[Fe(6-Me-py)₃tren](ClO₄)₂ in acetone

Figure 7. Changes with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)₃tren](ClO₄)₂ in acetone. The relative heights of the absorption bands are to scale. The tail of the CT band in the UV (not shown in Figure) was subtracted in the course of fitting.

of the complex **4** spectra in the two solvent resemble those of the low-spin complexes **2** and **3**, see Figures 1 and 7.

Comments and Conclusions

The main conclusion from this study of the effect of pressure on the CT bands of a series of Fe^{II} spin-crossover complexes is

that with pressure we are able to convert the spin state of [Fe-(6-Me-py)₃tren](ClO₄)₂ from mostly high spin to low spin in solution. There have been several studies wherein spin-crossover complexes in solution have been shown to convert from high spin to low spin upon decreasing the temperature of the solution. In these cases as the temperature of the solution is decreased presumably the main effect is a depopulation of the $^5T_2$ excited state of the Fe^{II} complex, and finally all complexes are in the $^1A_1$ ground state. That is, the energy difference between the $^5T_2$ and $^1A_1$ states is not affected appreciably by temperature, and the shift from more high-spin to all low-spin complexes with temperature just reflects a Boltzmann distribution. However, in the case of the pressure-driven conversion from high to low spin in solution the increased compression on the solvent tunes the energy difference between the $^5T_2$ and $^1A_1$ states such that the $^1A_1$ state of the Fe^{II} complex is stabilized at elevated pressures. One may, in principle, use the area under the peaks as a measure of the degree of spin conversion, assuming essentially all high-spin complexes below $\sim$5 kbar and all low-spin complexes at 10–11 kbar. This is a doubtful procedure in this case since in the intermediate pressure region there should be two pairs of peaks, one pair associated with each spin state. Nevertheless, if one proceeds in this manner it is possible to extract volume changes of −3.6 to −3.8 cc/mol in each solvent. A contributing factor to this value is certainly differences in ligand–metal bond length in the two solvents. However, there can also be differences in polarizability, dipole moment, and degree and type of solvation, and these intermolecular considerations can easily be a major consideration in the difference in volume observed.

Finally, we note that in solution this is clearly a stochastic chemical equilibrium which depends on the difference in free energy between the two states of the molecule. In the crystal the process is much more cooperative, and it is the free energy of the crystal which governs the conversion.

Silsesquioxanes as Models for Silica Surfaces

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Abstract: The hydrolytic condensation of cyclohexyltrichlorosilane (CySiCl₃) affords [Cy₇Si₇O₉(OH)₃] (**1**), [Cy₆Si₆O₉] (**2**), and [Cy₈Si₈O₁₁(OH)₂] (**3a**). Trisilanol **1** and **3b**, the bis(triphenyltin) derivative of **3a**, have been structurally characterized by single-crystal X-ray diffraction studies. Trisilanol **1** undergoes corner-capping reactions with trifunctional monomers (e.g., R'SiCl₃, MeGeCl₃, MeSnCl₃), is selectively monosilylated to [Cy₇Si₇O₉(OH)₂OTMS] (**6a**) with chlorotrimethylsilane, and can be dehydrated to [Cy₇Si₇O₁₀(OH)] (**7a**). Comparison of the molecular structure of **1** with (111) β-cristobalite and (0001) β-tridymite reveals many structural similarities. Silsesquioxanes **1**, **6a**, and **7a** are discussed as models for silica surfaces.

Heterogeneous silica-supported transition-metal complexes play an important role as catalysts in the petrochemical industry.[1]

Highly selective catalysts have been developed to catalyze an impressive range of chemical processes, such as hydrocarbon oxidation,[2] olefin and alkyne polymerization[3] and metathesis,[4,5]

(1) (a) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: New York, 1981. (b) Setyama, T., Tanabe, K., Eds. *New Horizons in Catalysis*; Elsevier: New York, 1980. (c) Thomas, C. *Catalytic Processes and Proven Catalysts*; Academic Press: New York, 1970. (d) Pearce, R.; Patterson, W. R. *Catalysis and Chemical Processes*; Blackie and Son: Glasgow, 1981. (e) Hartley, F. R. *Supported Metal Complexes*; Reidel: Boston, 1985. (f) Iwasawa, Y., Ed. *Tailored Metal Catalysis*; Reidel: Boston, 1986.

(2) Golodets, G. I. *Heterogeneous Catalytic Reactions Involving Molecular Oxygen*; Elsevier: New York, 1983.

(3) (a) Karol, F. J.; Wu, C.; Reichle, W. T.; Maraschin, N. J. *J. Catal.* **1979**, *60*, 68. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Lunsford, J. H.; Fu, S.-L.; Myers, D. L. *J. Catal.* **1988**, *111*, 231. (d) McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47.

CO reduction,[6] and the oxidative coupling of methane.[7] Recent advances in analytical techniques for probing surface structure have allowed great strides toward understanding reaction processes that occur on the surfaces of these catalysts, but detailed structural characterization and mechanistic studies of SiO_2-supported complexes are still inherently difficult. In some instances serious doubts exist as to whether or not the "observed" surface species have been properly identified and are, in fact, responsible for the observed chemical reactivity.

We have recently described a new approach for modeling the chemistry of silica-supported transition-metal complexes.[8] This approach is based on the synthesis of transition-metal-containing siloxane macromolecules, which structurally resemble surface sites that have been purportedly identified on silica surfaces. This paper provides a full account of the synthesis and characterization of several incompletely condensed silsesquioxanes and discusses their relevance as models for hydroxylated silica surfaces.

Results

Synthesis of 1, 2, and 3a. In a remarkable reaction first reported[9] by Brown and Vogt in 1965, trisilanol 1 is prepared by the kinetic hydrolytic condensation of cyclohexyltrichlorosilane ($CySiCl_3$) in aqueous acetone. In a typical reaction, 3.2 L of
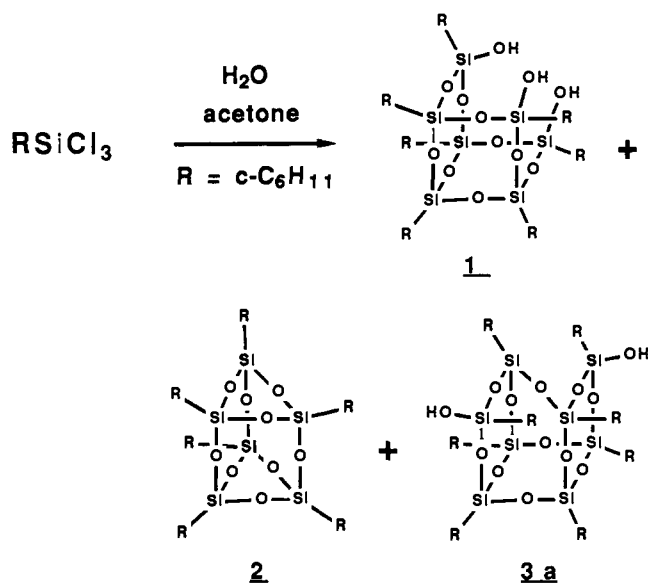
H_2O is carefully added to a solution of 3.0 mol of $CySiCl_3$ in 12 L of acetone in a 5-gal glass carboy and allowed to stand at room temperature. The desired product precipitates over a period of 2–36 months (vide infra) as a white microcrystalline solid, along with two minor components. Although repeated attempts to shorten the reaction time were largely unsuccessful, synthetically useful quantities of 1 can be obtained in a few weeks by performing the reaction on a large scale and filtering at early reaction times. The course of the reaction does not appear to be affected by
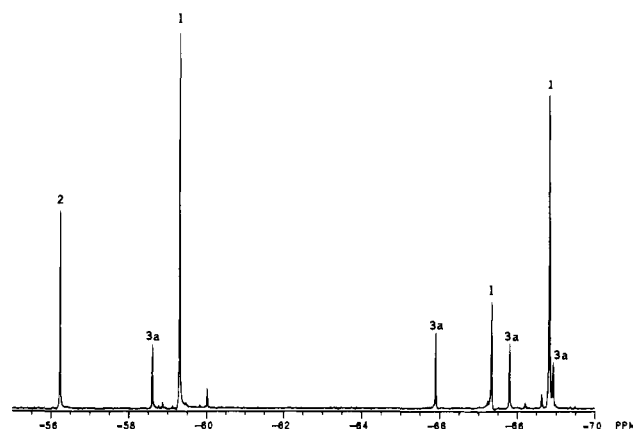
(4) (a) Moulijn, J. A.; Reitsma, H. J.; Boelhouwer, C. *J. Catal.* **1972**, *25*, 434. (b) Mortreux, A.; Blanchard, M. *Bull. Soc. Chim. Fr.* **1972**, 1641.

