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Facile Synthesis of Monomeric Alumatranes

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Abstract: Alumatranes, tricyclic neutral molecules featuring a transannular N → Al bond, can act as Lewis acids that activate substrates in the axial coordination site. Treatment of tris(2-hydroxy-3,5-dimethylbenzyl)-amine with $AlMe_3$ afforded dimeric $(AlL)_2$ **1** [wherein L = tris(2-oxy-3,5-dimethylbenzyl)amine]. X-ray diffraction analysis revealed bridging between AlL monomers by two Al−O bonds. Reactions of **1** with substrates containing O or N donors generated the alumatranes THF−AlL **2**, PhCHO−AlL **3**, $H_2NCH_2CH_2NH_2$−AlL **4**, and $[PhO{-}AlL]^-$ **5**, in which the apical added ligand on the five-coordinate aluminum center causes variation in the transannular bond distance. Water coordinates with **1** at −20 °C to form the alumatrane H_2O−AlL **6** that undergoes partial hydrolysis at room temperature to produce **7**, which X-ray crystallography showed to be composed of four AlL fragments linked by an $(H_2O)_2(HO)_2Al(OH)_2Al(OH)_2(H_2O)_2$ framework in which the $O_4AlO_2AlO_4$ moiety is of local D_{2h} symmetry. According to X-ray analysis, **7** can crystallize in at least two polymorphic modifications: triclinic **7a** and monoclinic **7b**. The reaction of **3** with water also generated **6** and **7**, depending on the reaction temperature. Dimeric **1** was found to promote the reaction of benzaldehyde with trimethylsilyl cyanide at room temperature to provide 2-trimethylsilyoxyphenylacetonitrile in 95% yield.

Introduction

Polydentate ligands can influence the reactivity of a metal center in a complex, not only by exerting steric and electronic effects, but also by imposing a specific coordination geometry on the metal ion. In the present context, Nelson et al. recently showed that an Al(III) complex with a trigonal monopyramidal coordination geometry is an active Lewis acid catalyst for a ketene aldehyde cycloaddition reaction, while its tetrahedral analogue is inactive in this process.[1] Tripodal tetradentate ligands define a large family of trigonal bipyramidal metal complexes commonly referred to as atranes.[2,3] These appealingly symmetrical compounds possess a pseudo threefold symmetric environment around the metal ion generated by the tripodal ligand and the exocyclic axial group,[3] a flexible transannular bond between the metal ion and an axial ligand atom in the tripodal ligand,[2] and the possibility of 3d orbital involvement for substrate binding at the exocyclic apical position,[3] provided that site is vacant or possesses a ligand that is relatively easily displaced. Thus, complexes of this type have been utilized for activation of small molecules[4−6] and for generating novel structural motifs,[3,5,7,8] such as ligand−metal multiple bonds.[7]

Although contributions from several laboratories including ours have led to the development of atrane chemistry involving a wide variety of metals,[2−7,9−11] examples of alumatranes are still relatively rare.[10] It is extensively documented that aluminum compounds can serve as powerful Lewis acid catalysts for organic transformations, and numerous studies of the mechanisms of such reactions implicate trigonal bipyramidal (TBP) alumatranes as active intermediates.[1,12] We therefore envisioned

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(1) Nelson, S. G.; Kim, B.-K.; Peelen, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 9318.

(2) (a) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 896. (b) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233.

(3) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9.

(4) (a) Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252. (b) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76. (c) Yandulov, D. V.; Schrock, R. R. *Inorg. Chem.* **2005**, *44*, 1103.

(5) (a) Macbeth, C. E.; Golombek, A. P.; Young, V. G., Jr.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. S. *Science* **2000**, *289*, 938. (b) Macbeth, C. E.; Gupta, R.; Mitchell-Koch, K. R.; Young, V. G., Jr.; Lushington, G. H.; Thompson, W. H.; Hendrich, M. P.; Borovik, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 2556. (c) Larsen, P. L.; Gupta, R.; Powell, D. R.; Borovik, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 6552.

(6) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *J. Am. Soc. Chem.* **2004**, *126*, 13464.

(7) (a) Cummings, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. (b) Johnson-Carr, J. A.; Zanetti, N. C.; Schrock, R. R.; Hopkins, M. D. *J. Am. Chem. Soc.* **1996**, *118*, 11305. (c) Hu, X.; Meyer, K. *J. Am. Chem. Soc.* **2004**, *126*, 16322.

(8) For examples of threefold symmetric metal complexes supported by tridentate ligands, which are similar to atranes and possess metal−ligand multiple bonds, see: (a) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238. (b) Brown, D. S.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322. (c) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252.

(9) (a) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **2000**, *19*, 5614. (b) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 1066. (c) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **2001**, *20*, 2331. (d) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 7035. (e) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **2000**, *39*, 5683. (f) Timosheva, N. V.; Chandrasekaran, A.; Holmes, R. R. *Inorg. Chem.* **2004**, *43*, 7403.

(10) (a) Kim, Y.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 4804. (b) Pinkas, J.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 2711. (c) Pinkas, J.; Gaul, B.; Verkade, J. G. *J. Am. Soc. Chem.* **1993**, *115*, 3925. (d) Waldner, K. F.; Laine, R. M.; Dhumrongvaraporn, S.; Tayaniphan, S.; Narayanan, R. *Chem. Mater.* **1996**, *8*, 2850.

(11) (a) Filippou, A. C.; Schneider, S.; Schnakenburg, G. *Inorg. Chem.* **2003**, *42*, 6974. (b) Groysman, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2005**, *44*, 5073. (c) Lehtonen, A.; Sillanpää, R. *Organometallics* **2005**, *24*, 2795. (d) Bull, S. D.; Davidson, M. G.; Johnson, A.; Robinson, D. E. J. E.; Mahon, M. F. *Chem. Commun.* **2003**, *14*, 1750. (e) Kol, M.; Shamis, M.; Goldberg, I.; Goldschmidt, Z.; Alfi, S.; Hayat-Salant, E. *Inorg. Chem. Commun.* **2001**, *4*, 177. (f) Hwang, J.; Govindaswamy, K.; Koch, S. A. *Chem. Commun.* **1998**, 1667. (g) Kim, Y.; Verkade, J. G. *Organometallics* **2002**, *21*, 2395.

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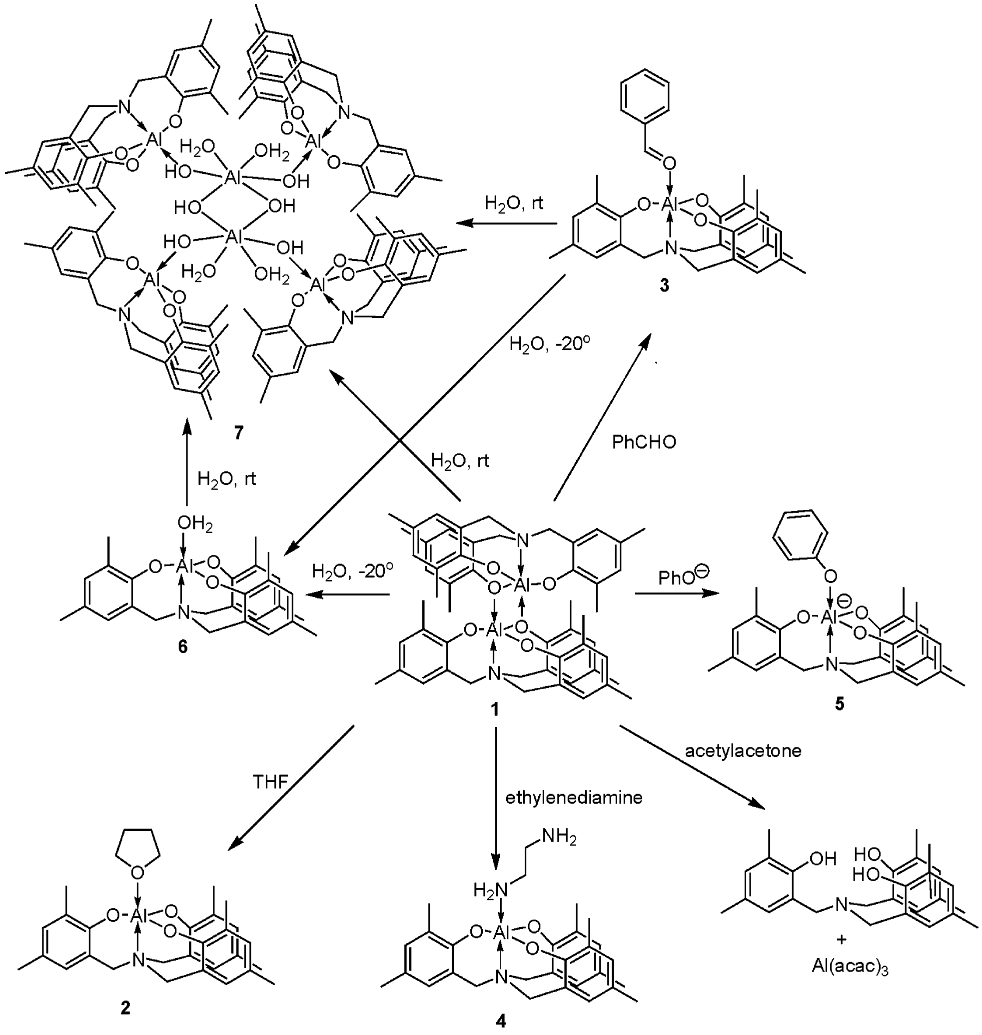
Scheme 1. Transformations Stemming from **1**[a]



