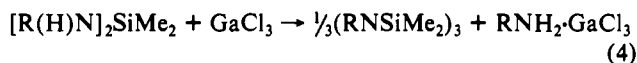


vary from 1.964 (4) to 2.012 (8) Å, and the Ga–N bond lengths (2.036 (7) and 2.016 (7) Å) in the cation fall at the upper end of this range. The Si–N bond lengths (1.833 (7) and 1.849 (7) Å) are within the range of values (1.744 (8)–1.874 (5) Å) observed in compounds where the silicon atom is bonded to a nitrogen atom with a tetrahedral coordination environment in this and other studies.<sup>3,22</sup>

The Ga–Cl (range: 2.149 (3)–2.180 (3) Å), Ga–N (1.995 (7) and 1.977 (6) Å), and C–N (average: 1.520 (12) Å) bond lengths in the anion  $[(\text{Cl}_3\text{Ga})_2\text{NEt}_2]^-$  (Figure 2) are similar to the corresponding bond lengths (range 2.149 (2)–2.176 (2) Å, 2.003 (5) Å, average 1.502 (7) Å) in  $\text{Me}_2\text{Si}(\text{NMe}_2)_2\cdot\text{GaCl}_3$ . The larger steric requirements of the ethyl groups versus the methyl groups on a nitrogen atom are reflected in the larger C(11)–N(3)–C(13) bond angle (113.8 (8)°) in the anion and the mean C–N–C bond angle (113.3 (7)°) in the cation in comparison to the C(1)–N(1)–C(2) bond angle (106.5 (5)°) in  $\text{Me}_2\text{Si}(\text{NMe}_2)_2\cdot\text{GaCl}_3$ . There are no abnormally close contacts between the ionic species in the unit cell.

The  $^1\text{H}$  NMR spectrum of  $[\text{Cl}_2\text{Ga}(\text{NEt}_2)_2\text{SiMe}_2]^-$   $[(\text{Cl}_3\text{Ga})_2\text{NEt}_2]$  in methylene- $d_2$  chloride exhibited three overlapping quartets at 3.41, 3.37, and 3.35 ppm; a triplet at 1.35 ppm; a triplet at 1.31 ppm; and a singlet at 1.07 ppm in the ratios of 12:6:12:6. The quartet at 3.41 ppm and the triplet at 1.35 ppm were assigned to the methylene and methyl protons of the ethyl groups in the anion, and the two upfield quartets (3.37 and 3.35 ppm) and the upfield triplet (1.31 ppm) were assigned to the methylene and methyl protons of the ethyl groups in the cation on the basis of decoupling experiments. When the triplet at 1.35 ppm was irradiated, the quartet at 3.41 ppm collapsed into a singlet, while irradiation of the triplet at 1.31 ppm resulted in the collapse of the two upfield quartets (3.37 and 3.35 ppm) into singlets. The singlet at 1.07 ppm was assigned to the protons in the methyl groups bonded to the silicon atom.

The reaction of  $[\text{Et}(\text{H})\text{N}]_2\text{SiMe}_2$  or  $[\text{n-Bu}(\text{H})\text{N}]_2\text{SiMe}_2$  with  $\text{GaCl}_3$  gave the N-alkylated hexamethylcyclotrisilazane and an alkylamine–gallium trichloride adduct (eq 4). The cyclotrisilazane



$(\text{EtNSiMe}_2)_3$  has been prepared previously by refluxing  $[\text{Et}$

$(\text{H})\text{N}]_2\text{SiMe}_2$  for 120 h in the presence of a catalytic amount of ammonium sulfate.<sup>8a,b</sup> Interestingly, no cyclosilazanes were isolated when  $[\text{n-Bu}(\text{H})\text{N}]_2\text{SiMe}_2$  was heated to 170–190 °C for 28 h in the presence of ammonium sulfate.<sup>8b</sup> The reaction pathway that leads to the formation of the N-alkylated hexamethylcyclotrisilazane and alkylamine–gallium trichloride in eq 4 is not known. However, the pathway probably does not involve a dehalosilylation reaction, in which  $[\text{Cl}_2\text{GaN}(\text{H})\text{R}]_n$  and  $\text{R}(\text{H})\text{NSi}(\text{Cl})\text{Me}_2$  are formed, and subsequently the elimination of HCl by  $\text{R}(\text{H})\text{NSi}(\text{Cl})\text{Me}_2$  with condensation to give  $(\text{RNSiMe}_2)_3$ . Autocondensation of  $\text{n-Bu}(\text{H})\text{NSi}(\text{Cl})\text{Me}_2$  at 70 °C for a period of 330 h was found to yield  $\text{n-BuNH}_2\text{Cl}$ ,  $\text{n-BuN}[\text{Si}(\text{Cl})\text{Me}_2]_2$ , and  $\text{n-BuN}[\text{Si}(\text{Cl})\text{Me}_2][\text{Si}(\text{N}(\text{H})(\text{n-Bu}))\text{Me}_2]$ . Similar N-ethylated disilazanes along with  $\text{EtNH}_2\text{Cl}$  were obtained when a petroleum ether solution of  $\text{EtNH}_2$  and  $\text{Me}_2\text{SiCl}_2$  in a 2:1 mole ratio was allowed to reflux for 320 h.<sup>23</sup>

While dehalosilylation has been observed in the reactions of  $(\text{Me}_3\text{Si})_2\text{NH}$  and  $(\text{Me}_3\text{Si})_2\text{NMe}$  with  $\text{GaCl}_3$ ,<sup>23,b</sup> only the reaction of  $(\text{Et}_2\text{N})_2\text{SiMe}_2$  with  $\text{GaCl}_3$  resulted in the metathetical elimination of  $\text{Et}_2\text{NSi}(\text{Cl})\text{Me}_2$ . Of the other substituted bis(amino)dimethylsilanes studied,  $(\text{Me}_2\text{N})_2\text{SiMe}_2$  formed a Lewis acid–base adduct with  $\text{GaCl}_3$  and  $[\text{Et}(\text{H})\text{N}]_2\text{SiMe}_2$  or  $[\text{n-Bu}(\text{H})\text{N}]_2\text{SiMe}_2$  reacted with  $\text{GaCl}_3$  to give the N-alkylated hexamethylcyclotrisilazane and alkylamine–gallium trichloride.

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**Supplementary Material Available:** Listings of crystallographic data, bond lengths, bond angles, selected dihedral angles, hydrogen coordinates, and anisotropic temperature factors and ORTEP diagrams illustrating the contents of the unit cells for  $\text{Me}_2\text{Si}(\text{NMe}_2)_2\cdot\text{GaCl}_3$  and  $[\text{Cl}_2\text{Ga}(\text{NEt}_2)_2\text{SiMe}_2][(\text{Cl}_3\text{Ga})_2\text{NEt}_2]$  (13 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

(23) Wannagat, U.; Schreiner, G. *Monatsh. Chem.* **1965**, *96*, 1895.