(5) (a) Boor, J. *Ziegler-Natta Catalysis and Polymerizations*; Academic Press: New York, 1979. (b) Keii, T., Soga, K., Ed. *Catalytic Polymerization of Olefins*; Elsevier: New York, 1985. (c) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. 3, pp 475–547. (d) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerizations of Cycloolefins*; Wiley: New York, 1986. (e) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1986.

(6) Nakajo, T.; Sano, K.-I.; Matsuhira, S.; Arakawa, H. *J. Chem. Soc., Chem. Commun.* **1987**, 647.

(7) (a) Sofranko, J. A.; Leonard, J. J.; Jones, C. A. *J. Catal.* **1987**, *103*, 302. (b) Jones, C. A.; Leonard, J. J.; Sofranko, J. A. *J. Catal.* **1987**, *103*, 311. (c) Zhen, K. J.; Khan, M. M.; Mak, C. H.; Lewis, K. B.; Somorjai, G. A. *J. Chem.* **1985**, *94*, 501. (d) Khan, M. M.; Somorjai, G. A. *J. Catal.* **1985**, *91*, 263.

(8) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850–52.

(9) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313–17.

Figure 1. ^{29}Si NMR spectrum of a 65:15:20 mixture of **1**, **2**, and **3a**.

periodic product isolations and the filtrate will continue to precipitate **1** for approximately 3 years. The eventual yield of crystalline products is typically 60–70%, based on $CySiCl_3$.

Filtration of a typical reaction mixture after 12 weeks affords 70 g of crude product, which contains 45% of heptameric **1**, 40% of hexameric **2**, and 15% of octameric **3a**. Subsequent filtrations of the reaction mixture yield crude product mixtures with progressively lower percentages of **2**. For example, a second filtration after an additional 12 weeks typically yields 40 g of material containing **1**, **2**, and **3a** in a 62:12:26 ratio. A third filtration after 12 months more typically gives 70 g of the three products in a 77:7:16 ratio. Crystalline material precipitating after 1.5 years is almost entirely **1**.

The three products of the reaction exhibit very different solubility properties and can be easily separated. Pyridine extraction of the crude product mixture quantitatively separates the insoluble **2** from the two silanol-containing products. Separation of **1** from **3a** can be effected by fractional crystallization from Et_2O: **1** is approximately 5 times less soluble in ether than **3a** and precipitates as analytically pure microcrystals upon concentration of hot ether solutions. Compound **3a** can be isolated in pure form by recrystallization from $CHCl_3$, in which it is 5 times less soluble than both **1** and **2**.

Characterization of 1, 2, and 3a. Despite their large sizes and close structural similarity, characterization of most silsesquioxanes is relatively straightforward. Compound **2** is easily identified by its mass spectrum and ^{13}C NMR spectrum ($CDCl_3$), which exhibits four resonances (δ 27.30, 26.64, 26.17, 22.67) for the six equivalent cyclohexyl groups. Trisilanol **1**, which has approximate C_{3v} symmetry, exhibits a more complex ^{13}C NMR spectrum, but its methine resonances appear several ppm farther upfield than the methylene resonances and are clearly resolved into the expected 3:3:1 multiplicity (δ 23.88, 23.54, 23.11). Disilanol **3a** is 2-fold rotationally symmetric and therefore exhibits four methine resonances (δ 23.70, 23.67, 23.37, 23.20) with relative intensities of 2:2:2:2. In addition, the ^1H NMR spectrum ($CDCl_3$) of **3a** exhibits a sharp singlet at δ 2.09 for the two equivalent hydroxy groups, compared to the broad deshielded resonance at δ 6.97 for the three hydrogen-bonded hydroxyl groups of **1** (vide infra).

^{29}Si NMR spectroscopy is particularly useful for characterizing these closely related compounds, as well as various admixtures.[10] For example, the ^{29}Si NMR spectrum of a typical crude product mixture is shown in Figure 1. The resonances for D_{3h}-symmetric **2** (one resonance), C_{3v} symmetric **1** (three resonances; 3:1:3), and C_2 symmetric **3a** (four resonances; 2:2:2:2) are well-resolved and can be accurately integrated if relaxation agents (e.g., $Cr(acac)_3$) are added to the sample. Surprisingly, $[(C_6H_{11})_8Si_8O_{12}]$ (δ 69.80), which is insoluble in aqueous acetone and would have been expected to precipitate from hydrolytic condensation reactions of this type,[9] is not detectable.

(10) For an excellent example of the dependence of ^{29}Si chemical shifts on siloxane framework structure: Marsmann, H. C.; Meyer, E. *Z. Anorg. Allg. Chem.* **1987**, *548*, 193–203.
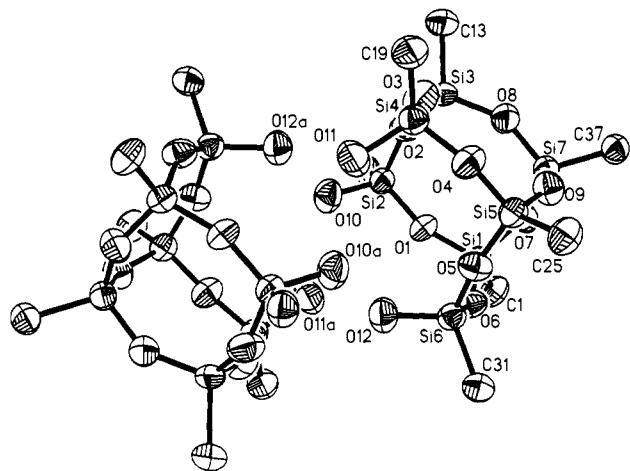
Figure 2. ORTEP plot of **1**. The molecules crystallize as a hydrogen-bonded dimer in the space group $P\bar{1}$. The two molecules that comprise the dimer are crystallographically related by $\bar{1}$. For clarity, thermal ellipsoids are shown at 20% probability and only C attached to Si are shown.

Table I. Selected Bond Distances and Angles for **1**

Bond Distances (Å)			
Si1–O1	1.609 (3)	Si4–O4	1.617 (3)
Si1–O6	1.609(3)	Si4–O11	1.620 (3)
Si2–O1	1.607 (3)	Si5–O4	1.608 (3)
Si2–O2	1.606 (3)	Si5–O5	1.610 (3)
Si2–O10	1.620 (3)	Si6–O5	1.613 (3)
Si3–O2	1.603 (3)	Si6–O6	1.615 (3)
Si3–O3	1.594 (3)	Si6–O12	1.626 (3)
Si4–O3	1.610 (3)	Si–C (av)	1.847 (5)

Bond Angles (deg)			
O1–Si1–O6	109.4 (2)	O4–Si4–O11	1078 (2)
O1–Si2–O2	110.2 (2)	O4–Si5–O5	108.9 (2)
O1–Si2–O10	108.5 (2)	O5–Si6–O6	110.2 (2)
O2–Si2–O10	107.6 (2)	O5–Si6–O12	107.1 (2)
O2–Si3–O3	109.5 (2)	O6–Si6–O12	108.5 (2)
O3–Si4–O4	110.2 (2)	O–Si–C (av)	110 (1)
O3–Si4–O11	108.4 (2)		
Si1–O1–Si2	160.5 (2)	Si6–O6–Si1	145.5 (2)
Si2–O2–Si3	152.4 (2)	Si1–O7–Si7	148.6 (2)
Si3–O3–Si4	160.8 (2)	Si3–O8–Si7	148.6 (2)
Si4–O4–Si5	148.1 (2)	Si5–O9–Si7	147.5 (2)
Si5–O5–Si6	161.1 (2)		

X-ray Structural Characterization of 1. The ORTEP plot from a single-crystal X-ray diffraction study of **1** is shown in Figure 2 and average bond distances and angles are collected in Table I. The molecule crystallizes as a strongly hydrogen-bonded dimer in the space group $P\bar{1}$ with both molecules comprising the dimer related by the crystallographic inversion center. The three siloxyl groups for each molecule of **1** are tilted slightly outward from their expected positions in octameric polyhedral oligosilsesquioxanes, but the bond distances and angles for the Si–O framework are not appreciably affected.[11]

Hydrogen-bonding between molecules of **1** in the solid-state dimer occurs in an interestingly symmetric fashion, with intermolecular O–O distances of 2.63–2.64 Å between adjacent oxygen atoms of the hydroxyl groups. Although the hydrogen-bonding protons could not be located in the final difference map, the highly symmetrical nature of the bonding is suggestive of a hydrogen-bonding interaction like the one shown in Figure 3.