[a] The cation for **5** is $[HP(i\text{-}PrNCH_2CH_2)_3N]^+$.

that a labile molecule serving as an exocyclic axial ligand on an alumatrane could potentially function as a substrate in a Lewis acid catalyzed reaction. Recently, we reported for the first time the molecular structure of a monomeric alumatrane, namely Me_2HNAlL, wherein L = tris(2-oxy-3,5-dimethylbenzyl)-amine.[10a]

Earlier work on atranes focused on examples containing three five-membered chelating rings.[2,3] Recently, however, Holmes et al. synthesized tris-(2-hydroxy-3,5-dimethylbenzyl)amine and its bulkier analogue tris-(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine to create a series of silatranes containing six-membered rings.[9] The flexibility of the six-membered rings in these compounds allowed these investigators to observe the effect of the exocyclic apical substituent on the transannular bond length.

Herein, we report the synthesis of the dimeric **1** and the cleavage of **1** into alumatranes **2**−**6** with ligands containing O or N donors, the reaction of **3** and **6** with water to give **7**, the reaction of **3** to give **6**, and a failed attempt to cleave **1** with acetylacetone with the aim of affording a higher-coordinate aluminum complex containing an acetylacetone moiety as well as ligand L (Scheme 1). We also demonstrate that **1** efficiently catalyzes the reaction of benzaldehyde with trimethylsilyl cyanide under mild conditions to give 2-trimethylsilyoxyphenylacetonitrile.

Experimental Section

General. All reactions were carried out under argon with the strict exclusion of moisture using Schlenk techniques, unless otherwise stated. Toluene, pentane, and THF were distilled from sodium/benzophenone under nitrogen, and CH_2Cl_2 was dried by distillation from CaH_2. All deuterated solvents and ethylenediamine were distilled from CaH_2 and stored over activated 3 Å molecular sieves under argon. Benzaldehyde was purchased from Aldrich and distilled under reduced pressure prior to use. Tris(2-hydroxy-3,5-dimethylbenzyl)amine was prepared according to a published procedure.[9b] Other chemicals were obtained from Aldrich and used as received. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Germini-300 spectrometer at 300 and 75.5 MHz, respectively. Electrospray MS analysis (ESI-MS) in toluene was recorded on a Finnigan AQA apparatus. Elemental analyses were carried out by Desert Analytics or 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 $(AlL)_2$ [L = Tris(2-oxy-3,5-dimethylbenzyl)amine] 1. To a suspension of 1.677 g of tris(2-hydroxy-3,5-dimethylbenzyl)-

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(12) (a) Ooi, T.; Uraguchi, D.; Kagoshima, N.; Maruoka, K. *J. Am. Chem. Soc.* **1998**, *120*, 5327. (b) Arai, T.; Sasai, H.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **1998**, *120*, 441. (c) Murakata, M.; Jono, T.; Mizuno, Y.; Hoshino, O. *J. Am. Chem. Soc.* **1997**, *119*, 11713. (d) Simonsen, K. B.; Svenstrup, N.; Roberson, M.; Jørgensen, K. A. *Chem.−Eur. J.* **2000**, *6*, 123.

amine (4.000 mmol) in 20 mL of toluene was slowly added 2 mL of a 2 M toluene solution of trimethylaluminum (4.000 mmol) via syringe. Stirring this reaction mixture for 2 min at room temperature afforded a yellow solution that was stirred for two more hours to generate a white precipitate. The solid was filtered off, washed with toluene (2 × 5 mL) and pentane (2 × 8 mL), and dried under vacuum to afford 1.507 g of **1** (yield, 85%) as a white solid. Single crystals suitable for X-ray diffraction were obtained from a toluene/pentane (v/v = 1:12) solution of **1** at room temperature. Anal. Calcd for **1**, $C_{54}H_{60}Al_2N_2O_6$: C, 73.12; H, 6.82; N, 3.16. Found: C, 73.49; H, 6.62; N, 3.06. ESI-MS (*m*/*z*): $[M + H]^+ = 887$. Because of very broad overlapped peaks from 2.3 to 5.9 ppm (assigned to the methylene groups), clear ^{1}H NMR spectra could not be obtained even at 50 °C. Poor solubility of **1** in toluene-d_8 and benzene-d_6 prevented us from obtaining ^{13}C NMR spectra for **1**.

Synthesis of THF−AlL, 2. Compound **1** (443 mg, 0.500 mmol) was dissolved in 15 mL of THF, giving a colorless solution. The solvent was evaporated from this solution under reduced pressure to afford 515 mg of **2** (yield, 99%) as a white solid. Single crystals suitable for X-ray diffraction were obtained from a THF/pentane (v/v = 1:12) solution of **2** at −20 °C. ^{1}H NMR ($CDCl_3$): δ 6.86 (s, 3H, *Ar*); 6.60 (s, 3H, *Ar*); 4.56 (b, 4H, CH_2CH_2O); 4.25 (d, *J* = 10.2 Hz, 3H, $ArCH_2N$); 2.83 (d, *J* = 10.2, 3H, $ArCH_2N$); 2.19−2.18 (m, 22H, $ArCH_3$ and CH_2-CH_2O). ^{13}C NMR ($CDCl_3$): δ 154.5 (Ar); 131.2 (Ar); 127.2 (Ar); 127.1 (Ar); 126.0 (Ar); 120.8 (Ar); 71.6 (CH_2O); 58.9 ($ArCH_2N$); 25.9 (CH_2-CH_2O); 20.7 ($ArCH_3$); 17.3 ($ArCH_3$). Anal. Calcd for **2**, $C_{31}H_{38}$-$AlNO_4$: C, 72.21; H, 7.43; N, 2.72. Found: C, 72.21; H, 7.44; N, 2.75.

Synthesis of PhCHO−AlL, 3. To a suspension of 443 mg of **1** (0.500 mmol) in 20 mL of toluene was added 0.200 mL of benzaldehyde (1.97 mmol). The reaction mixture was stirred at room temperature for 2 h to generate a yellowish solution that was concentrated under reduced pressure to 3 mL, followed by addition of 35 mL of pentane. This solution was stored at −20 °C for a few days to yield 368 mg of **3** (yield, 67%) as yellow crystals. ^{1}H NMR (C_6D_6): δ 10.06 (s, 1H, PhC*H*O); 7.61 (d, *J* = 7.0 Hz, 2H, ArCHO); 7.0 (s, 3H, Ar); 6.84−6.79 (m, 3H, ArCHO); 6.51 (s, 3H, Ar); 4.39 (b, 3H, $ArCH_2N$); 2.75 (b, 3H, $ArCH_2N$); 2.34 (s, 9H, $ArCH_3$); 2.23 (s, 9H, $ArCH_3$). ^{13}C NMR: 198.5 (Ph*C*HO); 155.1 (Ar); 136.3 (Ar); 134.6 (Ar); 131.7 (Ar); 131.5 (Ar); 128.1 (Ar); 127.7 (Ar); 127.1 (Ar); 125.7 (Ar); 121.0 (Ar); 58.9 ($ArCH_2N$); 20.6 ($ArCH_3$); 16.8 ($ArCH_3$). Anal. Calcd for **3**, $C_{34}H_{36}$-$AlNO_4$: C, 74.30; H, 6.60; N, 2.55. Found: C, 73.98; H, 6.84; N, 2.62.

