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The First Example of a Monomeric Alumatrane

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The novel five-coordinate aluminum adduct $Me_2HN\cdot AlL$ (**2**) [wherein L = tris(2-oxy-3,5-dimethylbenzyl)amine] containing three six-membered rings has been characterized by spectroscopic and by X-ray means. This adduct of an alumatrane is the first structurally characterized monomeric alumatrane derivative, and unlike its parent alumatrane $[Al(OCH_2CH_2)_3N]_x$, **2** is monomeric in the gas, solution, and solid states. The X-ray molecular structure of **2** reveals a tricyclic cage moiety of C_3 symmetry. The aluminum geometry is a slightly distorted trigonal bipyramid in which, quite unexpectedly, the metal atom is located somewhat below the plane formed by three equatorial oxygens and its $Al–N_{tertiary}$ bond is shorter than that in $Me_3N\cdot AlH_3\cdot NMe_3$ (Heitsch, C. W.; Nordman, C. E.; Parry, R. W. *Inorg. Chem.* **1963**, *2*, 508).

A wide variety of atoms in the periodic table have been utilized as core atoms in five-membered-ring atranes synthesized from triethanolamine.[1] Many studies of such atranes have focused on main group elements such as silicon,[2] phosphorus,[3] aluminum,[4] tin,[5] and alkali or alkali-earth metals[6] as well as transition metal elements such as titanium,[7] vanadium,[7e,8] iron,[9a] nickel,[9b] palladium,[9c] copper,[9d] and lanthanides.[9e,f] In contrast to other atranes, the monomeric form of alumatrane $[Al(OCH_2CH_2)_3N]$ might be expected to contain a four-coordinate metal with a paddle wheel structure featuring a nitrogen–aluminum bond, whereas oligomers would have a five- or six-coordinate structure owing to coordination of an apical position to the oxygen of a neighboring alumatrane molecule.[4g,k,l] Alumatrane has been described in the literature as dimeric in the gas phase; monomeric, hexameric, and octameric in solution; and tetrameric in the solid state.[4,10] In benzene, a cryoscopic determination of the molecular weight indicated octameric character,[4a] while an ebullioscopic measurement suggested

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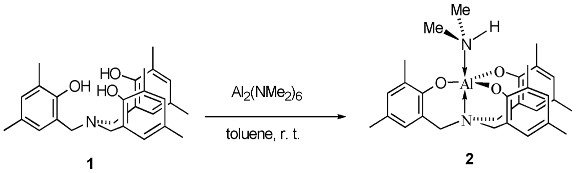
hexameric behavior.[4b] A mass spectrometric study revealed the stability of the dimer in the gas phase.[4c] A molecular X-ray structure for alumatrane ascertained the tetrameric nature in the solid state.[4d,g] However, examples of alumatranes having the same structure in the gas, solution, and solid states have to our knowledge not been reported. In addition, there is no example of a structurally characterized monomeric alumatrane-type molecule.

Recently, tripodal triphenoxyamine ligands made by deprotonating tris(2-hydroxy-3,5-dimethylbenzyl)amine (**1**) or other 3,5-dialkyl derivatives of **1** have been used to make silicon,[11] phosphorus,[12] titanium,[7j,13] tantalum,[14] indium,[15] and iron[16] complexes resembling the corresponding atranes except that the three chelating rings are six- instead of five-membered. The alkyl groups in the 5-position of these six-membered-ring atranes are expected to form a "picket fence" that could protect the metal atom from coordination sphere expansion through oligomer formation. This idea prompted us to determine whether the six-membered-ring alumatrane (possessing a four-coordinate aluminum) derived from **1** would be monomeric in the gas, solution, and solid states.



1 **2**

(1)

The alcoholysis of amides has proven to be a useful route to various metallic and metalloidal atranes.[1] Thus we allowed **1** to react with air-sensitive $Al_2(NMe_2)_6$ (reaction 1) which had been synthesized in 62% yield via the reaction of $LiNMe_2$ with $AlCl_3$ in pentane.[17] Another reason we employed the route in reaction 1 is that when we utilized $AlCl_3$ in a reaction with **1** in the presence of NEt_3 in dichloromethane solution or with trilithiated **1** in toluene or THF solution, an intractable mixture of compounds was obtained. However, after recrystallization of the product of reaction 1 from a toluene/pentane solution, we were somewhat surprised (in view of the volatility of dimethylamine) to obtain colorless crystals of adduct **2** (79% isolated yield) that were remarkably stable in the solid state for more than a month. In addition, **2** is very stable at room temperature for more than a week according to ^{1}H NMR spectroscopy in chloroform-*d$_1$*, acetone-*d$_6$*, and methanol-*d$_4$* solutions contained in capped NMR tubes. Compound **2** is soluble in a variety of solvents including toluene, methanol, acetone, and hexanes.