(11) (a) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Miller, D. M. *J. Am. Chem. Soc.* **1985,** *107,* 8262. (b) Smolin, Y. I.; Shepelev, Y. F.; Pomes, R. *Khim. Silik. Oksidov* **1982,** 68. (c) Baidina, I. A.; Podbenezskaya, N. V.; Alekseev, V. I.; Martynova, T. N.; Borisov, S. V.; Kanev, A. N. *Zh. Strukt. Khim.* **1979,** *20,* 648. (d) Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. *Acta Crystallogr., Sect. B* **1979,** *B35,* 2258. (e) Shklover, V. E.; Strchkov, Y. T.; Makarova, N. N.; Adrianov, K. A. *Zh. Strukt. Khim.* **1978,** *19,* 1107. (f) Larsson, K. *Ark. Kemi* **1960,** *16,* 203.
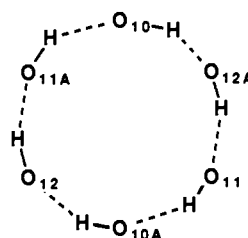

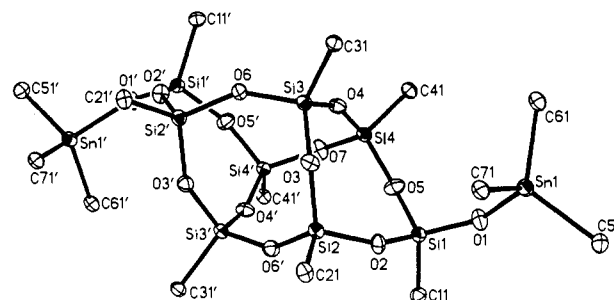**Figure 3.** Representation of the most probable hydrogen-bonding arrangement for **1**.

Figure 4. ORTEP plot of **3b**. The molecule is 2-fold rotationally symmetric about O7. For clarity, thermal ellipsoids are shown at 20% probability and only C attached to Si are shown.

Table II. Selected Bond Distances and Angles for **3b**

Bond Distances (Å)			
Si1–O1	1.605 (3)	Si3–O4	1.619 (9)
Si1–O5	1.626 (3)	Si3–O6	1.618 (3)
Si1–O2	1.626 (3)	Si4–O4	1.619 (3)
Si2–O2	1.614 (3)	Si4–O5	1.602 (3)
Si2–O3	1.624 (3)	Si4–O7	1.617 (3)
Si3–O3	1.620 (3)	Sn–O1	1.965 (3)
Si–C (av)	1.849 (10)	Sn–C (av)	2.123 (6)

| Bond Angles (deg)			
O1–Si1–O2	109.6 (2)	O3–Si3–O4	109.8 (2)
O1–Si1–O5	110.2 (2)	O3–Si3–O6	108.8 (2)
O2–Si1–O5	108.4 (2)	O4–Si3–O6	109.4 (2)
O2–Si2–O3	109.4 (2)	O4–Si4–O5	109.1 (2)
O2–Si2–O6'	108.7 (2)	O4–Si4–O7	109.5 (2)
O3–Si2–O6'	108.7 (2)	O5–Si4–O7	109.2 (2)
O1–Sn–C (av)	107 (5)	O–Si–C (av)	110 (4)
Sn–O1–Si1	160.2 (3)	Si1–O5–Si4	161.3 (3)
Si1–O2–Si2	152.4 (3)	Si3–O6–Si2'	145.5 (3)
Si2–O3–Si3	160.3 (4)	Si4–O7–Si4'	149.3 (3)
Si3–O4–Si4	148.8 (3)		

Interestingly, intermolecular distances between symmetry-related ($\bar{1}$) hydroxyl groups are 4.7–5.0 Å. The six silanol groups define a distorted octahedral coordination site approximately 2.1 Å in diameter, comparable to the O–O distances of octahedral coordination site in aluminosilicate minerals.[12]

X-ray Structural Characterization of 3b. The NMR, IR, mass spectral, and analytical data for **3a** are equally consistent with two isomeric structures, differing only by the stereochemistry of the siloxyl groups (e.g., **3a** vs **4**). A single-crystal X-ray diffraction study was therefore undertaken to unambiguously identify the structure of **3a**.

Although repeated attempts to obtain X-ray quality crystals and/or a satisfactory crystal structure of **3a** were unsuccessful,[13] suitable crystals of the bis(triphenyltin) derivative, **3b**, were obtained. The ORTEP plot from a single-crystal X-ray diffraction study of **3b** is shown in Figure 4, and selected bond distances and

(12) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: New York, 1985.

(13) Disilanol **3a** crystallizes from most solvents as extremely thin plates or needles in the space group $P2_1$. Although the relevant stereochemistry of the hydroxyl-bearing silicon atoms could be established, disorder problems prevented a satisfactory solution of the structure.

3a   R' = H
3b   SnPh₃

4
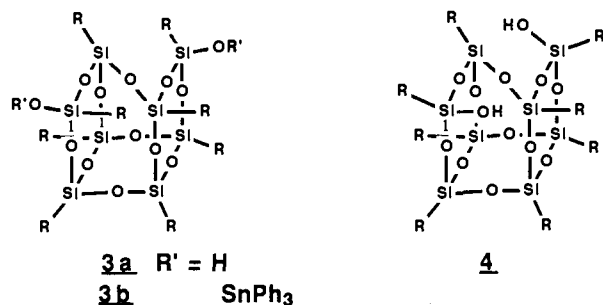
angles are collected in Table II.

The molecule crystallizes in the space group $C2/c$ and exhibits crystallographic 2-fold rotational symmetry about O7. The triphenyltin groups occupy nominally "exo" positions above nearby Si_4O_4 rings and have normal Sn–O–Si distances and angles.[14] The bond distances and angles for the siloxane framework are also within their normal ranges[11,15] and militate against substantial distortions of the Si–O skeleton: the Si–O–Si bond angles for fused Si_4O_4/Si_4O_4 rings are approximately 146–148°, while Si–O–Si bond angles for fused Si_5O_5/Si_4O_4 rings are expectedly somewhat larger (147–159°).

Reaction Chemistry of 1. Corner-Capping Reactions. Trisilanol 1 is formally derived from the hydrolytic removal of one silicon atom from a stable octameric silsesquioxane (i.e., "T_8"). It, therefore, exhibits a strong tendency to undergo reactions to fill the vacant vertex. Reactions of 1 with R'SiCl₃ in the presence of an amine, not surprisingly, lead to completely condensed products[8,16b] and provide a convenient method for synthesizing mixed T_8's with seven chemically inert cyclohexyl rings and one reactive functional group (e.g., R = p-$C_6H_4CH_2Cl$, p-$C_6H_4CCl_3$, etc.).[16b] Similarly, reactions of 1 with MeGeCl₃, MeSnCl₃, and *CpZrCl₃, as well as a large number of other transition-metal complexes,[16c,d] afford completely condensed products containing seven silicon atoms and one much larger metal atom. The reaction with *CpZrCl₃ is particularly notable because zirconium, one of the largest transition-metal atoms,[17] can be easily accommodated by the silsesquioxane framework of 1 and produces a relatively strain-free product, as determined by X-ray crystallography.

1   (R = c-C₆H₁₁)

5a   M = SiR'
5b   GeMe
5c   SnMe
5d   Zr(C₅Me₅)
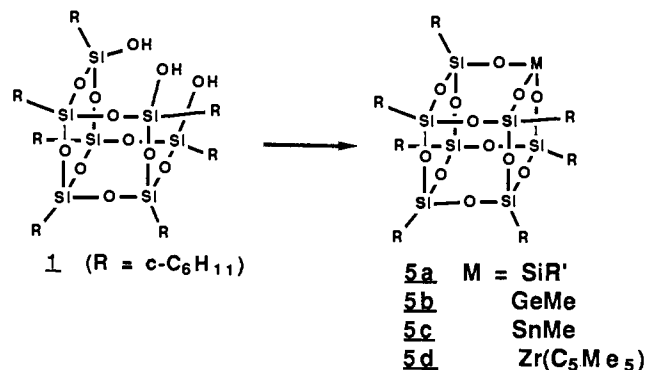
Silylation and Dehydration. Trisilanol 1 represents one of the best models for silica developed to date but is limited to modeling surface sites possessing three hydroxyl groups. Since there are many surface sites with fewer than three silanols, as well as sites with potentially coordinating siloxane oxygen atoms (i.e., Si–O–Si),

we have developed syntheses of several silsesquioxanes derived from 1 that may also be useful as models for silica.