Synthesis of $H_2NCH_2CH_2NH_2$−AlL, 4. To a suspension of 443 mg of **1** (0.500 mmol) in 20 mL of toluene was added 0.53 mL of ethylenediamine (7.9 mmol). The reaction mixture was stirred at room temperature for 3 h to generate a colorless solution. The volatiles were evaporated under vacuum to afford 490 mg of the desired product **4** (yield, 98%) as a white solid. Single crystals suitable for X-ray diffraction were obtained from a toluene/pentane (v/v = 1:10) solution of **4** at −20 °C. ^{1}H NMR (C_6D_6): δ 6.97 (s, 2H, Ar); 6.90 (s, 1H, Ar); 6.47 (s, 2H, Ar); 6.43 (s, 1H, Ar); 4.26 (d, *J* = 14.2 Hz, 3H, $ArCH_2N$); 3.02 (b, 2H, $AlNH_2CH_2$); 2.83 (m, 2H, $AlNH_2CH_2CH_2NH_2$); 2.46 (d, *J* = 14.0 Hz, 3H, $ArCH_2N$); 2.30 (s, 9H, $ArCH_3$); 2.23 (s, 6H, $ArCH_3$); 2.19 (s, 3H, $ArCH_3$), 2.09−2.05 (m, 2H, NH_2). ^{13}C NMR (C_6D_6): δ 155.1 (Ar); 131.2 (Ar); 129.2 (Ar); 126.6 (Ar); 125.5(Ar); 121.1 (Ar); 58.9 ($ArCH_2N$); 43.6 (NH_2CH_2); 41.8 (NH_2CH_2); 20.6 ($ArCH_3$); 17.0 ($ArCH_3$). Anal. Calcd for **4**, $C_{29}H_{38}AlN_3O_3$: C, 69.16; H, 7.61; N, 8.34. Found: C, 69.31; H, 7.72; N, 7.99.

Synthesis of PhO−AlL$^-$, 5. To a suspension of 443 mg (0.500 mmol) of **1** in 20 mL of CH_2Cl_2 was added the solution obtained by treatment of 94 mg (1.0 mmol) of phenol with 300 mg (1 mmol) of tri-isopropylproazaphosphatrane [P(*i*-$PrNCH_2CH_2)_3N$] in 20 mL of toluene. The reaction mixture was stirred at room temperature for 3 h to generate a colorless solution. The volatiles were evaporated under reduced pressure to afford 831 mg of [HP(*i*-$PrNCH_2CH_2)_3N$][**5**] (yield, 99%) as a white solid. Single crystals suitable for X-ray diffraction were obtained from a toluene/methylene chloride/pentane (v/v/v = 1:1:6) solution of [HP($C_3H_7NCH_2CH_2)_3N$][**5**] at −20 °C. ^{1}H NMR ($CDCl_3$): δ 7.09 (m, 5H, OPh); 6.78 (s, 3H, Ar); 6.54 (s, 3H, Ar); 5.38 (d, J_{PH} = 495.1 Hz, 1H, P*H*); 4.25 (b, 3H, $ArCH_2N$); 3.47−3.34 (m, 3H, NC*H*Me$_2$); 3.08−3.06 (m, 6H, CH_2NCHMe_2); 2.76−2.70 (m, 9H, $N(CH_2)_3$ and $ArCH_2N$); 2.16 (s, 9H, $ArCH_3$); 2.07 (s, 9H, $ArCH_3$); 1.02 (d, *J* = 6.7 Hz, 18H, $NCH(CH_3)_2$). ^{13}C NMR (CDCL$_3$): δ 164.8 (Ar); 155.9 (Ar); 130.4 (Ar); 129.3 (Ar); 128.5 (Ar); 128.3 (Ar); 127.0 (Ar); 126.9 (Ar); 125.5 (Ar); 124.1 (Ar); 122.1 (Ar); 121.3 (Ar); 114.1 (Ar); 59.4 ($ArCH_2N$); 46.9 (d, J_{PC} = 16.0 Hz, $NCHMe_2$); 46.5 (d, J_{PC} = 7.5 Hz, CH_2NCHMe_2); 32.9 (d, J_{PC} = 6.1 Hz, $N(CH_2)_3$); 21.3 (CH-$(CH_3)_2$); 20.7 ($ArCH_3$); 17.1 ($ArCH_3$). Anal. Calcd for $[HP(C_3H_7NCH_2$-$CH_2)_3N]^+$**5**, $C_{48}H_{69}AlN_5O_4P$: C, 68.79; H, 8.30; N, 8.36. Found: C, 68.76; H, 8.10; N, 8.01.

Synthesis of H_2O−AlL, 6. Method A. A −20 °C solution of water (18 mg, 1 mmol) in 70 mL of CH_2Cl_2 was added to a flask containing 443 mg (0.500 mmol) of **1**. The reaction mixture was stirred at −20 °C for 5 h to generate a colorless solution. This solution was concentrated to 5 mL, and then 30 mL of pentane was added. The resulting solution was stored at −20 °C for a few days to afford 194 mg of **6** (yield, 42%) as a colorless crystalline solid. Because **6** is unstable in solution at room temperature, its ^{1}H NMR spectrum showed several impurity peaks that are ascribable to decomposition. The peaks assigned to **6** are 6.72 (s, 3H, Ar); 6.42 (s, 5H, Ar and H_2O); 4.19 (b, 3H, $ArCH_2N$); 2.26, (s, 9H, $ArCH_3$); 2.10 (s, 9H, $ArCH_3$). Attempts to obtain satisfactory elemental analyses failed.

Method B. To a flask containing 275 mg (0.500 mmol) of **3** was added a mixture of 9 mg (0.5 mmol) of water in 70 mL of CH_2Cl_2 at −20 °C. This mixture was stirred at −20 °C for 5 h, giving rise to a colorless solution. Removal of the solvent under reduced pressure afforded a white residue that was dissolved in 5 mL of cold (−20 °C) toluene followed by addition of 40 mL of −20 °C pentane. After several days at −20 °C, 81 mg of **6** (yield, 35%) was obtained as colorless crystals.

Synthesis of 7 from 1 (Method A). A −20 °C solution of water (36 mg, 2.0 mmol) in 70 mL of CH_2Cl_2 was charged to a flask containing 443 mg (0.500 mmol) of **1** at −20 °C. The reaction mixture was allowed to warm slowly to room temperature while being stirred over 6 h to generate a colorless solution. Slow evaporation of the solvent under an argon flow afforded 153 mg of **7** (yield, 46%) as colorless crystals. ^{1}H NMR ($CDCl_3$): δ 9.09 (b, 2H, $AlOH_2$); 6.91 (s, 1H, Ar); 6.62−6.53 (m, 3H, Ar); 6.35 (s, 1H, Ar); 5.96 (s, 1H, Ar); 4.35 (d, *J* = 13.8 Hz, 1H, $ArCH_2N$); 4.16−4.04 (m, 2H, $ArCH_2N$); 3.07 (s, 1H, O*H*); 2.81−2.67 (m, 3H, $ArCH_2N$); 2.32 (s, 3H, $ArCH_3$); 2.25 (s, 3H, $ArCH_3$); 2.08 (s, 3H, $ArCH_3$); 1.96 (s, 3H, $ArCH_3$); 1.71 (s, 3H, $ArCH_3$); 1.67 (s, 3H, $ArCH_3$). ^{13}C NMR ($CDCl_3$): δ 153.9 (Ar); 153.4 (Ar); 152.7 (Ar); 132.6 (Ar); 131.6 (Ar); 130.3 (Ar); 127.7 (Ar); 127.4 (Ar); 127.2 (Ar); 125.6 (Ar); 125.1 (Ar); 121.9 (Ar); 121.8 (Ar); 118.2 (Ar); 59.4 ($ArCH_2N$); 58.7 ($ArCH_2N$); 20.8 ($ArCH_3$); 20.6 ($ArCH_3$); 20.3 ($ArCH_3$); 17.8 ($ArCH_3$); 16.9 ($ArCH_3$); 15.7 ($ArCH_3$). Anal. Calcd for **7**, $C_{108}H_{134}Al_6N_4O_{22}$: C, 64.79; H, 6.75; N, 2.80. Found: C, 64.62; H, 6.87; N, 2.72.

