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Synthesis, Spectral Studies, and Structural Characterization of a New Organosilanetriol, Its Amine Complexes, and a Surface Lewis Basic Cubic Aluminosilicate[§]

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The new trichlorosilane 2,6-$Et_2C_6H_3N(SiMe_3)SiCl_3$ (**2**) on controlled hydrolysis yields 2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (**3**). X-ray diffraction analysis of **3** reveals a rare structure type of aggregation where eight molecules of the silanetriol form an octameric cage through intermolecular O−H···O hydrogen bonding. Reaction of **3** with piperazine (PIP), 4,4′-bipyridine (BPY), and 1,4-diazabicyclo[2,2,2]octane (DABCO) yields [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}·{PIP}] (**4**), [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}·{BPY}] (**5**), and [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}·{DABCO}] (**6**), respectively. Treatment of **6** with HAl^iBu_2 affords the cubic aluminosiloxane [2,6-$Et_2C_6H_3N(SiMe_3)SiO_3Al(DABCO)]_4$·1,4-dioxane (**7**). The aluminum centers on the cubic core are coordinated by DABCO molecules in a monodentate fashion.

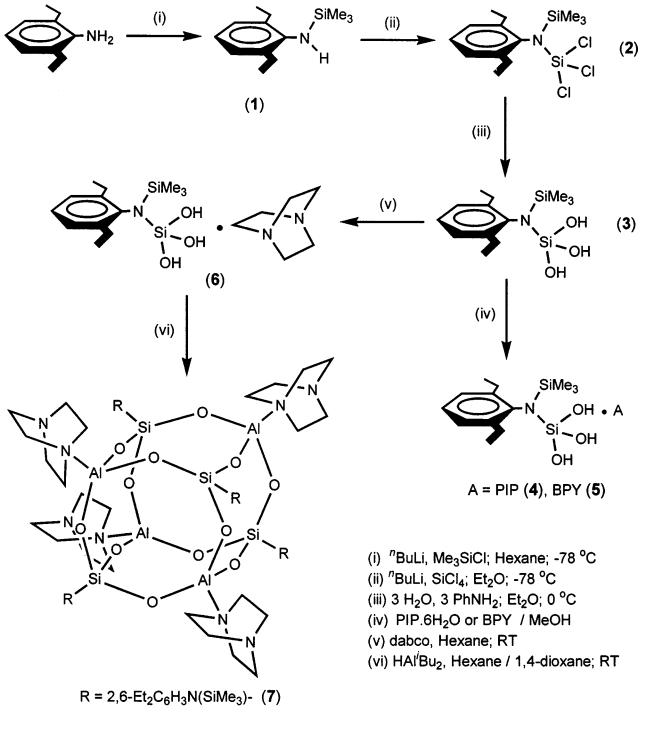
[4]Introduction

There has been a considerable interest in recent years in the synthesis of discrete silanols,[1] especially those containing three hydroxyl groups on the same silicon center (silanetriols) in view of their use as building blocks for metallosiloxanes.[2] Silanols are difficult to synthesize and handle under normal laboratory conditions due to the tendency of the Si−OH groups to self-condense and form siloxane rings and chairs. Despite these difficulties, a variety of silanetriols have been successfully synthesized and characterized in recent years.[3] The three −OH groups in these compounds often organize in the solid state to form different types of aggregate structures. We have recently shown that a somewhat less stable N-bonded silanetriol could be further stabilized by forming complexes with diamines such as 4,4′-bipyridine, DABCO, and piperazine.[4] Continuing our studies on silanetriols, we report herein the synthesis and characterization of a new N-bonded silanetriol and its reaction chemistry.

Results and Discussion

2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (3). Using the synthetic methodology outlined in Scheme 1, a new silanetriol, 2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$, was synthesized in a three-step procedure starting from 2,6-$Et_2C_6H_3NH_2$. Initially 2,6-diethylaniline was treated with 1 equiv of ^nBuLi at −78 °C to yield its mono-lithium salt. Without isolating, this monolithium salt was treated with trimethylsilyl chloride to yield the secondary amine 2,6-$Et_2C_6H_3N(SiMe_3)H$ (**1**). The lithium salt of **1** when reacted with $SiCl_4$ yields 2,6-$Et_2C_6H_3N(SiMe_3)SiCl_3$ (**2**). Compounds **1** and **2** were characterized by IR, CHN, EI-MS, and NMR spectroscopic techniques. The electron

Scheme 1. Synthesis of 1−7



[§] Dedicated to Professor G. Mehta on his 62nd birthday.

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(1) (a) Lickiss, P. D. *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 2001; Vol. 3, Chapter 12, Polysilanols; pp 695−744. (b) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147.

(2) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205. (b) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183. (c) Murugavel, R.; Bhattacharjee, M.; Roesky, H. W. *Appl. Organomet. Chem.* **1999**, *13*, 227.