Trimethylsilylation of 1 provides the simplest means by which the number of silanols can be reduced. The reaction of (TMS)Cl and 1 in THF/Et₃N (95:5, v/v) is remarkably selective. For example, the reaction of 1 with 0.80 equiv of (TMS)Cl in THF/Et₃N at 25 °C affords 6a in 79% (NMR) yield, along with

1

6a

6b

6c
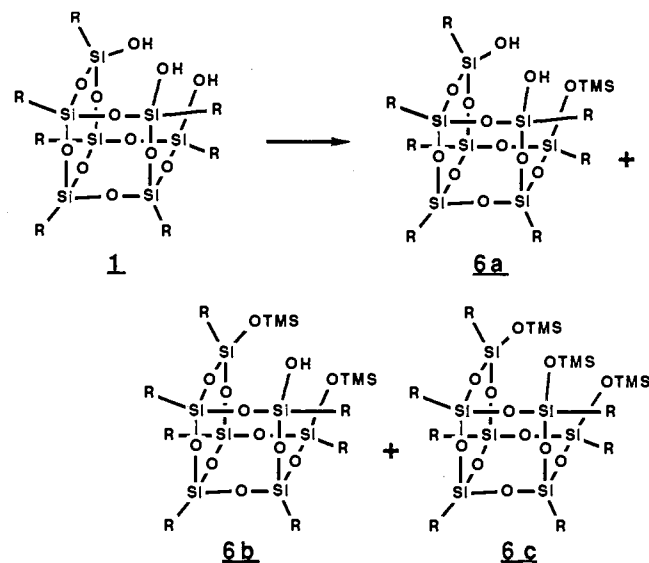
20% of unreacted 1 and traces (<1%) of 6b and 6c. Preparatively, the monosilylation of 1 is most conveniently performed by using slightly more that 1 equiv of (TMS)Cl, in order to ensure the complete reaction of 1 (which cannot be easily separated from 6a). The separation of 6a from both 6b and 6c is conveniently effected by fractional recrystallization from pentane or hexane. Disilylation of 1 is substantially less selective than monosilylation and produces mixtures of 6b and 6c that are very difficult to separate. Pure 6b is most readily obtained as a side product from the synthesis of 6a, as described in the Experimental Section. The trisilylated compound (6c) can be cleanly prepared from 1 and 3 equiv of (TMS)Cl in pyridine/CHCl₃.

Dehydration of 1 to 7a also reduces the number of available silanols and provides an important silica model to complement 1.

1

7a   R' = H
7b   SiMe₃
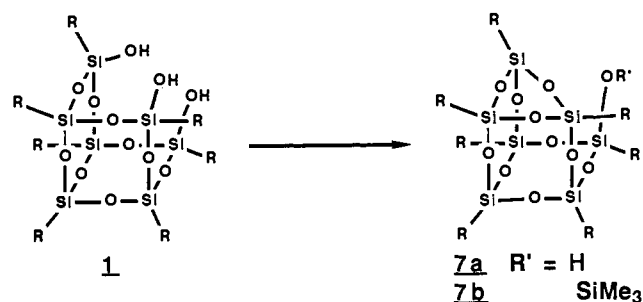
The dehydration of 1 itself requires heating above 200 °C and produces complicated mixtures of products. However, it can be easily condensed to 7a using a trace of Et₃N and highly activated 4-Å molecular sieves. Although 7a has resisted all recrystallization attempts and slowly decomposes on standing, it can be isolated as a stable trimethylsilylated derivative (7b).

Discussion

Trisilanol 1 and Its Derivatives as Models for Silica Surface Sites. The use of highly siliceous compounds to approximate silica seems quite reasonable, but the mere presence of a large siloxane network does not necessarily provide a model any better than one based on simple silanols, such as Me₃SiOH or Ph₃SiOH. Useful models for both spectroscopic comparisons and chemical reactivity studies must structurally resemble specific surface morphologies

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(15) (a) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554–6. (b) Smolin, Y. I.; Shepelev, Y. F.; Ershov, A. S.; Hoebbel, D.; Wieker, W. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1984**, *29*, 421. (c) Clegg, W.; Sheldrick, G. M.; Vater, N. *Acta Crystallogr., Sect. B* **1980**, *B36*, 3162. (d) Baidina, I. A. *Zh. Strukt. Khim.* **1980**, *21*, 125.

(16) (a) Feher, F. J.; Gonzales, S. L.; Ziller, J. W. *Inorg. Chem.* **1988**, *27*, 7. (b) Feher, F. J.; Budzichowski, T., to be submitted for publication. (c) Feher, F. J.; Walzer, J. F., to be submitted for publication. (d) Feher, F. J.; Newman, D. A., to be submitted for publication.

(17) Weast, R. C. *Handbook of Chemistry and Physics*, 57th ed.; CRC Press: Cleveland, OH, 1976; pp F231–4.
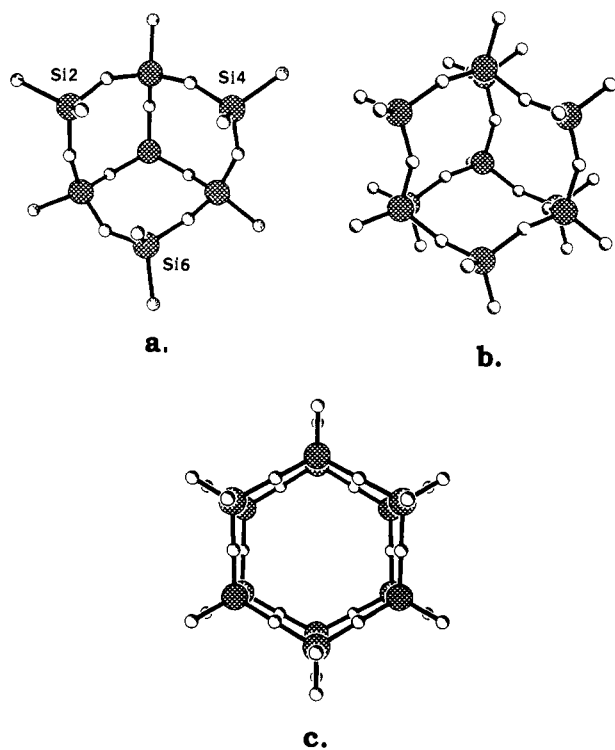
Silsequioxanes as Models for Silica Surfaces

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Figure 5. (a) ORTEP plot of **1** viewed down pseudo-C_3 axis. For clarity, only C attached to Si are shown. (b) ORTEP plot of idealized (111) octahedral face of β-cristobalite. (c) ORTEP plot of idealized (0001) rhombohedral face of β-tridymite. Figures 5a–c are plotted on the scale. Silicon atoms are large cross-hatched circles, carbon atoms are small shaded circles, and oxygens atoms are open circles.

Figure 6. (a) ORTEP plot of **1**. For clarity, only C attached to Si are shown. (b) ORTEP plot of an idealized portion of β-cristobalite. (c) ORTEP plot of an idealized portion of β-tridymite. The three upper-most hydroxyl groups shown in parts b and c are located on β-cristobalite (111) and β-tridymite (0001), respectively. Parts a–c are plotted on the scale. Silicon atoms are large cross-hatched circles, carbon atoms are small shaded circles, and oxygens atoms are open circles.

that are believed to occur on silica. Trisilanol **1** is ideally suited for such purposes. Its close-range geometric similarity to known SiO_2 morphologies makes it the best model for silica that has been developed to date.

An ORTEP plot of **1**, viewed down the C_3 axis of the vacant vertex, is illustrated in Figure 5a. This figure bears a close similarity to potential coordination sites available on the (111) octahedral face of the cristobalite form of SiO_2 (Figure 5b).[18,20] There is also a short-range geometric similarity to comparable sites on the (0001) rhombohedral face of the tridymite form of SiO_2 (Figure 5c).[19,20]

The similarity between cristobalite and **1** is particularly striking. Both coordination environments possess a small siliceous cavity with an outer rim of six silicon and six oxygen atoms. The separation of siloxyl groups on cristobalite is 5.04 Å (Si–Si and O–O), which is very similar to the Si–Si separation of 4.9 Å for the three siloxyl groups of **1**. The OH–OH separation of **1** is only 4.0 Å, but this difference should be of relatively minor importance since the bending potentials of Si–O–M (M = Si, metal or other atoms) linkages are relatively small and broad.[21] To a first approximation, the bonding capabilities of both sites should be quite similar, since slight deformations of the siloxyl groups of both **1**, and cristobalite toward a common intermediate geometry should be relatively easy.

The similarity of **1** to the (0001) face of tridymite is less striking because tridymite does not have geometrically comparable "cavities" on the surface (vide infra). However, the surface to-

pography of tridymite (0001) is virtually identical with cristobalite (111) and would be expected to adopt similar geometries. To the extent that immediate coordination environments dictate the properties of the surface, trisilanol **1** would also model tridymite-like surface morphologies.

Side views of the coordination environments provided by **1**, cristobalite (111), and tridymite (0001) illustrate the major differences between the structures (parts a–c of Figure 6).

