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Synthesis and Structure of 1,3,5-Tris(diorganohydroxysilyl)benzenes. Novel Building Blocks in Supramolecular Silanol Chemistry

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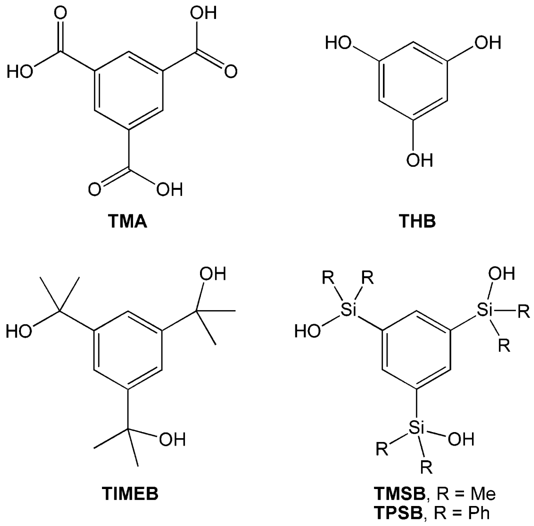
The 1,3,5-tris(diorganohydroxysilyl)benzenes 1,3,5-$(HOR_2Si)_3C_6H_3$ (TMSB, R = Me; TPSB, R = Ph) have been prepared and fully characterized by X-ray crystallography. The crystal structure of TMSB features pairwise connected layers, in which the molecules are involved in interlayer hydrogen bonding. The supramolecular hydrogen bond motif may be described as a 12-membered ring that adopts a chair conformation. TPSB forms an equimolar inclusion complex with water, which is associated via hydrogen bonding and apparently fills a void in the crystal packing. In this case, the supramolecular hydrogen bond motif may be described as an eight-membered ring. Two of the water molecules are also associated, giving rise to a water dimer entrapped in the silanol matrix. Besides the hydrogen bonds, the crystal structure of the TPSB·H_2O complex reveals intra- and intermolecular C−H···π stacking of most of the phenyl groups. Electrospray mass spectrometry shows that TPSB undergoes supramolecular complex formation with a variety of N-donors such as 4-(dimethylamino)pyridine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, imidazole, 2-(dimethylamino)pyridine, and 2,2′-dipyridylamine.

Introduction

In supramolecular organic chemistry, considerable efforts have been directed toward the design of clathrates, interpenetrating networks or nanoporous solids, which are often based on hydrogen-bonded assemblies of molecular building blocks having suitable donor and acceptor sites with preorganized directionality.[1] An important family of molecular building blocks comprises 1,3,5-trifunctionalized benzene derivatives including the frequently employed trimesic acid (TMA) and 1,3,5-trihydroxybenzene (THB),[2] or the less often used 1,3,5-tris(1-hydroxy-1-methylethyl)benzene (TIMEB) (Chart 1).[3] Organosilanols, the silicon congeners of alcohols, are well-known for their extensive self-organization in the solid state, which makes them potentially useful building blocks for the emerging field of supramolecular organometallic chemistry.[4,5] Organosilanols possess both excellent donor and acceptor sites for the formation of hydrogen-bonded assemblies with themselves,[6] alcohols,[7,8] ethers,[9−11] or amines.[12−18] For instance, the supramolecular structures of Ph_3SiOH[19] and Me_3SiOH[20] give rise to two cyclic tetramers and a polymeric array, respectively (Chart 2). Sterically more encumbered

Chart 1



TMA

THB

TIMEB

TMSB, R = Me
TPSB, R = Ph

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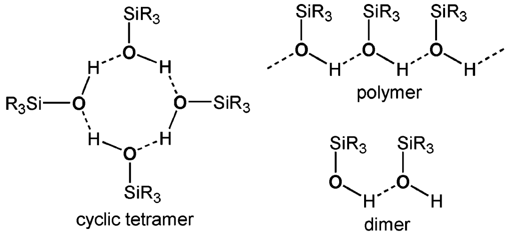
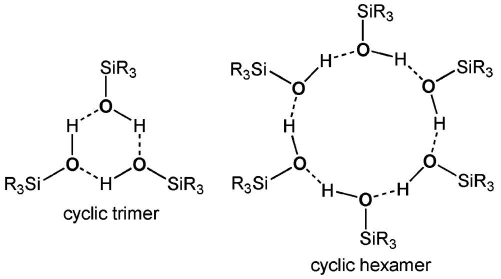
Chart 2