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Table 1. ^{29}Si NMR Chemical Shifts of Nitrogen-Bonded Trichlorosilanes and Silanetriols

	δ $NSiMe_3$	δ $SiCl_3$	δ $Si(OH)_3$	ref
$C_6H_5N(SiMe_3)SiCl_3$	12.8	−28.2		3l
2,6-$Me_2C_6H_3N(SiMe_3)SiCl_3$	12.5	−28.2		3l
2-^{i}Pr-6-$MeC_6H_3N(SiMe_3)SiCl_3$	12.2	−27.9		3l
2,4,6-$Me_3C_6H_2N(SiMe_3)SiCl_3$	12.3	−28.3		3l
2,6-$^i Pr_2C_6H_3N(SiMe_3)SiCl_3$	12.3	−27.5		3b
2,6-$Et_2C_6H_3N(SiMe_3)SiCl_3$ (**2**)	11.9	−28.2		*a*
2,6-$Me_2C_6H_3N(SiMe_3)Si(OH)_3$	7.7		−66.2	3l
2-^{i}Pr-6-$MeC_6H_3N(SiMe_3)Si(OH)_3$	7.5		−65.3	3l
2,4,6-$Me_3C_6H_2N(SiMe_3)Si(OH)_3$	7.3		−65.8	3l
2,6-$^i Pr_2C_6H_3N(SiMe_3)Si(OH)_3$	3.8		−67.3	3b
2,6-$^i Pr_2C_6H_3N(SiMe_2{}^iPr)Si(OH)_3$	11.1^b		−65.0	3m
2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (**3**)	2.7		−70.7	*a*
[{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}{PIP}] (**4**)	7.7		−63.4	*a*
[{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}] (**5**)	4.7		−66.4	*a*
[{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}] (**6**)	5.6		−66.0	*a*

[a] This work. [b] $SiMe_2{}^iPr$ resonance.

impact mass spectra of **1** and **2** yield the molecular ion peaks [M^+] at *m/z* 221 and 355, respectively. The ^{29}Si NMR spectral data for **2** (δ 11.9 and −28.2 ppm) compare well with the resonances reported for similar silyltrichlorides (Table 1).[3]

Hydrolysis of **2** was carried out by addition of 3 equiv of H_2O to **2** in the presence of aniline to obtain 2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (**3**) as a beige solid in 96% yield (Scheme 1). The product is moderately air- and moisture-stable (turns brown after a few weeks in air) and is highly soluble in common organic solvents. In the EI mass spectrum, the M^+ ion appears at *m/z* 299. The infrared spectrum of **3** shows a strong, broad absorption band at 3368 cm^{-1}, indicating that all three −OH groups are probably involved in hydrogen bonding.[5] The ^{1}H and ^{29}Si NMR spectral data are consistent with the formulation of **3** and compare well with the reported chemical shifts for the other N-bonded silanetriols (Table 1).[3]

A perspective view of one of the silanetriol molecules in the asymmetric part of the unit cell is shown in Figure 1. The asymmetric part of the unit cell of **3** is made up of an octameric cage consisting of eight monomeric silanetriol molecules (formed through extensive hydrogen-bonding between the Si−OH groups of the silanetriol molecules) and a solvent toluene molecule. The hydrophobic 2,6-$Et_2C_6H_3N(SiMe_3)$− organic groups form the surface of the cage-like structure and shield the hydrophilic hydrogen-bonded Si−OH core. The O···O hydrogen bond distances and O−H···O angles in the cluster lie in the range 2.637−2.889 Å and 149−178°, respectively. The 24 different Si−O bond lengths in the cluster are in the range 1.598−1.661 Å. The O−Si−O bond angles lie in the range 102.2−112.5°. These values are in good agreement with the corresponding bond distances and angles found for other silanetriols (vide infra).[3]

Amine Adducts 4−6. The reaction of silanetriol **3** with piperazine hexahydrate, 4,4′-bipyridine, or DABCO in methanol affords [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}-{PIP}] (**4**), [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}] (**5**), or [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}{DABCO}] (**6**), respectively. Amine complexes **4−6** have been characterized by elemental analysis and IR, ^{1}H NMR, and ^{29}Si NMR spectroscopy. The IR and NMR spectral data for **4−6** are consistent with the formulation.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with one silanetriol and one piperazine molecule in the asymmetric unit (Figure 2). The octameric structure of silanetriol in **3** breaks down to lower aggregates in the presence of added amines, which interact with amines through H-bonds to form extended polymeric solids. Thus, the overall structure of **4** can be described as a polymeric arrangement of molecular subunits based on hydrogen bonding (see Supporting Information). Two molecules of silanetriols form a dimer via two intermolecular hydrogen bonds (O(3)−H(3O)···O(2)), which results in the formation of eight-membered cyclic subunits. Each of these subunits is linked by O−H···N and N−H···O hydrogen bonding. The silanetriol hydroxyl groups O(1)−H(1O) and O(2)−H(2O) form hydrogen bonds with the piperazine nitrogen atoms N(3) and N(2), respectively.