Contribution from the Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7 Canada, and Merck Sharp and Dohme Research Laboratories, Rahway, New Jersey 07065

## Multidentate Lewis Acids. Synthesis and Structure of Complex Aluminum Chloride Alkoxides

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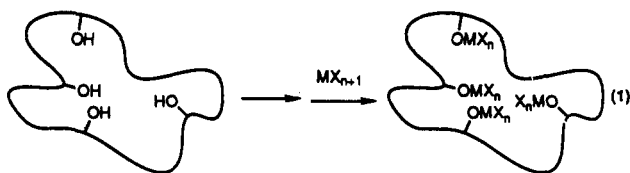
Received October 12, 1990

Complexes of simple aluminum chloride alkoxides with THF can be prepared by treating the corresponding alcohols or trimethylsilyl ethers with aluminum chloride and THF. Low-temperature  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{27}\text{Al}$  NMR spectra suggest that the products of these reactions are inhomogeneous and exist in solution as mixtures resulting from redistribution. More complex aluminum chloride alkoxides and their adducts can be prepared from the bis(trimethylsilyl) ethers of cyclic 1,2-diols. These chloride alkoxides also appear to undergo redistribution in solution, but some adopt well-defined structures in the solid state. An X-ray crystallographic study of representative chloride alkoxide **8b**, derived from a *trans*-1,2-cyclohexanediol, reveals a characteristic pentacyclic structure organized around a central  $\text{Al}_2\text{O}_2$  ring containing approximately trigonal oxygens and trigonal-bipyramidal aluminums. Compound **8b** crystallizes in the triclinic space group  $P\bar{1}$  with unit cell parameters  $a = 8.710$  (3) Å,  $b = 9.309$  (5) Å,  $c = 9.600$  (3) Å,  $\alpha = 88.82$  (3)°,  $\beta = 82.02$  (3)°,  $\gamma = 75.31$  (4)°,  $V = 745.6$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.333$  g cm<sup>-3</sup>, and  $Z = 1$  (dimer). Full-matrix least-squares refinement of 1425 reflections ( $I \geq 3.00\sigma(I)$ ) converged at  $R = 0.054$  and  $R_w = 0.050$ .

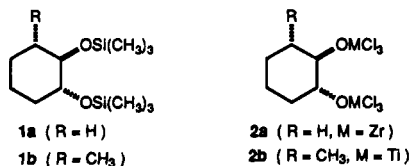
Host molecules with suitably oriented sites of Lewis acidity can recognize, bind, transport, and chemically activate complementary

basic guests.<sup>2</sup> We have recently shown that potential multidentate hosts with sites of strong Lewis acidity can be created conveniently

by adding inorganic halides  $\text{MX}_{n+1}$  to derivatives of alcohols (eq 1).<sup>3</sup> For example, treatment of bis(trimethylsilyl) ethers **1a**<sup>4</sup> and



**1b**<sup>3a</sup> with 2 equiv of zirconium tetrachloride or titanium tetrachloride produces bidentate trichloride alkoxides **2a** and **2b**, and we have described the structures of their adducts with representative Lewis bases.<sup>3</sup>

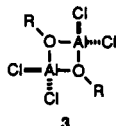


Strong  $\pi$  bonding involving the p orbitals of oxygen and d orbitals of zirconium and titanium in trichloride alkoxides **2a** and **2b** and related compounds favors C–O–M angles close to 180°. This geometrical arrangement creates a wide divergence of the Lewis acidic sites in structures **2a** and **2b** and helps disfavor cooperative binding of a single basic site by both metals. We reasoned that similar bidentate chloride alkoxides of metals without empty low-energy d orbitals would incorporate smaller C–O–M angles,<sup>5b</sup> allowing the Lewis acidic sites to converge and bind guests cooperatively. To test this hypothesis, we decided to study the synthesis and structure of various dichloride alkoxides of aluminum.

The hypothetical transmetalation reaction of eq 2 should be distinctly exothermic and should provide convenient access to aluminum dichloride alkoxides. The existence of aluminum



chloride as a dimer in condensed phases and the likely preference of aluminum chloride alkoxides for the dimeric structure **3**<sup>6</sup> make

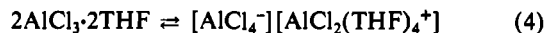


- (1) (a) Université de Montréal. (b) Merck Sharp and Dohme.
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- (3) (a) Bachand, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015–2025. Phan Viet, M. T.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026–3032. Bachand, B.; Bélanger-Gariépy, F.; Wuest, J. D. *Organometallics* **1990**, *9*, 2860–2862. (b) Sharma, V.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 579–581. (c) Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955–958.
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the stoichiometry of the actual transmetalation more complex but do not prevent it from occurring. As expected, treatment of a suspension of  $\text{Al}_2\text{Cl}_6$  in dichloromethane with 2 equiv of the trimethylsilyl ether of 2-propanol,<sup>8</sup> followed by evaporation of solvent and volatile products, yielded an aluminum chloride alkoxide. This material could not be purified by crystallization, however, and the complexity of its <sup>1</sup>H, <sup>13</sup>C, and <sup>27</sup>Al NMR spectra at low temperatures suggested that the crude product was not homogeneous or that pure dimeric aluminum dichloride alkoxide **3** (R = CH(CH<sub>3</sub>)<sub>2</sub>) was formed but undergoes extensive redistribution in solution. Likely products of redistribution include aluminum chloride and aluminum chloride diisopropoxide (eq 3), as well as mixed aggregates derived from the various species present in solution.<sup>9</sup>



Since we could not prepare and characterize pure, uncomplexed aluminum dichloride alkoxides, we then attempted to make stable adducts by adding trimethylsilyl ethers to equivalent amounts of complexes of aluminum chloride. We began by using the well-studied adducts of aluminum chloride with tetrahydrofuran (THF).<sup>10</sup> The chemistry of the interaction of aluminum chloride with THF is remarkably subtle, and two completely different 1:2 adducts have been characterized by X-ray crystallography. One form, obtained by an indirect procedure, is a normal trigonal-bipyramidal complex in which both molecules of THF are axial,<sup>10a</sup> the other form, prepared directly from aluminum chloride and THF, is the ionic species  $[\text{AlCl}_4^-][\text{AlCl}_2(\text{THF})_4^+]$ .<sup>10a,b,f</sup> We obtained a crystalline 1:2 complex in 80% yield by chilling a solution of appropriate amounts of the components in dichloromethane and established by X-ray powder diffraction that this procedure gives the known ionic adduct. Studies of this material by variable-temperature <sup>1</sup>H and <sup>27</sup>Al NMR spectroscopy confirmed earlier work showing that at least two species are present in solution.<sup>10c,d,f</sup> At 25 °C, the <sup>1</sup>H NMR spectrum in  $\text{CDCl}_3$  showed peaks at  $\delta$  2.01 and 4.18 due to bound THF, while at –78 °C in  $\text{CD}_2\text{Cl}_2$  at 0.09 M concentration the upfield multiplet further split into signals of approximately equal intensity at  $\delta$  1.93 and 2.05. This is presumably because interconversion of the ionic and molecular adducts is slow at –78 °C (eq 4).<sup>11</sup> Similarly, the <sup>27</sup>Al

