The Influence of Bulky Ligands in the Synthesis of Aluminosiloxanes: X-ray Crystal Structures of a Sterically Hindered Silanetriol $RSi(OH)_3$ and the Aluminosiloxanes $[RSiO_3Al\cdot THF]_4$ and $[RSiO(OH)_2]_2AlC(SiMe_3)_3\cdot 3THF$ ($R = (2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)$)[†]

Andreas Klemp, Hagen Hatop, Herbert W. Roesky,* Hans-Georg Schmidt, and Mathias Noltemeyer

Institut für Anorganische Chemie, Georg-August-Universität, Tammannstrasse 4,
D-37077 Göttingen, Germany

Received July 21, 1999

Reactions of the new aminosilanetriol $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)Si(OH)_3$ (**2**) with the trialkylalanes $AlMe_3$ at 0 °C and $(Me_3Si)_3CAlMe_2\cdot THF$ at room temperature in THF afford the new cubic aluminosiloxane $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)SiO_3Al\cdot THF]_4$ (**3**) and the new acyclic aluminosiloxane $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)SiO(OH)_2]_2AlC(SiMe_3)_3\cdot 3THF$ (**4**) in good yield. These compounds have been characterized by mass, IR, and multinuclear NMR spectroscopy. The X-ray structures of **2**−**4** are described. The molecular structure of **3** reveals an $Al_4Si_4O_{12}$ cubic core while the molecular structure of **4** is represented by an acyclic $AlSi_2O_2(OH)_4$ unit. In **4** the silicon atoms containing the hydroxo groups are connected by an O−Al−O unit.

Introduction

Aluminosilicates are part of a wide variety of naturally occurring minerals. They contain the Al−O−Si unit as the basic fragment. Many synthetic and natural zeolites are built upon the same construction principle. Examples of aluminosilicates are feldspars like gismondine $[CaAl_2Si_2O_8(H_2O)]_n$,[1] cancrinite $[Na_6Al_6Si_6O_{24}(CaCO_3)(H_2O)]_n$,[2] and sodalite $[Na_8Al_6Si_6O_{24}(OH)_2(H_2O)]_n$.[3] Although the Al:Si ratio is fixed in these three examples, different structures are found depending on the metal cation. Additionally, among zeolites which are composed of three-dimensional networks of SiO_4 and AlO_4 tetrahedra, there is a large variation of their composition.[4] These different structural properties and compositions give important reactivity differences which are shown in industrial processes: zeolites are used as ion exchangers, molecular sieves, and catalysts.[5] Due to this, it is surprising that the first steps in the synthesis of soluble model compounds for these important and complex materials were made only 20 years ago. The history of the synthesis of anionic aluminosilicates suffered from the absence of suitable synthons. Feher et al. reported the preparation of aluminosilsesquioxanes with $Si_7O_{12}Al$ units using $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$.[6]

Five years ago our group started with the synthesis of silanetriols as synthons for generating soluble model compounds of naturally occurring aluminosilicates. A number of silicates obtained from the reaction of N-bonded silanetriols with various aluminum compounds were structurally characterized.[7] Those silicates can be classified in three structural types: eight-membered ring systems and polyhedral frameworks with drum- or cubane-like cages. In recent years we discovered that the variation of the organic ligand bonded to the silicon of the silanetriols has no substantial influence on the structure of the aluminosilicate. Consequently we prepared a new silanetriol as starting material which contains a $SiMe_2\text{-}i\text{-}Pr$ group instead of the $SiMe_3$ group. The increased steric demand of the substituent should lead to a variation of the structural properties of the resulting aluminosilicates.

Results and Discussion

Preparation of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)Si(OH)_3$ (2). The controlled hydrolysis of the N-substituted silicon trichloride $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)SiCl_3$ (**1**) affords the new silanetriol $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)Si(OH)_3$ (**2**) in good yield. The

---

* To whom correspondence should be addressed.

[†] Dedicated to Professor Jean'ne Shreeve on the occasion of her 65th birthday.

(1) Fischer, K. *Am. Mineral.* **1963**, *48*, 664.

(2) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.

(3) Hoebbel, D.; Garzó, G.; Ujszászi, K.; Engelhardt, G.; Fahlke, B.; Vargha, A. *Z. Anorg. Allg. Chem.* **1982**, *484*, 7.

(4) Liebau, F. *Structural Chemistry of Silicates*; Springer: Berlin, 1985; pp 244−260.