The bonding cavity presented by **1** is "cubelike" with a depth of nearly 3.8 Å, measured from Si7 to the plane containing Si2, Si4, and Si6. This is somewhat more shallow than the corresponding cavity depth of cristobalite (5.1 Å), since cristobalite contains additional planes of silicon and oxygen atoms. The structural similarity between tridymite (0001) and cristobalite (111) surfaces is clearly evident. Although bulk cristobalite has a zinc-blend structure and tridymite a wurtzite structure, the dimensions of their hydroxylated surface layers, which determine the chemical reactivity and many of the physical properties, are virtually identical.

Cristobalite and tridymite are two of the three substantially different known crystalline modifications of silica that crystallize from aqueous solutions under normal ($T < 300$ °C; $P < 100$ atm) hydrothermal conditions.[22–28] The other is quartz, which seems to bear surprisingly little similarity to amorphous silica.[22] Although the exact nature of the silica surface (if there is one!) is still the subject of immense controversy,[25] the occurrence of

(18) (a) Figures of cristobalite produced using X-ray structural data reported for β-cristobalite.[17b,19] (b) Wright, A. F.; Leadbetter, A. J. *Philos. Mag.* **1975**, *31*, 1391.

(19) (a) Figures of tridymite produced using X-ray structural data reported for β-tridymite.[18b,19] (b) Kihara, K. *Z. Kristallogr.* **1978**, *148*, 237.

(20) Cristobalite and tridymite occur in several different crystalline modifications. The differences between the phases involve very small changes in atomic positions. These slight changes are unimportant for the sake of the arguments presented here.

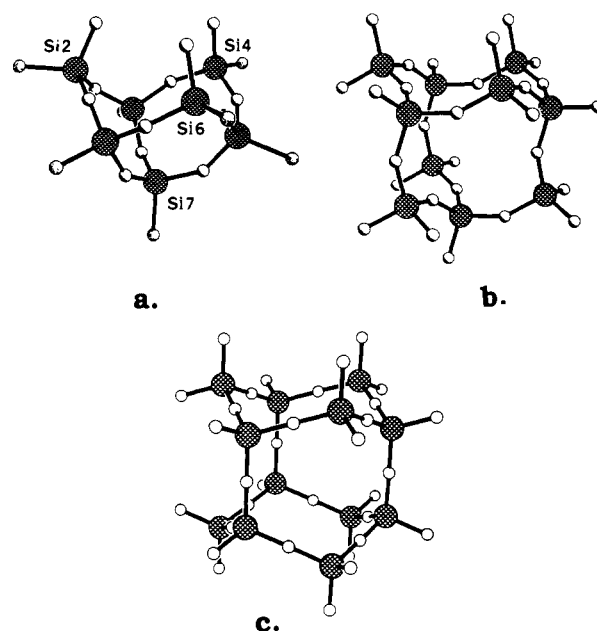(21) Tossel, J. A.; Gibbs, G. V. *Acta Crystallogr., Sect. A* **1978**, *A34*, 463.

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(27) *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed.; McGraw-Hill: New York, 1982; Vol. 12, p 397–400.

(28) Although it has been argued[23,25] that tridymite is not a pure form of SiO_2, it is nevertheless a very commonly observed form of "silica".

cristobalite-like and tridymite-like surface structures has been frequently suggested[22] and is supported by both experimental[22,26,27,29] and theoretical data.[22,30] Of particular relevance is the observation that fully hydroxylated, heat-stabilized amorphous silica (a standard silica gel support) contains a "commonly observed"[22,38] value of 4.6 SiOH groups per 100 Å^2. This is in remarkably close agreement with the calculated[22,25] hydroxyl group concentration on the (111) octahedral face of β-cristobalite (4.55) and the (0001) rhombohedral face of β-tridymite (4.56). (The corresponding hydroxyl group concentration modeled by trisilanol 1 is 4.81).[31]

Although arguments of this nature are frequently oversimplifications that lead to heated controversies,[25] the close similarity between the bulk physical properties of amorphous silica, cristobalite, and tridymite,[26,27] as well as the observation that crystalline cristobalite and tridymite have been detected in samples of amorphous silica,[32] do suggest that some regions of bulk amorphous silica can be reasonably represented by cristobalite-like and tridymite-like structures. The extrapolation of such structures to the surface is natural.

Compounds **6a** and **7a** show short-range geometric similarties to known SiO$_2$ morphologies and should also be useful models for silica. Disilanol **6a** provides a model for the many surface sites possessing two vicinal hydrogen-bonded siloxy groups and potentially coordinating Si–O–Si linkages. Monosilanol **7a**, on the other hand, represents surface sites with isolated, non-hydrogen-bonded siloxy groups and is an excellent complement to **1** for silica modeling studies: to the extent that **1** represents a hydroxylated silica surface, **7a** represents its (partially) dehydrated form. It is also interesting to note that the siloxyl group in **7a** is in close proximity to a strained Si$_3$O$_3$ ring. Compound **7a** should, therefore, be useful for modeling reactions of strained surface siloxane bonds that are assisted by adjacent siloxy groups (e.g., hydration). Such reactions have been frequently invoked to rationalize the sometimes curious reactivity of silica.[22,33]

Other Silsesquioxanes? Silsesquioxanes **1, 6a–c**, and **7a** have great potential as models for silica in homogeneous analogues of silica-supported catalysts. Exploration of their interesting chemistry, however, requires an inconvenient gestation period for ligand synthesis and frequent access to high-field multinuclear (^{13}C and ^{29}Si) NMR spectrometers for routine product characterization. Less time-intensive syntheses of silsesquioxanes with potentially well-resolved ^{1}H NMR spectra (e.g., Me$_7$Si$_7$O$_9$(OH)$_3$) would be highly desirable. Surprisingly, however, the large volume of work with polyhedral oligosilsesquioxanes ([RSiO$_{1.5}$]$_n$), since their discovery[34a] in 1946, has produced only a few examples in which incompletely condensed silsesquioxanes (e.g., **1, 3a, 6a**) can be prepared and isolated in synthetically useful quantities.[34b]

Brown has reported[35] the isolation of many incompletely condensed silsesquioxanes from the hydrolytic condensation of phenyltrichlorosilane, but product separation was extremely difficult, definitive characterization data for most compounds were lacking, and many structural assignments are questionable. Voronkov, Lavrent'ev, Kovrigin, and co-workers have identified a large number of incompletely condensed intermediates in mixtures of oligoethylsilsesquioxanes using GC/MS analysis.[36] The major products are completely condensed octamers and decamers (i.e., [EtSiO$_{1.5}$]$_n$: $n = 8, 10$)], but heptamers **8** and **9**, which are structurally analogous to **1** and **7a**, can constitute 15–40% of the $n = 6$–12 oligomers. Nonamer **10** has also been observed in comparable yields.

8   **9**

10
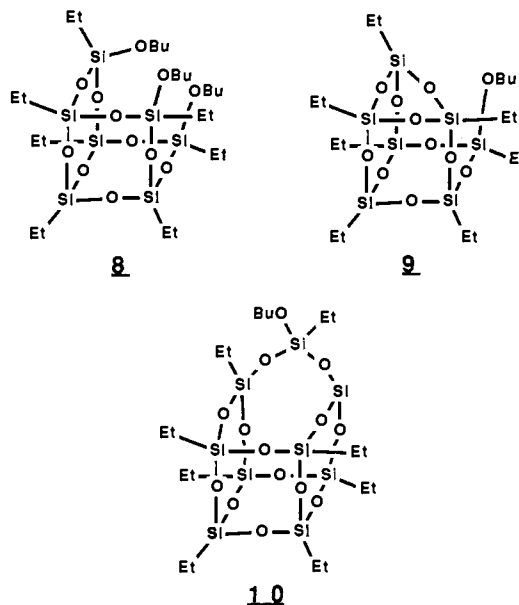
To our knowledge, these are the only other examples in which significant yields of incompletely condensed silsesquixanes can be synthesized and there is a reasonable possibility of separating the product mixture.

Conclusions

This paper has described straightforward procedures for the synthesis of **1, 2,** and **3a** from the hydrolytic condensation of cyclohexyltrichlorosilane. The structures of **1** and **3b** (the bis-(triphenyltin) derivative of **3a**) have been unequivocally established by single-crystal X-ray diffraction studies. The molecular structure of **1** has been compared with cristobalite and tridymite, two crystalline polymorphs of SiO$_2$ that purportedly resemble the hydroxylated surfaces of amorphous silica. There is a close geometric similarity between the structure of **1** and idealized trisilanol sites available on cristobalite (111) and tridymite (0001).

As part of our goal to develop useful new models for hydroxylated silica surfaces, several chemical reactions of **1** have been explored. Corner-capping reactions occur readily with trifunctional monomers (e.g., RSiCl$_3$, MeGeCl$_3$, MeSnCl$_3$, (C$_5$Me$_5$)ZrCl$_3$)), suggesting that a variety of models for isolated metal atoms attached to three surface silanols could be synthesized.