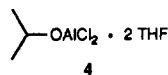


NMR spectrum at 25 °C in  $\text{CH}_2\text{Cl}_2$  at 0.07 M concentration contained a single broad peak at  $\delta$  86.2, which split at –35 °C into a sharp peak at  $\delta$  104 characteristic of  $[\text{AlCl}_4^-]$ , a broad peak at  $\delta$  63 typical of the pentacoordinate aluminum in the molecular adduct, and an even broader signal near  $\delta$  20 assigned to the hexacoordinate aluminum of  $[\text{AlCl}_2(\text{THF})_4^+]$ .<sup>12</sup> As expected,

- (6) Related aluminum dihalide alkoxides are known to be dimeric in solution and in the solid state.<sup>7</sup>
- (7) Bonamico, M.; Dessy, G. *J. Chem. Soc. A* **1967**, 1786–1790.
- (8) Prepared by the method of: Klebe, J. F. *Acc. Chem. Res.* **1970**, *3*, 299–305. Klebe, J. F.; Finkbeiner, H.; White, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 3390–3395.
- (9) The structure of a complex aluminum chloride isopropoxide aggregate has been described by: Yanovskii, A. I.; Kozunov, V. A.; Turova, N. Y.; Furmanova, N. G.; Struchkov, Y. T. *Dokl. Akad. Nauk* **1979**, *244*, 119–122.
- (10) (a) Means, N. C.; Means, C. M.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1987**, *26*, 1466–1468. (b) Strel'tsova, N. R.; Bel'skii, V. K.; Ivakina, L. V.; Storozhenko, P. A.; Bulychev, B. M. *Koord. Khim.* **1987**, *13*, 1101–1108. (c) Tarasov, V. P.; Kirakosyan, G. A.; Randarevich, S. B.; Buslaev, Y. A. *Koord. Khim.* **1984**, *10*, 950–955. (d) Nöth, H.; Rurländer, R.; Wolfgardt, P. Z. *Naturforsch.* **1982**, *37B*, 29–37. (e) Cowley, A. H.; Cushner, M. C.; Davis, R. E.; Riley, P. E. *Inorg. Chem.* **1981**, *20*, 1179–1181. (f) Derouault, J.; Granger, P.; Forel, M. T. *Inorg. Chem.* **1977**, *16*, 3214–3218. Derouault, J.; Forel, M. T. *Inorg. Chem.* **1977**, *16*, 3207–3213. (g) Han, O. H.; Oldfield, E. *Inorg. Chem.* **1990**, *29*, 3666–3669.
- (11) This also requires that the molecules of THF in each adduct be equivalent by symmetry, become equivalent by rapid exchange, or have hydrogens that cannot be distinguished by <sup>1</sup>H NMR spectroscopy.
- (12) Aikitt, J. W. *Prog. Nucl. Magn. Reson. Spectrosc.* **1989**, *21*, 1–149. Benn, R.; Janssen, E.; Lehmkuhl, H.; Ruffinska, A. *J. Organomet. Chem.* **1987**, *333*, 155–168.

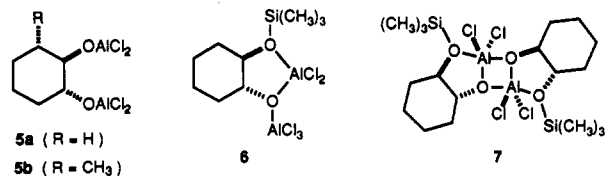
the more strongly solvated and entropically unfavorable ionic species becomes increasingly important as the temperature decreases.

Addition of 2-propanol or its trimethylsilyl ether to a 1:2 mixture of aluminum chloride and THF in dichloromethane, followed by removal of solvent and volatile products, yielded a substance that initially appeared to be the desired 1:2 adduct **4** of aluminum



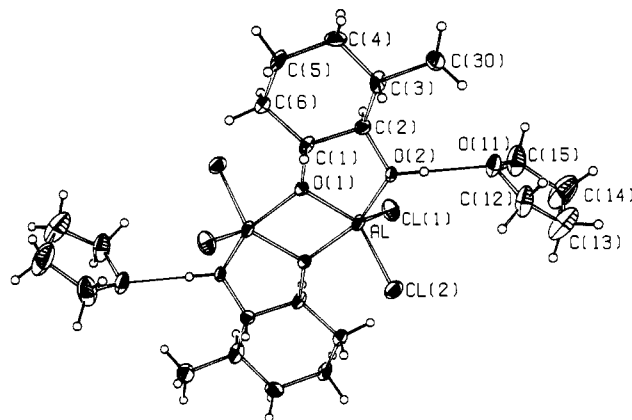
dichloride isopropoxide with THF.<sup>13</sup> Since this material could not be crystallized, it was studied by NMR spectroscopy without further purification. At 25 °C in CDCl<sub>3</sub>, its <sup>1</sup>H NMR spectrum consisted of a doublet at δ 1.45 (6 H) and a septet at δ 4.70 (1 H). In addition, multiplets at δ 2.00 (8 H) and 4.06 (8 H) could be assigned with confidence to bound THF, since they were shifted downfield by 0.17 and 0.35 ppm, respectively, from those of free THF. Unexpectedly, however, a <sup>1</sup>H NMR spectrum recorded at -85 °C in CD<sub>2</sub>Cl<sub>2</sub> showed more signals, including a pair at δ 1.88 and 1.98 in a 1:2 ratio that correspond to bound THF in at least two different environments. The signals assigned to THF were similar to those observed in <sup>1</sup>H NMR spectra of [AlCl<sub>4</sub>][AlCl<sub>2</sub>(THF)<sub>4</sub>]<sup>+</sup> under similar conditions, so putative adduct **4**, like uncomplexed aluminum dichloride isopropoxide itself, may undergo extensive redistribution in solution. Likely products of this hypothetical redistribution include the molecular and ionic adducts of aluminum chloride with THF, as well as complexes of aluminum chloride diisopropoxide with THF. Additional support for this proposal was provided by <sup>13</sup>C NMR spectra of a 0.31 M solution of putative adduct **4** in CD<sub>2</sub>Cl<sub>2</sub>. At 22 °C, the spectrum consisted of only two signals at δ 23.6 and 73.4 characteristic of an isopropoxy group, as well as two signals at δ 25.5 and 71.7 attributed to bound THF. At -85 °C, however, both regions of the spectrum became much more complicated, indicating that several distinct species containing isopropoxy groups and bound THF were present. Further evidence of complex behavior in solution was provided by the <sup>27</sup>Al NMR spectrum of a solution of putative adduct **4** in CH<sub>2</sub>Cl<sub>2</sub> at -78 °C. A sharp peak characteristic of [AlCl<sub>4</sub>]<sup>-</sup> appeared at δ 104 (w<sub>1/2</sub> = 200 Hz), and broader signals attributable to tetra-coordinate and penta-coordinate aluminum were apparent at δ 98, 87, and 63.

