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Silsesquioxane chemistry☆
Part 5. New silyl-functionalized silsesquioxanes

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Abstract

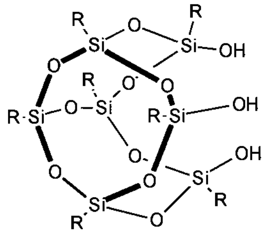
Treatment of $Cy_7Si_7O_9(OH)_3$ (**1**) with Me_2SiCl_2 (molar ratio 2:3) in the presence of triethylamine affords the Me_2Si-bridged bis(silsesquioxane) derivative $Me_2Si[Cy_7Si_7O_{10}(O_2SiMe_2)]_2$ (**5**). The novel silsesquioxane vinyl monomer $Cy_7Si_7O_9(OSiMe_2CH{=}CH_2)_3$ (**7**) has been synthesized by reacting in situ generated $Cy_7Si_7O_9(OLi)_3$ (**6**) with three equivalents of $Me_2SiCl(CH{=}CH_2)$. The molecular structures of **5** and **7** as well as that of the known silyl-functionalized silsesquioxane precursor $Cy_7Si_7O_9(OH)(OSiMe_3)_2$ (**3**) have been determined by X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silsesquioxanes; Silylation; Vinylsilanes; X-ray structure

1. Introduction

Polyhedral silsesquioxanes of the general formula $(RSiO_{1.5})_n$ form an interesting class of organosilicon compounds which currently have a tremendous impact on catalysis research [1] and materials science [2] alike. Due to their chemical composition they can be viewed as hybrids between silica (SiO_2) and the silicones $(R_2SiO)_n$. In accordance with several unique properties the polyhedral silsesquioxanes have been termed the 'smallest particles of silica possible' [3] or 'small soluble chunks of silica' [1]. With respect to catalysis the chemistry of metallasilsesquioxanes is receiving considerable current interest [4,5]. Incompletely condensed silsesquioxanes such as $Cy_7Si_7O_9(OH)_3$ (**1**) share structural similarities with β-cristobalite and β-tridymite and are thus quite realistic models for the silanol sites on silica surfaces [6–10]. Metal complexes derived from **1** are therefore regarded as 'realistic' models for metal catalysts immobilized on silica surfaces [1,7].

The fact that silsesquioxane molecules like **1** contain covalently bonded reactive functionalities also makes them promising monomers for polymerization reactions or for grafting these monomers to polymer chains. In recent years this has been the basis for the development of novel hybrid materials which offer a variety of useful properties [2,3]. The preparation and derivative chemistry of **1** have been mainly developed by Feher and co-workers. These authors were the first to show that silylation is an excellent way of selectively functionalizing such incompletely condensed silsesquioxanes. For example, the reactivity of **1** can be modified and tuned by silylation of the Si–OH functions using Me_3SiCl/NEt_3 in different stoichiometric amounts [5,11]. This way the silylated derivatives $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ (**2**), $Cy_7Si_7O_9(OH)(OSiMe_3)_2$ (**3**), and $Cy_7Si_7O_9(OSiMe_3)_3$ (**4**) can be selectively prepared starting from **1**.



1: R = cyclohexyl

Scheme 1.

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We report here the molecular structure of the disilylated silsesquioxane derivative **3** as well as the preparation and structural characterization of two new silyl-functionalized cage compounds derived from **1**.

2. Experimental

2.1. General information

The reactions were carried out in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents 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 (^{1}H 400.13 MHz, ^{13}C 101.62 MHz, ^{29}Si 79.49 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C) or an internal standard (^{1}H, ^{29}Si: TMS = 0 ppm). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. Melting and decomposition points were measured on an Electrothermal IA 9100 apparatus. The compounds $Cy_7Si_7O_9(OH)_3$ (**1**) and $Cy_7Si_7O_9(OH)$ (**3**) [5] were prepared according to literature procedures.

