The dimeric structure of **2** was confirmed by X-ray analysis. It is interesting that although the core structure of **2** is similar to that of **6**, there are significant differences in some of the corresponding bond lengths and bond angles. The apical Al−O bond of **2** [1.930(6) Å] is significantly longer than that in **6** [1.888(3) Å], giving rise to a shorter N→Al transannular bond [2.028(8) Å] in **2** compared to that in **6** [2.083(3) Å]. This effect could be attributed to the proximity of the electron-donating *t*-Bu groups in **2** to the nitrogen (the donor properties of which exceed those of the methyl groups in **6**) thus enhancing the ability of the latter to transannulate to the aluminum of **2**. The longer bridging Al−O bonds permit the $N-Al-O_{axial}$ angle [161.8(3)°] in **2** to be considerably larger than that in **6** [141.41(13)°] thus allowing the coordination geometry around each Al center in **2** to approach ideal TBP geometry more closely than in **6**.

In an attempt to grow crystals of **1** by evaporating pentane (sodium dried) from a pentane solution of **1** using a slow flow of argon, sufficient adventitious water was apparently still present to facilitate the deposition of colorless crystals of adduct **3**. This adduct was also obtained from the reaction of **1** with 1 equiv of water in CH_2Cl_2. The structure of **3**, established by X-ray crystallographic analysis, showed that in addition to the apically coordinated water molecule, four free water molecules were incorporated into the unit cell. The coordination geometry around the aluminum in **3** is nearly ideally TBP. The transannular bond distance in **3** [2.081(2) Å] is somewhat longer than that in **2** [2.028(8) Å]. The average value of the $O_{eq}-Al-N$ angle of 92.39(10)° in **3** indicates a slight displacement of the aluminum atom from the plane of the equatorial oxygen atoms toward the nitrogen. The $O_{apical}-Al-N$ angle [176.47(10)°] is nearly linear, the $O_{equatorial}-Al-O_{equatorial}$ bond angles are 118.77(10), 119.95(11), and 120.77(11)°, respectively, and the sum of the latter is 359.49°. ^1H NMR and ^{13}C NMR spectra of **3** are consistent with a 3-fold symmetry of this adduct, indicating that the coordinated water molecule rapidly rotates around its $Al-O_{apical}$ bond on the NMR time scale. NMR monitoring of a solution of **3** under argon in $CDCl_3$ showed stability for at least 1 week.

The bond lengths and bond angles involving the aluminum center in **7** are within three times the estimated standard deviation of the corresponding parameters in **3**. X-ray analysis revealed that **7** is a dimer linked by a hydrogen bond between a water ligand of one alumatrane unit and an aryloxide oxygen atom in a neighboring alumatrane unit.[10b] This intermolecular hydrogen bond could provide a proton-transfer route from a water ligand to an aryloxy oxygen in a neighboring molecule of **7**, thus facilitating decomposition/hydrolysis. By contrast, the solid-state structure of **3** does not possess such an intermolecular hydrogen bond, owing to the presence of bulky *tert*-butyl groups. Blockage of this type of proton transfer in **3** may account for its stable nature at room temperature, despite the enhancement of the acidity of the water ligand coordinated to the Lewis-acidic aluminum. An alternative proton-transfer process could involve additional water molecules that bridge, via intermolecular hydrogen bonding, a proton donor on a ligating water molecule (i.e., on the Al atom in **3**) to a proton acceptor (here, an aryloxide oxygen atom) for proton delivery.[18] Whereas **7** underwent hydrolysis in the presence of water at room temperature to yield an aluminum cluster containing