(5) (a) Shannon, R.; Gardner, K. H.; Staley, R. H.; Bergeret, G.; Gallezot, P.; Auroux, A. *J. Phys. Chem.* **1985**, *89*, 4778. (b) Perego, G.; Bellussi, G.; Corno, C.; Taramasso, M.; Buonomo, F.; Esposito, A. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijiama, A., Ward, J. W., Eds.; Studies in Surface Science and Catalysis 28; Elsevier: Amsterdam, 1986, p 129. (c) Camblor, M. A.; Corma, A.; Martinez, A.; Pérez-Pariente, J. *J. Chem. Soc., Chem. Commun.* **1992**, 589. (d) Blasco, T.; Camblor, M. A.; Corma, A.; Peréz-Pariente, J. *J. Am. Chem. Soc.* **1993**, *115*, 11806. (e) Serrano, D. P.; Li, H.-X.; Davis, M. E. *J. Chem. Soc., Chem. Commun.* **1992**, 745. (f) Inui, T.; Makino, Y.; Okazumi, F.; Miyamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 571. (g) Marchenko, L. S.; Levin, D. Z.; Plakhotnik, V. A.; Mortikov, E. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 94; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1986**, *35*, 81. (h) Giannetto, G.; Montes, A.; Gnep, N. S.; Florentino, A.; Cartraud, P.; Guisnet, M. *J. Catal.* **1994**, *145*, 86.

(6) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638.

(7) (a) Ritter, U.; Winkhofer, N.; Schmidt, H.-G.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 591; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 524. (b) Montero, M. L.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2761; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504. (c) Montero, M. L.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1994**, *106*, 2198; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103. (d) Voigt, A.; Murugavel, R.; Parisini, E.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 823; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 748. (e) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918.

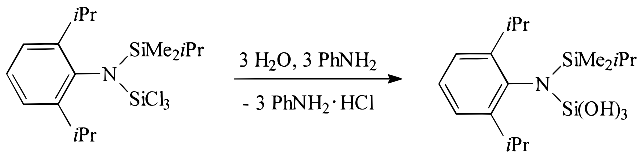
10.1021/ic990861c CCC: $18.00

Table 1

	2	**3**	**4**
empirical formula	$C_{19}H_{37}NO_4Si_2$ incl 0.5 dioxane	$C_{84}H_{152}Al_4N_4O_{16}Si_8$	$C_{56}H_{115}AlN_2O_9Si_7$
fw	399.68	1806.74	1184.11
temp (K)	203(2)	193(2)	200(2)
cryst size (mm)	0.90 × 0.40 × 0.20	1.00 × 0.40 × 0.40	1.00 × 0.60 × 0.60
cryst syst	triclinic	tetragonal	monoclinic
space group	$P\bar{1}$	$I4(1)/a$	$P2_1/n$
a (Å)	10.395(5)	15.415(2)	10.940(10)
b (Å)	14.001(8)	15.415(2)	25.189(5)
c (Å)	16.747(8)	50.725(10)	25.589(6)
α (deg)	96.17(5)	90	90
β (deg)	105.65(5)	90	91.950(19)
γ (deg)	94.11(3)	90	90
cell vol V (Å^3)	2320(2)	11947(3)	7024(2)
Z	4	4	4
ρ_c (g mm^{-3})	1.144	1.005	1.120
μ (mm^{-1})	0.174	0.169	0.196
F(000)	872	3904	2592
2θ range (deg)	3.57−24.95	3.58−20.04	3.57−22.57
data measd, unique	10328, 8088 [R(int) = 0.0823]	11388, 2788 [R(int) = 0.0374]	14842, 9213 [R(int) = 0.0336]
R,[a] wR_2[b]($I > 2\sigma(I)$)	0.0675, 0.1713	0.0694, 0.2146	0.0872, 0.2253
R, wR_2 (all data)	0.0934, 0.1980	0.0811, 0.2596	0.1087, 0.2547
goodness of fit, S[c]	1.016	1.128	1.033
refined param	483	270	676
restraints	0	0	499
largest diff peak, hole (e Å^{-3})	+1.147/−0.694	+0.877/−0.314	+1.614/−1.009

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma(n - p)]^{1/2}$.

Scheme 1



1 **2**

method of hydrolysis has been described previously.[8] The silanetriol **2** has been characterized by elemental analysis, IR, multinuclear NMR, mass spectroscopy, and X-ray diffraction studies. Scheme 1 depicts the synthesis of the silanetriol **2**.