Known supramolecular motifs of triorganosilanols



Hitherto unknown supramolecular motifs of triorganosilanols



triorganosilanols including Ph_2(fluorenyl)SiOH and $(PhCH_2)_3SiOH$ show a somewhat limited ability to form hydrogen-bonded complexes and contain dimers or even monomers in the solid state (Chart 2).[21]

Cyclic trimers and hexamers, frequently encountered supramolecular motifs in the crystal structures of alcohols,[4] have not yet been observed for organosilanols (Chart 2). Recently reported were the first theoretical efforts undertaken to estimate strain energies associated with cyclic hydrogen-bonded motifs of organosilanol assemblies.[22] Most interestingly, Ph_3SiOH forms a selective inclusion complex with ethanol, in which the tetrameric structure is retained, even in the presence of a large excess of water, methanol, or propanol.[7] On the other hand, *t*-$BuMe_2SiOH$ readily crystallizes as a hemihydrate, but forms no complexes with small alcohols.[23] Furthermore, complexes of Ph_3SiOH are known with 12-crown-4, 1,4-dioxane, DMSO, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tris(2-aminoethylamine), 4-phenylpyridine, 4,4′-dipyridyl, and acridine, respectively.[6,11,13,15] While the latter examples demonstrate that simple organosilanols undergo formation of a variety of hydrogen-bonded complexes, their potential as building blocks in supramolecular chemistry is somewhat limited due to the lack of directional preorganization of the silanol sites at the molecular level.

We now describe the preparation and full characterization of two 1,3,5-tris(diorganohydroxysilyl)benzenes, 1,3,5-$(HOR_2Si)_3C_6H_3$ (TMSB, R = Me; TPSB, R = Ph), which possess three directionally preorganized silanol groups and therefore hold potential as building blocks in supramolecular organometallic chemistry (Chart 1).

Results and Discussion

TMSB and TPSB were prepared by the oxidation of the corresponding 1,3,5-tris(diorganosilyl)benzenes adopting literature procedures for similar compounds. Thus, 1,3,5-$(HMe_2Si)_3C_6H_3$ and 1,3,5-$(HPh_2Si)_3C_6H_3$ were oxidized using Pearlman's catalyst, $Pd(OH)_2/C$,[24] in aqueous THF and $AgNO_3$ in water, respectively (eq 1).[25] TMSB and TPSB consist of high-melting colorless crystalline solids that are sparingly soluble in unpolar solvents and readily soluble in polar solvents.

$$\text{1,3,5-}(HR_2Si)_3C_6H_3 \xrightarrow[(i)\text{ or }(ii)]{\text{oxidation}} \text{1,3,5-}(HOR_2Si)_3C_6H_3 \quad \begin{matrix}\text{TMSB, R = Me}\\ \text{TPSB, R = Ph}\end{matrix} \tag{1}$$

(*i*) Pearlman's catalyst in THF/H_2O;
(*ii*) $AgNO_3$ in H_2O

Crystal and Molecular Structure of 1,3,5-$(HOMe_2Si)_3C_6H_3$ (TMSB). The molecular structure of TMSB is depicted in Figure 1, and two perspective views of the crystal structure are shown in Figures 2 and 3; selected bond and hydrogen bond parameters are collected in the captions of Figures 1 and 3. As observed for the great majority of organosilanols, all three silanol sites in TMSB act as both hydrogen bond donors and acceptors.[6] Owing to the orientation of the molecules in the crystal lattice, the three dimethylhydroxysilyl substituents adopt aligned conformations, so that the silanol groups are situated on the same side of the benzene ring (Figure 1). The individual molecules are packed in layers, in which the symmetry-related ben-

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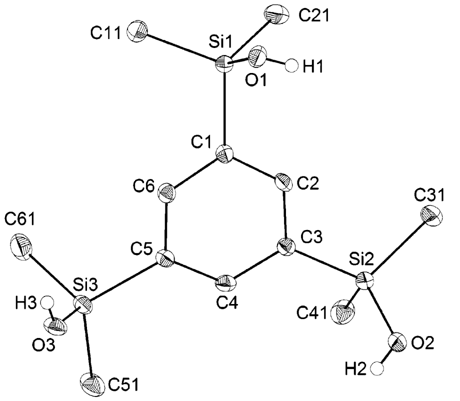

Figure 1. Molecular structure of TMSB showing 30% probability displacement ellipsoids and the atom-numbering scheme. Selected bond parameters [Å, deg]: Si−O 1.645(2)−1.653(2); Si−C 1.846(4)−1.875(2); C−Si−O 104.57(12)−111.69(9); C−Si−C 107.43(12)−112.72(13).