Compound **2** apparently binds its dimethylamine moiety quite tightly, and long periods of drying under vacuum at elevated temperatures even above 200 °C were unsuccessful in expelling $HNMe_2$. Attempts to purify **2** by sublimation at 250 °C at 7 μm resulted in decomposition after extended periods. It is interesting to note, moreover, that attempts to displace the $HNMe_2$ group with excess acetone, water, or more bulky amines such as HN(*i*-Pr)$_2$ and NEt_3 in refluxing THF solution also failed and only starting material **2** was recovered.

Compound **2** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{27}Al NMR spectroscopies and EI mass spectrometry, and also by elemental analysis and X-ray crystallography. The electron-impact mass spectrum (70 eV) of **2** indicates monomeric behavior in the gas phase. The 443 *m*/*e* peak stems from loss of a molecule of $HNMe_2$ from **2**, and the absence of other peaks between 500 and 1000 *m*/*e* rules out stability of a dimeric species under these conditions, a species generally accepted to exist in the gas phase of alumatrane itself.[4c] The ^{1}H NMR spectrum of **2** displays well-defined sharp resonances with the expected integrations. The aryl and methyl proton resonances appear as singlets because of the presence of the two methyl substituents on each aryl ring. The $NCH_2C_6H_2$ protons are diastereotopic on the NMR time scale and appear as two well-separated ($\Delta\delta$ 1.4) doublets. This nonequivalency of the benzylic protons is confirmed by the X-ray-derived molecular structure of **2**, which reveals pseudo-C_3 symmetry (see below). Also, six and four resonances for the aromatic and aliphatic carbons, respectively, are contained in the ^{13}C{^{1}H} NMR spectrum, and there is no indication of the presence of higher oligomers because the resonances consist of very sharp and intense singlets. These results are consistent with a monomeric structure of **2** in the solution phase. Despite a high quadrupolar relaxation rate for the ^{27}Al nucleus ($I = {}^5/_2$) and our observance of a broad background signal at 61 ppm in the spectrum,[18] a single broad ^{27}Al NMR chemical shift at 37.15 ppm was detected at room temperature in chloroform-*d*$_1$. The latter peak is reasonably assigned to a single pentacoordinated aluminum atom, which is normally observed in the range 33−44 ppm.[4h,i,19] Thus the ^{27}Al NMR spectral results are also consistent with monomeric behavior for **2** in the solution state.[19]

To elucidate the nature of the metal−ligand bonding and the solid-state structural nature of **2**, we carried out a single-crystal X-ray diffraction study.[20] The ORTEP plot, selected

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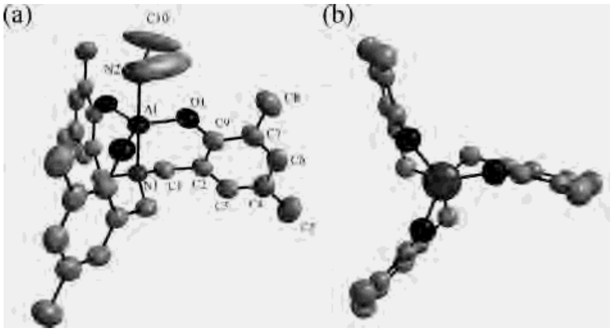

Figure 1. (a) Ball and stick drawing of **2** showing 50% probability thermal ellipsoids with H atoms and benzene-d_6 molecule omitted for clarity. Selected bond distances (Å): Al1−O1 = 1.7613(18), Al1−N2 = 2.048(4), Al1−N1 = 2.083(3), C1−N1 = 1.490(2), N2−C10 = 1.285(5). Selected bond angles (deg): N1−Al1−N2 = 180.00(8), O1−Al1−N1 = 92.34(6), O1−Al1−N2 = 87.66(6), Al1−O1−C9 = 133.08(15), Al1−N2−C10 = 119.7(3), Al1−N1−C1 = 109.95(13). (b) Perspective drawing showing the "propeller" arrangement of of **2**, viewed along the N−Al−N axis, with $HNMe_2$ in the foreground. The methyl groups of $HNMe_2$ are omitted for clarity.