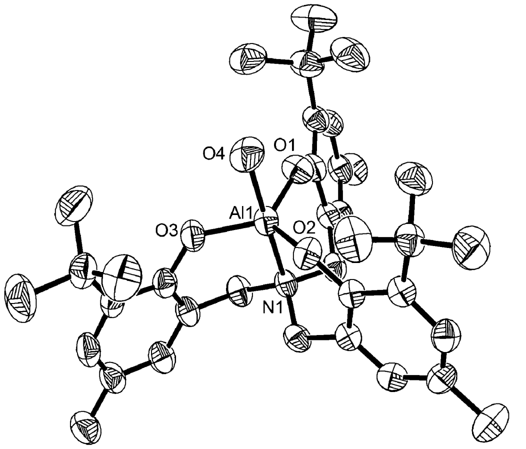
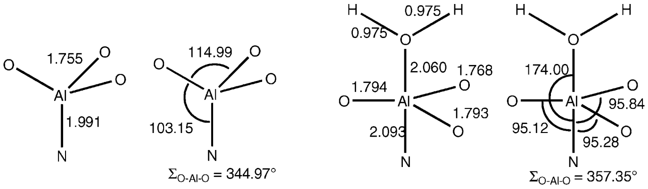


Figure 3. ORTEP of compound **3** at the 50% probability level with hydrogen atoms omitted for clarity.

aluminum hydroxide moieties,[10b] treatment of **3** with a saturated solution of water in CH_2Cl_2 at room-temperature did not lead to detectable hydrolysis. Noteworthy here is the fact that even though **3** cocrystallizes with water molecules in the unit cell, none of them are hydrogen bonded to **3**, presumably owing to the steric shielding of the *tert*-butyl groups.

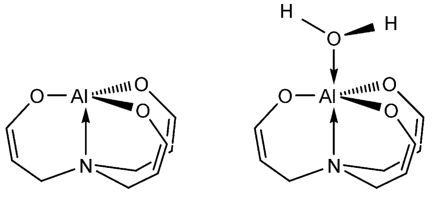
Water-coordinated alumatranes **3** and **7** model intermediates in the hydrolysis pathways of aluminum salts, an important route to the synthesis of porous and nanosized materials.[16] For a metal alkoxide or halide, this reaction sequence is proposed to be initiated by the nucleophilic attack of water at the metal center, followed by proton migration from coordinating water molecules to leaving groups (for the formation of HOR or HX, respectively) plus metal hydroxide.[17] The latter product then undergoes polycondensation to yield the corresponding metal oxide. The initial attack of water at the metal center is expected to involve the temporary formation of a water-coordinated intermediate. Because subsequent steps are apparently too fast to stop hydrolysis at the water-coordinated intermediate stage, no such complex has, to our knowledge, been reported for a stable water-coordinated neutral aluminum alkoxide. In this regard, however, Kawashima and co-workers did recently report a water-coordinated carbasilatrane which models an intermediate in the hydrolysis of alkoxysilanes.[13]



8 **8** **9** **9**

Figure 4. Selected bond lengths (angstroms) and angles (degrees) of model compounds **8** and **9**.

In an attempt to gain an idea of the Lewis acidity of tetracoordinate **1**, DFT calculations were performed at the B3LYP level[19] using the Gaussian03 package.[20] To reduce computation time, model compounds **8** and **9** containing olefinic bridges instead of benzene rings were employed.



8 **9**

Structural optimizations were performed with the 6-31G(d) basis set with C_3 symmetry for tetracoordinate **8** and C_1 symmetry for water-coordinated **9**. Optimized bond lengths and bond angles are summarized in Figure 4. The Al−O bond lengths (1.755 Å) and the Al−N bond length (1.991 Å) calculated for **8** match those for structurally determined **1** within 0.07 Å. The N−Al−O bond angles calculated for **8** were 103.15°, the O−Al−O bond angles were 114.99°, and the sum of the O−Al−O bond angles was 344.97°. These angles are reasonably close to those expected for **1** in the absence of disorder.