The asymmetric part in the molecular structure of **5** shows the presence of one silanetriol and one BPY molecule (Figure 3). As in the case of **4**, the hydroxyl group O(2)−H(2) from one silanetriol interacts with

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(3) (a) Toshio, T. *J. Am. Chem. Soc.* **1959**, *75*, 2339. (b) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Noltemeyer, M.; Reller, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352. (c) Cerveau, G.; Corriu, R. J. P.; Dabiens, B.; Le Bideau, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4533. (d) Cerveau, G.; Chappellet, S.; Corriu, R. J. P.; Dabiens, B.; Le Bideau, J. *Organometallics* **2002**, *21*, 1560. (e) Unno, M.; Tanaka, T.; Matsumoto, H. *J. Organomet. Chem.* **2003**, *686*, 175. (f) Lindemann, H. M.; Schneider, M.; Neumann, B.; Stammler, H.-G.; Stammler, A.; Jutzi, P. *Organometallics* **2002**, *21*, 3009. (g) Nolte, J.-O.; Schneider, M.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Organometallics* **2003**, *22*, 1010. (h) Malisch, W.; Lankat, R.; Schmitzer, S.; Reising, J. *Inorg. Chem.* **1995**, *34*, 5701. (i) Ishida, H.; Koenig, J. L.; Gardner, K. C. *J. Chem. Phys.* **1982**, *77*, 5748. (j) Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599. (k) Jutzi, P.; Strassburger, G.; Schneider, M.; Stammler, H.-G.; Neumann, B. *Organometallics* **1996**, *15*, 2842. (l) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298. (m) Klemp, A.; Hatop, H.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem.* **1999**, *38*, 5832. (n) Schneider, M.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Monats. Chem.* **1999**, *130*, 33. (o) Jutzi, P.; Schneider, M.; Stammler, H.-G.; Neumann, B. *Organometallics* **1997**, *16*, 5377. (p) Seyferth, D.; Rudie, C. N.; Nestle, M. O. *J. Organomet. Chem.* **1979**, *178*, 227. (q) Ritter, U.; Winkhofer, N.; Schmidt, H.-G.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 524. (r) Damja, R. I.; Eaborn, C. *J. Organomet. Chem.* **1985**, *290*, 267. (s) Buttrus, N. H.; Damja, R. I.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *Chem. Commun.* **1985**, 1385. (t) Morrison, C. A.; Rankin, D. W. H.; Robertson, H. E.; Lickiss, P. D.; Masangane, P. C. *J. Chem. Soc., Dalton Trans.* **1999**, 2293. (u) 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. (v) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682. (w) Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 10454.

(4) Prabusankar, G.; Murugavel, R.; Butcher, R. J. *Organometallics* **2004**, *23*, 2305.

(5) Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley-VCH: Great Britain, 1980.

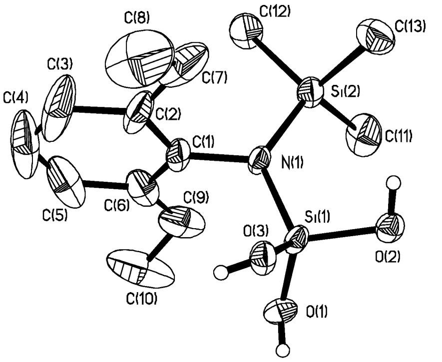

Figure 1. ORTEP of 2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (**3**) at 40% probability level. Selected bond lengths and angles: Si(1)−O(1) 1.620(4), Si(1)−O(2) 1.624(3), Si(1)−O(3) 1.651(3), Si(1)−N(1) 1.704(3), Si(2)−N(1) 1.754(3) Å, O(1)−Si(1)−O(2) 110.0(2), O(3)−Si(1)−N(1) 112.9(2), O(1)−Si(1)−O(3) 110.2(2), C(1)−N(1)−Si(1) 115.3(3), O(2)−Si(1)−O(3) 104.1(2), C(1)−N(1)−Si(2) 119.3(3), O(1)−Si(1)−N(1) 111.0(2), Si(1)−N(1)−Si(2) 125.4(2), O(2)−Si(1)−N(1) 108.5(2)°.