Method B. A solution of **6** (100 mg, 0.217 mmol) in CH_2Cl_2 was exposed to air for a few days via a needle through the septum of the flask to afford 27 mg of colorless crystals of **7** in 37% yield. For the ^{1}H NMR spectrum, see Method A.

Method C. A toluene solution of **3** (200 mg, 0.364 mmol) was exposed to air for a few days via a needle through the septum of the flask to generate 52 mg of colorless crystals of **7** in a 43% yield. For the ^{1}H NMR spectrum of the product, see Method A.

X-ray Structure Determination. Crystals suitable for X-ray analysis were selected from underneath a solvent layer and were covered with premixed epoxy glue to prevent decomposition, as almost all of the substances investigated were extremely unstable in the atmosphere. The sample was immediately mounted under a stream of cold nitrogen and centered in the X-ray beam using a video camera.

Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å, graphite monochromator) radiation with a detector to crystal distance of 5.03 cm. As almost all of the aforementioned samples were twinned, three series of ω scans at different starting angles were obtained to analyze the reflection profiles and to estimate the exposure time for data collection. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω, with an exposure time of 30 s per frame. Members of this class of compounds diffracted very weakly and were limited to low-resolution angles (usually, above 0.9 Å). No preliminary indexing was performed. The data were obtained using the full sphere routine by harvesting four sets of frames with 0.3° scans in ω with an exposure time 30−120 s per frame. The dataset was integrated with SMART software[14] and analyzed with RLATT software[14] to separate the reflections belonging to one crystal for further calculations. Those datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements[13] using SADABS software.[14]

The positions of some core non-hydrogen atoms for all the structures were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps using SHELXTL[14] software. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation. Typically, all other hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. In some cases, hydrogen atoms belonging to water ligands were found objectively on Fourier difference maps, and after that their parameters were constrained. Atomic coordinates, bond lengths and angles, and anisotropic parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 297572−297580).

Structure of 1. A colorless plate (0.20 mm × 0.20 mm × 0.08 mm), $C_{54}H_{60}Al_2N_2O_6 \times C_7H_8$, M = 979.13, at 298 K is monoclinic, space group $C2/c$, a = 30.924(15), b = 11.069(5), c = 17.077(8) Å, β = 97.377(3)°, Z = 4, V = 5247(4) Å^3, R_1 = 0.072, wR_2 = 0.206, GOF = 1.058.

Structure of 2. A colorless plate (0.20 mm × 0.20 mm × 0.08 mm), $C_{31}H_{38}AlNO_4$, M = 515.60, at 298 K is monoclinic, space group $P2_1/c$, a = 9.3865(16), b = 17.609(3), c = 16.824(3) Å, β = 116.153(13)°, Z = 4, V = 2757.8(8) Å^3, R_1 = 0.046, wR_2 = 0.124, GOF = 1.024.

Structure of 3. A colorless block (0.40 mm × 0.30 mm × 0.30 mm), $C_{34}H_{36}AlNO_4$, M = 549.62, at 183 K is rhombohedral, space group $R\bar{3}$, $a = b = c$ = 11.7638(15) Å, $\alpha = \beta = \gamma$ = 116.153(13)°, Z = 2, V = 1508.8(3) Å^3, R_1 = 0.053, wR_2 = 0.139, GOF = 1.056.

Structure of 4. A colorless plate (0.28 mm × 0.22 mm × 0.10 mm), $C_{35}H_{44}AlN_3O_3'$, M = 575.66, at 173 K is triclinic, space group $P\bar{1}$, a = 10.631(3), b = 12.816(3), c = 13.411(4) Å, α = 71.575(4)°, β = 71.114(4)°, γ = 81.389(5)°, Z = 2, V = 1637.9(8)A^3, R_1 = 0.060, wR_2 = 0.162, GOF = 1.032.

Structure of 5. A colorless plate (0.30 mm × 0.20 mm × 0.10 mm), $(C_{15}H_{34}AlNO_4)^+(C_{33}H_{35}PN_4)^- \times CH_2Cl_2$, M = 922.96, at 183 K is monoclinic, space group $P2_1/n$, a = 13.024(6), b = 18.322(8), c = 20.516(10) Å, β = 96.352(9)°, Z = 4, V = 4866(4) Å^3, R_1 = 0.073, wR_2 = 0.180, GOF = 1.064.

Structure of 6. A colorless block (0.20 mm × 0.20 mm × 0.15 mm), $2(C_{27}H_{32}AlNO_4)\cdot C_7H_8$, M = 1015.17, at 173 K is triclinic, space group $P\bar{1}$, a = 13.350(5), b = 14.565(6), c = 15.156(6) Å, α = 73.818(6)°, β = 68.657(6)°, γ = 79.629(6)°, Z = 2, V = 2627.4(17) Å^3, R_1 = 0.058, wR_2 = 0.140, GOF = 1.040.

Structure of 7a. A colorless plate (0.10 mm × 0.10 mm × 0.03 mm), $C_{108}H_{134}Al_6N_4O_{22}$, M = 2002.07, at 293 K is triclinic, space group $P\bar{1}$, a = 18.433(7), b = 19.237(7), c = 22.352(9) Å, α = 104.229(7)°, β = 106.203(7)°, γ = 104.718(7)°, Z = 2, V = 6920(5) Å^3, R_1 = 0.106, wR_2 = 0.295, GOF = 1.167.

Structure of 7b. A colorless block (0.40 mm × 0.20 mm × 0.18 mm), $C_{108}H_{134}Al_6N_4O_{22}$, M = 2002.07, at 203 K is monoclinic, space group $C2/c$, a = 37.345(11), b = 18.611(5), c = 26.234(7) Å, β = 134.62(1)°, Z = 4, V = 12978(6) Å^3, R_1 = 0.071, wR_2 = 0.218, GOF = 1.059.

Structure of 7c. A colorless block (0.20 mm × 0.20 mm × 0.15 mm), $C_{108}H_{134}Al_6N_4O_{22}\cdot C_6H_{14}\cdot 6(CH_2Cl_2)$, M = 2597.80, at 173 K is orthorhombic, space group $Aba2$, a = 27.854(10), b = 25.160(8), c =18.562(8) Å, Z = 4, V = 13009(8) Å^3, R_1 = 0.069, wR_2 = 0.182, GOF = 1.041.

The Reaction of 3 with Trimethylsilyl Cyanide in Toluene. To a solution of 275 mg (0.500 mmol) of compound **3** in 10 mL of toluene was added 64 mg (0.65 mmol) of trimethylsilyl cyanide. After being stirred at room temperature for 12 h, all volatiles were removed under reduced pressure at 40 °C. The reaction mixture was diluted with 50 mL of hexanes and filtered, and the filtrate was concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel (eluent: 5% ethyl acetate in hexanes) to give 101 mg of α-trimethylsilyoxyphenylacetonitrile (yield, 98%). The ^{1}H NMR and ^{13}C NMR spectra are in accord with those reported in the literature.[15d]

Trimethylsilyl Cyanation of Benzaldehyde Catalyzed by 1. To each of the following suspensions of 5 mol % (44.4 mg, 0.500 mmol), 10 mol % (88.8 mg, 0.100 mmol), and 25 mol % (222 mg, 0.250 mmol) of **1** in 10 mL of toluene was added 106 mg (1.00 mmol) of benzaldehyde, whereupon a bright yellow solution formed. The reaction mixtures were stirred for 30 min, and then 129 mg (1.3 mmol) of trimethylsilyl cyanide was added, causing the solution to become pale yellow immediately. The reaction mixtures were stirred at room temperature for 12 h, during which time a white solid precipitated in the presence of the highest concentration of catalyst and a turbid solution was obtained when the two lower concentrations of catalyst were present. To remove excess trimethylsilyl cyanide, all volatiles were removed under reduced pressure at 40 °C. Then 50 mL of hexanes was added, and the precipitated catalyst was filtered off. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: 5% ethyl acetate in hexanes) to produce 191 mg (93% yield, 5 mol % catalyst), 201 mg (98% yield, 10 mol % catalyst), and 205 mg (99% yield, 25 mol % catalyst) of α-trimethylsilyoxyphenylacetonitrile for which the ^{1}H NMR and ^{13}C NMR spectra were in accord with those reported in the literature.[15d] The reactants were also added in reverse order. Thus, to a suspension of 10 mol % (88.8 mg, 0.100 mmol) of compound **1** in 10 mL of toluene was added 129 mg (1.30 mmol) of trimethylsilyl cyanide, giving a brownish solution. The reaction mixture was stirred for 30 min, after which 106 mg (1.00 mmol) of benzaldehyde was added, causing the solution to became pale yellow. The reaction mixture was stirred at room temperature for 12 h, during which time a turbid solution was obtained. Workup followed the same procedure as above, and after column chromatography on silica gel, 189 mg (92% yield) of α-trimethylsilyoxyphenylacetonitrile was obtained.