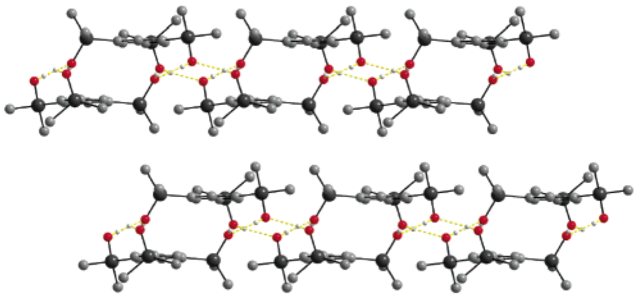

Figure 2. Crystal structure of TMSB, as viewed along the *c*-axis, showing two stacks of hydrogen-bonded double layers.

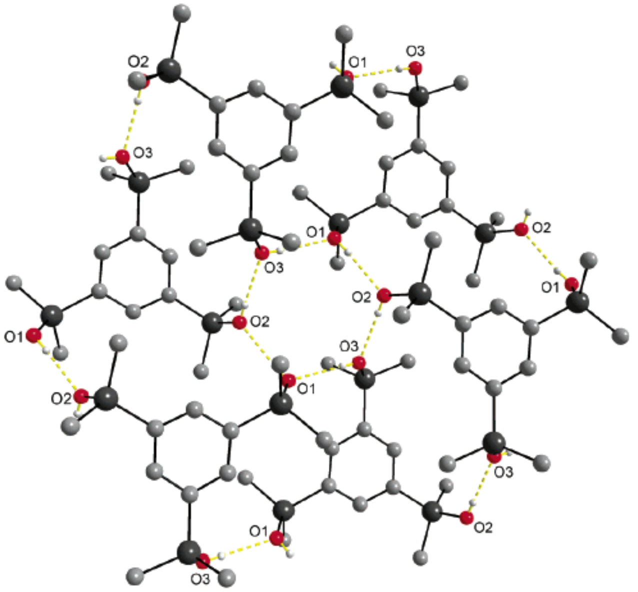

Figure 3. Crystal structure of TMSB showing the hydrogen bond assembly of six oxygen and hydrogen atoms. Hydrogen-bonding parameters [Å, deg]: O1−H1 0.701(14); H1···O2 1.994(13); O1···O2 2.693(5); O1−H1···O2 176(2); O2−H2 0.694(21); H2···O3 2.011(21); O2···O3 2.703(3); O2−H2···O(3) 176(2); O3−H3 0.684(25); H3···O1 2.031(24); O3···O1 2.704(3); O3−H3···O1 168(2).

zene rings are coplanar (Figure 2). The silanol groups are located on the same side of the layer, which consequently possesses a strongly hydrophilic character. Adjacent layers are pairwise connected through their hydrophilic sides, whereby all three silanol groups of the molecules are involved in interlayer hydrogen bonding. Stacks of these pairwise connected layers are linked only by the van der Waals interactions of their hydrophobic exterior sides (Figure 2). The supramolecular motif defined by the hydrogen bond interactions may be described as a 12-membered quasi ring of six oxygen and hydrogen atoms that features a chair conformation (Figures 2 and 3); the bond parameters are consistent with medium-strength hydrogen bonding.[26] It is interesting to note that such a cyclic hexamer structure has not yet been observed for simple triorganosilanols (Chart 2) and that the supramolecular structure of TIMEB (Chart 1), the carbon analogue of TMSB,[3] features both polymeric arrays and eight-membered rings, i.e., cyclic tetramers, although 12-membered rings are frequently encountered supramolecular motifs in the crystal structures of alcohols.[4] By comparison with the recently reported crystal structure of 1,3-bis(dimethylhydroxysilyl)benzene comprising hexagonal arrays of stacked dimers,[27] it can be further surmised that all three silanol sites of TMSB are essential for the stabilization of the supramolecular motif (Figures 2 and 3).

