Silyl-functionalized Silsesquioxanes: New Building Blocks for Larger Si-O-Assemblies, including the First Si-Si-Bonded Silsesquioxanes

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Dedicated to Professor Michael Veith on the Occasion of his 60th Birthday

Abstract.
Novel silyl-functionalized silsesquioxane building blocks have been prepared by treatment of Cy7Si7O9(OH)3 (1, Cy = c-C6H11) with hexachlorodisilane or hexachlorodisiloxane, respectively, in the presence of triethylamine. Reactions in a 1:1 molar ratio afforded the trichlorosilyl-functionalized silsesquioxane derivatives Cy7Si8O12SiCl3 (2) and Cy7Si8O12OSiCl3 (3). Related bis(silsesquioxanes), (Cy7Si8O12)2 (4) and (Cy7Si8O12)2O (5) are accessible in a similar manner by employing a 2:1 molar ratio of the reactants. Compound 1 also served as a starting material in the preparation of the partially closed silsesquioxane cages Cy7Si11(OH)SiMe2 (6) and Cy7Si11(OH)Si(OEt)2 (7), while the related condensation product Cy7Si10(OSiMe3) (9) was made by AlCl3-catalyzed elimination of water from Cy7Si7O9(OH)2-OSiMe3 (8). The molecular structure of 9 was determined by X-ray diffraction.

Keywords: silicon; silsesquioxanes; Si-Si-bond; disilane; disiloxane; X-ray structure

Introduction
Silsesquioxanes of the general formula (RSiO1.5)n form an unusual class of organosilicon compounds which are formally hybrids between silica (SiO2) and the silicones (R2SiO)n. They offer numerous exciting applications in catalysis [1, 2] as well as materials science [3, 4]. Of particular current interest is the chemistry of incompletely condensed polyhedral silsesquioxanes (“POSS”) [1, 5, 6] as these Si/O cage structures can be viewed as small soluble fragments of silica. Fehér et al. were the first to demonstrate that incompletely condensed silsesquioxanes such as Cy7Si9(OH)1 (1) share structural similarities with β-cristobalite and β-tridymite and are thus quite realistic models for the silanol sites on silica surfaces [7−14].

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the first examples of silsesquioxanes incorporating an Si-Si bond.

**Results and Discussion**

Hexachlorodisilane, Si₂Cl₆, and hexachlorodisiloxane, Si₂OCl₆, were chosen as suitable reagents for the synthesis of novel functional silsesquioxanes. Reactions between 1 and either Si₂Cl₆ or Si₂OCl₆, respectively, were carried out in toluene solution. Reactions in a 1:1 molar ratio in the presence of 3 equivalents of triethylamine according to Scheme 2 afforded the novel trichlorosilanes 2 and 3:

![Scheme 2 Preparation of Cy₇Si₈O₁₂SiCl₃ (2) and Cy₇Si₈O₁₂OSiCl₃ (3).](image)

**Scheme 2** Preparation of Cy₇Si₈O₁₂SiCl₃ (2) and Cy₇Si₈O₁₂OSiCl₃ (3).

Cy₇Si₈O₁₂SiCl₃ (2) was isolated in 43% yield as a colorless, high-melting solid, which is significantly moisture-sensitive. The Cl mass spectrum of 2 shows the protonated molecular ion (m/z 1133) with 100% relative intensity. Other peaks with high relative intensity result from elimination of one or two Cl atoms or a cyclohexyl group, respectively. Thus the mass spectrum confirms the formation of 2. The ²⁹Si NMR spectrum is also consistent with the structure of 2 as shown in Scheme 2. It consists of four signals in the range of −67.7 to −68.4 ppm (intensity ratio 1:2:3:1) for the seven cage silicon atoms bearing the cyclohexyl substituents, and one signal at −31.4 ppm for the cage silicon atoms bonded to the SiCl₃ group. The ²⁹Si resonance of the latter is found at −62.0 ppm. ¹H and ¹³C NMR data of this related compounds are generally much less informative as they show only signals attributable to the cyclohexyl substituents.