The calculated transannular Al−N bond length in **9** was 2.093 Å, and the equatorial Al−O bond lengths were 1.768, 1.793, and 1.794 Å on the basis of its C_1 structure (avg = 1.785 Å). The bond lengths around the aluminum atom in **9** are within 0.04 Å of the experimental values obtained for **3** with the exception of the apical Al−O bond length (2.064 Å), which was 0.1 Å longer than that in **3**. Calculated values

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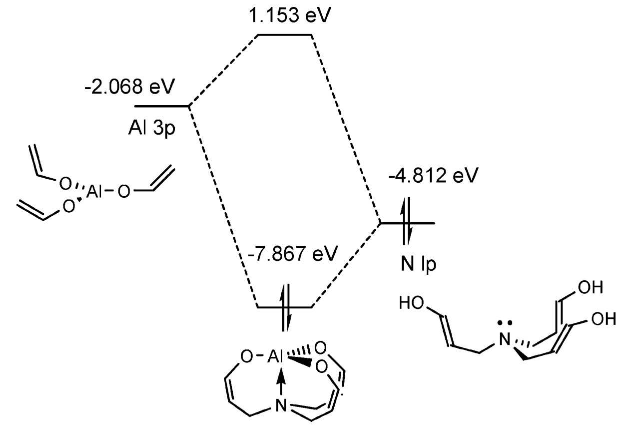

Figure 5. Energy diagram of tetracoordinate proalumatrane **8**.

for the $O_{apical}-Al-N$ bond angle (174.00°), the $O_{equatorial}-Al-O_{equatorial}$ bond angles (117.52, 119.89, and 119.94°), and the sum of the latter angles (357.35°) in **9** are within 2.5 degrees of the corresponding angles in **3** [176.47, 118.77(10), 119.95(11), 120.77(11), and 359.49°, respectively].

Because olefinic model compounds **8** and **9** appeared to mimic quite well the structures of **1** and **3**, respectively, the stabilization energy achieved upon the addition of a water molecule to **1** to form **3** was of interest to calculate on the basis of the aquation of **8** to give **9**. Upon the application of a frequency analysis with zero-point energy correction to **8** and **9**, proalumatrane **1** is stabilized by 17.29 kcal/mol upon aquation to give **3**. By contrast, BF_3 acquires a stabilization of only 9.41 kcal/mol in this process at the same level of theory.

The aluminum $3p_z$ orbital and the nitrogen $2sp^{4.48}$ lone-pair orbital correspond to the LUMO+3 (1.153 eV) and the HOMO−3 (−7.867 eV) molecular orbitals, respectively (Figure 5). The energy of the aluminum $3p_z$ orbital in **8** is elevated above that calculated for trivinyloxyalane (−2.068 eV); whereas, the nitrogen lone-pair energy in **8** is decreased from −4.812 eV in trishydroxypropenylamine to −7.867 eV. The relatively high aluminum $3p_z$ orbital energy indicates that the Lewis acidity of the aluminum center in **8** is weakened through $N\rightarrow Al$ transannulation. Even so, the large stabilization energy achieved by aquation in **9** is consistent with the postulate that proalumatrane **8** is a stronger Lewis acid than boron trifluoride.

Conclusion

In summary, we have demonstrated that steric hindrance near the vacant fifth coordination site of aluminum in **1** permits its isolation as a monomeric TMP proalumatrane, whereas the use of a less-hindered isomeric tetradentate ligand gives the five-coordinate dimer of **1**, namely **2**, which contains two alumatrane units. Proalumatrane **1** in the presence of water gives the isolable TBP adduct **3**, the first example of a stable water-coordinated neutral aluminum alkoxide. The stability of **3** with respect to hydrolysis relative to **7** stems from steric protection afforded by bulky *tert*-butyl groups, which apparently inhibit proton migration from a water molecule to the Aryl−O−Al oxygen in **3**. DFT calculations are consistent with the suggestion that **1** is a stronger Lewis acid than BF_3. Experiments are underway to evaluate the activity of compounds such as **1** in Lewis-acid-catalyzed organic reactions.