The indication that simple aluminum dichloride alkoxides and their adducts are unstable species prone to redistribution in solution made us doubt that we would be able to prepare and characterize more complex multidentate derivatives. Nevertheless, we attempted to prepare bidentate dichloride alkoxide **5a** by adding



the corresponding bis(trimethylsilyl) ether **1a** to 2 equiv of aluminum chloride. This reaction, described elsewhere in detail,<sup>3b</sup> did not lead to the product of complete desilylation but to the novel aluminum chloride alkoxide **6**. An analogous reaction with 1 equiv of aluminum chloride produced a less soluble material with a similar <sup>1</sup>H NMR spectrum. Although this compound could not be crystallized and characterized fully, we propose that it is dimer **7** or a stereoisomer. This hypothesis is reasonable because it accounts for the close chemical relationship and spectroscopic similarity of compounds **6** and **7**. In addition, it proposes a polycyclic structural motif consisting of linearly fused five- and four-membered rings with trigonal-bipyramidal aluminums similar to those found in related aluminum alkoxides.<sup>14</sup>

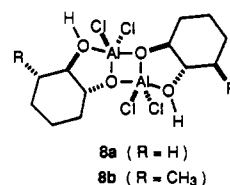
(13) A related compound has been reported by: Flagg, E. E.; Schmidt, D. L. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2329–2341.



**Figure 1.** ORTEP drawing of one of the two structures that constitute crystals of the THF solvate of aluminum chloride alkoxide **8b**. Non-hydrogen atoms are represented by ellipsoids corresponding to 33% probability, and hydrogen atoms are shown as spheres of arbitrary size.

Transfer of trimethylsilyl from compounds **6** and **7** to suitable bases is apparently facilitated by internal coordination of the trimethylsilyloxy groups to aluminum. As a result, addition of THF to compound **6** or the direct reaction of bis(trimethylsilyl) ether **1a** with a mixture of 2 equiv of aluminum chloride and 4 equiv of THF yielded a new product that no longer contained a trimethylsilyl group. Its <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> at 25 °C showed peaks at δ 2.01 and 4.12 attributable to 4 equiv of bound THF but was otherwise very similar to spectra of compounds **6** and **7**. The new compound may therefore be a complex of bidentate aluminum chloride alkoxide **5a** with two molecules of THF bound to each of the two aluminums. An analogous reaction with bis(trimethylsilyl) ether **1b** appeared to produce a similar THF complex of derivative **5b**.

Despite careful efforts, neither complex could be crystallized without decomposition, and solutions of the THF adduct of putative compound **5a** in mixtures of THF and pentane slowly deposited crystals of a new compound. Its <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> at 25 °C was generally similar to that of the starting material, but the peaks due to THF appeared farther upfield at δ 1.93 and 3.87, close to those of free THF. In addition, a broad band attributable to O–H stretching appeared unexpectedly in its IR spectrum. We propose that the new substance is a THF solvate of compound **8a** or a stereoisomer and that it results from



partial hydrolysis of the THF complex of precursor **5a** caused by adventitious water introduced during the long crystallization.<sup>15</sup> Similarly, crystals of a solvate of derivative **8b** could be obtained from the THF complex of compound **5b** by an analogous procedure.

Support for the speculative pentacyclic structures assigned to compounds **7**, **8a**, and **8b** was provided by an X-ray crystallographic study of the THF solvate of aluminum chloride alkoxide **8b**. Crystals of this compound proved to be disordered and to consist of equal populations of two closely related structures. One has the configuration of structure **8b** and appears in Figure 1, while the other resembles its mirror image and is shown in Figure 2 of

(14) For references, see: Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409–427. Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2486–2488. van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K.; Kojič-Prodič, B.; Spek, A. L. *Organometallics* **1985**, *4*, 1701–1707.

(15) Slow cleavage of THF occurs when solutions prepared by dissolving [AlCl<sub>4</sub>]<sup>-</sup>[AlCl<sub>2</sub>(THF)<sub>4</sub>]<sup>+</sup> in CHCl<sub>3</sub> are kept at 25 °C.

**Table I.** Crystallographic Data for the THF Solvate of Aluminum Chloride Alkoxide **8b** and Experimental Parameters

formula	C <sub>14</sub> H <sub>26</sub> Al <sub>2</sub> Cl <sub>4</sub> O <sub>4</sub> ·2C <sub>4</sub> H <sub>8</sub> O
fw	598.348
system	triclinic
space group	P1
cell const	
<i>a</i> , Å	8.710 (3)
<i>b</i> , Å	9.309 (5)
<i>c</i> , Å	9.600 (3)
α, deg	88.82 (3)
β, deg	82.02 (3)
γ, deg	75.31 (4)
cell vol. Å <sup>3</sup>	745.6
Z	1 (dimer)
T, K	173
ρ(calcd), g cm <sup>-3</sup>	1.333
μ(calcd), cm <sup>-1</sup>	4.88
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71069)
cryst dimens, mm	0.10 × 0.19 × 0.21
scan width	1.00 + 0.35 tan θ
2θ <sub>max</sub> , deg	50.0
data colln range	± <i>h</i> , ± <i>k</i> , <i>l</i>
no. of reflns colld	2611
no. of reflns retained	1425
no. of params refined	240
goodness-of-fit	2.076
R	0.054
R <sub>w</sub>	0.050