Results and Discussion

In earlier work, we synthesized the alumatrane $Me_2HN{-}AlL$ via the reaction of tris(2-hydroxy-3,5-dimethylbenzyl)amine with $Al_2(NMe_2)_6$.[10a] The dimethylamine liberated in this reaction formed a robust adduct with the AlL moiety, and attempts to synthesize other alumatranes by displacing dimethylamine from

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[13] Blessing, R. H. *Acta Crystallogr*. **1995**, *A51*, 33.

[14] *SHELXTL* program library and NT version, version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 2003.

[15] (a) Yang, W.-B.; Fang, J.-M. *J. Org. Chem*. **1998**, *63*, 1356. (b) Whitesell, J. K.; Apodaca, R. *Tetrahedron Lett*. **1996**, *37*, 2525. (c) Sasai, H.; Arai, S.; Shibasaki, M. *J. Org. Chem*. **1994**, *59*, 2661. (d) Costa, D. J.; Boutin, N. E.; Riess, J. G. *Tetrahedron* **1974**, *30*, 3793.

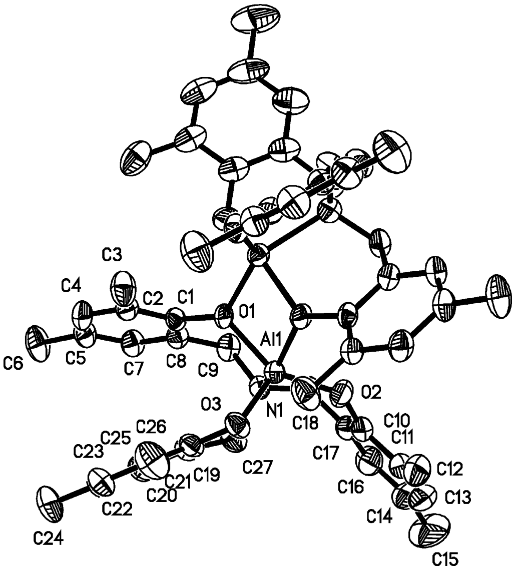

Figure 1. ORTEP of the molecular structure of **1** at the 50% probability level with atomic labeling. Hydrogen atoms were omitted for clarity.

$Me_2HN-AlL$ with other ligands such as benzaldehyde and phenol were unsuccessful.[16] To achieve the goal of synthesizing a coordinately unsaturated alumatrane that would readily be ligated by a substrate molecule and hence activate it, we sought to use trimethylaluminum as the metal source for the reaction with tris(2-hydroxy-3,5-dimethylbenzyl)amine in toluene, in which unreactive methane would be generated. Because only dimeric **1** was formed in this reaction, we turned our attention to the possibility of cleaving dimeric **1**.

Synthesis and Structural Characterization of 1. This compound was synthesized in 85% yield by combining trimethylaluminum with tris(2-hydroxy-3,5-dimethylbenzyl)amine in equimolar quantities in toluene at room temperature. As shown in Figure 1, the molecular structure determined by X-ray means is composed of two alumatrane units (related by a C_2 axis through the molecular center) linked by two Al−O bonds. To our knowledge, the dimeric structure of **1** in the solid state represents the only structurally characterized example of an alumatrane dimer thus far reported. The aluminum atoms in this structure adopt a distorted TBP geometry with a $N_{ax}-Al-O_{ax}$ angle of 141.41(13)°.

Two $Al-O_{eq}$ bonds [1.733(3) and 1.755(3) Å] are significantly shorter than those between the Al−O bonds involving the bridging oxygen atoms [ave = 1.886(3) Å]. The shorter aryloxide Al−O distances, which are also observed in $Me_2HN-AlL$[10a] and in other alumatranes (see below), suggest a degree of π-bonding between the oxygen lone pairs and aluminum-centered σ^* orbitals.[17] The transannular interaction distance $Al-N_{ax}$ in **1** [2.083(3) Å] is the same as the N−Al bond length in $Me_2HN-AlL$ [2.083(3) Å].[10a] This distance is essentially equal to the sum of the covalent radii of the Al and N atoms (2.05 Å),[18] which suggests a substantial degree of single bond character. This conjecture is supported by our observation in the molecular structures reported in the present work that, in the absence of overriding effects, the aluminum atom is displaced from the plane of the equatorial oxygens toward N_{ax} (see below). It should be noted, however, that transannular distances in atranes can also be influenced in the solid state by dipole forces, and differences in these distances may not be entirely due to substituent effects.[19] The average obtuse $O_{eq}-Al-N_{ax}$ angle of 93.26(5)° indicates that the Al atom is slightly displaced toward N_{ax} from the plane defined by three equatorial oxygen atoms, as also occurs in $Me_2HN-AlL$.[10b]

The positive ion electrospray MS spectrum of a solution of **1** in toluene displayed a peak at $m/z = 887$, corresponding to its dimeric structure. The absence of additional peaks in the ESI MS spectrum suggests that other species in toluene solution are absent or are present in undetectably low concentration. In previous literature reports,[10b,c,20] evidence was presented for various degrees of association of alumatranes: dimeric in the gas phase; monomeric, hexameric, and octameric in solution; and tetrameric in the solid phase. The aforementioned ESI MS results given for **1** point to the persistence of a dimeric structure for solid **1** in solution.

Cleavage of Dimeric 1 to Monomeric Alumatranes and Their Structural Characterization. In view of the distortion of the trigonal bipyramidal geometry adopted by the aluminum atoms in **1**, we hypothesized that there might be sufficient strain in this dimer to permit its symmetrical cleavage with selected ligands. Dissolving **1** in THF at room temperature allowed adduct **2** to be formed in virtually quantitative isolated yield. Adduct **2** is also easily synthesized in quantitative yield by combining **1** with 2 equiv of THF in toluene. The expected molecular structure of **2** was confirmed by X-ray diffraction analysis (Figure 2). Here the Al atom adopts a nearly ideal trigonal bipyramidal (TBP) structure with a THF molecule at the apical position. The sum of the $O_{eq}-Al-O_{eq}$ angles is 359.63(3)°, and the $N_{ax}-Al-O_{ax}$ angle [179.15(8)°] is quite linear. The average of the three $O_{eq}-Al$ bonds in **2** [1.7535(17) Å] is significantly shorter than the $O_{ax}-Al$ bond [1.9613(16) Å]. The transannular N−Al bond length in **2** [2.0685(18) Å] is within 3 times the estimated standard deviation (esd) of that in **1** [2.083(3) Å]. The average acute $O_{eq}-Al-O_{ax}$ bond angle [87.98(7)°] and the average obtuse $O_{eq}-Al-N_{ax}$ [92.02(7)°] indicates slight displacement of the aluminum atom in **2** from the equatorial plane toward N_{ax}, as is also found in **1** and in $Me_2HN-AlL$.[10c]

In the ^1H and ^{13}C NMR spectra of **2**, equivalency of the three identical arms of the ligand was observed, indicating average

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(16) Attempts to remove the dimethylamine ligand in Me_2HNAlL by protonation with 1 equiv of F_3CCOOH or F_3CSO_3H failed, resulting in decomposition. Benzaldehyde and phenol also did not displace the dimethylamine ligand from Me_2HNAlL.

(17) (a) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086. (b) Healy, M. D.; Wielda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543. (c) Healy, M. D.; Ziller, J. W.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2949.

(18) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and* Reactivity, 4th ed.; Harper-Collins: New York, 1993; p 292.

(19) Kárpáti, T.; Veszprémi, T.; Thirupathi, N.; Liu, X.; Wang, Z.; Ellern, A.; Nyulászi, L.; Verkade, J. G. *J. Am. Chem. Soc.* **2006**, *128*, 1500−1512.