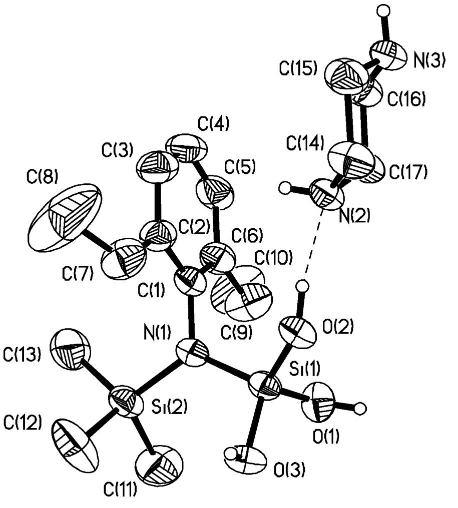

Figure 2. ORTEP of [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}·{PIP}] (**4**) at 40% probability level. Selected bond lengths and angles: Si(1)−O(1) 1.616(2), Si(1)−O(2) 1.620(2), Si(1)−O(3) 1.613(2), Si(1)−N(1) 1.721(2), Si(2)−N(1) 1.746(2), Å; O(3)−Si(1)−O(1) 107.4(1), O(3)−Si(1)−N(1), 108.8(1), O(3)−Si(1)−O(2) 107.8(1), O(1)−Si(1)−N(1), 109.4(1), O(1)−Si(1)−O(2) 112.1(1), O(2)−Si(1)−N(1), 111.3(1), C(1)−N(1)−Si(2) 118.3(2), C(1)−N(1)−Si(1), 118.3(2), Si(1)−N(1)−Si(2) 123.4(1)°.

O(1), leading to the formation of a silanetriol dimer. Each silanetriol dimer unit interacts with two BPY molecules on either side, leading to the formation of a zigzag chain-like structure (see Supporting Information). The Si−O bond distances (1.600(3)−1.626(2) Å) and O−Si−O bond angles (105.3(4)−112.6(2)°) are comparable with those found for **3**. A comprehensive comparison of the structurally characterized silanetriols is listed in Table 2.[3]

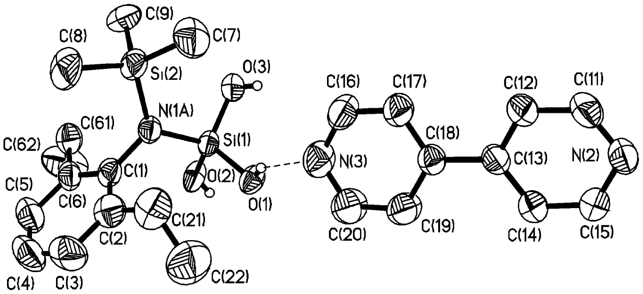

Figure 3. ORTEP of [{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}·{BPY}] (**5**) at 40% probability level. Selected bond lengths and angles: Si(1)−O(1) 1.626(2), Si(1)−O(2) 1.600(3), Si(1)−O(3) 1.607(3), Si(1)−N(1) 1.708(2), Si(2)−N(1) 1.749(3) Å; O(2)−Si(1)−O(3) 112.6(2), O(1)−Si(1)−N(1) 115.2(1), O(2)−Si(1)−O(1) 105.3(1), O(3)−Si(1)−O(1) 110.6(1), O(2)−Si(1)−N(1) 108.2(1), O(3)−Si(1)−N(1) 105.1(1)°.

[2,6-$Et_2C_6H_3N(SiMe_3)SiO_3Al(DABCO)]_4$·1,4-dioxane (7). Although aluminosilicates are widely found in nature and have achieved great practical and commercial significance as zeolites, there are only a few soluble derivatives of these compounds.[6] However, these molecules are not suitable for the construction of extended structures by the sol−gel or any other suitable processes because of the presence of stable Si−C or Si−N bonds. In an attempt to synthesize ideal precursors for rational construction of aluminosilicate superstructures, we used compound **6** as the building block to synthesize the desired aluminosilicate. Addition of HAl^iBu_2 to **6** in *n*-hexane/1,4-dioxane yields moderately stable [2,6-$Et_2C_6H_3N(SiMe_3)SiO_3Al(DABCO)]_4$·1,4-dioxane (**7**). The IR spectrum shows absorptions at 944 and 1077 cm^{-1}, attributable to Al−O−Si stretching. The ^{29}Si NMR chemical shift for the SiO_3 silicon centers in **7** appears at δ −80.8 ppm.

Crystals suitable for diffraction studies were grown from a hexane/dioxane mixture at 0 °C. The molecular structure of **7** comprises a cubic polyhedral structure with an $Al_4Si_4O_{12}$ core (Figure 4).[7] Four silicon and four aluminum atoms occupying the alternate corners of the cube are bridged by 12 μ_2-O ligands, defining the core structure. Thus, there are six $Al_2Si_2O_4$ eight-membered rings that define the faces of the cube, with each of these rings adopting a pseudo-C_4 crown conformation. The aluminum centers of the cubic polyhedra are coordinated by DABCO ligands in a monodentate fashion. The $Al_4Si_4O_{12}$ polyhedron is completely enclosed by 2,6-$Et_2C_6H_3N(SiMe_3)$− and DABCO groups, thus leading to a high solubility of this compound even in nonpolar solvents such as hexane. In addition, the absence of any interactions between the molecules in the lattice is attributable to the steric bulk of the groups wrapped around the cube. The average Si−O bond length (1.61(2) Å) is shorter than the Si−O distances observed for the parent silanetriol **3**. The Al−O bond length falls in the range 1.67(2)−1.77(2) Å, and the Al−N bond length is 1.99(3) Å. The average Si···Al edge length is 3.13 Å. The average Si−O−Al angle formed is 140.8(12)°. The body diagonal of the Al_4Si_4 cube is approximately 5.43 Å. The observed bond lengths and angles are within the range of the corresponding values for reported aluminosilicate cubes. An interesting aspect of this compound is the presence of four DABCO molecules on the surface of the cube. The presence of an uncoordinated nitrogen atom

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(6) (a) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918. (b) Montero, M. L.; Voigt, A.; Teichert, M.; Usón, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504.