Experimental Section

General. All of the reactions were carried out under argon with, the strict exclusion of moisture using Schlenk techniques, unless otherwise stated. Toluene and pentane were distilled from sodium/benzophenone under nitrogen, and CH_2Cl_2 was dried by distillation from CaH_2. All of the deuterated solvents and ethylenediamine were distilled from CaH_2 and stored over activated 3 Å molecular sieves under argon. Tris(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)amine was prepared according to a published procedure.[11c] Other chemicals were obtained from Aldrich and used as received. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Gemini-300 spectrometer at 300 MHz and 75.5 MHz, respectively. Elemental analyses were carried out by Desert Analytics or by Instrument Services of this department. Single-crystal X-ray diffraction data were collected under N_2 flow at −100 °C on a Bruker 1000 CCD diffractometer.

Synthesis of AlL (L = Tris(3-*tert*-butyl-5-methyl-2-oxidobenzyl)amine) 1. To a solution of 1.090 g of tris(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine[11c] (2.000 mmol) in 20 mL of toluene was slowly added 1 mL of a 2 M toluene solution of trimethylaluminum (2 mmol) via a syringe. The room-temperature reaction mixture was stirred for 3 h to generate a light-yellow solution. The solvent was evaporated from this solution under reduced pressure to afford 1.140 g of **1** (yield: 100%) as an off-white solid. Single crystals suitable for X-ray diffraction were obtained by storing a concentrated solution of **1** in toluene (2 mmol of **1** in 4 mL of toluene). ^1H NMR (300 MHz, C_6D_6): δ 7.20 (s, 3H, *Ar*), 6.39 (s, 3H, *Ar*), 3.16 (b, 6H, $ArCH_2N$), 2.22 (s, 9H, $ArCH_3$), 1.58 (s, 27H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6): δ 155.12 (Ar); 139.37 (Ar); 128.70 (Ar); 128.60 (Ar); 126.98 (Ar); 122.03 (Ar); 57.74 ($ArCH_2N$); 34.99 ($ArC(CH_3)_3$); 29.75 ($ArC(CH_3)_3$); 20.87 ($ArCH_3$). Anal. Calcd for **1**, $C_{36}H_{48}AlNO_3$: C, 75.89; H, 8.49; N, 2.46. Found: C, 75.49; H, 8.02; N, 2.37.

Synthesis of Tris(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)amine. This compound was made analogously to the procedure reported for the synthesis of tris(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)amine[11c] except that chromatography was used for product isolation. The material generated from this reaction was loaded onto a silicon gel column and 5−10% ethyl acetate in hexanes was used as the eluent. Fractions containing the desired product were collected and then concentrated to about 20 mL. The concentrated solution was stored at −20 °C to afford an off-white crystalline solid, which was washed with ethanol and air-dried (yield: 7.5 g, 33.3%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.07 (s, 3H, *Ar*), 6.97 (s, 3H, *Ar*), 6.36 (b, 3H, OH), 3.69 (s, 6H, $ArCH_2N$), 2.23 (s, 9H, $ArCH_3$), 1.28 (s, $C(CH_3)_3$, 27H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.38 (Ar); 142.69 (Ar); 127.86 (Ar); 125.60 (Ar); 124.29 (Ar); 121.65 (Ar); 56.64 ($ArCH_2N$); 34.13 ($ArC(CH_3)_3$); 31.82 ($ArC(CH_3)_3$); 16.48 ($ArCH_3$). Anal. Calcd for $C_{36}H_{51}NO_3$: C, 79.22; H, 9.42; N, 2.57. Found: C, 79.26; H, 9.38; N, 2.59.