(20) (a) Hein, F.; Albert, P. W. *Z. Anorg. Allg. Chem.* **1952**, *269*, 67. (b) Mehrotra, R. C.; Mehrotra, R. K. *J. Indian Chem. Soc.* **1962**, *39*, 677. (c) Lacey, M. J.; McDonald, C. G. *Aust. J. Chem.* **1967**, *29*, 1119. (d) Shkklover, V. E.; Struchkov, Yu. T.; Voronkov, M. G.; Ovchinnikova, Z. A.; Baryshok, V. P. *Dokl. Akad. Nauk SSSR (Engl. Transl.)* **1984**, *277*, 723. (e) Voronkov, M. G.; Baryshok, V. P. *J. Organomet. Chem.* **1982**, *239*, 199. (f) Paz-sandoval, M. A.; Fernandez-Vincent, C.; Uribe, G.; Contreras, R.; Klaebe, A. *Polyhedron* **1988**, *7*, 679. (g) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398. (h) Mehrotra, R. C.; Rai, A. K. *Polyhedron* **1991**, *10*, 1967. (i) Narayanan, R.; Laine, R. M. *Appl. Organomet. Chem.* **1997**, *11*, 919. (j) Opornsawad, Y.; Ksapabutr, B.; Wongkasemjit, S.; Laine, R. M. *Eur. Polym. J.* **2001**, *37*, 1877.

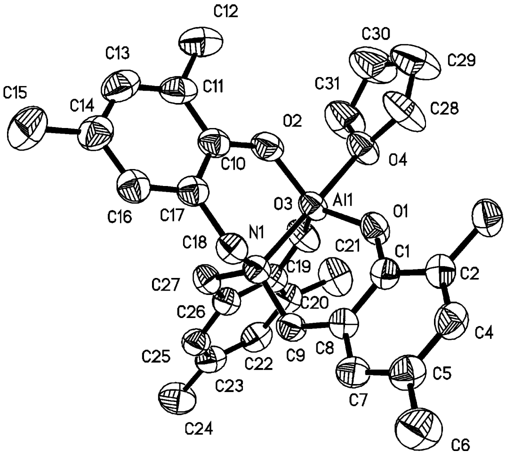


Figure 2. ORTEP of the molecular structure of **2** at the 50% probability level with atomic labeling. Hydrogen atoms were omitted for clarity.

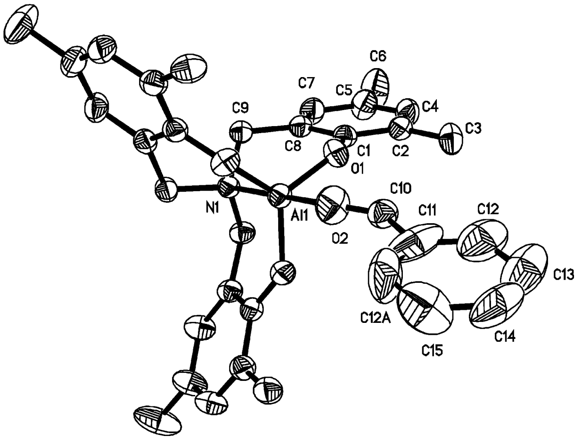


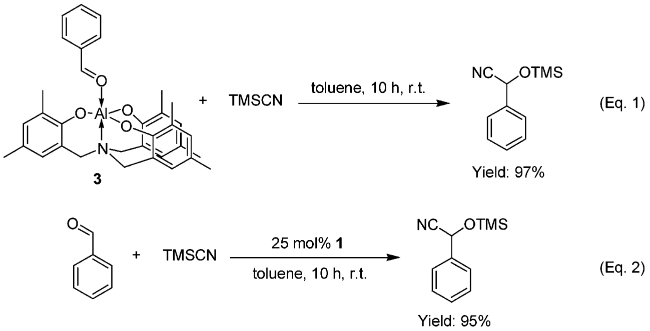
Figure 3. ORTEP of the molecular structure of **3** at the 50% probability level with atomic labeling. Hydrogen atoms were omitted for clarity.

pseudo C_{3v} molecular symmetry in solution owing to a rapid twisting molecular motion around the molecular axis on the NMR time scale, in contrast to the mirror symmetry of the molecular crystal structure.

Treatment of a suspension of **1** in toluene with 4 equiv of benzaldehyde gave a solution of the benzaldehyde adduct **3** that was isolated as yellow crystals. We were prompted to synthesize **3** by the realization that many reactions catalyzed by aluminum complexes involve carbonyl-bearing substrates whose carbonyl group can be activated by oxygen coordination to the metal.[1,12,21−23] The molecular structure of **3** shown in Figure 3, like that of **2**, possesses a near-ideal TBP coordination geometry featuring a linear $O_{ax}-Al-N_{ax}$ linkage [180.00(18)°] and an aluminum center somewhat displaced toward N_{ax} as indicated by the $O_{eq}-Al-N_{ax}$ angle [92.95(6)°]. Although the $Al-O_{ap}$ bond length [1.9815(15) Å] in **3** is only slightly longer than that in **2** [1.9613(16) Å], the transannular bond distance in **3** [2.0983(15) Å] is distinctly longer than that in **2** [2.0685(18)] Å. The differences in these distances are consistent with the expected poorer donor character of the benzaldehyde oxygen compared with the oxygen in THF.

The ^1H NMR and ^{13}C NMR spectra of **3**, like those of **2**, are consistent with threefold symmetry in solution. It is interesting to note that the ^{13}C NMR spectrum of **3** exhibits a downfield shift of 8 ppm for the carbonyl carbon compared with that of uncoordinated benzaldehyde, consistent with the presence of a more electrophilic carbonyl carbon in **3** as the result of a shift of lone pair density from the carbonyl oxygen to aluminum.

The activation of benzaldehyde in compound **3** was demonstrated by its reaction with an equivalent of trimethylsilyl cyanide (eq 1). Compound **1** serves in such a catalytic capacity for the addition of trimethylsilyl cyanide to benzaldehyde (eq 2), a transformation that Lewis acids readily facilitate.[15] Here, benzaldehyde apparently symmetrically cleaves dimeric **1**, generating **3** in situ as an intermediate. Only one literature report was found stating that this reaction proceeds in high yield in the absence of a catalyst.[24] In our hands, only a 15% yield of product was obtained under such conditions. However, in the presence of 5, 10, or 25 mol % loading of **1**, we obtained excellent isolated yields (93−100%) of α-trimethylsilyoxyphenylacetonitrile. Because this compound is easily hydrolyzed in the presence of moisture, the HCN thus generated could function as a catalyst unless strong precautions are taken. On the other hand, adventitious water could also be expected to destroy catalyst **1** by producing catalytically inactive **6** and/or **7**. In our reaction of 1 equiv of **1** with excess benzaldehyde for 30 min prior to addition of the trimethylsilyl cyanide, 2 equiv of intermediate **3** would be expected to form from the 5, 10, or 25 mol % loading of dimeric **1** via its cleavage into 10, 20, and 50 mol % of monomeric **1**, respectively. By reversing the order of addition of the reagents (see Experimental Section), a 92% isolated yield of product was obtained. In that experiment, the brownish solution obtained on initial addition of the trimethylsilyl cyanide suggests it ligates to the aluminum center in the monomeric cleavage product of dimeric **1**. Subsequent addition of benzaldehyde could then displace the trimethylsilyl cyanide Lewis base to form **3**, as was suggested by the replacement of the brownish color of the solution of the trimethylsilyl cyanide adduct by the yellow color of the benzaldehyde adduct **3**. Nucleophilic attack of the liberated trimethylsilyl cyanide on the carbonyl carbon would then follow.



The reaction of **1** with ethylenediamine (en) in toluene yielded alumatrane **4** in which the en is coordinated to the aluminum center by only one nitrogen. The molecular structure of **4**, established by X-ray diffraction analysis, is shown in Figure 4. The transannular bond in **4** [2.1079(19) Å] is slightly longer than those in **2** [2.0685(18) Å] and **3** [2.0983(15) Å], and it is

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(21) (a) *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000; Vols. 1 and 2. (b) *Lewis Acid Reagents: A Practical Approach*; Yamamoto, H., Ed.; Oxford University Press: Oxford, 1999.

(22) Saito, S.; Nagahara, T.; Shiozawa, M.; Nakadai, M.; Yamamoto, H. *J. Am. Chem. Soc.* **2003**, *125*, 6200.