In the IR spectrum of **2** a sharp absorption (3625 cm^{-1}) and a very broad one (3334 cm^{-1}) indicate the presence of OH groups. In addition to the expected resonances of aryl, SiMe$_2$-*i*-Pr, and *i*-Pr protons, the OH signals are observed as a singlet (δ 4.40) in the ^{1}H NMR spectrum. Compound **2** shows two ^{29}Si NMR resonances due to the SiO$_3$ silicon center (δ_{Si} −65.0) and the SiMe$_2$-*i*-Pr group (δ_{Si} 11.1). Moreover, the parent ion is clearly seen in the electron impact mass spectrum.

X-ray Crystal Structure of 2. The molecular structure of **2** is shown in Figure 1. Details of the data collection, structure solution, and refinement are given in Table 1. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules and one dioxane in the asymmetric unit.

The aromatic ring is almost perpendicular with reference to the Si$_2$N plane. The crystal structure of **2** represents the third example of a structurally characterized silanetriol with Si−N bonds. In this compound, there are two types of Si−N bonds, with the shorter bond length (1.704(3) Å) being associated with the silicon atom bearing three oxygen atoms. The other Si−N bond length is substantially longer (1.764(3) Å). This observation is consistent with multiple bonding effects found in compounds containing group 14 and 15 elements that are bonded to electron-withdrawing substituents.[9] The average Si−O bond length (1.627(3) Å) is comparable with that observed for other silanetriols. The observed O−Si−O bond angles in the molecule are 106.33(14)°, 105.51(14)°, and 112.05(15)°. These values are comparable to those found in *t*-BuSi(OH)$_3$,[9] in (Me$_3$Si)$_3$-SiSi(OH)$_3$,[8a] and especially in (2,4,6-Me$_3$C$_6$H$_2$)N(SiMe$_3$)Si(OH)$_3$.[11] Compound **2** is involved in a huge network of intra- and intermolecular hydrogen bonds. A view showing the hydrogen-bonding interactions between the silanetriol molecules is given in Figure 2.

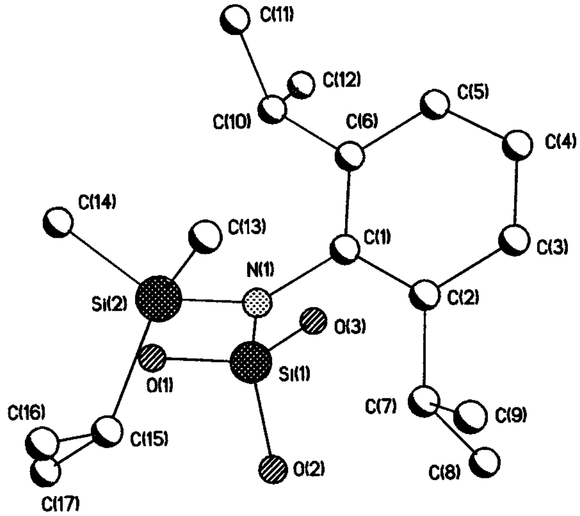


Figure 1. Molecular crystal structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−O(1) 1.634(3), Si(1)−O(2) 1.628(3), Si(1)−O(3) 1.619(3), Si(1)−N(1) 1.704(3), Si(2)−N(1) 1.764(3); Si(1)− N(1)−Si(2) 122.8(2), C(1)−N(1)−Si(1) 118.0(2), C(1)−N(1)−Si(2) 119.2(2), O(1)−Si(1)−O(2) 106.33(14), O(1)−Si(1)−O(3) 105.51(14), O(2)−Si(1)−O(3) 112.05(15).

---

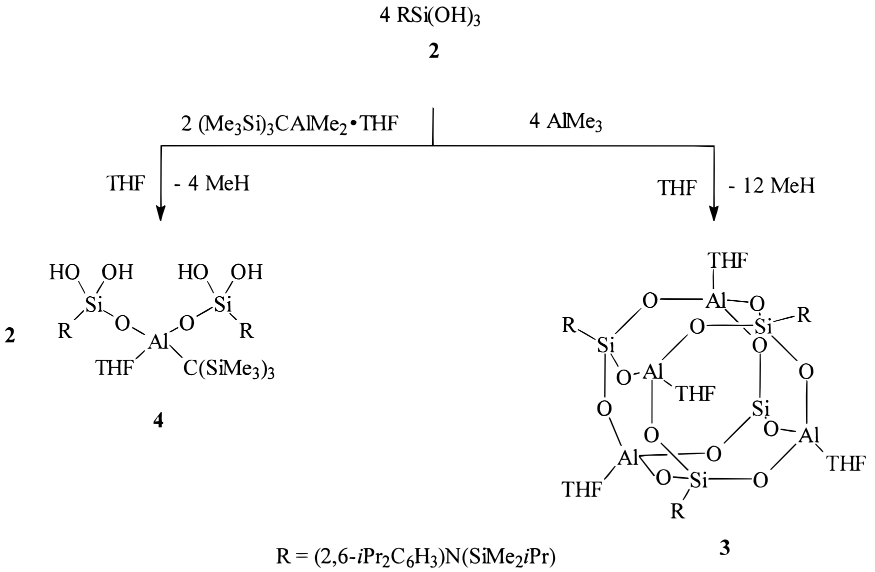
[8] (a) Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem.* **1992**, *104*, 670; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599. (b) Takiguchi, T. *J. Am. Chem. Soc.* **1959**, *81*, 2359.