(7) The X-ray diffraction data collection was carried out twice on two different diffractometers at low temperature. However, due to poor data quality obtained both times, the final residuals (*R* factors) at the end of the refinement are rather high. The peripheral carbon atoms of the silicon and aluminum substituents show large thermal motions (see Figure 4 and Supporting Information).

Table 2. Comparison of Structural Parameters of Silanetriols, Their Adducts, and Amine Complexes

silanetriol	structure	Si−O, Å	O−Si−O, deg	O−H···O, Å	ref
$CySi(OH)_3$	double sheet	1.608−1.637	105.94−112.77	2.722−2.724	3i
$^{t}BuSi(OH)_3$	corrugated layer	1.613−1.634	105.8−110.5	2.704−2.705	3j
$Cp^{*}Si(OH)_3 \cdot 0.5H_2O$	layer	1.627−1.629	106.13−108.61		3k
$2,4,6\text{-}Me_3C_6H_2N(SiMe_3)Si(OH)_3$	tubular	1.612−1.644	103.5−113.3	2.579−2.819	3l
$2,6\text{-}{}^{i}Pr_2C_6H_3N(SiMe_2{}^{i}Pr)Si(OH)_3$	tubular	1.619−1.634	105.51−112.05		3m
(9-methylfluoren-9-yl)-$Si(OH)_3 \cdot H_2O$/EtOH	tubular	1.628−1.643	103.94−111.60	2.71−2.88	3n
(9-methylfluoren-9-yl)-$Si(OH)_3 \cdot 2MeOH$	tubular	1.599−1.632	107.49−111.76	2.66−2.85	3n
(9-methylfluoren-9-yl)-$Si(OH)_3 \cdot H_2O$	double sheet	1.619−1.631	107.11−110.05	2.66−2.85	3n
$Cp(SiMe_3)Si(OH)_3$	tubular	1.611−1.645	104.0−111.7	2.693−2.787	3o
$(CO)_9Co_3CSi(OH)_3$	octameric cage	1.61−1.648	105.9−111.7		3q
$(Me_3Si)_3CSi(OH)_3$	hexameric cage	1.64−1.79	97−116.8	2.82−3.12	3r
$(PhMe_2Si)_3CSi(OH)_3$	tetramer	1.615−1.638			1b
$(Me_3Si)_3SiSi(OH)_3$	hexameric cage	1.65−1.69	105−109.1	2.71−2.95	3u
$[(Ph_3P)_3OsCl(CO)Si(OH)_3$	monomer	1.624−1.649			3v
2-naphthalene-$Si(OH)_3$	monomer	1.635−1.646	103.4−112.5		3w
$[\{2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3\} \cdot \{PIP\}]$	layer	1.616−1.626	107.35−111.73	2.72	4
$[\{2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3\} \cdot \{DABCO\} \cdot \{1,4\text{-dioxane}\}_{0.5}]$	layer	1.617−1.624	108.4−111.2	2.81	4
$[\{2,6\text{-}Me_2C_6H_3N(SiMe_3)Si(OH)_3\} \cdot \{BPY\}_{1.5}]$	layer	1.613−1.639	108.7−111.4		4
$2,6\text{-}Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (**3**)	octameric cage	1.598−1.661	102.2−112.5	2.637−2.889	*a*
$[\{2,6\text{-}Et_2C_6H_3N(SiMe_3)Si(OH)_3\} \cdot \{PIP\}]$ (**4**)	layer	1.613−1.620	107.4−112.1	2.77	*a*
$[\{2,6\text{-}Et_2C_6H_3N(SiMe_3)Si(OH)_3\} \cdot \{BPY\}]$ (**5**)	layer	1.600−1.626	105.3−112.6	2.756	*a*

[a] This work.