2.2. Preparation of $Me_2Si[Cy_7Si_7O_{10}(O_2SiMe_2)]_2$ (**5**)

To a solution of **1** (2.0 g, 2.1 mmol) in THF (100 ml) were added successively triethylamine (0.62 g = 0.86 ml, 6.2 mmol) and Me_2SiCl_2 (0.40 g = 0.37 ml, 3.1 mmol). The mixture was stirred for 24 h at room temperature. Evaporation to dryness afforded a white solid residue which was extracted with pentane (3 × 20 ml). Filtration and cooling of the clear filtrate to −20°C yielded **5** (1.65 g, 76%) as colorless crystals. M.p. 155–158°C. MS(CI): *m*/*z* 1029 [$Cy_7Si_7O_{10}(O_2SiMe_2)$, 60%], 945 [$Cy_7Si_7O_{10}(O_2SiMe_2) - C_6H_{11}$, 100%]. IR (KBr, ν (cm^{-1})): 2923vs, 2850vs, 2793w, 2667w, 1460w, 1448s, 1407w, 1347m, 1327w, 1261s, 1197vs, 1113vs, 1038vs, 1028vs, 895s, 849s, 826s, 802s, 749s, 612w, 579w, 509vs, 459s, 415s. ^{1}H-NMR (C_6D_6, 25°C): δ 1.73 (m, 70H C*H*$_2$), 1.22 (m, 70H C*H*$_2$), 0.72 (m, 14H C*H*), 0.13, 0.12 (s, 18H C*H*$_3$Si) ppm. ^{13}C-NMR (C_6D_6, 25°C): δ 27.7, 27.7, 27.6, 27.6, 27.5, 26.9, 26.8, 26.7, 26.7 (*C*H$_2$), 24.8, 24.3, 24.1, 23.8 23.2 (*C*H, rel. int. 1:2:1:2:1), 1.2, 0.8 (*C*H$_3$Si) ppm. ^{29}Si-NMR (C_6D_6, 25°C): δ −17.6, −18.8 (*Si*CH$_3$, rel. int. 2:1); −67.2, −67.4, −68.8, −69.1, −70.4 (*Si*C$_6$H$_{11}$) ppm. Anal. Calc. for $C_{90}H_{172}O_{24}Si_{17}$ (2115.81): C, 51.1; H, 8.2. Found: C, 50.6; H, 8.5%.

2.3. Preparation of $Cy_7Si_7O_9(OSiMe_2CH{=}CH_2)_3$ (**7**)

$LiN(SiMe_3)_2$ was prepared in situ by addition of *n*-BuLi (10.3 ml of a 1.5 molar solution in hexane, ≈ 15.4 mmol) to hexamethyldisilazane (2.48 g = 3.2 ml, 15.4 mmol) in THF (150 ml) and stirring for 1 h. 5.0 g (5.1 mmol) **1** were added as a solid and stirring at 20°C was continued for 24 h. To the resulting solution of **6** was added via a syringe chlorodimethylvinylsilane (2.0 g = 2.6 ml, 19 mmol). After stirring for another 12 h the reaction mixture was evaporated to dryness. The residue was extracted with pentane (50 ml). The precipitated LiCl was washed with pentane (20 ml) and the combined extracts were concentrated in vacuo to a total volume of ca. 25 ml. Cooling to −20°C afforded 5.4 g (86%) **7** as colorless crystals. M.p. 260°C (dec.). MS (CI): *m*/*z* 1227 [M + 1, 8%], 1211 [M − (CH_3), 30%], 1199 [M − ($CH{=}CH_2$), 75%], 1143 [M − (C_6H_{11}), 100%], 1060 [M − 2(C_6H_{11}), 6%]. IR (KBr, ν (cm^{-1})): 3052vw, 2923vs, 2849s, 2666vw, 1636 vw, 1596vw, 1447m, 1407w, 1347vw, 1326vw, 1260m(sh), 1256m, 1197m, 1118vs, 1037s, 995m(sh), 956w, 896m, 835s, 786m, 758w, 714vw, 639w, 610vw, 576w, 516m, 500m, 466m. ^{1}H-NMR (C_6D_6, 25°C): δ 6.14 (dd, 3 H, Si–C*H*=), 5.91 (dd, $^{cis}J_{HH}$ = 14.9 Hz, $^{geminal}J_{HH}$ = 4.0 Hz, 3H, *cis* =CH*H*), 5.73 (dd, $^{trans}J_{HH}$ = 20.3 Hz, $^{geminal}J_{HH}$ = 4.0 Hz, 3H, *trans* =C*H*H), 1.73 (m$_c$, 35H, C*H*$_2$ *c*-C$_6$H$_{11}$), 1.22 (m$_c$, 35H, C*H*$_2$ *c*-C$_6$H$_{11}$), 0.67 (m$_c$, 7H, C*H* *c*-C$_6$H$_{11}$), 0.18 (s, 18H, Si–C*H*$_3$) ppm. ^{13}C-NMR (C_6D_6, 25°C): δ 23.1, 24.9, 25.2 (1:3:3, *C*H, *c*-C$_6$H$_{11}$), 26.6, 26.8, 26.9, 26.9, 27.0, 27.1, 27.5, 27.7, 27.9 (*C*H$_2$, *c*-C$_6$H$_{11}$), 131.7 (=*C*H$_2$), 139.3 (Si–*C*H=) ppm. ^{29}Si-NMR (C_6D_6, 25°C): δ −2.7 (–*Si*Me$_2$CH=CH$_2$), −68.4, −69.3, −70.1 ppm. Anal. Calc. for $C_{54}H_{104}Si_{10}O_{12}$ (1226.27): C, 52.9; H, 8.6. Found: C, 52.7; H, 8.5%.