[9] Reed, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

[10] Al-Juaid, S. S.; Buttrus, N. H.; Damja, R. I.; Derouiche, Y.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1989**, *371*, 287.

[11] Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298.

Scheme 2



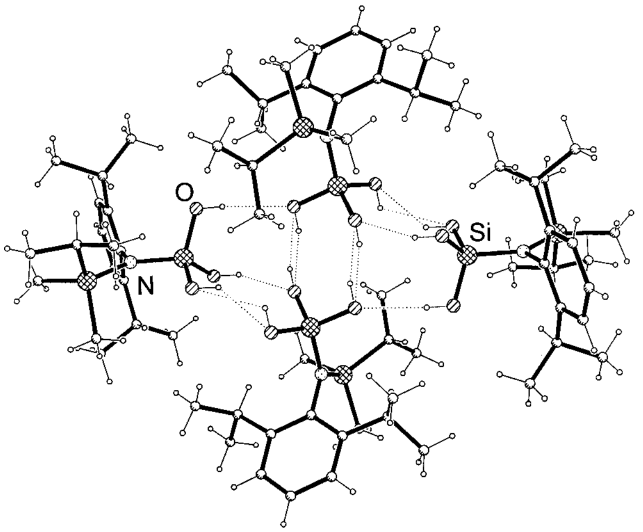


Figure 2. Crystal packing of **2** showing the hydrophilic interior and hydrophobic exterior.

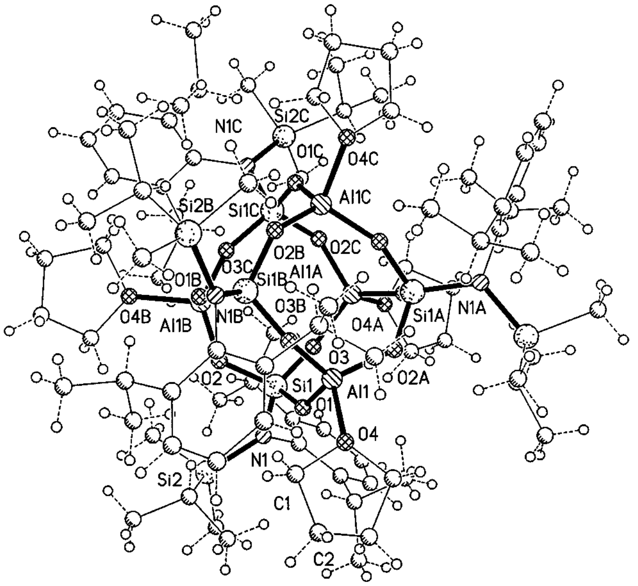


Figure 3. Molecular crystal structure of **3**. Selected bond distances (Å) and angles (deg): Si(1)−O(1) 1.620(4), Si(1)−O(2) 1.624(4), Si(1)−O(3) 1.608(4), Al(1)−O(1) 1.714(4), Al(1)−O(2) 1.710(4), Al(1)−O(3) 1.704(4), Al(1)−O(4) 1.866(4), Si(1)−N(1) 1.736(4), Si(2)−N(1) 1.750(4); O(1)−Si(1)−O(2) 108.9(2), O(3)−Si(1)−O(1) 109.0(2), O(3)−Si(1)−O(2) 112.7(2), O(2)−Al(1)−O(1) 116.8(2), O(3)−Al(1)−O(2) 113.4(2), O(3)−Al(1)−O(1) 115.8(2).