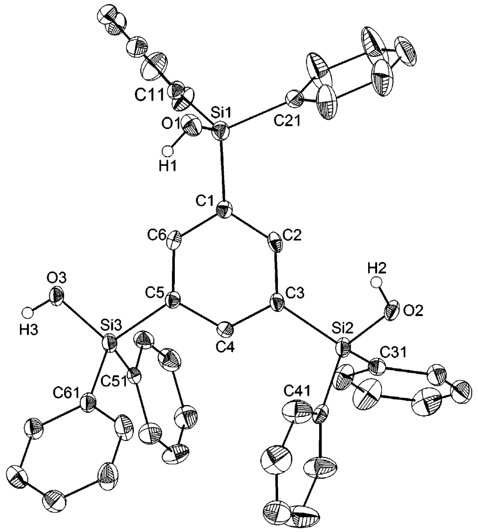

Figure 4. Molecular structure of TPSB showing 30% probability displacement ellipsoids and the atom-numbering scheme. Selected bond parameters [Å, deg]: Si−O 1.651(4)−1.662(3); Si−C 1.850(6)−1.870(6); C−Si−O 105.95(9)−112.21(10); C−Si−C 104.87(11)−111.90(11).

Crystal and Molecular Structure of 1,3,5-(HOPh$_2$Si)$_3$C$_6$H$_3$·H$_2$O (TPSB·H$_2$O). The molecular structure of TPSB is depicted in Figure 4, and one perspective view of the crystal structure is shown in Figure 5; selected bond and hydrogen bond parameters are collected in the captions of Figures 4 and 5. TPSB forms an equimolar inclusion complex with water, which is associated via hydrogen bonding and fills a void in the crystal packing. The supramolecular motif defined by the hydrogen bond interactions is best described as an eight-membered ring of four oxygen and hydrogen atoms

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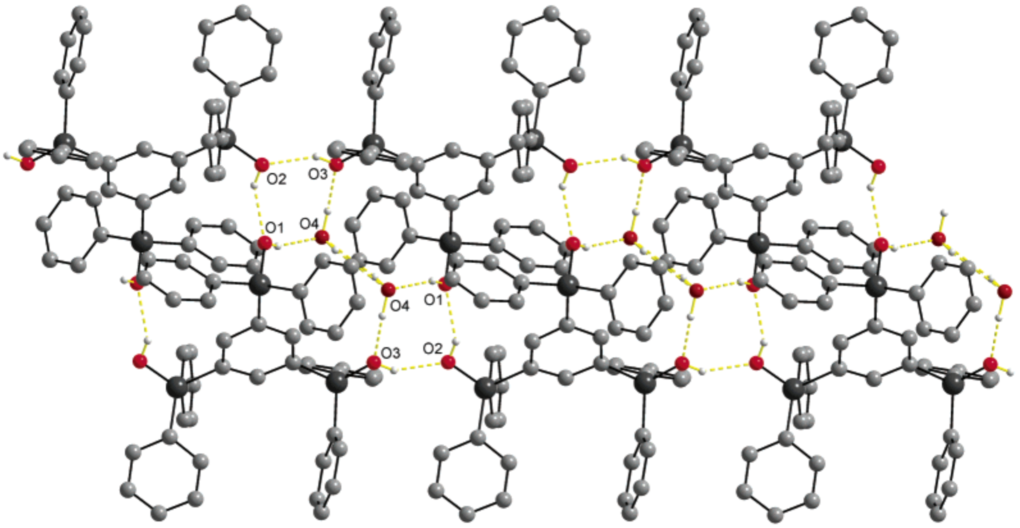

Figure 5. Crystal structure of TPSB·H_2O showing the C−H···π stacking and the hydrogen bond assembly including the entrapped water dimer. Hydrogen-bonding parameters [Å, deg]: O1−H1 0.820(4); H1···O4 1.969(9); O1···O4 2.733(13); O1−H1···O4 154.74(16); O4−H4 0.947(34); H4···O3 1.832(34); O4···O3 2.755(4); O4−H4···O3 164.23(309); O3−H3 0.820(2); H3···O2 1.999(4); O3···O2 2.745(6); O3−H3···O2 150.86(10); O2−H2 0.820(2); H2···O1 2.058(2); O2···O1 2.721(2); O2−H2···O1 137.66(12); O4−H5 0.749(48); H5···O4 2.313(40); O4···O4a 3.008(8); O4−H5···O4a 155.03(375) (symmetry operation: $a = -x, -y, -z$).