Synthesis of $(AlL)_2$ (L = Tris(5-*tert*-butyl-3-methyl-2-oxidobenzyl)amine) 2. To a solution of 1.090 g of tris(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)amine (2.000 mmol) in 20 mL of toluene was slowly added 1 mL of a 2 M toluene solution of trimethylaluminum (2 mmol) via a syringe at room temperature. The reaction mixture was stirred for 5 h to generate a light-yellow solution. The

Table 1. Crystal Data for **1**, **2**, **2′**, and **3**

	compound			
cryst data	**1**	**2**	**2′**	**3**
formula	$C_{36}H_{48}AlNO_3$	$C_{86}H_{112}Al_2N_2O_6$	$C_{86}H_{112}Al_2N_2O_6$	$C_{36}H_{52}AlNO_5$
fw	569.73	1323.74	1323.74	605.77
cryst habit	colorless cubes	colorless block	colorless needle	colorless cubes
cryst size (mm^3)	0.20 × 0.10 × 0.10	0.30 × 0.26 × 0.23	0.30 × 0.10 × 0.07	0.30 × 0.30 × 0.15
unit cell	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*Cmc*2$_1$	*C*2/*c*	*Pbcn*	*P*2$_1$/*c*
a	17.616(3)	25.550(10)	26.105(5)	13.702(4)
b	22.889(3)	12.363(4)	12.446(3)	11.208(3)
c	9.5032(13)	26.166(8)	24.267(5)	23.007(7)
β (deg)	90	106.023(10)	90	90.944(5)
V (Å^3)	3831.9(9)	7944(5)	7884(3)	3532.7(17)
T (°C)	193	193	173	173
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	0.988	1.107	1.115	1.139
μ (Mo Kα) (mm^{-1})	0.082	0.088	0.089	0.097
F(000)	1232	2864	2864	1312
total reflns	12 477[a]	25 239[b]	25 239[c]	19 262[d]
independent reflns	2865	9377	3111	4305
params	232	450	405	412
R1$_{obs}$	0.0730	0.0797	0.0924	0.0456
wR2$_{obs}$	0.1937	0.1811	0.2529	0.1136
R1$_{all}$	0.0847	0.1926	0.1247	0.0718
wR2$_{all}$	0.2015	0.2439	0.2753	0.1263
GOF	1.236	0.975	1.041	1.063
diff. density max/min (e Å^{-3})	0.281/−0.218	0.567/−.535	1.219/−0.725	0.209/−0.283

[a] Up to h(−19/19), k(−25/25), l(−10/10) measured in a range of 1.46° ≤ Θ ≤ 23.25°. [b] Up to h(−33/32), k(−16/15), l(−34/34) measured in a range of 1.56° ≤ Θ ≤ 18.85. [c] Up to h(−23/23), k(−9/11), l(−20/22) measured in a range of 1.56° ≤ Θ ≤ 18.85°. [d] Up to h(−14/14), k(−11/11), l(−24/24) measured in a range of 2.02° ≤ Θ ≤ 21.94°.

solvent was evaporated from this solution under reduced pressure to afford 1.138 g of **2** (yield: 100%) as an off-white solid. Single crystals suitable for X-ray diffraction were obtained by storing a concentrated solution of **2** in toluene (2 mmol of **2** in 6 mL of toluene). Because of very broad overlapped proton peaks from 2.2 to 6.1 ppm (assigned to the methylene groups), clean ^1H NMR spectra could not be obtained even at 50 °C.^{13}C NMR (75 MHz, C_6D_6): δ 152.60 (Ar); 152.55 (Ar); 141.33 (Ar); 137.70 (Ar); 129.14 (Ar); 128.38 (Ar); 127.99 (Ar); 127.75 (Ar); 127.70 (Ar); 125.51(Ar); 124.45 (Ar); 123.43 (Ar); 123.41(Ar); 123.39 (Ar); 123.37 (Ar); 121.36 (Ar); 59.70 (Ar*C*H$_2$N); 33.88 (Ar*C*(CH$_3$)$_3$); 31.74 (ArC(*C*H$_3$)$_3$); 21.29 (Ar*C*H$_3$). Anal. Calcd for **2**, $C_{72}H_{96}Al_2N_2O_6$: C, 75.89; H, 8.49; N, 2.46. Found: C, 75.94; H, 8.26; N, 2.58.