Preparation of [(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_2$-*i*-Pr)SiO$_3$Al·THF]$_4$ (3) and [(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_2$-*i*-Pr)SiO(OH)$_2$]$_2$AlC(SiMe$_3$)$_3$·3THF (4). Addition of AlMe$_3$ to a solution of the silanetriol **2** in 1:1 stoichiometry in tetrahydrofuran at 0 °C leads to the cubic aluminosiloxane **3** (Scheme 2). From this result, one can assume that the steric demand of **2** is not sufficient to produce new structural motifs. Consequently, we carried out the reaction of the silanetriol **2** with (Me$_3$Si)$_3$CAlMe$_2$·THF in a 2:1 stoichiometry at room temperature. The resulting product **4** is a disilanediol bridged by an O−Al−O unit shown in Scheme 2. In contrast to the reaction of the silanetriol **2** and AlMe$_3$, this reaction affords an intermediate containing two hydroxo groups on each silicon.

The aluminosiloxanes **3** and **4** are fully characterized by IR, electronic impact mass spectroscopy (EI), multinuclear NMR, and single-crystal X-ray structural determination. In the IR spectrum of **4**, two sharp absorptions (3660 and 3632 cm^{-1}) and a broad one (3384 cm^{-1}) indicate the presence of OH groups. However, no absorption for OH groups is detected in the IR spectrum of **3**. In the ^{1}H NMR spectra of **3** and **4** the expected resonances due to aryl, SiMe$_2$-*i*-Pr, and *i*-Pr protons are observed. Additionally, a singlet (δ 5.35) for hydroxo protons is detected in the ^{1}H NMR spectrum of **4**, while no corresponding signal is found for **3**. The ratio of the intensities for compound **4** indicate that only one OH group of each silicon atom has been involved in the reaction. Each ^{29}Si NMR spectrum gives two signals due to the SiO$_3$ silicon centers (**3**, δ −80.6; **4**, δ −71.9) and the SiMe$_2$-*i*-Pr groups (**3**, δ 5.1; **4**, δ 8.0). Moreover, for compound **3** a parent ion is seen in the electron impact mass spectrum; in the case of **4** only smaller fragment ions are found.

X-ray Single-Crystal Structure of 3. The molecular structure of **3** is shown in Figure 3. Details of the data collection, structure solution, and refinement are given in Table 1. The compound crystallizes in the tetragonal space group *I*4(1)/*a* as a tetrahydrofuran solvate. A cubic polyhedron can be defined with four silicon and four aluminum atoms occupying the alternate corners. The Si···Al edges are bridged by an oxygen atom in a