**Table II.** Coordinates (×10<sup>4</sup>) and Equivalent Isotropic Thermal Parameters (×10<sup>3</sup>) for the Non-Hydrogen Atoms of the THF Solvate of Aluminum Chloride Alkoxide **8b**

atom	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
Al	1193 (2)	5456 (2)	3992 (2)	39
Cl(1)	403 (2)	6546 (2)	2142 (2)	71
Cl(2) <sup>a</sup>	3344 (6)	3580 (4)	3523 (5)	60
Cl(2') <sup>a</sup>	3545 (6)	4119 (4)	3647 (6)	59
O(1)	146 (4)	5838 (3)	5790 (3)	37
O(2) <sup>a</sup>	2392 (8)	6635 (8)	4663 (7)	48
C(1) <sup>a</sup>	610 (10)	6775 (10)	6684 (8)	39
C(2) <sup>a</sup>	1572 (13)	7653 (11)	5783 (10)	45
C(3) <sup>a</sup>	2313 (10)	8577 (11)	6610 (9)	53
C(4) <sup>a</sup>	1284 (15)	9358 (12)	7898 (11)	78
C(5) <sup>a</sup>	163 (14)	8481 (13)	8607 (11)	54
C(6) <sup>a</sup>	-667 (12)	7568 (11)	7828 (10)	65
C(30) <sup>a</sup>	3172 (15)	9556 (16)	5644 (16)	71
O(2') <sup>a</sup>	1773 (8)	7428 (7)	4342 (6)	35
C(1') <sup>a</sup>	196 (10)	7157 (9)	6476 (8)	35
C(2') <sup>a</sup>	1713 (12)	7566 (10)	5850 (9)	37
C(3') <sup>a</sup>	1701 (10)	9130 (10)	6259 (9)	41
C(4') <sup>a</sup>	1610 (14)	9063 (12)	7836 (10)	62
C(5') <sup>a</sup>	258 (15)	8550 (12)	8684 (14)	60
C(6') <sup>a</sup>	255 (11)	7069 (9)	8057 (8)	33
C(30') <sup>a</sup>	3258 (14)	9572 (16)	5695 (17)	71
O(11)	4324 (5)	7610 (5)	2680 (4)	74
C(12)	5855 (7)	6578 (8)	2450 (7)	90
C(13)	6352 (9)	6470 (10)	949 (8)	131
C(14)	5362 (11)	7677 (10)	342 (8)	154
C(15)	3969 (8)	8287 (8)	1382 (9)	117

<sup>a</sup> Atom with an occupancy factor of 0.50.

the supplementary material. Crystallographic data and experimental parameters are summarized in Table I, atomic coordinates and isotropic thermal parameters for both structures are listed in Table II, and selected bond lengths and angles are compiled in Table III. Both structures incorporate several noteworthy features. Two five-membered rings are linearly fused to a central four-membered ring consisting of approximately trigonal oxygens and trigonal-bipyramidal aluminums. The Al–O bond lengths in the four-membered rings (1.833 (3) and 1.868 (4) Å) and average Al–Cl bond lengths (2.146 Å) are similar to those found in related aluminum chloride alkoxides.<sup>3b,7,9,16</sup> As expected, the

**Table III.** Selected Bond Lengths (Å) and Angles (deg) in the THF Solvate of Aluminum Chloride Alkoxide **8b**<sup>a</sup>

Bond Lengths			
Al(1)–Cl(1)	2.137 (2)	Al–O(2)	1.873 (7)
Al–Cl(2)	2.214 (5)	Al–O(2)'	2.069 (7)
Al–Cl(2)'	2.096 (5)	O(2)···O(11)	2.664 (8)
Al–O(1)	1.833 (3)	O(2)'···O(11)	2.590 (8)
Al–O(1)*	1.868 (4)		
Bond Angles			
Cl(1)–Al–Cl(2)	112.9 (2)	O(1)–Al–O(1)*	76.1 (2)
Cl(1)–Al–Cl(2)'	113.4 (2)	O(2)–Al–O(1)*	153.6 (3)
Cl(1)–Al–O(1)	125.8 (1)	O(2)'–Al–O(1)*	153.8 (2)
Cl(1)–Al–O(2)	104.7 (2)	Al–O(1)–C(1)	119.9 (4)
Cl(1)–Al–O(2)'	83.4 (2)	Al–O(1)–C(1)'	118.2 (4)
Cl(1)–Al–O(1)*	98.1 (1)	Al–O(2)–C(2)	115.8 (6)
Cl(2)–Al–O(1)	121.1 (2)	Al–O(2)'–C(2)'	106.3 (5)
Cl(2)'–Al–O(1)	120.1 (2)	C(2)–O(2)···O(11)	116.9 (6)
Cl(2)–Al–O(2)	91.7 (3)	C(2)'–O(2)'···O(11)	120.0 (5)
Cl(2)'–Al–O(2)'	96.8 (2)	Al–O(1)–Al*	103.9 (2)
Cl(2)–Al–O(1)*	91.4 (2)	Al*–O(1)–C(1)	135.5 (4)
Cl(2)'–Al–O(1)*	106.3 (2)	Al*–O(1)–C(1)'	135.4 (4)
O(1)–Al–O(2)	79.9 (2)	Al–O(2)···O(11)	114.6 (3)
O(1)–Al–O(2)'	81.8 (2)	Al–O(2)'···O(11)	110.6 (3)

<sup>a</sup> Asterisks indicate atoms with equivalent positions  $-x, 1-y, 1-z$ .

apical Al–O distance in the four-membered ring is somewhat longer than the equatorial Al–O distance.<sup>14</sup> In addition, both five-membered rings are trans-fused to cyclohexane rings that adopt chair conformations with equatorial substituents. Trans-fusion is undoubtedly facilitated by the distorted trigonal-bipyramidal hybridization of aluminum, which creates O–Al–O angles close to 80° within each five-membered ring. Finally, two molecules of THF are associated with compound **8b** via hydrogen bonds to hydroxyl groups made unusually acidic by internal coordination to aluminum. Despite extensive similarity, the two structures that constitute crystals of aluminum chloride alkoxide **8b** have significantly different distances from aluminum to the oxygen not incorporated in the four-membered ring (O(2) and O(2)'). In one structure, this distance is normal (1.873 (7) Å), but in the other it is unexpectedly long (2.069 (7) Å) and close to the limits observed for Al–O bonds.<sup>14,17</sup> Careful attempts to solve the structure by imposing a more normal distance led to increased values of *R*, and we found no evidence that the crystals have a larger unit cell or belong to space group *P1* without disorder. We therefore attribute the anomaly to disorder created by the presence of diastereomers of structure **8b** derived from two methylcyclohexanediol units of the same absolute configuration. The longer Al–O(2)' bond length is associated with other geometrical changes, including significant pyramidalization at O(2)' (sum of angles = 336.9°), an unusually small O(2)'–C(2)'–C(1)'–O(1) dihedral angle (46.5 (8) °), and bending of Cl(1) toward O(2)'. Furthermore, the hydroxyl group appears to be more strongly hydrogen bonded to THF, since the O(2)'···O(11) distance (2.590 (8) Å) is somewhat shorter than O(2)···O(11) (2.664 (8) Å). The disorder inherent in crystals of aluminum chloride alkoxide **8b** raises doubts about the significance and origin of these anomalies, but the basic features common to both structures are firmly established.