Reactions of the silsequioxane framework have also been examined in order to develop syntheses of less extensively hydroxylated ligands. Trisilanol **1** can be monosilylated to **6a** and dehydrated to **7a**, providing two silica models complementary to **1**. Compound **6a** represents a vicinal disilanol surface site with hydrogen-bonded hydroxyl groups and a potentially coordinating Si–O–Si linkage. Compound **7a** represents the (partially) dehydrated state of surface sites modeled by **1**.

Silsesquioxanes such as **1, 3a, 6a–c**, and **7a** offer great potential as models for silica in homogeneous analogues of silica-supported transition-metal catalysts. Forthcoming work from our laboratory will the demonstrate the utility of silsesquioxanes as models for

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(31) The hypothetical SiOH concentration was calculated by assuming that trisilanol **1** was derived from the (111) octahedral face of a β-cristobalite-like lattice with a Si–Si separation of 4.9 Å (the Si–Si separation in **1**).

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silica surfaces, as well as the unique coordinating ability of **1**.

Experimental Section

General Procedures. Except where noted, all operations were performed under a nitrogen atmosphere, either on a high-vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-lab.

Tetrahydrofuran (THF) and diethyl ether were distilled from dark purple solutions of potassium benzophenone ketyl under nitrogen. Aliphatic and aromatic hydrocarbon solvents were distilled from dark purple solutions of potassium benzophenone ketyl containing tetraglyme. Before distillation, aliphatic hydrocarbon solvents were stirred for 48 h over two portions of concentrated H_2SO_4, washed successively with saturated $KMnO_4$ in 10% H_2SO_4, three portions of H_2O, and one portion of saturated Na_2CO_3, and dried over $CaCl_2$. Cyclohexane, dichloromethane, chloroform, pyridine, triethylamine, chlorotrimethylsilane, and acetonitrile were distilled from CaH_2 under nitrogen immediately before use. $CDCl_3$ was vacuum distilled [25 °C (0.1 Torr)] from CaH_2 or P_2O_5, while C_6D_6 was vacuum distilled [25 °C (0.1 Torr)] from sodium benzophenone ketyl. Trichlorosilane obtained from Strem Chemcial Co., methyl trichlorogermane and methyl trichlorostannane obtained from Alpha Products, and triphenyltin chloride and hexachloroplatinic acid obtained from Aldrich Chemical Co. were used without further purification.

NMR spectra were recorded on Bruker WM-250 (^1H, 250.1 MHz; ^{13}C, 62.5 MHz; ^{29}Si, 49.7 MHz), General Electric QE-300 (^1H, 300.15 MHz; ^{13}C, 75.04 MHz), or GN-500 (^1H, 500.1 MHz; ^{13}C, 125.03 MHz; ^{29}Si, 99.36 MHz) NMR spectrometers. All chemical shifts are reported in units of δ (downfield from tetramethylsilane) but were most often measured relative to (residual) ^1H or ^{13}C resonances in the deuterated solvents: $CDCl_3$ (δ 7.260 for ^1H, δ 77.000 for ^{13}C), C_6D_6 (δ 7.150 for ^1H, δ 128.000 for ^{13}C). Most ^{29}Si NMR spectra were recorded with inverse-gated proton decoupling in order to increase resolution and minimize nuclear Overhauser enhancement effects. To ensure integrated intensities, all ^{29}Si NMR samples contained 0.02 M $Cr(acac)_3$ in order to reduce T_1's to <2 s, and at least three T_1's were allowed to elapse between observation pulses. Infrared spectra were recorded in dilute solutions or pressed KBr pellets on a Perkin-Elmer PE-281 IR Spectrophotometer. Electron impact mass spectral analyses were conducted on a VG 7070e high-resolution mass spectrometer. Melting points were measured with a Mel-temp melting point apparatus and are uncorrected.

Full details regarding the X-ray crystal structures of **1** and **3b** are reported in the supplementary material.

Preparation of Cyclohexyltrichlorosilane (CySiCl₃). $CySiCl_3$ was prepared by a modification of the procedure described by Selin and West.[37] Trichlorosilane (6.00 L, 62 mol) was added via cannula to cyclohexene (4 L, 39.5 mol) and hexachloroplatinic acid (1 g) in a 12-L round-bottomed flask. The mixture was refluxed under nitrogen for 10 days with a condensor maintained at -20 °C by a circulated bath of refrigerated methanol. The reflux condenser was replaced by a distillation head, and then the mixture was fractionally distilled under nitrogen at atmospheric pressure: bp 30–40 °C, $HSiCl_3$, 1.5 L; bp 50–60 °C, $SiCl_4$, 0.75 L; bp 201–207 °C, $CySiCl_3$, 7.86 kg (92% based on cyclohexene).

General Procedure for the Hydrolytic Condensation of CySiCl₃. Preparation of 1, 2, and 3a. Distilled H_2O (3.2 L) was carefully added with stirring to a solution of $CySiCl_3$ (650 g, 3.0 mol) in 12 L of technical-grade acetone in a 5-gal glass carboy. The carboy was stoppered and then allowed to stand for 3–36 months (vide infra).

To facilitate isolation of the crystalline products, most of the solvent and resinous liquid were first decanted into another 5-gal glass carboy. After acetone (~200–300 mL) was added to dissolve the resin, the precipate was collected in a large sintered-glass Buchner funnel and washed with acetone. The wet filter cake inevitably contained large amounts of occluded resinous material, which was most efficiently removed by finely pulverizing the crude product, stirring with approximately 300–500 mL of acetone for 1 h, and then vacuum filtering. After the material was dried overnight at 40–50 °C, approximately 70 g of product containing 45% of **1**, 40% of **2**, and 15% of **3a** were obtained. The combined acetone washes were added to the aqueous acetone, which had been decanted earlier. The carboy was again stoppered and allowed to stand for 3 months, whereupon an additional 40 g of product containing **1**, **2**, and **3a** in a 62:12:26 ratio precipitated. Isolation of this material as described above and an additional 12 months of standing produced another 70 g of product containing 77% of **1**, 7% of **2**, and 16% of **3a**. The reaction continues to precipitate product for approximately 3 years. The combined yield of the three products from a typical reaction is 60–70% (240–280 g).

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Isolation of 2. The crude product mixture was stirred with 5 times its weight of pyridine for approximately 30 min. Hexamer **2** was collected in a medium sintered-glass Buchner funnel, washed with a small amount of pyridine, and dried overnight at 25 °C in a fume hood. Since **2** is practically insoluble in pyridine, it is almost quantitatively removed from the crude product mixture. Recrystallization from boiling chloroform affords pure material. For **2**. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 1.73 (vbr m, 36 H), 1.26 (vbr m, 24 H), 0.84 (vbr m, 6 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, 25 °C): δ 27.30, 26.64, 26.17 (s, 2:1:2 for CH_2), 22.67 (s, CH). $^{29}Si\{^1H\}$ NMR (49.7 MHz, 1:1 $CDCl_3/Et_3N$, 25 °C, 0.02 M $Cr(acac)_3$): δ -56.23. MS (70 eV, 200 °C); relative intensity): m/e 810 (M^+, 18%), 729 ($M^+ - C_6H_{11}$, 77%). Mp: 266–269 °C.

Isolation of 1. The pyridine extract from the solution of **2** was carefully poured into 5 times its volume of ice-cold aqueous HCl (1 mL of concentrated HCl/mL of pyridine). Any large clumps of precipitated product were broken up as finely as possible and then collected on a large Buchner funnel. It was essential to remove any mechanically entrained pyridine, pyridinium hydrochloride, or HCl before continuing. This was most efficiently accomplished by very finely pulverizing the filter cake, stirring with a large excess of water for 1 h, collecting the product on a very large Buchner funnel, and then washing with copious amounts of water. The mixture of **1** and **3a** was dried overnight at 40–50 °C and then dissolved in a minimum amount of hot diethyl ether (approximately 30 mL/g of **1**) and filtered to remove particulates. The volume of the solution was reduced to approximately 10 mL/g of **3a** in the original crude product mixture, whereupon analytically pure **1** precipitated as small microcrystals. The isolated yield of **1** was typically 80% of that in the original crude reaction mixture. For **1**. ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ 6.97 (vbr s, 3 H), 1.72 (vbr, m 35 H), 1.23 (vbr, m, 35 H), 0.73 (vbr m, 7 H). $^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$, 25 °C): 27.55, 26.89, 26.66 (s, 2:1:2 for CH_2), 23.88, 23.54, 23.11 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (49.7 MHz, 1:1 $CDCl_3/Et_3N$, 25 °C, 0.02 M $Cr(acac)_3$): δ -60.16, -67.99, -69.54 (s, 3:1:3). MS (65 eV, 200 °C); relative intensity): m/e 871 ($M^+ - C_6H_{11} - H_2O$, 100%), 789 ($M^+ - C_6H_{11} - C_6H_{10} - H_2O$, 6%). MP: 250 °C (dec).