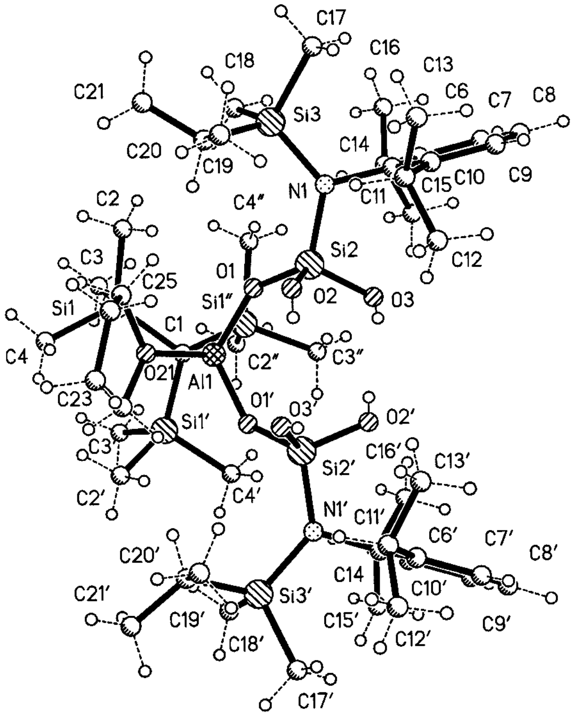


Figure 4. Molecular crystal structure of **4**. Selected bond distances (Å) and angles (deg): Al(1)−O(1) 1.742(4), Al(1)−O(1′) 1.744(4), Al(1)−O(21) 1.927(4), Al(1)−C(1) 1.994(5), Si(2)−O(1) 1.610(3), Si(2)−O(2) 1.647(4), Si(2)−O(3) 1.625(4), Si(2’)−O(1′) 1.604(4), Si(2′)−O(2′) 1.617(4), Si(2′)−O(3′) 1.654(4), Si(2)−N(1) 1.729(4), Si(3)−N(1) 1.758(5), Si(2′)−N(1′) 1.724(5), Si(3′)−N(1′) 1.757(5); O(1)−Al(1)−O(1′) 115.4(2), O(1′)−Al(1)−O(21) 99.0(2), O(1)−Al(1)−O(21) 99.4(2), O(1)−Al(1)−C(1) 114.5(2), O(1′)−Al(1)−C(1) 115.1(2), O(21)−Al(1)−C(1) 110.9(2), Si(2)−O(1)−Al(1) 140.4(2), Si(2′)−O(1′)−Al(1) 139.5(2), Si(2)−N(1)−Si(3) 128.3(3), Si(2′)−N(1′)−Si(3′) 130.3(3), O(1)−Si(2)−O(3) 108.3(2), O(1)−Si(2)−O(2) 106.3(2), O(3)−Si(2)−O(2) 111.3(2), O(1′)−Si(2′)−O(3′) 103.7(2), O(1′)−Si(2′)−O(2′) 110.2(2), O(3′)−Si(2′)−O(2′) 110.6(2).

μ fashion. The cube is composed of six puckered $Al_2Si_2O_4$ eight-membered rings, each of which exists in a C_4 crownlike conformation. The average bond length within the polyhedron (1.713(4) Å) is considerably shorter than the exocyclic Al−O bond length (1.866(4) Å). This is consistent with the different bonding types within and outside the framework. The average Si−O bond length (1.617(4) Å) is shorter than the Si−O distances observed for the parent silanetriol **2**. This is consistent with the observations made in other cubic aluminosiloxanes.[7a,b,e] The Al−O−Si angles are in the range 133.2−151.9°. A comparable situation is found in the structurally related $[NMe_4]_4[Al_4Si_4O_{12}(OH)_8]\cdot 24H_2O$.[12]

X-ray Single-Crystal Structure of 4. The molecular structure of **4** is shown in Figure 4. Details of the data collection, structure solution, and refinement are given in Table 1. The compound crystallizes in the monoclinic space group $P2_1/n$ with two additional molecules of tetrahydrofuran in the asymmetric unit. The lattice tetrahydrofuran molecules do not show any substantial interaction with the aluminosiloxane molecule. The structure consists of an $AlSi_2O_2(OH)_4$ unit. The silicon atoms containing the OH groups are connected by an O−Al−O bridge. The cis conformation of the hydroxo groups is also found in the tetrahydroxodisiloxane $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)Si(OH)_2]_2O$.[13] The aluminum atom in **4** possesses a distorted tetrahedral environment. Without regard to the slightly longer Al−O bond length of the coordinated tetrahydrofuran (1.927(4) Å), the average Al−O bond length (1.740(4) Å) is comparable to the Al−O distances (1.720 Å) found in the dimeric ring system $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_2(OH)]_2Al_2(i\text{-}Bu)_2(THF)_2$.[7c] The oxygen-bearing silicon atoms possess a tetrahedral coordination sphere with angles from 103.7(2)° to 111.3(2)°. The average distance to the hydroxo oxygen atoms is 1.64 Å while the average Si−O bond length to the bridging oxygen atoms is somewhat shorter (1.61 Å). Compound **4** can be regarded as an intermediate in the synthesis of the as yet known aluminosiloxanes such as compound **3**. Due to the large steric demand of the $(Me_3Si)_3C$ ligand, the reaction can be stopped at the intermediate state of the acyclic system.

Conclusion

The introduction of bulky ligands in silanetriols using aluminum compounds does not lead to new structural systems of aluminosiloxanes. However, in the case of the sterically demanding $(Me_3Si)_3C$ ligand, an aluminosiloxane with a new structural motif is obtained. Furthermore, the hydroxo groups in **4** could make it possible to synthesize new bimetallic molecules.

Experimental Section

General Experimental Procedures. All reactions were carried out using standard Schlenk techniques. Solvents were purified and dried according to standard methods. The samples for spectral measurements were prepared in a drybox. Trimethylaluminum (2 M solution in hexanes, Aldrich) and trimethylgallium (Witco) were used as received. The trichlorosilane and $(Me_3Si)_3CAlMe_2\cdot THF$[14] were prepared as described. Aniline (Aldrich) was refluxed and distilled over CaH_2. NMR spectra were recorded on a Bruker AM 200 or a Bruker AM 250 instrument, and the chemical shifts are reported with reference to TMS. The upfield shifts are negative. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer (only the strong absorption bands are given). Mass spectra were obtained on Finnigan MAT CH5 and Finnigan MAT 95 spectrometers. Melting points were obtained on a HWS-SG-3000 or a Bühler SPA-1 apparatus. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen.