(23) Ooi, T.; Takahashi, M.; Maruoka, K. *J. Am. Chem. Soc.* **1996**, *118*, 11307.

(24) Manju, K.; Trehan, S. *J. Chem. Soc., Perkin Trans. 1* **1995**, *19*, 2383.

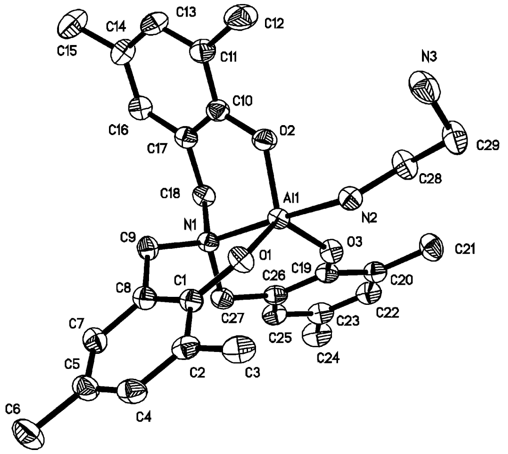

Figure 4. ORTEP of the molecular structure of **4** at 50% probability level with atomic labeling. Hydrogen atoms were omitted for clarity.

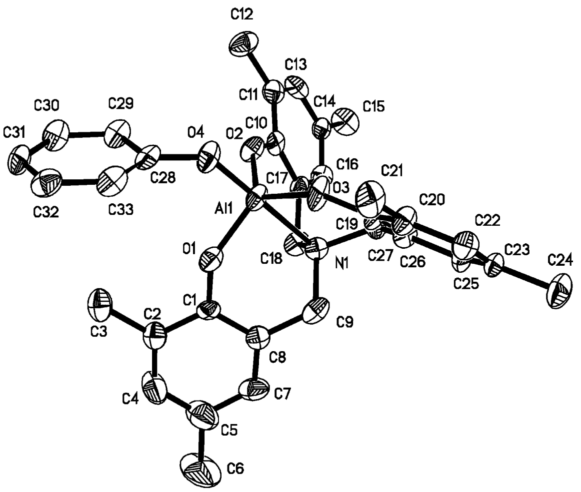

Figure 5. ORTEP of the molecular structure of **5** at the 50% probability level with atomic labeling. Hydrogen atoms were omitted for clarity.

also slightly longer than the Al−$NH_2CH_2CH_2NH_2$ bond in **4** [2.0146(19) Å]. Neither intermolecular nor intramolecular hydrogen bonds were observed in the structure.

The reaction of **1** with en was carried out in an attempt to synthesize a six-coordinate complex possessing a bidentate ethylenediamine ligand, or a five-coordinate en complex in which the tripodal ligand did not coordinate its central nitrogen to the aluminum (or did so only weakly). The preservation of the characteristic atrane structure is indicative of the stereoelectronic stability of its tris-chelated structure involving three six-membered rings. The ^1H NMR spectrum of compound **4** in C_6D_6 shows the presence of two chemically different phenyl rings in a 2:1 ratio which may be associated with sterically hindered rotation of the en ligand around the Al−N axis and/or intramolecular hydrogen bonding between the hydrogens of the free $-NH_2$ group of the en ligand with an oxygen atom of the aryloxide.

Unlike the reaction of **1** with en, its reaction with acetylacetone produced tris-acetylacetonatato aluminum(III) along with free tris(2-hydroxy-3,5-dimethylbenzyl)amine. In view of the comparatively great strength of the Al−O bond, it is reasonable to suppose that the reaction was driven by formation of six Al−O bonds at the cost of breaking only three Al−O bonds and one Al−N bond.

Combination of a solution of [HP(*i*-$PrNCH_2CH_2N)_3N$][OPh] (made from an equimolar mixture of P(*i*-$PrNCH_2CH_2N)_3N$ and phenol) with **1** afforded [HP(*i*-$PrNCH_2CH_2N)_3N$][**5**]. This compound allowed us the opportunity to gauge the influence of an anionic exocyclic ligand on the alumatrane structure in view of the fact that the exocyclic ligands in **2**−**4** and in Me_2-HN−AlL[10a] are charge neutral. Of particular interest here was the effect of the phenolate ligand on the length of the transannular bond in anionic **5** whose molecular structure we obtained by X-ray analysis. As depicted in Figure 5, the metal adopts a TBP coordination geometry with an average Al−O_{eq} bond length [1.752(6) Å] close to that in **2**−**4**. Coordination of the anionic phenolate to aluminum, however, gives rise to a short Al−O_{ax} bond [1.768(6) Å] in **5** that is significantly shorter by about 0.2 Å than that in **2**. Moreover, the aluminum position is above the plane defined by the three equatorial O atoms, in contrast to its location in **1**−**4** and in Me_2HN−AlL,[10a] where it is below this plane in each case. The metal location in **5** is reflected by the average of the acute O_{eq}−Al−N angles [85.9(2)°] and the obtuse O_{eq}−Al−O_{ax} angles [94.2(2)°]. The phenolate anion in **5** is expected to function as a stronger electron donor than the neutral ligands present in **2**−**4** and in Me_2HN−AlL.[10a] This supposition is consistent with the observation of a distinctly longer transannular bond in **5** [2.233(6) Å] compared with that in **1** [2.083(3) Å], **2** [2.0685(18) Å], **3** [2.0983(15) Å], **4** [2.1079(19) Å], and Me_2HN−AlL [2.083(3) Å].[10a]

Synthesis of 6 and 7. The reaction of **1** with water at −20 °C yielded the water-coordinated monomeric alumatrane **6** in 42% yield, while the reaction of **1** with water at room temperature led to its partial hydrolysis giving **7** which consists of four alumatrane units symmetrically connected into a ring by a tetra-aqua dimeric aluminum hydroxide molecule (see later). These observations suggested that **6** is unstable at room temperature, probably undergoing hydrolysis to generate **7**. Further experiments showed that indeed **6** reacted with atmospheric moisture at room temperature to give **7** in 37% yield. The sensitivity to atmospheric moisture of the benzaldehyde-coordinated alumatrane **3** at room temperature and at −20 °C gave rise to the formation of **7** in 43% yield and **6** in 35% yield.

Both **6** and **7** were structurally characterized by single-crystal X-ray diffraction experiments. It should be mentioned that it was possible to crystallize two different polymorphs of **7** (triclinic **7a** and monoclinic **7b**) as well as solvate **7c**. As depicted in Figure 6, two molecules of **6** are linked by an unsymmetrical hydrogen bond between a water ligand of one alumatrane unit and an aryloxide oxygen atom in the neighboring alumatrane unit. Although the two alumatranes in this dimer are inequivalent because of the hydrogen bond, all the corresponding bond distances and angles are very similar. The aluminum atoms in a dimeric unit of **6** each possess a TBP coordination geometry with an average O_{eq}−Al bond distance [1.755(3) Å] close to that in **1**−**5** and Me_2HN−AlL.[10a] The average of the O_{ax}−Al bonds in the two units of dimeric **6** [1.933(4) Å] is slightly shorter than that in **2** [1.9613(16) Å], and the average of the transannular bond distances in **6** [2.063(4) Å] is shorter than those in **1**−**5** and in Me_2HN−AlL.[10a] The transannular distance in **6** is, however, within 3 times the esd of that in **2**.

As depicted in Figure 7, the molecular structure of **7a** can be viewed as a tetramer consisting of four alumatrane units

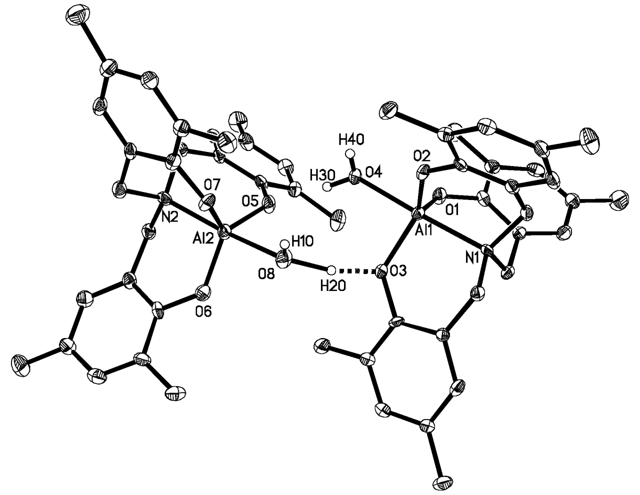

Figure 6. ORTEP of the molecular structure of **6** showing the dimer formed by hydrogen bonding. All hydrogen atoms were omitted except those participating in dimerization.