incorporating three silanol sites (O1−O3) and one water molecule (O4). In this way it resembles the supramolecular tetramer of the parent compound Ph_3SiOH (Chart 1),[19] rather than the hydrogen-bonding pattern of the inclusion complex $(Ph_3SiOH)_4$·EtOH, which forms a distorted 10-membered ring.[7] The bond parameters of TMSB are also consistent with medium-strength hydrogen bonding.[26] The water molecule (O4) is further associated with a symmetry-related water molecule (O4a; symmetry operation: $a = -x, -y, -z$), giving rise to a water dimer[28] entrapped in a silanol matrix (Figure 5). The related O4···O4a distance of 3.008(8) Å is somewhat larger than the gas-phase value of the water dimer (2.967(3) Å), as determined by microwave spectroscopy.[29] Although all hydrogen atoms situated near oxygen atoms have been located in the final refinement cycle of the X-ray structure analysis, there is evidence that some of the hydrogen atoms, e.g., H4, are disordered.[30] It is noteworthy that most of the phenyl rings in the crystal structure of TPSB adopt edge-to-face conformations, indicative of significant C−H···π stacking (Figure 5).[31]

Supramolecular Gas-Phase Complexes of TPSB with Selected N-Donors. In general, the nucleation of cocrystals should be facilitated when the components also interact in solution, e.g., via hydrogen bonding. In an effort to probe such interactions, electrospray mass spectrometry (ESMS) studies of TPSB and additional N-donors have been performed. ESMS allows the rapid and unambiguous gas-phase detection of supramolecular complex ions already preformed in solution.[32] The ESMS spectrum (positive mode, cone voltage 20 V, MeCN; measured range 0−2800 Da) of TPSB shows mass clusters of $[\text{TPSB} + \text{Na}]^+$ (695.2 Da), $[2\ \text{TPSB} + \text{Na}]^+$ (1368.4 Da), $[3\ \text{TPSB} + \text{Na}]^+$ (2041.6 Da), and $[4\ \text{TPSB} + \text{Na}]^+$ (2715.8 Da), which are assigned to hydrogen-bonded silanol complexes. Upon addition of equimolar amounts of 4-(dimethylamino)pyridine (4-DMAP), these peaks disappear and new mass clusters evolve that are related to $[\text{TPSB} + \text{4-DMAP} + \text{H}]^+$ (795.3 Da), $[2\ \text{TPSB} + \text{4-DMAP} + \text{H}]^+$ (1467.5 Da), and $[3\ \text{TPSB} + \text{4-DMAP} + \text{H}]^+$ (2141.7 Da) and which are unambiguously assigned to the protonated supramolecular 1:1, 2:1, and 3:1 complexes of the silanol with the amine; the ESMS spectrum is shown in Figure 6. In these complexes, SiO−H···N hydrogen bonding presumably plays an important role.[12−18] In addition, two mass clusters of very low intensity were observed of $[\text{TPSB} + 2\ \text{4-DMAP} + \text{H}]^+$ (917.4 Da) and $[2\ \text{TPSB} + 2\ \text{4-DMAP} + \text{H}]^+$ (1590.6 Da), which belong to the protonated supramolecular 1:2 and 2:2 complexes of the silanol with the amine (Figure 6). Upon addition of equimolar amounts of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and imidazole (IMDAZ), similar mass clusters were observed of $[\text{TPSB} + \text{TMEDA} + \text{H}]^+$