Preparation of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)Si(OH)_3$ (2). To a suspension of water (12.9 g, 0.72 mol) and $PhNH_2$ (62.1 g, 0.72 mol) in diethyl ether (400 mL) was added a solution of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)SiCl_3$ (97.7 g, 0.24 mol) in Et_2O (200 mL) dropwise at 0 °C with vigorous stirring. The reaction mixture was stirred for 12 h and allowed to come to room temperature. The precipitated $PhNH_3Cl$ was filtered off, and the solvent was removed from the filtrate in vacuo, affording $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)Si(OH)_3$ as an off-white solid, which was purified by recrystallization in pentane (150 mL).Yield: 58.7 g (71%). Mp: 149 °C. ^1H NMR (200.13 MHz, C_6D_6, 25 °C): δ 7.04 (m, 3 H, Ar−*H*), 4.40 (s, 3 H, O*H*), 3.72 (sept, 2 H, $^3J(H,H) = 6.8$ Hz, $CCH(CH_3)_3$), 1.31 (m, 1 H, $SiCH(CH_3)_2$), 1.26 (d, 6 H, $^3J(H,H) = 6.8$ Hz, $CCH(CH_3)_2$), 1.22 (d, 6 H, $^3J(H,H) = 6.8$ Hz, $CCH(CH_3)_2$), 1.07 (d, 6 H, $^3J(H,H) = 6.8$ Hz, $SiCH(CH_3)_2$), 0.14 (s, 6 H, $SiCH_3$). ^{29}Si NMR (49.63 MHz, $CDCl_3$, 25 °C): δ 11.1 ($SiCH(CH_3)_2$), −65.0 ($Si(OH)_3$); IR(KBr, Nujol): $\tilde{\nu}$ 3625, 3334, 1425, 1365, 1313, 1254, 1179, 1104, 953, 931, 803, 771, 723, 676 cm^{-1}. MS (EI) *m*/*e* (%): 355 [M, 3], 312 [M − (*i*-Pr), 100]. Anal. Calcd for $C_{17}H_{33}NO_3Si_2$: C, 57.4; H, 9.4; N; 3.9. Found: C, 57.7; H, 9.2; N, 3.9.

Preparation of $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)SiO_3Al\cdot THF]_4$ (3). A solution of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_2\text{-}i\text{-}Pr)Si(OH)_3$ (1.76 g, 4.95 mmol) in THF (40 mL) was cooled to 0 °C. To this was added $AlMe_3$ (2.48 mL, 4.95 mmol of 2 M solution in hexane) dropwise. The reaction

---

[12] Smolin, Yu. I.; Shepelev, Yu. F.; Ershow, A. S.; Hoebbel, D. *Dokl. Akad. Nauk SSSR* **1987**, *297*,1377; *Chem. Abstr.* **1988**, *108*, 229950f.

[13] Murugavel, R.; Böttcher, P.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W.; Parisini, E.; Teichert, M.; Noltemeyer, M. *Chem. Commun.* **1996**, 2417.

[14] Schnitter, C.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Röpken, C.; Parisini, E.; Sheldrick, G. M. *Chem. Eur. J.* **1997**, *3*, 1783.

mixture was allowed to attain room temperature and stirred for 12 h. The solvent was removed in vacuo affording $[(2,6\text{-}i\text{-Pr}_2C_6H_3)N(SiMe_2\text{-}i\text{-Pr})SiO_3Al\cdot THF]_4$ as a white solid. The product was recrystallized from 2:1 v/v hexane and THF. Yield: 0.95 g (78%). Mp: >300 °C. ^{1}H NMR (200.12 MHz, THF-d_8, 25 °C): δ 6.96 (m, 3 H, Ar−*H*), 3.92 (sept, 2 H, ^3J(H,H) = 6.9 Hz, CC*H*(CH$_3$)$_2$), 1.27 (m, 1 H, SiC*H*(CH$_3$)$_2$), 1.25 (d, 6 H, ^3J(H,H) = 6.9 Hz, CCH(C*H*$_3$)$_2$), 1.17 (d, 6 H, ^3J(H,H) = 6.9 Hz, CCH(C*H*$_3$)$_2$), 0.83 (d, 6 H, ^3J(H,H) = 7.4 Hz, Si(CH(C*H*$_3$)$_2$), −0.09 (s, 6 H, Si(C*H*$_3$)). ^{29}Si NMR (79.46 MHz, THF-d_8, 25 °C): δ 5.1 (SiMe$_2$-*i*-Pr), −80.6 (SiO$_3$). IR(KBr, Nujol): $\bar{\nu}$ 1577, 1438, 1360, 1322, 1313, 1245, 1185, 1108, 1092, 1043, 1022, 1003, 960, 937, 911, 880, 825, 803,766, 678, 645, 615, 564, 542 cm^{-1}. MS (EI) *m*/*e* (%): 1474 [M − (*i*-Pr) − 4THF, 30], 162 [2,6-*i*-Pr$_2$C$_6$H$_4$, 72], 42 [C$_3$H$_6$, 100]. Anal. Calcd for $C_{84}H_{152}Al_4N_4O_{16}Si_8$: C, 55.8; H, 8.5; N; 3.1. Found: C, 55.7; H, 8.1; N, 3.3.