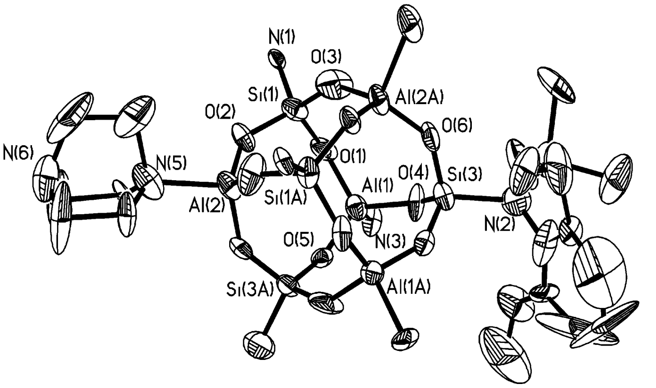

Figure 4. ORTEP of $[2,6\text{-}Et_2C_6H_3N(SiMe_3)SiO_3Al(DABCO)]_4 \cdot 1,4$-dioxane (**7**) at 40% probability level. Substituents on only one of the Al and Si corners of the cube shown for clarity.

on the alternate corners of the cube offers interesting opportunities to carry out cluster expansion reactions.

Experimental Section

$2,6\text{-}Et_2C_6H_3N(SiMe_3)H$ (1). To a vigorously stirred solution of 2,6-diethylaniline (29.9 g, 200 mmol) in hexane (250 mL) was added dropwise $^{n}BuLi$ (125 mL, 200 mmol) at −78 °C. After the addition, the reaction mixture was allowed to attain room temperature and stirred for 8 h. Subsequently, the reaction mixture was cooled to −78 °C and Me_3SiCl (18.5 g, 200 mmol) in hexane (25 mL) was added dropwise, allowed to warm to room temperature, and stirred for 12 h. Precipitated LiCl was removed by filtration and solvent was removed. The resultant pale brown oil was purified by fractional distillation. Yield: 42.8 g (96%). Bp: 120 °C/0.5 mmHg. Anal. Calcd for $C_{13}H_{22}NSi$ (mol wt 220.41): C, 70.84; H, 10.06; N, 6.35. Found: C, 70.76; H, 10.30; N, 6.71. MS (EI, 70 eV): *m/z* 221 (M^+), 206 ($M^+ - Me$, 100%). IR (neat, cm^{-1}): $\bar{\nu}$ 3384(m), 3063(m), 3026(m), 2964(vs), 2930 (s), 2898(s), 2874(s), 1592(w), 1454(vs), 1335(m), 1263(s), 1251(vs), 1203(m), 1109(w), 1059(w), 1036(w), 905(vs), 842(vs), 777(m), 748(m), 694(m), 682(w), 615(w). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.32 (s, 9H, Si−CH_3), 1.37 (t, 6H, CH_3, $^3J_{HH} = 6$ Hz), 2.80 (q, 4H, CH_2, $^3J_{HH} = 7$ Hz), and 6.83−7.18 (m, 3H, aryl−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.25 (Si−CH_3), 14.44 (CH_3), 25.62 (CH_2), 122.22, 125.91, 137.49, 141.95 (aryl C) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 4.6 (s, *Si*−CH_3) ppm.

$2,6\text{-}Et_2C_6H_3N(SiMe_3)SiCl_3$ (2). $^{n}BuLi$ (96.3 mL, 154 mmol) in diethyl ether (50 mL) was added dropwise at 0 °C to **1** (34.1 g, 154 mmol) in Et_2O (150 mL) and stirred for 12 h at 25 °C. Subsequently, this solution was heated under reflux for 4 h. This mixture was added to $SiCl_4$ (17.7 mL, 154 mmol) in Et_2O (100 mL) at 0 °C and stirred for 12 h. The LiCl was filtered off and the volatiles were removed. The resultant pale brown oil was purified by fractional distillation under reduced pressure to obtain **2** as a colorless viscous liquid. Yield: 44.3 g (81%). Bp: 140 °C/0.5 mmHg. Anal. Calcd for $C_{13}H_{22}NSi_2Cl_3$ (mol wt 354.86): C, 44.00; H, 6.25; N, 3.95. Found: C, 44.76; H, 6.66; N, 4.11. MS (EI, 70 eV): *m/z* 355 (M^+), 93 (100%). IR (neat, cm^{-1}): $\bar{\nu}$ 3065(w), 2966(s), 2934(s), 2876(s), 1510(w), 1400(w), 1444(s), 1325(w), 1255(vs), 1170(vs), 1112(s), 1032(m), 987(vs), 876(vs), 841(vs), 804(m), 760(m), 640(w), 620(w), 572(s), 490(w). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.20 (s, 9H, Si−CH_3), 1.24 (t, 6H, CH_3, $^3J_{HH} = 8$ Hz), 2.50−2.81 (m, 4H, CH_2), and 7.12−7.14 (m, 3H, aryl−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.85 (Si−CH_3), 15.10 (CH_3), 24.98 (CH_2), 126.11, 126.18, 139.31, 142.32 (aryl C) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 11.9 (s, *Si*−CH_3) and −28.2 (s, *Si*−Cl) ppm.