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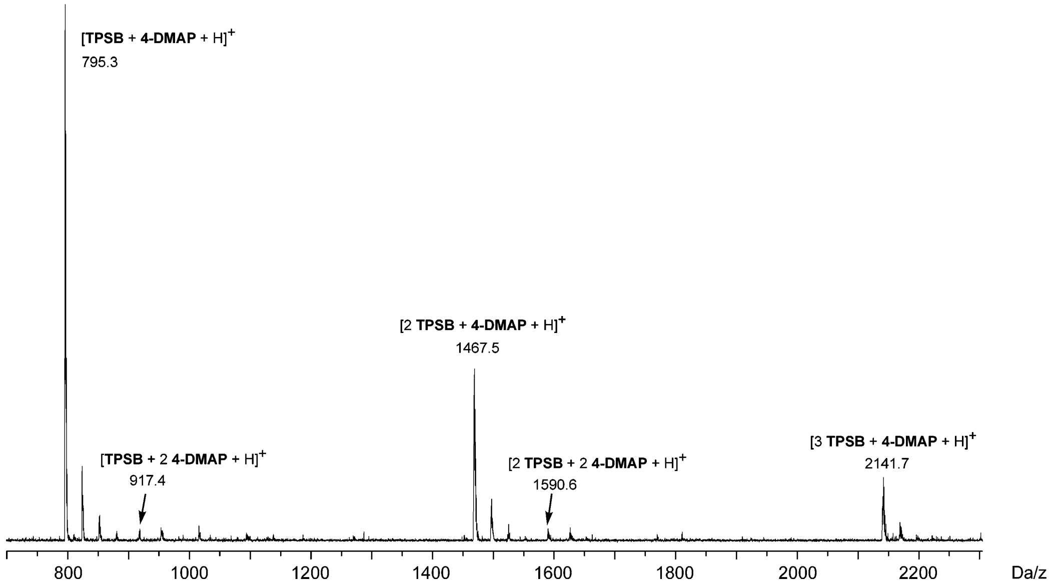

Figure 6. Electrospray mass spectrum (positive mode, cone voltage 20 V, MeCN) of a mixture of TPSB and 4-DMAP (1:1) in the range from 700 to 2300 Da.

(789.3 Da), [2 TPSB + TMEDA + H]$^+$ (1462.5 Da), [3 TPSB + TMEDA + H]$^+$ (2135.7 Da), [TPSB + IMDAZ + H]$^+$ (741.2 Da), [2 TPSB + IMDAZ + H]$^+$ (1414.4 Da), and [3 TPSB + IMDAZ + H]$^+$ (2087.6 Da). However, 2-(dimethylamino)pyridine (2-DMAP) and 2,2′-dipyridylamine (DPA) show a somewhat reduced tendency to undergo complex formation with TPSB, as only mass clusters of [TPSB + DPA + H]$^+$ (844.3 Da), [2 TPSB + DPA + H]$^+$ (1517.5 Da), and [TPSB + 2-DMAP + H]$^+$ (795.3 Da) were detected. Interestingly, no evidence was found for mass clusters related to supramolecular complexes of TPSB with 4,4′-dipyridyl, pyrazine, and 1,3,5-triazine.

We are currently engaged in cocrystallization studies of TMSB, TPSB, and related organosilanols possessing multiple silanol sites of preorganized directionality, with selected N-donors.

Experimental Section

General Procedures. All solvents were distilled prior to use. The 1,3,5-tris(diorganosilyl)benzenes, 1,3,5-$(HMe_2Si)_3C_6H_3$ and 1,3,5-$(HPh_2Si)_3C_6H_3$, were prepared by the in-situ Grignard method by reacting 1,3,5-tribromobenzene with $HSiMe_2Cl$ and $HSiPh_2Cl$, respectively, in the presence of Mg.[33] Pearlman's catalysts, $Pd(OH)_2/C$ (20 wt % Pd (dry basis) on carbon, water content ≤50%), was purchased from Aldrich. The NMR spectra were measured using a JEOL Eclipse Plus 400 spectrometer (at 399.78 Mz (^{1}H), 100.54 (^{13}C), and 79.42 (^{29}Si)) and were referenced against $SiMe_4$. The IR spectra were recorded using a BioRad FTIR spectrometer. The ESMS spectra were obtained with a Platform II single quadrapole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min^{-1}. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 200 and 20 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. Typically 10 signal-averaged spectra were collected at a cone voltage of 20 V in the positive detection mode. Microanalyses were carried out by CMAS, Belmont, Australia.

Synthesis of 1,3,5-Tris(dimethylhydroxysilyl)benzene (TMSB). To an ice-cooled suspension of Pearlman's catalyst (50 mg) in THF (80 mL) and water (5 mL) was slowly added a solution of 1,3,5-$(HMe_2Si)_3C_6H_3$ (5.05 g, 20.0 mmol) in THF (20 mL). After the evolution of hydrogen had ceased, the mixture was stirred at room temperature for 15 min. Then, the catalyst was filtered off and the solvent removed under reduced pressure so that the temperature did not exceed 30 °C. Diethyl ether (150 mL) and *n*-hexane (50 mL) were added to the remainder, and most of the water layer was separated with a pipet. The solvent was dried over Na_2SO_4, which also absorbed residues of the catalyst still present. Removal of approximately half of the solvent in a vacuum induced crystallization of TMSB (yield: 5.47 g, 18.2 mmol, 91%; mp 170−172 °C). ^{29}Si NMR (d_4-MeOH) δ: 9.1. ^{13}C NMR (d_4-MeOH) δ: 140.6, 139.5, 1.1. ^{1}H NMR (d_4-MeOH) δ: 9.27 (3H), 6.30 (3H), 1.75 (18H). IR (KBr) ν_{OH}: 3157 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_3Si_3$ (300.58): C, 47.95; H, 8.05. Found: C, 47.85; H, 7.98.