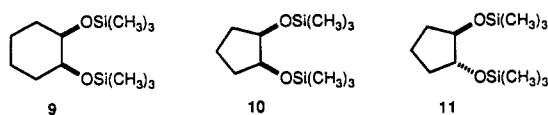
It is tempting to conclude that the pentacyclic structure revealed by this crystallographic study is a characteristic motif that compounds **7**, **8a**, **8b**, and related aluminum chloride alkoxides adopt dependably, both in the solid state and in solution. This is not true. At –78 °C, the <sup>27</sup>Al NMR spectrum of a solution prepared by dissolving the pure, crystalline THF solvate of compound **8a** in CH<sub>2</sub>Cl<sub>2</sub> consisted of a sharp signal at δ 102 characteristic of [AlCl<sub>4</sub>]<sup>-</sup>, as well as a broad signal at δ 55 assigned to penta-coordinate aluminum. A similar spectrum of compound **8b** showed distinct peaks at δ 102, 55, and 10 even at +30 °C. The observation of major peaks at δ 55 in both spectra provides evidence that substances with penta-coordinate aluminum, possibly intact

(16) Thewalt, U.; Stollmaier, F. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 133–134.

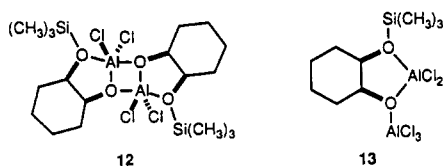
(17) Boardman, A.; Small, R. W. H.; Worrall, I. J. *Acta Crystallogr.* **1983**, *C39*, 433–435.

structures **8a** and **8b** or stereoisomers, are present in solution. Nevertheless, the simultaneous detection of  $[\text{AlCl}_4]^-$  demonstrates that compounds **8a** and **8b**, and presumably related aluminum chloride alkoxides as well, undergo at least partial redistribution and that the pentacyclic structures favored in the solid state are not the only species in solution. Additional support for this hypothesis was provided by  $^{13}\text{C}$  NMR spectra of a 0.12 M solution prepared by dissolving the pure, crystalline THF solvate of compound **8b** in  $\text{CD}_2\text{Cl}_2$ . At 25 °C, the spectrum showed seven major signals at  $\delta$  17.7, 23.2, 31.1, 33.6, 35.8, 76.4, and 84.0 derived from the methylcyclohexanediol framework, as well as two signals at  $\delta$  25.8 and 68.8 that were attributed to THF. This indicates that a single major species, possibly intact structure **8b**, is present in solution. However, an additional set of seven minor signals could be detected at  $\delta$  17.7, 23.3, 31.0, 33.5, 36.0, 76.3, and 84.5. We attribute these minor signals to the methylcyclohexanediol framework of the product of partial redistribution. At -60 °C, signals in the  $^{13}\text{C}$  NMR spectrum broadened somewhat, but no further splitting was observed.

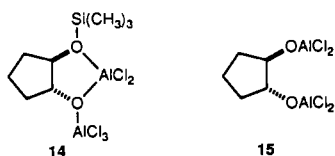
Although redistribution threatened to be a general feature of the chemistry of aluminum chloride alkoxides derived from diols, we decided to pursue our investigation by studying the effect of small structural modifications of the diol framework. In this study, we added bis(trimethylsilyl) ethers **9–11**<sup>4</sup> to suspensions of alu-



minum chloride in dichloromethane. As expected, the reactions of cis ether **9** with 1 or 2 equiv of aluminum chloride were similar to those of trans isomer **1a** and yielded products that retained trimethylsilyloxy groups internally coordinated to aluminum. By analogy, we assign them structure **12**, or a stereoisomer, and



structure **13**. The  $^1\text{H}$  NMR spectrum of compound **13** showed multiplets at  $\delta$  4.44 (1 H,  $w_{1/2} = 21$  Hz) and 4.85 (1 H,  $w_{1/2} = 8$  Hz) assigned to the carbinolic hydrogens. The upfield signal presumably corresponds to the hydrogen geminal to the oxygen bearing silicon. This hydrogen has a larger half-width, so the trimethylsilyloxy group must be equatorial. Similarly, the upfield carbinolic hydrogen in compound **12** has a larger half-width, so again the trimethylsilyloxy group must be equatorial. Analogously, addition of the bis(trimethylsilyl) ether **10** of *cis*-1,2-cyclopentanediol to 1 or 2 equiv of aluminum chloride also gave products that retained trimethylsilyloxy groups. In contrast, no characterizable trimethylsilyl ethers could be obtained from the reaction of trans isomer **11** with 2 equiv of aluminum chloride. This observation supports the hypothesis that internal coordination to aluminum protects the trimethylsilyl ethers of compounds **6** and **13** against cleavage by external aluminum chloride.<sup>3b</sup> Hypothetical intermediate trans-fused adduct **14** is probably strained, so we suggest that further cleavage to bidentate aluminum dichloride alkoxide **15** can take place and that compound **15** then undergoes extensive redistribution reactions.



The creation of useful multidentate Lewis acids by the simple expedient of treating derivatives of alcohols with inorganic halides presents an immensely difficult challenge. The sites of Lewis acidity must be close enough together to allow cooperative binding

of substrates but not so close that counterproductive bridging can take place. Furthermore, destructive redistribution reactions must be avoided. The observations summarized in this paper demonstrate that useful multidentate aluminum dichloride alkoxides will be particularly hard to prepare.

### Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. A Varian VXR-300 spectrometer was used to obtain  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra at 300 MHz,  $^{13}\text{C}$  NMR spectra at 75.4 MHz, and  $^{27}\text{Al}$  NMR spectra at 78.2 MHz. In addition, a Bruker WH-400 instrument was used to record  $^1\text{H}$  NMR spectra at low temperature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in parts per million downfield from internal tetramethylsilane ( $\delta$ ), and  $^{27}\text{Al}$  chemical shifts are relative to an external 1.5 N solution of  $\text{Al}(\text{NO}_3)_3$  in  $\text{D}_2\text{O}$ . Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus. Dichloromethane was dried by distillation from  $\text{CaH}_2$ , and pentane and tetrahydrofuran (THF) were dried by distillation from the sodium ketyl of benzophenone. Aluminum chloride was purified twice by sublimation in vacuo.