Synthesis of H_2O-AlL Adduct 3. A −20 °C solution of water (18 mg, 1.0 mmol) in 70 mL of CH_2Cl_2 was added to a flask containing 570 mg (1.00 mmol) of **1**. The reaction mixture was slowly warmed to room temperature with stirring, and then it was stirred at room temperature for 5 h to generate a light-yellow solution. The solvent was evaporated from this solution under reduced pressure to afford 584 mg of **3** (99% yield) as an off-white solid. Single crystals suitable for X-ray diffraction were obtained from a solution of **3** in pentane maintained under a slow argon flow for 3 days. ^1H NMR (300 MHz, $CDCl_3$): δ 7.00 (s, 3H, *Ar*), 6.67 (s, 3H, *Ar*), 4.22 (b, 3H, ArC*H*$_2$N), 3.56 (b, 2H, Al−O*H*$_2$), 2.85 (b, 3H, ArC*H*$_2$N); 2.23 (s, 9H, ArC*H*$_3$); 1.40(s, 27H, C(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.06 (Ar); 137.82 (Ar); 127.93 (Ar); 127.48 (Ar); 124.29 (Ar); 125.87 (Ar); 122.11 (Ar); 58.64 (Ar*C*H$_2$N); 34.81 (Ar*C*(CH$_3$)$_3$); 29.72 (ArC(*C*H$_3$)$_3$); 21.01 (Ar*C*H$_3$). Anal. Calcd for **3**, $C_{36}H_{50}AlNO_4$: C, 73.56; H, 8.57; N, 2.38. Found: C, 73.40; H, 8.88; N, 2.23.

Crystallographic Studies. Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation and a detector-to-crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. The final cell constants were calculated from a set of 946 strong reflections from the actual data collection. All of the structures were solved using direct methods. Non-hydrogen atoms were refined in full-matrix anisotropic approximation. Hydrogen atoms were placed at the calculated positions and were refined using a riding model. All attempts to crystallize **1**, **2**, **2′** (below), and **3** led to small, unstable, and extremely solvent-dependent crystals. The actual resolution of the data obtained is limited to 0.9−1.1 Å. However, the X-ray analyses (even on the basis of high-angle reflections) prove unambiguously the molecular and crystal structure of all of the samples. Atomic coordinates, bond lengths and angles, and anisotropic parameters have been deposited with the Cambridge Crystallographic Data Center (CCDC 611313−611316). Crystal data for **1**, **2**, **2′**, and **3** are summarized in Table 1. The disorder of O and C atoms within the asymmetric unit of **1** together with the mirror plane of the space group led to a highly disordered model. It can be described as a disorder of two shifted configurations around the 3-fold axis. The electron densities in the voids definitely indicated the existence of the solvent in the crystal structure; however, all of the attempts to locate molecules of the only two possible solvents (toluene and hexanes) resulted in unstable refinement. All of the attempts to refine H atoms on theoretically calculated positions led to unstable refinement. Therefore, the SQUEEZE routine from the PLATON software package was used to treat the diffuse-solvent problem. After the SQUEEZE routine was applied, final least-squares refinement of 232 parameters against 2865 independent reflections converged to R (on the basis of F^2 for $I \geq 2\sigma$) and wR (on the basis of F^2 for $I \geq 2\sigma$) of 0.073 and 0.205, respectively.

Crystal structures of two polymorphs of **2** with toluene molecules have been determined. Both substances were extremely unstable and solvent dependent. In both structures, one toluene molecule was found per half of a cluster.

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Supporting Information Available: Table of atomic coordination, anisotropic thermal parameters, and bond lengths and angles for **1**, **2**, **2′**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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