Isolation of 3a. If necessary, the mother liquors from the fractional crystallization of **1** from ether were further concentrated to approximately 10 mL of ether/g of **3a** in the original crude product mixture to precipitate additional **1** (which was collected by filtration). The remaining solution was evaporated to dryness and then recrystallized from a minimum amount of hot chloroform (10 mL/g of **3a**). The isolated yield of pure **3a** was typically 60–70% of that in the original crude reaction mixture. Additional cycles of fractional crystallizations from ether and chloroform will naturally increase the isolated yields of **1** and **2a** but were normally not performed. The mother liquors were evaporated and then combined with pyridine extracts from subsequent reactions. For **3a**. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 2.09 (s, 2 H), 1.75 (vbr m, 40 H), 1.23 (vbr m, 40 H), 0.77 (m, 8 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, 25 °C): δ 27.53, 27.51, 27.47, 27.42, 26.82, 26.78, 26.71, 26.69, 26.63, 26.53, 26.51, 26.49, (s, CH_2), 23.70, 23.67, 23.37, 23.20 (s, 2:2:2:2 for CH). $^{29}Si\{^1H\}$ NMR (99.36 MHz, 9:1 (v/v) pyridine/C_6D_6, 25 °C, 0.02 M $Cr(acac)_3$): δ -58.46, -65.66, -67.51, -68.58 (s, 2:2:2:2). IR (CCl_4): 3700 (m), 2925 (s), 2855 (s), 1448 (m), 1197 (m), 1120 (s), 1100 (s), 1040 (m), 1030 (m), 892 (m) cm⁻¹. MS (22 eV, 200 °C): relative intensity): m/e 1015 ($M^+ - C_6H_{11}$, 100%), 997 ($M^+ - C_6H_{11} - H_2O$, 16.5%). Anal. Calcd for $C_{48}H_{90}O_{13}Si_8$ (found): C, 52.42 (52.33); H, 8.25 (8.35). MP: 316–326 °C (dec).

Preparation of 3b. Triethylamine (50 µL, 0.359 mmol) was added to slurry of **3a** (100 mg, 0.091 mmol) and triphenyltin chloride (70 mg, 0.182 mmol) in benzene (0.5 mL). After the solution was stirred for 1 h at 25 °C, the volatiles were removed in vacuo [25 °C (0.1 Torr)], and the residue was extracted with toluene (0.4 mL). Colorless plates of the toluene solvate of **3b** (130 mg, 77%) were obtained by carefully layering acetonitrile (1 mL) onto the toluene solution and cooling to 10 °C for 2 days. For **3b**. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 7.70 (m, 12 H, *o*-H), 7.46 (m, 18 H, *m*- + *p*-H), 1.69 (vbr m, 40 H), 1.19 (vbr m, 40 H), 0.62 (m, 6 H), 0.52 (m, 2 H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, 25 °C): δ 138.95; 136.27 ($J_{^{13}C^{-117,119}Sn}$ = 46.1 Hz); 129.85; 128.67 ($J_{^{13}C^{-117,119}Sn}$ = 61.7 Hz); 27.74, 27.69, 27.57, 27.51, 27.17, 26.91, 26.87, 26.85, 26.79, 26.65, 26.53 (s, CH_2); 25.02, 23.77, 23.43, 23.29 (s, 2:2:2:2 for CH). MP: 188–192 °C after desolvation at ~100 °C.

Preparation of 5b. A benzene (2-mL) solution of methyl trichlorogermane (41 mg, 0.21 mmol) was rapidly added to a solution of **1** (194 mg, 0.200 mmol) in 5 mL of 4:1 (v/v) C_6H_6/Et_3N and stirred for 2 h at 25 °C. Evaporation of the volatiles [25 °C (0.1 Torr)], extraction with pentane, and solvent removal in vacuo [25 °C (0.1 Torr)] gave a virtually quantitative yield of crude **5b** as an amorphous white foam. Recrystallization by slow diffusion of acetonitrile into a concentrated benzene solution of **5b** afforded 195 mg (92%) of colorless crystals. For **5b**. ^1H

NMR (250.13 MHz, CDCl₃, 25 °C): δ 1.73 (vbr m, 35 H), 1.24 (vbr m, 35 H), 0.74 (vbr m, 7 H), 0.715 (s, 3 H). ¹³C{¹H} NMR (62.5 MHz, CDCl₃, 25 °C): δ 27.61, 27.55, 26.95, 26.72 (s, CH₂), 23.81, 23.35, 23.29 (s, 3:3:1 for CH), 0.93 (s, CH₃). ²⁹Si{¹H} NMR (49.7 MHz, CDCl₃, 25 °C): δ −67.41, −68.40, −68.92 (s, 3:1:3). MS (65 eV, 200 °C; relative intensity): *m/e* 1043 (M⁺ − CH₃, 1%), 975 (M⁺ − C₆H₁₁, 50%), 893 (M⁺ − C₆H₁₁ − C₆H₁₀, 100%).

Preparation of 5c. A benzene (2-mL) solution of methyl trichlorostannane (50 mg, 0.21 mmol) was rapidly added to a solution of 1 (194 mg, 0.200 mmol) in 5 mL of 4:1 (v/v) C₆H₆/Et₃N and stirred for 2 h at 25 °C. Evaporation of the volatiles [25 °C (0.1 Torr)], extraction with pentane, and solvent removal in vacuo [25 °C (0.1 Torr)] gave a virtually quantitative yield of crude 5c as an amorphous white foam. Recrystallization by slow diffusion of acetonitrile into a concentrated benzene solution of 5c afforded 212 mg (96%) of colorless crystals. For 5c. ¹H NMR (250.13 MHz, CDCl₃, 25 °C): δ 1.72 (vbr m, 35 H), 1.24 (vbr m, 35 H), 0.939 (s, 3 H), 0.73 (vbr m, 7 H). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, 25 °C): δ 27.70, 27.56, 27.19, 26.96, 26.73, 26.67 (s, CH₂): 24.36, 23.44, 23.25 (s, 3:3:1 for CH); −3.12 (s, CH₃). ²⁹Si{¹H} NMR (49.7 MHz, CDCl₃), 25 °C): δ −65.00, −68.24, −69.55 (s, 3:1:3). MS (65 eV, 200 °C; relative intensity): *m/e* 1089 (M⁺ − CH₃, 1.2%), 1021 (M⁺ − C₆H₁₁, 80%), 939 (M⁺ − C₆H₁₁ − C₆H₁₀, 100%).

Preparation of 6a and 6b. Chlorotrimethylsilane (1.799 g, 16.57 mmol) was added dropwise to a solution of 1 (14.00 g, 14.40 mmol) and triethylamine (14.57 g, 144.0 mmol) in THF (280 mL). Triethylammonium hydrochloride, which began to precipitate soon after mixing, was removed by vacuum filtration after 18 h of stirring at 25 °C. Removal of the volatiles in vacuo [25 °C (0.1 Torr)] afforded a 9:1 mixture of 6a and 6b. This white solid was extracted with hexane (700 mL), filtered, and concentrated to 125 mL by distillation [68 °C (1 atm)]. After the solution stood for 2 days at 22 °C, pure 6a (9.551 g, 63.4%) precipitated as colorless crystals. Cooling to −10 °C produced an additional 424 mg (20%) of material. Two additional crops (2.786 g, 17.3%) of 6a were collected by further concentrating the solution and cooling to −10 °C. Total yield: 12.337 g (80.7%). For 6a. ¹H NMR (500.1 MHz, CDCl₃, 25 °C): δ 4.187 (s, 2 H, OH), 1.73 (vbr m, 35 H), 1.23 (vbr m, 35 H), 0.77 (brm, 6 H), 0.67 (brm, 1 H), 0.157 (s, 9 H, SiMe₃). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, 25 °C): δ 27.59, 27.57, 27.51, 27.48, 26.86, 26.82, 26.77, 26.68, 26.62, 26.57, 26.52 (s, CH₂); 24.61, 23.79, 23.40, 23.16, 23.04 (s, 1:2:2:1:1 for CH); 1.65 (s, SiMe₃). ²⁹Si{¹H} NMR (99.36 MHz, CDCl₃, 25 °C, 0.02 M Cr(acac)₃): δ 11.24 (s, SiMe₃); −58.53, −67.57, −67.80, −68.00, −69.50 (s, 2:1:1:1:2). IR (CCl₄): 3450 (m), 2920 (s), 2853 (s), 1447 (m), 1270 (m), 1253 (sh), 1195 (m), 1112 (s), 1038 (sh), 1028 (sh), 895 (m), 847 (m) cm⁻¹. Anal. Calcd for C₄₅H₈₈O₁₂Si₈ (found): C, 51.68 (52.04); H, 8.48 (8.83). MP: 236−238 °C.