2.4. X-ray structure determinations (cf. Table 1)

All measurements were performed on a Siemens SMART CCD system with Mo–K$_\alpha$ X-ray radiation (λ = 0.71073 Å) and graphite monochromator. Selected crystals of **3**, **5**, and **7** were coated with mineral oil, mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. As an absorption correction the SADABS routine was applied. The crystal structures were solved by direct methods (SHELXS 86 for **3**, SHELXS 97 for **5** and **7**). For structure refinement the programs SHELXL 93 (**3**) and SHELXL 97 (**5** and **7**) were used [12,13].

3. Results and discussion

The silylated products **2** and **4** can be readily isolated as pure materials by fractional crystallization from pentane or hexane [5,11]. In contrast, the disilylated silsesquioxane **3** is not easily prepared as it is very soluble in hydrocarbon solvents and thus somewhat difficult to purify. Recently an analytically pure sample of **3** was

Table 1
Summary of crystal structure determination data for **3**, **5**, and **7**

	3	**5**	**7**
Formula	$C_{48}H_{96}O_{12}Si_9$	$C_{90}H_{172}O_{24}Si_{17}$	$C_{54}H_{104}O_{12}Si_{10}$
M_r	1118.06	2115.81	1226.27
Habit, color	Colorless prism	Colorless prism	Colorless column
Crystal dimension (mm^3)	$0.60 \times 0.30 \times 0.20$	$0.42 \times 0.42 \times 0.14$	$0.76 \times 0.27 \times 0.26$
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$C2/c$	$P\bar{1}$	$Pna2_1$
Unit cell constants			
a (Å)	40.7499(2)	11.065(2)	31.4917(2)
b (Å)	14.3308(2)	22.274(2)	45.9617(3)
c (Å)	21.2215(2)	23.374(2)	19.3271(2)
α (°)	90	94.331(3)	90
β (°)	94.711(2)	92.525(3)	90
γ (°)	90	93.225(3)	90
V ($Å^3$)	12351	5728	27974
Z	8	2	16
$D_{x(calc)}$ ($Mg\ m^{-3}$)	1.203	1.227	1.165
μ (mm^{-1})	0.25	0.25	0.24
$F(000)$	4848	2284	10624
T (°C)	−100	−120	−100
$2\theta_{max}$	56.7	60.0	56.5
Reflections collected	40056	68682	86551
Independent reflections	15153	33161	59000
R_{int}	0.055	0.053	0.044
Refined parameters	739	1181	2687
wR (F^2, all reflections)	0.154	0.156	0.174
R ($F > 4\sigma(F)$)	0.058	0.053	0.080
S	1.04	1.00	1.09
Maximum Δ/σ	<0.001	0.001	0.001
Maximum $\Delta\rho$ ($e\ Å^{-3}$)	0.65	1.95	0.76

obtained by repeated crystallization from acetonitrile and this enabled us to determine its molecular structure (Table 1). Fig. 1 depicts how the single Si–OH function is sterically shielded by a cyclohexyl substituent and two $-OSiMe_3$ units.

In contrast to the monomeric nature of **3**, the parent trisilanol **1** had previously been reported to crystallize as a hydrogen-bonded dimer [5]. A monomeric structure related to **3** was also reported by Abbenhuis et al. for the monosilylated derivative $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_3)$ (**8**), which was structurally characterized in connection with a study of platinum silsesquioxane complexes [14]. In this case, however, the poor quality of the structure determination did not allow a detailed discussion of the structural features, although the overall structure could be unambiguously determined. The Si–O distance of the remaining silanol function in **3** (Si(5)–O(12)) is 162.6(2) pm, which can be favorably compared to corresponding values of 165.0(8) pm and 161.9(8) pm reported for **8** [14]. Si–O–Si angles in the latter compound fall in the range of 149–156°. In **3** the exocyclic Si–O–Si angles have been found to be 157.0(2)° and 147.2(2)°, respectively.