Preparation of $[(2,6\text{-}i\text{-Pr}_2C_6H_3)N(SiMe_2\text{-}i\text{-Pr})SiO(OH)_2]_2AlC(SiMe_3)_3\cdot 3THF$ (4). To a solution of $(2,6\text{-}i\text{-Pr}_2C_6H_3)N(SiMe_2\text{-}i\text{-Pr})Si(OH)_3$ (3.08 g, 8.64 mmol) in THF (40 mL) was added $(Me_3Si)_3CAlMe_2\cdot THF$ (1.56 g, 4.32 mmol) in THF (40 mL) at room temperature. The evolution of methane ceased within 25 min, and the reaction mixture was stirred for another 6 h. Subsequently, the solvent was removed in vacuo and the white residue was washed with hexane (30 mL), affording $[(2,6\text{-}i\text{-Pr}_2C_6H_3)N(SiMe_2\text{-}i\text{-Pr})SiO(OH)_2]_2AlC(SiMe_3)_3\cdot 3THF$ as a white solid. Yield: 4.06 g (85%). Mp: 100 °C. ^{1}H NMR (200.13 MHz, THF-d_8, 25 °C): δ 7.01 (m, 6 H, Ar−*H*), 5.34 (s, 1H, O*H*), 5.10 (s, 2 H, O*H*), 4.91 (s, 1 H, O*H*), 3.62 (m, 4 H, CC*H*(CH$_3$)$_2$), 1.23 (m, 2 H, SiC*H*(CH$_3$)$_2$), 1.20 (m, 24 H, CCH(C*H*$_3$)$_2$), 0.86 (d, ^3J(H,H) = 7.4 Hz, 6 H, CCH(C*H*$_3$)$_2$), 0.84 (d, ^{3}J(H,H) = 7.4 Hz, 6 H, CCH(C*H*$_3$)$_2$), 0.32 (s, 27 H, C(Si(C*H*$_3$)$_3$)$_3$), 0.11 (s, 12 H, SiC*H*$_3$). ^{29}Si NMR (79.46 MHz, THF-d_8, 25 °C): δ 8.0 (Si(CH$_3$)$_3$), −3.8 (C(Si(CH$_3$)$_3$)$_3$), −71.9 (SiO(OH)$_2$). IR (KBr, Nujol): $\bar{\nu}$ 3660, 3632, 3384, 1645, 1378, 1366, 1313, 1257, 1170, 1104, 1052, 1024, 934, 860, 805, 722, 669, 574 cm^{-1}. MS (EI) *m*/*e* (%): 1067 [M − SiMe$_2$-*i*-Pr − Me, 21], 162 [2,6-*i*-Pr$_2$C$_6$H$_4$, 100]. Anal. Calcd for $C_{56}H_{115}AlN_2O_9Si_7$: C, 56.8; H, 9.8; N, 2.4. Found: C, 55.2; H, 9.9; N, 2.5.

X-ray Structure Determination of 2−4. Colorless single crystals suitable for X-ray diffraction studies were grown from hexane/1,4-dioxane for **2** at 5 °C. Single crystals of compounds **3** and **4** were obtained from THF/hexane at 5 °C and room temperature, respectively. A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil.[15] Diffraction data were collected on a Siemens-Stoe AED diffractometer (at −70 °C for **2** and **4**, and at − 80 °C for **3**), with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods[16] using and refined against F^2 on all data by full-matrix least squares with SHELXL-93.[17] All non-hydrogen atoms were refined anisotropically. In the case of **4**, a total of 499 restraints were applied to eventually disordered isopropyl groups. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model (in the case of hydroxo groups with torsion angles). Other details of the data collection, structure solution, and the refinement are listed in Table 1.

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft and the Witco GmbH for support of this work.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990861C

---

(15) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *46*, 615.

(16) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(17) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1993.