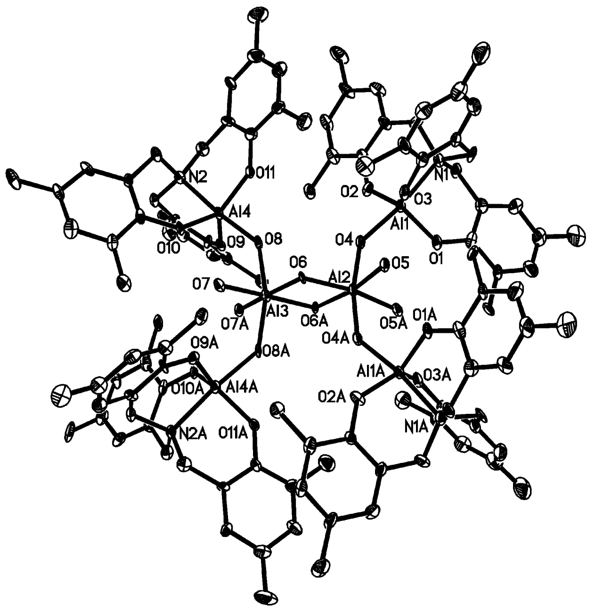

Figure 7. Computer drawing of the molecular structure of **7a**. Ellipsoids for the carbon atoms and hydrogen atoms were not displayed for clarity. The full ORTEP diagram can be found in the Supporting Information.

bridged by the dimeric aluminum hydroxide tetra-aqua fragment $(H_2O)_2(HO)_2Al(OH)_2Al(H_2O)_2(OH)_2$ in which both aluminum atoms are octahedrally coordinated. In this framework, the pairs of terminal OH and H_2O groups on each aluminum are mutually trans and cis, respectively, with the terminal hydroxyls each shared with an AlL fragment. The two six-coordinate aluminum centers are linked by two hydroxyl bridges. The seven Al$-\mu_2$-OH bond distances in **7a** fall in the range of 1.852−1.891 Å, distances that are comparable to those for such linkages reported in the literature.[25] The four Al−OH_2 bond lengths in **7a** range from 1.900(5) to 1.907(5) Å, of which the upper end of the range is within 3 times the esd of the Al−OH_2 bond length in **6** [(1.933(4) Å) and close to Al(III)−OH_2 bond distances reported in the literature (1.916 Å).[25] The four alumatranyl units in **7** are related by a C_2 symmetry axis, and each of these units features a TBP aluminum coordination geometry. The metal centers in these units are located in the plane defined by their three equatorial oxygen atoms as indicated by the sum of the O_{eq}−Al−O_{eq} angles of 360.0(8)°. The average Al−O_{eq} bond length of [1.777(5) Å] is within the range (1.745−1.759 Å) of those observed in **1**−**6**. The four alumatranyl Al atoms in **7** are each bound to an anionic hydroxyl ligand. The average transannular bond distance in **7** [2.073(6) Å] is significantly shorter than that in compound **5** [2.233(6) Å] which also bears an anionic ligand. The marked difference in the transannular bond distance in these two compounds can be attributed to the fact that the hydroxyl in **7** is a bridging ligand, while the ligand in **5** is monodentate and bears a full negative charge. As an expected consequence, the average Al−O_{ax} bond distance in **7** [1.854(5) Å] is longer than that in **5** [1.768(6) Å].

Although the instability of **6** at room temperature precluded obtaining definitive ^{1}H NMR spectra, such a spectrum of **7** shows that there are three inequivalent arms of the tripodal ligand in the four alumatranyl units owing to sterically restricted rotation of these units around their pseudo threefold axis. Interestingly, the hydroxyl proton (3.07 ppm) and ligated water proton (9.09 ppm) resonances appear at separate chemical shifts at room temperature.

The hydrolysis of aluminum alkoxides is a reaction that has been widely used for the synthesis of porous or nanosized materials.[26] For a metal alkoxide or halide, this process is proposed to be initiated by nucleophilic attack of water at the metal center, followed by formation of HOR or HX, and metal hydroxide, of which the latter then undergoes polycondensation to provide the corresponding metal oxide.[27] Water attack at the metal center is expected to involve the temporary formation of a water-coordinated complex. Because departure of the alkoxide or halide is apparently too fast to stop hydrolysis at the stage of a water-coordinated complex, no such complex has yet been reported for a neutral water-coordinated aluminum alkoxide. In this regard, however, Kawashima and co-workers recently reported a water-coordinated silicon atrane that is representative of an intermediate in the hydrolysis of alkoxysilanes.[28] Our observations that **1** and **3** are easily converted to **6** and that **6** is converted to **7** under mild conditions suggest that **6** is a model of the first intermediate in the hydrolysis of an aluminum alkoxide. Our observation that **6** is easily transformed to **7** is consistent with the notion that **7** is representative of a subsequent condensed intermediate that could well be formed in such hydrolyses.

Conclusions

As summarized in Scheme 1, dimeric **1** is a versatile starting material for the synthesis of monomeric alumatranes with a

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(25) Casey, W. H.; Olmstead, M. M.; Phillips, B. L. *Inorg. Chem*. **2005**, *44*, 4888.

(26) (a) Kim, H. J.; Lee, H. C.; Rhee, C. H.; Chung, S. H.; Lee, H. C.; Lee, K. H.; Lee, J. S. *J. Am. Chem. Soc*. **2003**, *125*, 13354. (b) Cabrera, S.; Haskouri, J. E.; Alamo, J.; Beltrán, A.; Beltrán, D.; Mendioroz, S.; Marcos, M. D.; Amoros, P. *Adv. Mater*. **1999**, *11*, 379. (c) Pu, L.; Bao, X.; Zou, J.; Feng, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1490. (d) Zou, J.; Pu, L.; Bao, X.; Feng, D. *Appl. Phys. Lett*. **2002**, *80*, 1079. (e) Lee, H. C.; Kim, H. J.; Chung, S. H.; Lee, K. H.; Lee, H. C.; Lee, J. S. *J. Am. Chem. Soc*. **2003**, *125*, 2882. (f) Hant, S. M.; Attard, G. S.; Riddle, R.; Ryan, K. M. *Chem. Mater*. **2005**, *17*, 1434. (g) Li, Y.; Zhang, W.; Zhang, L.; Yang, Q.; Wei, Z.; Feng, Z.; Li, C. *J. Phys. Chem. B* **2004**, *108*, 9739. (h) Yue, Y.; Cedeon, A.; Bonardet, J. L.; Melosh, N.; D'Esinose, J. B.; Fraissard, J. *Chem. Commun*. **1999**, 1967.

(27) (a) Cerveau, G.; Corriu, R. J. P.; Framery, E. *Chem. Mater*. **2001**, *13*, 3373. (b) Misra, C. *Industrial Alumina Chemicals*; ACS Monograph 184; American Chemical Society: Washington, DC, 1986; p 133.

(28) Kobayashi, J.; Kawaguchi, K.; Kawashima, T. *J. Am. Chem. Soc*. **2004**, *126*, 16318.

variety of substituents, including a novel water-coordinated alumatrane. Comparison of the transannular bond lengths in the alumatrane monomers **2**−**7** and $Me_2HN-AlL$[10b] allowed insights into the influence of the axial ligands on the transannular bond length, although these distances lie in a somewhat narrow range (2.063−2.233 Å). It has been shown by ^{13}C NMR spectroscopy that coordination of the aluminum center in **3** to the oxygen of a carbonyl group appears to reduce the electron density on the carbonyl carbon, thereby enhancing the electrophilicity of this atom. Moreover, the fact that **3** is an isolable compound is indicative of considerable Lewis acidity of the aluminum center. We believe these findings are consistent with promising prospects for the utility of alumatranes such as **1** as Lewis acidic catalysts, and investigations along these lines are underway. On the basis of the literature and our observations of the facile conversion of **1** and **3** to **6**, and of **6** to **7**, we can suggest that **6** models the initial intermediate in the hydrolysis of an aluminum alkoxide and that **7** models a condensed intermediate formed later in such hydrolyses.

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Supporting Information Available: Crystallographic data (CIF), chromatograms, ORTEP, and experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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