**Reaction of the Trimethylsilyl Ether of 2-Propanol with Aluminum Chloride.** A stirred suspension of aluminum chloride (0.906 g, 6.79 mmol) in dichloromethane (4 mL) was cooled to -78 °C under dry Ar and treated dropwise with a solution of the trimethylsilyl ether of 2-propanol<sup>8</sup> (0.904 g, 6.83 mmol) in dichloromethane (4 mL). The cooling bath was removed, and the mixture was kept at 25 °C for 20 h. Removal of volatiles by evaporation in vacuo left a residue of putative aluminum dichloride alkoxide **3** as a yellow oil (0.941 g, 5.99 mmol, 88.2%): IR (liquid film) 2990, 1390, 1370, 1260, 1180, 1135, 1030, 890, 840, 750, 680, 440, 350, 300  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  1.55 (d, 6 H), 4.75 (sept, 1 H);  $^{27}\text{Al}$  NMR (78.2 MHz,  $\text{CH}_2\text{Cl}_2$  containing 20%  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  90 ( $w_{1/2} = 400$  Hz), 100 ( $w_{1/2} = 200$  Hz).

**Preparation of  $[\text{AlCl}_4][\text{AlCl}_2(\text{THF})_4]^+$ .** A stirred suspension of aluminum chloride (0.875 g, 6.56 mmol) in dichloromethane (5 mL) was cooled to -78 °C under dry Ar and treated dropwise with THF (0.975 g, 13.5 mmol). The cooling bath was removed, the mixture was filtered, and a layer of pentane (5 mL) was carefully added to the filtrate. Slow diffusion at -25 °C induced the formation of colorless crystals of  $[\text{AlCl}_4][\text{AlCl}_2(\text{THF})_4]^+$  (1.46 g, 5.26 mmol, 80.2%): mp 88–90 °C; IR (Nujol mull) 1000, 840  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  2.01 (m, 16 H), 4.18 (m, 16 H);  $^{27}\text{Al}$  NMR (78.2 MHz, 0.07 M in  $\text{CH}_2\text{Cl}_2$  containing 20%  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  86.2. Anal. Calcd for  $\text{C}_{16}\text{H}_{32}\text{Al}_2\text{Cl}_6\text{O}_4$ : C, 34.62; H, 5.81. Found: C, 34.03; H, 5.93. The X-ray powder diffraction pattern of this compound was essentially identical with that of the known ionic adduct of aluminum chloride with THF.<sup>10a</sup>

**Reaction of 2-Propanol with Aluminum Chloride and Tetrahydrofuran.** A stirred suspension of aluminum chloride (0.394 g, 2.95 mmol) in dichloromethane (2 mL) was cooled to -78 °C under dry Ar and treated dropwise with THF (0.424 g, 5.88 mmol). The mixture was warmed briefly to 25 °C, recooled to -78 °C, and treated dropwise with 2-propanol (0.177 g, 2.95 mmol). The cooling bath was removed, and the mixture was kept at 25 °C for 76 h. Removal of volatiles by evaporation in vacuo left a residue of putative aluminum dichloride alkoxide **4** as a white solid (0.762 g, 2.53 mmol, 85.8%): IR (Nujol mull) 1100, 1040, 1000, 910, 840, 800, 520, 490, 450, 355  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  1.45 (d, 6 H), 2.00 (m, 8 H), 4.06 (m, 8 H), 4.70 (sept, 1 H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CD}_2\text{Cl}_2$ , 22 °C)  $\delta$  23.6, 25.5, 71.7, 73.4;  $^{27}\text{Al}$  NMR (78.2 MHz,  $\text{CH}_2\text{Cl}_2$  containing 20%  $\text{CD}_2\text{Cl}_2$ , -78 °C)  $\delta$  104, 98, 87, 63.

**Reaction of the Bis(trimethylsilyl) Ether **1a** of *trans*-1,2-Cyclohexanediol with Aluminum Chloride (1 equiv).** Similar procedures converted aluminum chloride (0.321 g, 2.41 mmol) and the bis(trimethylsilyl) ether **1a**<sup>4</sup> of *trans*-1,2-cyclohexanediol (0.626 g, 2.40 mmol) into aluminum chloride alkoxide **7**, a colorless solid (0.679 g, 1.19 mmol, 99.2%): IR (Nujol mull) 1260, 1090, 1070, 990, 850, 700, 630, 540, 515, 390, 350, 320  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.50 (s, 18 H), 1.3 (m, 4 H), 1.6 (m, 4 H), 1.8 (m, 4 H), 2.4 (m, 4 H), 3.9 (m, 4 H).

**Reaction of the Bis(trimethylsilyl) Ether **1a** of *trans*-1,2-Cyclohexanediol with Aluminum Chloride and Tetrahydrofuran.** Similar procedures converted aluminum chloride (0.399 g, 2.99 mmol), THF (0.431 g, 5.98 mmol), and the bis(trimethylsilyl) ether **1a**<sup>4</sup> of *trans*-1,2-cyclohexanediol (0.390 g, 1.50 mmol) into a colorless solid that is presumed to be a 1:4 complex of aluminum chloride alkoxide **5a** with THF (0.868 g, 1.45 mmol, 97.0%). This material was redissolved in THF (5 mL), the solution was filtered, and a layer of pentane (13 mL) was carefully added to the filtrate. Slow diffusion at 25 °C induced the formation of crystals of the 1:2 solvate of aluminum chloride alkoxide **8a** with THF as colorless transparent plates (0.230 g, 0.403 mmol, 53.7%): mp

128–134 °C dec; IR (Nujol mull) 3600–2300, 1090, 1060, 1040, 1000, 920, 850, 680, 490, 360 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.30 (m, 4 H), 1.51 (m, 4 H), 1.76 (m, 4 H), 1.93 (m, 8 H), 2.03 (d, 2 H), 2.41 (d, 2 H), 3.87 (m, 12 H); <sup>27</sup>Al NMR (78.2 MHz, CH<sub>2</sub>Cl<sub>2</sub> containing 20% CD<sub>2</sub>Cl<sub>2</sub>, -78 °C) δ 102, 55. Anal. Calcd for C<sub>20</sub>H<sub>38</sub>Al<sub>2</sub>Cl<sub>4</sub>O<sub>6</sub>: C, 42.12; H, 6.72; Cl, 24.87. Found: C, 39.79; H, 6.65; Cl, 22.04.