When 1 was reacted in a similar manner with hexachlorodisiloxane, Si₂OCl₆, the trichlorosiloxane derivative 3 was isolated in 62% yield. This compound too forms colorless, moisture-sensitive crystals which melt at 184-185 °C. It was fully characterized by its elemental analysis and spectroscopic data. Once again the proposed structure as depicted in Scheme 2 was confirmed mainly by mass spectrometry and the ²⁹Si NMR data. At m/z 1147 the mass spectrum displays the protonated molecular ion with 100% relative intensity. Signals at m/z 1111 (rel. int. 50%) and 1065 (rel. int. 77%) can be attributed to fragments resulting from the molecular ion via elimination of one Cl atom or one cyclohexyl group, respectively. Signals in the ²⁹Si NMR spectrum in the range of −67.8 to −70.2 ppm can be clearly assigned to the cage silicon atoms bearing the cyclohexyl moieties. A peak at −56.6 ppm originates from the SiCl₃ group, while the peak at −66.0 ppm is attributed to the silicon bonded to four oxygen atoms [18].

With the same combinations of precursors it was also possible to prepare dimeric silsesquioxanes by employing a 2:1 molar ratio as illustrated in Scheme 3. These reactions were again conducted in toluene solution, and 6 equivalents of triethylamine (4) or pyridine (5) were used to facilitate the elimination of hydrogen chloride. In both cases the products were purified by recrystallization from CHCl₃ and isolated in the form of colorless, very high-melting (m.p. >400 °C), air-stable solids.

The disiloxane derivative Cy₇Si₈O₁₂₂ (4) is especially remarkable as it represents the first dimeric silsesquioxane incorporating an Si-Si bond. In this case too the most important information came from the mass spectrum and the ²⁹Si NMR data. In the Cl mass spectrum it was possible to detect the protonated molecular ion at m/z 1995 with 9% relative intensity. Among the characteristic fragment ions is M-C₆H₁₁⁺ at m/z 1667 (2%). The ²⁹Si NMR spectrum exhibits five resonances for the seven cyclohexyl-substituted silicon atoms at −68.1, −68.6, −68.8, −69.0 and −69.5 ppm in an intensity ratio of 1:2:2:1:1. The signal at −79.0 ppm is clearly attributable to the central silicon atoms. Full characterization of the disiloxane derivative Cy₇Si₈O₁₂₂O (5) was achieved analogously. In this case the ²⁹Si resonance of the silicon atoms comprising the central SiOSi unit is found at δ −94.9 ppm, as each of these silicon atoms is bonded to four oxygens.

Reactions of 1 with monofunctional silylating agents such as Me₃SiCl generally lead to mixtures of mono-, di-

![Scheme 3 Preparation of (Cy₇Si₈O₁₂)₂ (4) and (Cy₇Si₈O₁₂)₂O (5).](image)
St. Gießmann, A. Fischer, F. T. Edelmann

Scheme 4 Preparation of \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})\text{SiMe}_2 \) (6) and \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Si(}\text{OEt}\text{)}_2 \) (7).

and trisilylated products, which have to be separated by fractional crystallization in order to obtain pure products. Especially disilation using 2 equivalents of \( \text{Me}_3\text{SiCl/NEt}_3 \) is tedious, and the monosilanol product \( \text{Cy}_7\text{Si}_7\text{O}_{9}(\text{OH})\text{OSiMe}_3 \) can be isolated only in low yield by fractional crystallization [6]. We found that this problem can easily be circumvented by using difunctional silylating agents to block two silanol functions in 1 simultaneously (Scheme 4).

For example, treatment of 1 with \( \text{Me}_2\text{SiCl}_2 \) in a molar ratio of 1:1 in diethyl ether and in the presence of triethylamine afforded the silsesquioxane monosilanol 6 in 62 % yield:

A salt-free synthetic route to the related silsesquioxane monosilanol derivative \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Si(}\text{OEt}\text{)}_2 \) (7) was achieved by treatment of 1 with one equivalent of tetraethoxysilane according to Scheme 4. Ethanol formed as by-product in this reaction was removed by azeotropic distillation together with the solvent toluene. Silanol 7 was isolated in 48 % yield as a colorless crystalline solid. Full characterization of the new compounds \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})\text{SiMe}_2 \) (6) and \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Si(}\text{OEt}\text{)}_2 \) (7) was readily achieved by elemental analysis and the usual combination of spectroscopic methods. These two compounds can be expected to become useful precursors for new metallosilsesquioxanes, as they both retain one reactive Si-OH functional group.