Synthesis of 1,3,5-Tris(diphenylhydroxysilyl)benzene (TPSB). A mixture of 1,3,5-tris(diphenylsilyl)benzene (12.3 g, 28.0 mmol), $AgNO_3$ (11.2 g, 92.0 mmol), and water (20 mL) was heated to 90 °C until the evolution of nitrous oxides had ceased. Water (50 mL) was added and the residue thoroughly extracted with diethyl ether (4 × 50 mL). The combined organic extracts were dried over Na_2SO_4 before the solvent was removed in a vacuum under reduced pressure. The crude product was recrystallized once from CH_2Cl_2/*n*-hexane and then from toluene to give TPSB·H_2O (yield: 5.7 g, 8.2 mmol, 41%; mp 146−148 °C). ^{29}Si NMR ($CDCl_3$) δ: 13.3. ^{13}C NMR ($CDCl_3$) δ: 143.1, 134.9, 133.7, 130.0, 127.9. ^{1}H NMR ($CDCl_3$) δ: 8.04 (3H), 7.58−7.28 (30H). IR (KBr) ν_{OH}: 3240 cm^{-1}. Anal. Calcd for $C_{42}H_{36}O_3Si_3 \cdot H_2O$ (691.02): C, 73.00; H, 5.54. Found: C, 72.91; H, 5.38.

Crystallography. Single crystals suitable for X-ray crystallography were obtained from a diethyl ether/*n*-hexane (TMSB) or toluene solution (TPSB·H_2O) at room temperature. Crystal data for TMSB: $C_{12}H_{24}O_3Si_3$, $M = 300.58$, triclinic, $a = 9.8881(2)$ Å, $b = 10.5524(3)$ Å, $c = 10.8173(3)$ Å, $\alpha = 105.6718(13)°$, $\beta = 103.8305(13)°$, $\gamma = 116.6279(11)°$, $V = 882.36(4)$ Å^3, $T = 173(1)$ K, space group $P\bar{1}$, $Z = 2$, $D_x = 1.131$ Mg/m^3, $F(000) = 324$, λ(Mo Kα) = 0.71073 Å, $\mu = 0.268$ mm^{-1}. $R_1 = 0.037$ for 2226 [$I > 2\sigma(I)$] and $wR_2 = 0.091$ for 4010 independent reflections. Crystal data for TPSB·H_2O: $C_{42}H_{38}O_4$-

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[33] (a) Chaffee, R. G.; Beck, H. N. *J. Chem. Eng. Data* **1963**, *8*, 453. (b) Chaffee, R. G. Poly(silylbenzenes). Dow Corning Patent 1966, 9 p. (c) Plenio, H. *J. Organomet. Chem.* **1992**, *435*, 21.

Si_3, $M = 690.99$, monoclinic, $a = 10.7744(8)$ Å, $b = 19.892(3)$ Å, $c = 17.827(3)$ Å, $\beta = 102.349(8)°$, $V = 3732.4(9)$ Å^3, $T = 293(1)$ K, space group $P2_1/n$, $Z = 4$, $D_x = 1.230$ Mg/m^3, $F(000) = 1456$, λ(Mo Kα) = 0.71073 Å, $\mu = 0.168$ mm^{-1}. $R_1 = 0.034$ for 2283 [$I > 2\sigma(I)$] and $wR_2 = 0.060$ for 6650 independent reflections.

Intensity data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα (0.7107 Å) radiation. The data were not corrected for absorption effects. The structure was solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[34−36] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to oxygen atoms were located in the difference Fourier map and refined isotropically.[34−36] All other hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The figures were created using DIAMOND.[37]

Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 239007 for TMSB and no. 239008 for TPSB·H_2O. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for TMSB and TPSB·H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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