bond distances, and selected bond angles are shown in Figure 1, which reveals a monomeric molecular structure for adduct **2**. The tricyclic cage moiety resembles a three-bladed turbine of C_3 symmetry (Figure 1b). In addition to the three "anionic" oxygens, the aluminum atom is ligated by means of a transannular interaction stemming from the bridgehead amino nitrogen, as well as via coordinate bonding with the dimethylamine molecule, giving a very slightly distorted trigonal bipyramidal geometry around aluminum. The equatorial oxygens form a regular triangle with sides of 3.048(3) Å, and the average distance between these oxygens and the axial secondary nitrogen ($NHMe_2$) is shorter than that between the oxygens and the axial tertiary nitrogen [2.646(3) and 2.782(3) Å, respectively]. The sum of the $O_{eq}-Al-O_{eq}$ angles is 359.50(6)° [av $O_{eq}-Al-O_{eq}$ angle = 119.83(6)°], and the $N_{secondary}-Al-N_{tertiary}$ angle (180.00(8)°) is nearly linear. It is interesting to note that the acute $O_{eq}-Al-N_{secondary}$ angles [av = 87.66(5)°] and obtuse $O_{eq}-Al-N_{bridgehead}$ angles [av = 92.34(5)°] reflect a displacement of the aluminum atom toward the bridgehead nitrogen by 0.235(2) Å. By contrast, the metal atom in all structured metallatranes is consistently located above the triangle formed by the three equatorial oxygens.[1,11,13−16] Moreover, the $Al-N_{tertiary}$ bond in **2** [2.083(3) Å] is somewhat longer than the $Al-N_{secondary}$ distance [2.048(4) Å] but is shorter than that in trigonal bipyramidal $Me_3N{\cdot}AlH_3{\cdot}NMe_3$ [2.18(1) Å] which is of local C_{3v} symmetry.[21] The average Al−O [1.761(1) Å] and Al−N [2.066(4) Å] bond distances in **2** are similar to the average of these distances observed for other structurally characterized aluminum alkoxides or aluminum amides, respectively.[22] Interestingly, there is only one other known example of a structurally characterized aluminum compound containing a dimethylamine molecule, namely, $Me_2NH{\cdot}AlH_3$, which is dimeric.[22b]

In conclusion, we find the stability of **2** to dissociation to be rather remarkable. Dissociation of volatile dimethylamine with formation of a strong coordinate bond to a four-coordinate aluminum might have been expected in view of the apparently less strain in the six-membered rings of the product that (according to crude molecular models) would then contain a tetrahedral rather than a trigonal bipyramidal metal in the tricyclic paddle wheel structure. Such a structure would be analogous to that of boratrane $[B(OCH_2CH_2)_3N]$ which possesses a N→B transannular bond [1.6764(3) Å] involving a tetrahedral boron at the bridgehead of three five-membered rings.[23] Loss of dimethylamine from **2** might also be expected to strengthen the transannular bond in the alumatrane product, as seems to be suggested by the ca. 0.2 Å displacement of the aluminum toward the tertiary nitrogen in **2** and by the shorter $Al-N_{tertiary}$ bond in **2** compared with that in $Me_3N{\cdot}AlH_3{\cdot}NMe_3$ (see above). It is possible that further shortening of the $Al-N_{tertiary}$ bond in **2** is inhibited by developing strain in the six-membered rings owing to the existence of two adjacent sp^2 carbons in the aromatic moiety fused to each of the rings, which impose two 120° angles in each of these rings. An interesting balance may therefore be established between adding too much strain in a completely dissociated free tricyclic alumatrane product and the formation of two weaker (although more delocalized) "half-bonds" along the trigonal axis of **2** which, in an MO interpretation, can arise from a filled 3-center BMO and a filled 3-center NBMO. The formation of an alumatrane adduct under our reaction conditions, rather than an alumatrane oligomerized via intermolecular O→Al coordinate links, may be ascribed to steric protection afforded by the "picket fence" of methyl groups around the metal in our free alumatrane which disfavor the approach of additional equally large identical molecules. Experiments aimed at synthesizing an appropriately sterically protected free alumatrane are in progress.

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Supporting Information Available: Details of the synthesis, X-ray data collection, structure solution, and structure refinement; tables of crystal data, atomic coordinates, thermal parameters, bond distances, and bond angles; ORTEP diagrams for compound **2**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Crystal data for **2** (173 K): space group $R\bar{3}$ with a = 14.250(2) Å, b = 14.250(2) Å, c = 26.738(4) Å, α = 90°, β = 90°, γ = 120°, V = 4702.1(12) Å^3, Z = 6, d_{calc} = 1.201 Mg/m^3, 7993 reflections measured (1782 unique). R (based on F^2 for $I > 2\sigma$) = 0.0525, R_w (based on F^2 for $I > 2\sigma$) = 0.1380, and GOF = 1.032.

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