The monosilylated derivative \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})_2\text{OSiMe}_3 \) (8) served as starting material for the closely related silsesquioxane cage compound \( \text{Cy}_7\text{Si}_7\text{O}_{10}(\text{OSiMe}_3)_2 \) (9). The latter has been first mentioned in an early paper by Feher et al. [6]. We obtained this compound in an attempt to prepare an aluminasilsesquioxane by reacting 8 with anhydrous \( \text{AlCl}_3 \) in the presence of triethylamine. It was surprisingly found that under the chosen reaction conditions metal-free 9 was the only isolable reaction product (40 % yield) (Scheme 5).

IR and NMR data of 9 were in good agreement with those reported by Feher et al. [6]. Slow cooling of a saturated solution of 9 in diethyl ether to 4 °C afforded large, colorless X-ray quality single-crystals (prisms). The compound crystallizes in the monoclinic space group P2_1/n. The molecular structure of 9 is depicted in Figure 1. Crystal data and selected bond lengths and angles are listed in Tables 1 and 2, respectively. Formally 9 is formed by elimination of a water molecule from the precursor \( \text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OH})_2\text{OSiMe}_3 \) (8) under formation of an oxygen bridge between the silicon atoms Si4 and Si5. This results in the formation of a strained six-membered Si3O3 ring within the silsesquioxane cage with a small angle of 130.0(2)° at O7. The bending of the \( \text{Me}_3\text{SiO} \) group towards O7 (Si7-O-Si8 140.3(2)°) can be traced back to the steric influence of the neighboring cyclohexyl substituents. It leads to a roughly spherical molecular structure of 9.

In summarizing these results, we have established synthetic routes leading to trichlorosilyl-substituted silsesquioxanes as well as dimeric silsesquioxanes, including the first Si-Si-bonded representatives. Several silsesquioxane building blocks described in this work are promising precursors for further investigations, e.g. the synthesis of novel metallosilsesquioxanes.
Experimental Section

General Procedures. The reactions were carried out in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents (with the exception of CHCl₃) were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer System 2000. NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer (¹H 400.13 MHz, ¹³C 101.62 MHz, ²⁹Si 79.49 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (H, ¹³C) or an internal standard (H, ²⁹Si: TMS = 0 ppm). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leuco CHNS 932 apparatus. Melting and decomposition points were measured on a Electrothermal IA 9100 apparatus. X-ray data collection and structure refinement: The measurement on SADAB. 1H NMR (CDCl₃, 25 °C): δ = 1.74 (m br, 35 H, CH₃); 1.23 (m br, 35 H, CH₂), 0.76 (m br, 7 H, CH); ¹³C NMR (CDCl₃, 25 °C): δ = 27.5, 27.4, 27.3, 26.8, 26.7, 26.6, 26.5, 26.4, 26.3, 26.2 (t, CH₂); 23.5, 23.4, 23.0, 22.9 (d, 21.3:1, CH); ²⁹Si NMR (CDCl₃, 25 °C): δ = -56.6 (OSiCl₃); -66.0 (OSiCl₂); -67.8, -68.0, -68.0, -69.0, -69.8, -70.2 (SiH); MS (CI): m/z 133 (M + H, 100 %); 1195 (M–Cl, 58 %), 1049 (M–C₂H₅, 54 %), 1033 (M–C₂C₁H₇, 93 %); IR (KBr): ν = 3436-2949 cm⁻¹, 2369 cm⁻¹; ²⁹Si(CH₃)₃ (1): A rapidly stirred solution of 1 (1.00 g, 1.03 mmol) in toluene (ca. 50 ml) was treated at room temperature subsequently with Si(OEt)₃ (0.32 g, 1.16 mmol) and NEt₃ (0.40 ml, 0.29 g, 2.89 mmol). Stirring was continued for 18 h. A white precipitate of [NEt₃H]Cl was filtered off, and the colorless filtrate was evaporated to dryness. Recrystallization from a minimum amount of hot CHCl₃ afforded colorless crystals of 2. M.p. 284-288 °C; yield: 0.50 g (43 %); Elemental analysis calcd (%) for C₅₄H₁₀₂Cl₂O₁₂Si₁₄: C 56.25, H 7.08, Cl 8.65. 