The volatiles were removed from the mother liquor in vacuo [25 °C, (0.1 Torr)] to yield a white foam, which was dissolved in warm acetone (15 mL). After the mixture stood for 12 h at 22 °C, colorless crystals of 6b precipitated (0.850 g, 5.3%). A second crop (0.791 g, 4.9%) was obtained by slowly concentrating the solution at 22 °C over 2 days. Total yield: 1.641 g (10.2%). Analytically pure material was obtained by slow diffusion of acetonitrile into a benzene solution of 6b. For 6b. ¹H NMR (500.1 MHz, CDCl₃, 25 °C): δ 2.79 (s, 2 H, OH), 1.75 (vbr m, 35 H), 1.24 (vbr m, 35 H), 0.75 (br m, 5 H), 0.65 (br m, 2 H), 0.146 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, 25 °C): δ 27.89, 27.72, 27.69, 27.65, 27.52, 26.97, 26.93, 26.90, 26.83, 26.75, 26.57 (s, CH₂), 24.95, 24.78, 23.80, 23.63, 23.07 (s, 2:1:2:1:1 for CH), 1.79 (s, SiMe₃). IR (CCl₄): 3550 (m br), 2920 (s), 2850 (s), 1449 (m), 1270 (sh), 1253 (sh), 1195 (m), 1108 (s), 1038 (sh), 1028 (sh), 895 (m), 845 (m) cm⁻¹. Anal. Calcd for C₄₈H₉₆O₁₂Si₉ (found): C, 51.57 (51.36); H, 8.66 (8.86). MP: 207−209 °C.

Preparation of 6c. Chlorotrimethylsilane (196 μL, 1.546 mmol) was added to a solution of 1 (500 mg, 0.514 mmol) in 25 mL of chloroform containing 1 mL of pyridine. After the solution was stirred for 4 h at 25 °C, the solvent was removed in vacuo (10⁻⁴ Torr). The white residue was extracted with pentane and filtered and the solvent again removed in vacuo (10⁻⁴ Torr) to yield 600 mg (98%) of crude 6c. Colorless crystals (582 mg, 95%) were obtained by carefully layering acetonitrile onto a concentrated benzene solution of 6c and allowing it to stand for 48 h. For 6c. ¹H NMR (500.1 MHz, CDCl₃, 25 °C): δ 1.75 (vbr m,

35 H), 1.22 (vbr m, 35 H), 0.72 (br m, 4 H), 0.60 (br m, 3 H), 0.11 (s, 27 H). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, 25 °C): δ 27.91, 27.76, 27.13, 26.98, 26.93, 26.84, 26.52 (s, CH₂), 25.25, 24.87, 23.04 (s, 3:3:1 for CH), 1.99 (s, CH₃). IR (CCl₄): 2918(s), 2855 (s), 1448 (m), 1255 (s), 1200 (s), 1119 (sh), 1114 (sh), 1110 (s), 1105 (s), 1094 (s), 1090 (s), 1084 (sh), 1055 (sh), 1038 (sh), 897 (s), 843 (m) cm⁻¹. MS (10 eV, 200 °C; relative intensity): *m/e* 1174 (M⁺ − CH₃, 9%), 1106 (M⁺ − C₆H₁₁, 100%). Anal. Cald for C₅₁H₁₀₄O₁₂Si₁₀ (found): C, 51.46 (51.36); H, 8.82 (8.94). MP (sealed capillary under N₂): 297−300 °C.

Preparation of 7a. Trisilanol 1 (100.0 mg, 0.514 mmol) was dissolved in 10 mL of benzene containing 0.25 mL of Et₃N and refluxed for 12 h over freshly activated 4-Å molecular sieves. The solution was allowed to cool to room temperature and filtered and the solvent removed in vacuo (10⁻⁴ Torr) to give a white amorphous foam. Extraction of the crude material with pentane, vacuum filtration, and solvent evaporation [25 °C (10⁻⁴ Torr)] afforded 40 mg (41%) of 7a as an amorphous white foam. The product slowly decomposes in both the solid and solution states. For 7a. ¹H NMR (500.1 MHz, C₆D₆, 25 °C): δ 2.997 (s, 1 H), 2.06 (vbr m, 15 H), 1.62 (vbr m, 35 H), 1.23 (vbr m, 20 H), 0.96 (m, 7 H). ¹³C{¹H} NMR (125.76 MHz, C₆D₆, 25 °C): δ 27.89, 27.77, 27.75, 27.62, 27.58, 27.32, 27.27, 27.21, 27.17, 27.00, 26.95, 26.93, 26.74 (s, CH₂), 23.82, 23.71, 23.64, 23.05 (s, 3:1:2:1 for CH). The chemical shifts of the methine resonances are very sensitive to traces of Et₃N in the sample: 23.98, 23.87, 23.70, 23.66, 23.07 (s, 1:2:1:2:1 for CH with traces of Et₃N present). ²⁹Si{¹H} NMR (49.7 MHz, CDCl₃, 25 °C, 0.02 M Cr(acac)₃): δ −55.28, −56.91, −57.08, −66.07, −66.40 (s, 1:1:2:1:2). IR (CCl₄): 2925 (s), 2856 (s), 1547 (sh), 1545 (w), 1448 (m), 1276 (w), 1268 (w), 1197 (m), 1115 (sh), 1108 (s), 1105 (sh), 1103 (sh), 1091 (sh), 1086 (s), 1083 (sh), 1071 (sh), 1065 (s), 1040 (sh), 1030 (w), 982 (w), 895 (m), 850 (w) cm⁻¹. MS (70 eV, 230 °C; relative intensity): *m/e* 871 (M⁺ − C₆H₁₁, 100%). Anal. Calcd for C₄₂H₇₈O₁₁Si₇ (found): C, 52.77 (52.93); H, 8.24 (8.88).

Preparation of 7b. Trimethylsilylchloride (65 μL, 0.514 mmol) was added to a solution of 7a (500 mg, 0.514 mmol) in 35 mL of benzene containing 0.5 mL of triethylamine. After the solution was stirred for 4 h at 25 °C, the solvent was removed in vacuo (10⁻⁴ Torr). The white residue was extracted with pentane and filtered and the solvent again removed in vacuo (10⁻⁴ Torr) to yield 650 mg (99%) of crude 7b. Colorless crystals (617 mg, 94%) were obtained by carefully layering acetonitrile onto a concentrated benzene solution of 7b and standing for 48 h. For 7b. ¹H NMR (500.1 MHz, C₆D₆, 25 °C): δ 2.09 (vbr m, 15 H), 1.68 (vbr m, 35 H), 1.27 (vbr m, 20 H), 1.06 (m, 7 H), 0.357 (s, 9 H). ¹³C{¹H} NMR (125.76 MHz, C₆D₆, 25 °C): 27.96, 27.78, 27.75, 27.69, 27.67, 27.56, 27.34, 27.33, 27.31, 27.19, 27.18, 27.16, 27.04, 26.92, 26.82 (s, CH₂), 25.00, 24.12, 23.85, 23.83, 23.18 (s, 1:2:2:1:1 for CH), 1.96 (s, CH₃). ²⁹Si{¹H} NMR (49.7 MHz, CDCl₃, 25 °C, 0.02 M Cr-(acac)₃): δ 9.06 (s, SiMe₃), −56.33, −59.02, −66.68, −68.76, −68.84 (s, 1:2:1:1:2 for SiCH). IR (CCl₄): 2920 (s), 1447 (m), 1275 (w), 1271 (w), 1251 (w), 1215 (m), 1197 (m), 1142 (sh), 1138 (sh), 1133 (sh), 1128 (sh), 1114 (s), 1107 (sh), 1096 (s), 1067 (sh), 1060 (s), 1057 (s), 1038 (sh), 1028 (w), 988 (w), 896 (m), 847 (m) cm⁻¹. MS (70 eV, 230 °C; relative intensity): *m/e* 943 (M⁺ − C₆H₁₁, 32%), 871 (M⁺ − C₆H₁₁ − SiMe₃, 100%). Anal. Cald for C₄₅H₈₆O₁₁Si₈ (found): C, 52.57 (53.09); H, 8.45 (8.86). MP: 144−146 °C.

Supplementary Material Available: X-ray crystal data for 1 and 3b including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (23 pages); listing of calculated and observed structure factors (62 pages). Ordering information is given on any current masthead page.