$2,6\text{-}Et_2C_6H_3N(SiMe_3)Si(OH)_3$ (3). Compound **2** (7.1 g, 20 mmol) in Et_2O (50 mL) was added at 0 °C dropwise to a stirred solution of aniline (5.62 g, 60 mmol) and water (1.1 g, 60 mmol) in diethyl ether (300 mL). The reaction mixture was slowly allowed to attain room temperature and stirred for a further 12 h. The precipitated aniline hydrochloride was filtered off, and volatiles were removed from the filtrate under vacuum. Compound **3** was obtained as beige solid, which was further purified by crystallization from hexane at 0 °C. Yield: 8.6 g (96%). Mp: 135−137 °C. Anal. Calcd for $C_{13}H_{25}NO_3Si_2$ (mol wt 299.52): C, 52.13; H, 8.41; N, 4.68. Found: C, 51.64; H, 8.26; N, 4.64. MS (EI, 70 eV): *m/z* 299 (M^+), 284 ($M^+ - Me$). IR (KBr, cm^{-1}): $\bar{\nu}$ 3368(s), 3063(w), 2964(s), 2935(m), 2878(w), 1444(s), 1328(w), 1252(vs), 1185(s), 1114(w), 981(vs), 907(vs), 839(vs), 810(vs), 957(m), 686(w), 640(w), 545(w). ^1H NMR ($CDCl_3$, 300 MHz): δ 0 (s, 9H, Si−CH_3), 1.12 (t, 6H, CH_3, $^3J_{HH} = 8$ Hz), 2.61 (q, 4H, CH_2, $^3J_{HH} = 8$ Hz), 4.60 (s, 3H, O*H*), and 6.95 (s, 3H, aryl−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.60 (Si−CH_3), 14.65 (CH_3), 24.13 (CH_2), 124.48, 125.35, 140.64, 142.56 (aryl C) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 2.7 (s, *Si*−CH_3) and −70.7 (s, *Si*−OH) ppm.

$[\{2,6\text{-}Et_2C_6H_3N(SiMe_3)Si(OH)_3\}\{AMINE\}]$ (4−6). Piperazine hexahydrate (0.58 g, 3 mmol) was added to a solution of

3 (0.90 g, 3 mmol) in methanol (30 mL) at room temperature and stirred for 24 h. The solvent was removed, and the solid obtained was dried for 3 h and crystallized from a hexane/dioxane mixture (1:3, v/v) Yield: 0.26 g (67%). Mp: 123−125 °C. Anal. Calcd for $C_{17}H_{35}N_3O_3Si_2$ (mol wt 385.66): C, 52.95; H, 9.15; N, 10.90. Found: C, 52.57; H, 9.22; N, 10.96. IR (KBr, cm^{-1}): $\bar{\nu}$ 3290(s), 3263(s), 3062(m), 2960(s), 2844(m), 1443(m), 1366(w), 1325(w), 1248(s), 1188(w), 1115(W), 951(vs), 908(vs), 836(vs), 813(vs), 758(s), 683(w), 594(w), 547(W), 469(w), 431(m), 408(m). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.10 (s, 9H, Si−CH_3), 1.01−1.05 (m, 6H, CH_3), 2.50−2.59 (m, 4H, Et−CH_2), 2.67−2.69 (s, 8H, CH_2), and 6.81−6.86 (m, 3H, aryl−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.62 (Si−*C*H_3), 14.53 (*C*H_3), 23.96 (Et−*C*H_2), 45.95 (*C*H_2), 123.74, 124.97, 142.82 (aryl *C*) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 7.7 (s, *Si*−CH_3) and −63.4 (s, *Si*−OH) ppm.

[{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}{BPY}] (**5**) was synthesized as described above for **4**. Yield: 0.58 g (63%). Mp: 150−152 °C. Anal. Calcd for $C_{23}H_{33}N_3Si_2O_3$ (mol wt 455.71): C, 60.62; H, 7.30; N, 9.22. Found: C, 60.58; H, 7.52; N, 9.13. IR (KBr, cm^{-1}): $\bar{\nu}$ 3329(s), 3057(s), 2963(s), 2879(s), 2855(s), 1596(s), 1536(w), 1443(m), 1410(m), 1323(w), 1247(m), 1188(m), 1065(w), 975(s), 950(vs), 914(s), 838(m), 807(m), 754(w), 681(w), 617(w), 545(w), 477(m). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.08 (s, 9H, Si−CH_3), 1.20 (t, 6H, −CH_3, $^3J_{HH}$ = 7 Hz), 2.69−2.93 (m, 4H, −CH_2), 6.96−7.04 (m, 3H, aryl−C*H*), and (7.42 (s), 7.42−7.56 (d), 8.71−8.72 (d)) (8H, bpy−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.77 (Si−*C*H_3), 14.67 (*C*H_3), 24.09 (*C*H_2), 121.34, 123.66, 124.86, 142.25, 142.66, 145.31, 150.29 (aryl *C*) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 4.7 (s, *Si*−CH_3) and −66.4 (s, *Si*−OH) ppm.