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<td>Si–C₅</td>
<td>1.671 (3)</td>
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578 vw, 515 s, 464 m, 410 m cm
895 m, 863 sh, 849 m, 820 sh, 801 vs, 741 vw, 703 vw, 662 vw, 625 vw br,
1449 m, 1413 vw, 1397 vw, 1348 vw d, 1263 vs, 1198 s, 1104 vs br, 1028 vs br,
(2.71 g, 1.64 mmol) and 

Cy-Si-O$_2$(OH)SiMe$_2$ (6): A solution of 1 (3.00 g, 3.08 mmol) in diethyl ether (ca. 300 ml) was added dropwise over a period of 4 h to a stirred solution of Me$_2$SiCl$_2$ (0.50 ml, 0.54 g, 4.18 mmol) and NEt$_3$ (8.00 ml, 5.84 g, 28.86 mmol) in diethyl ether (ca. 300 ml). The reaction mixture was stirred at room temperature for 80 h, filtered and evaporated to dryness. Recrystallization of the residue from CHCl$_3$ afforded colorless crystals of 6. M.p. 85 °C (dec.); yield: 1.97 g (62 %); Elemental analysis calcd (%) for C$_{47}$H$_{84}$O$_{12}$Si$_8$: C 51.32, H 8.22; found: C 49.73, H 7.98.

1H NMR (CDCl$_3$, 25 °C): δ = 4.27 (2 vbr, v$\nu$OH), 3.87 (q, 2H, OC$_3$H$_7$); 27.7, 27.6, 27.0, 26.9, 26.8, 26.7 (t, Cy$_3$); 24.3, 24.1, 23.9, 23.2, 23.1 (d, 2:2:1:1:1, CH); 0.9 (SiMe$_3$); 2Si NMR (CDCl$_3$, 25 °C): δ = −15.6 (OSiMe$_3$); −58.8, −59.0, −67.4, −67.7, −68.7, −69.7, −70.3 (SiCH$_3$); MS (Cl): m/z 1029 (M + H, 74 %), 1013 (M−CH$_2$, 14 %), 945 (M−Cy, 100 %); IR (KBr): v = 3437 vw br, 2922 vs, 2850 to 1634 vw br, 1448 s, 1356 vw, 1197 m, 1110 vs br, 1062 vs, 1038 s, 1027 sh, 895 w, 849 w, 824 w, 803 m, 760 vw sh, 742 vw, 670 vw, 601 vw, 516 s & 463 m, 417 w cm$^{-1}$.

To a stirred solution of Me$_2$SiCl$_2$ (0.50 ml, 0.54 g, 4.18 mmol) and NEt$_3$ (8.00 ml, 5.84 g, 28.86 mmol) in diethyl ether (30 ml) was added neat Si(OEt)$_4$ (0.50 ml, 0.47 g, 2.24 mmol) at 0 °C. After 1 h the solution was cooled to room temperature and the mixture was left in situ for further 2 h. The reaction mixture was filtered to remove the unreacted Si(OEt)$_4$ and the filtrate was concentrated on a rotatory evaporator to give a colorless oil, which was distilled over a short column (200 °C). Yield: 1.97 g (62 %); Elemental analysis calcd (%) for C$_{47}$H$_{84}$O$_{12}$Si$_8$: C 52.36, H 8.15.

1H NMR (CDCl$_3$, 25 °C): δ = 4.27 (s vbr, v$\nu$OH), 3.87 (q, 2H, OC$_3$H$_7$); 27.7, 27.6, 27.0, 26.9, 26.8, 26.7 (t, Cy$_3$); 24.3, 24.1, 23.9, 23.2, 23.1 (d, 2:2:1:1:1, CH); 0.9 (SiMe$_3$); 2Si NMR (CDCl$_3$, 25 °C): δ = −15.6 (OSiMe$_3$); −58.8, −59.0, −67.4, −67.7, −68.7, −69.7, −70.3 (SiCH$_3$); MS (Cl): m/z 1029 (M + H, 74 %), 1013 (M−CH$_2$, 14 %), 945 (M−Cy, 100 %); IR (KBr): v = 3437 vw br, 2922 vs, 2850 to 1634 vw br, 1448 s, 1356 vw, 1197 m, 1110 vs br, 1062 vs, 1038 s, 1027 sh, 895 w, 849 w, 824 w, 803 m, 760 vw sh, 742 vw, 670 vw, 601 vw, 516 s & 463 m, 417 w cm$^{-1}$.

References