**Reaction of the Bis(trimethylsilyl) Ether 1b of (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ )-3-Methyl-1,2-cyclohexanediol with Aluminum Chloride and Tetrahydrofuran.** A similar procedure converted aluminum chloride (0.389 g, 2.92 mmol), THF (0.419 g, 5.81 mmol), and the bis(trimethylsilyl) ether 1b<sup>3a</sup> of (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ )-3-methyl-1,2-cyclohexanediol (0.400 g, 1.46 mmol) into a colorless solid that is presumed to be a 1:4 complex of aluminum chloride alkoxide 5b with THF (0.863 g, 1.41 mmol, 97.1%). This material was redissolved in THF (2.5 mL), the solution was filtered, and a layer of pentane (8 mL) was carefully added to the filtrate. Slow diffusion at 25 °C induced the formation of crystals of the 1:2 solvate of aluminum chloride alkoxide 8b with THF as colorless transparent plates (0.251 g, 0.419 mmol, 57.4%): mp 94–98 °C; IR (Nujol mull) 1240, 1100, 1060, 1035, 990, 920, 900, 870, 840, 670 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.0–1.8 (m, 12 H), 1.05 (d, 6 H), 1.89 (m, 8 H), 2.40 (d, 2 H), 3.52 (m, 2 H), 3.81 (m, 10 H); <sup>13</sup>C NMR (75.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ 17.7, 23.2, 23.3, 25.8, 31.0, 31.1, 33.5, 33.6, 35.8, 36.0, 68.8, 76.3, 76.4, 84.0, 84.5; <sup>27</sup>Al NMR (78.2 MHz, CH<sub>2</sub>Cl<sub>2</sub> containing 20% CD<sub>2</sub>Cl<sub>2</sub>, 30 °C) δ 102, 55, 10. Anal. Calcd for C<sub>32</sub>H<sub>42</sub>Al<sub>2</sub>Cl<sub>4</sub>O<sub>6</sub>: C, 44.16; H, 7.08; Cl, 23.70. Found: C, 40.64; H, 7.32; Cl, 22.89.

**Reactions of the Bis(trimethylsilyl) Ether 9 of *cis*-1,2-Cyclohexanediol with Aluminum Chloride (1 and 2 equiv).** A similar procedure converted aluminum chloride (0.133 g, 0.997 mmol) and the bis(trimethylsilyl) ether 9<sup>a</sup> of *cis*-1,2-cyclohexanediol (0.258 g, 0.990 mmol) into a colorless solid that is presumed to be aluminum chloride alkoxide 12 (0.278 g, 0.487 mmol, 98.4%): IR (Nujol mull) 1260, 980, 850, 710, 515, 460, 430 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.47 (s, 18 H), 1.14 (q, 2 H), 1.4 (m, 4 H), 1.80 (m, 6 H), 2.10 (q, 2 H), 2.52 (d, 2 H), 4.02 (m,  $w_{1/2}$  = 22 Hz, 2 H), 4.40 (m,  $w_{1/2}$  = 9 Hz, 2 H).

An analogous reaction of aluminum chloride (0.718 g, 5.38 mmol) and bis(trimethylsilyl) ether 9<sup>a</sup> (0.700 g, 2.69 mmol) provided a sample of the putative aluminum chloride alkoxide 13, a yellow solid (1.10 g, 2.62 mmol, 97.4%): IR (Nujol mull) 1270, 950, 860, 810, 730 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.62 (s, 9 H), 1.34 (q, i H), 1.60 (d, 1 H), 1.9 (m, 3 H), 2.1 (m, 2 H), 2.73 (d, 1 H), 4.44 (m,  $w_{1/2}$  = 21 Hz, 1 H), 4.85 (m,  $w_{1/2}$  = 8 Hz, 1 H).

**Reaction of the Bis(trimethylsilyl) Ether 10 of *cis*-1,2-Cyclopentanediol with Aluminum Chloride (2 equiv).** A similar procedure converted aluminum chloride (0.412 g, 3.09 mmol) and the bis(trimethylsilyl) ether 10<sup>a</sup> of *cis*-1,2-cyclopentanediol (0.380 g, 1.54 mmol) into a yellow solid that is presumably analogous to aluminum chloride alkoxide 13 (0.591 g, 1.46 mmol, 94.8%): IR (Nujol mull) 1260, 1110, 1010, 990, 860, 810, 750 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.64 (s, 9 H), 1.81 (m, 1 H), 2.0–2.4 (m, 4 H), 2.7 (m, 1 H), 4.85 (m, 1 H), 5.05 (m, 1 H).

**X-ray Crystallographic Study of Aluminum Chloride Alkoxide 8b.** Crystallographic data and experimental parameters are summarized in

Table I. A single crystal of compound 8b was mounted quickly in air on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 well-centered reflections in the range 10.0° ≤  $\theta$  ≤ 11.5°. The orientation was checked every 200 measurements, and intensity was checked every 1 h with seven standard reflections. The largest variations were within ±1.7% of the mean. Corrections were introduced for the Lorentz effect and polarization but not for absorption. The structure was solved by direct methods (SHELXS-86) and difference-Fourier calculations (SHELXL-76).<sup>18</sup> Refinement of the occupancy factors indicated that two equally populated structures were present. The structure was refined on  $|F_o|$  by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found by difference-Fourier synthesis or by calculation and then were fixed at ideal coordinates. Refinement converged to  $R = 0.054$ ,  $R_w = 0.050$ , and goodness-of-fit ratio  $S = 2.076$  for 240 parameters refined. The final  $\Delta F$  map was essentially featureless, with a general background below ±0.31 e Å<sup>-3</sup>. The scattering curves for the non-hydrogen atoms<sup>19</sup> and the hydrogen atoms<sup>20</sup> were taken from standard sources.

Atomic coordinates and isotropic thermal parameters for both structures are listed in Table II, and selected bond lengths and angles are compiled in Table III. A figure showing the second occupant of the unit cell and tables of complete bond lengths and angles, anisotropic thermal parameters, fixed hydrogen atom coordinates, and observed and calculated structure factors are included as supplementary material.

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**Registry No.** 1a, 39789-21-4; 1b, 129493-35-2; 3, 135366-83-5; 4, 135366-84-6; 7, 135366-85-7; 8a, 135366-86-8; 8b, 135366-88-0; 9, 39789-20-3; 10, 41235-26-1; 12, 135416-42-1; 13, 135366-89-1; (CH<sub>3</sub>)<sub>2</sub>CHO(TMS), 1825-64-5; [AlCl<sub>4</sub>]<sup>-</sup>[AlCl<sub>2</sub>(THF)<sub>4</sub>]<sup>+</sup>, 64200-55-1; [Cl<sub>3</sub>Al(μ<sub>2</sub>-η<sup>3</sup>-*cis*-1,2-*c*-C<sub>3</sub>H<sub>5</sub>-O-(TMS)AlCl<sub>2</sub>)]<sub>2</sub>, 135366-90-4.

**Supplementary Material Available:** A figure showing the second occupant of the unit cell and tables containing complete bond lengths and angles, anisotropic thermal parameters, and fixed hydrogen atom coordinates (8 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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