[{2,6-$Et_2C_6H_3N(SiMe_3)Si(OH)_3$}·{DABCO}] (**6**) was synthesized as described above for **4.** Yield: 0.91 g (74%). Mp: 128−130 °C. Anal. Calcd for $C_{19}H_{37}N_3O_3Si_2$ (mol wt 411.69): C, 55.43; H, 9.06; N, 10.21. Found: C, 55.99; H, 9.56; N, 10.29. IR (KBr, cm^{-1}): $\bar{\nu}$ 3337(m), 3061(m), 2963(s), 2881(s), 2303(w), 1781(w), 1462(s), 1443(s), 1361(m), 1325(s), 1246(vs), 1190(vs), 1120(s), 1061(vs), 1003(vs), 963(vs), 920(vs), 839(vs), 811(vs), 777(vs), 682(s), 548(s), 471(s), 439(s). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.11 (s, 9H, Si−CH_3), 1.19 (t, 6H, −CH_3, $^3J_{HH}$ = 7 Hz), 2.77 (s, 12H, CH_2−DABCO), 3.57−3.67 (m, 4H, −CH_2) and 7.05 (s, 3H, aryl−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.74 (Si−*C*H_3), 14.56 (*C*H_3), 23.93 (*C*H_2), 46.66 (*C*H_2−DABCO), 123.40, 124.65, 142.34, 142.56 (aryl *C*) ppm. ^{29}Si NMR (59.593 MHz, $CDCl_3$): δ 5.6 (s, *Si*−CH_3) and −66.0 (s, *Si*−OH) ppm.

[2,6-$Et_2C_6H_3N(SiMe_3)SiO_3Al(DABCO)]_4$·1,4-dioxane (7). To a suspension of **6** (0.654 g, 1.5 mmol) in *n*-hexane (25 mL)/1,4-dioxane (5 mL) was added $HAl^{i}Bu_2$ (1.5 mmol, 1.0 M solution in *n*-hexane) at 25 °C and stirred for 12 h. The reaction mixture was heated under reflux for 3 h, and the volatiles were removed to obtain **7**. Single crystals were obtained at room temperature from an *n*-hexane/1,4-dioxane mixture (v/v, 1:2). Yield: 1.21 g (47%). Mp: >250 °C. Anal. Calcd for $C_{80}H_{144}N_{12}Si_8O_{14}Al_4$ (mol wt 1830.71): C, 52.49; H, 7.93; N, 9.18. Found: C, 51.84; H, 8.11; N, 8.88. IR (KBr, cm^{-1}): $\bar{\nu}$ 3057(w), 2959(s), 2879(m), 1536(w), 1446(m), 1326(w), 1247(s), 1194(m), 1121(m), 1077(vs), 1034(vs), 964(vs), 944(vs), 912(s), 869(w), 839(s), 756(w), 545(m), 491(m), 411(w). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.02 (s, 36H, Si−CH_3), 1.14 (t, 24H, CH_3, $^3J_{HH}$ = 7 Hz), 2.86−2.91 (s, 16H, CH_2), 2.52−2.77 (m, 48H, CH_2−DABCO), 3.73 (s, 8H, CH_2−dioxane), and 6.97 (s, 12H, aryl−C*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 2.33 (Si−*C*H_3), 14.95 (*C*H_3), 24.69 (*C*H_2), 43.94 (*C*H_2−DABCO), 45.60 (*C*H_2−DABCO), 67.27 (*C*H_2−dioxane), 122.04, 124.27, 143.20, 147.80 (aryl *C*) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −0.5 (s, *Si*−CH_3) and −80.8 (s, *Si*−O−Al) ppm.

Single-Crystal X-ray Structure Solution and Refinement. The structures of compounds **3**, **4**, **5**, and **7** were determined by single-crystal X-ray diffraction studies. Crystals suitable for X-ray diffraction were grown from hexane for **3** at 0 °C and from a hexane/dioxane mixture for **4** and **7** at room temperature and for **5** at 8 °C. Intensity data were collected on a STOE AED-2 four-circle diffractometer for **3**, on a Bruker CCD area detector for **6**, and on a Nonius MACH-3 four-circle diffractometer for **5** and **7**. The structure solution was achieved by direct methods (SIR-92).[8] The final refinement of the structure was carried using full matrix least-squares methods on F^2 using SHELXL-97.[9] All the hydrogen atoms attached to oxygen (hydroxyl hydrogen atoms) were located from the difference map and included in the subsequent refinement. All non-hydrogen atoms were refined anisotropically. Details of crystallographic data collection, structure solution, and refinement are given in the Supporting Information.

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Supporting Information Available: Crystal data, listing of hydrogen bonds, and DIAMOND plots of aggregation of silanetriol molecules in **3**−**5** (PDF); tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Altomare, A.; Cascarano, G.: Giacovazzo, C.; Gualardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(9) Sheldrick, G. M. *SHELXL-97*, Program for Structure Refinement; University of Göttingen: Germany, 1997.