In an extension of this chemistry the reaction of **1** with the difunctional reagent dichlorodimethylsilane was studied. A pure reaction product, the bis(silsesquioxane) derivative **5**, can be isolated in 76% yield when the reaction is carried out in a 2:3 molar

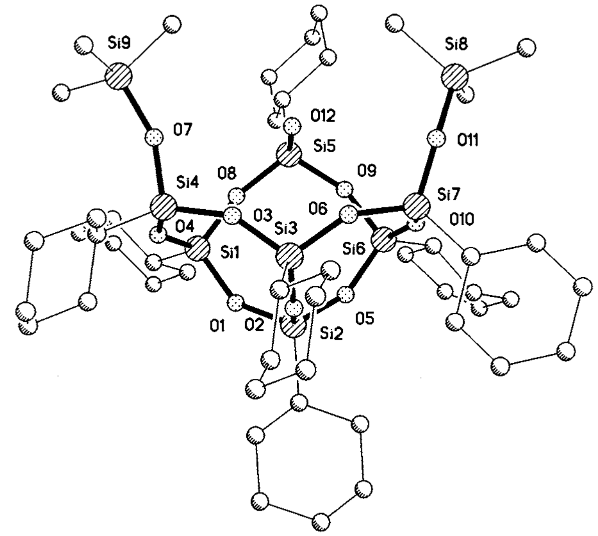
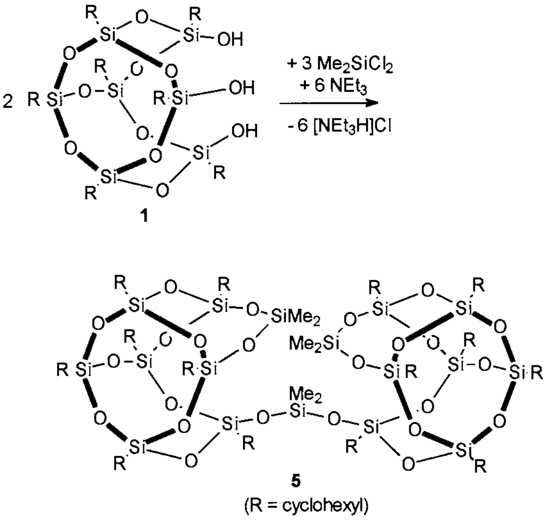


Fig. 1. Structure of **3** in the crystal. Selected interatomic distances (pm) and bond angles (°): Si(5)–O(12) 162.6(2), Si(4)–O(7) 159.5(2), Si(9)–O(7) 163.3(2), Si(7)–O(11) 160.4(2), Si(8)–O(11) 164.4(2), Si(4)–O(7)–Si(9) 157.0(2), Si(7)–O(11)–Si(8) 147.2(2).

ratio according to Scheme 1. The white crystalline solid was structurally characterized by X-ray diffraction (Table 1, Fig. 2). In this molecule one corner of the original incompletely condensed silsesquioxane is capped by a Me_2Si unit. A third Me_2Si group connects two of these partially closed silsesquioxane cages. The Si–O and Si–C distances in **5** are unexceptional and there is little variation between the Si–O bond lengths within the silsesquioxane cages and those constituting the bridging unit. With 108.0(1)° the O(7)–Si(9)–O(7′) angle at the central silicon atom comes close to the ideal tetrahedral angle.

Synthetic routes leading to functionalized silsesquioxanes are not limited to reactions of the parent silanols with appropriate halide reagents in the presence of triethylamine. The use of the recently discovered lithium silsesquioxane derivative $Cy_7Si_7O_9(OLi)_3$ (**6**) [15,16] as precursor has now been found to be a valuable alternative route. In the present study it served as a highly useful starting material for the preparation of a new silsesquioxane vinyl monomer. For this purpose the lithium reagent **6** was generated in situ by reacting **1** with three equivalents of $LiN(SiMe_3)_2$ [17] in THF solution. Subsequent treatment with three equivalents of chlorodimethylvinylsilane according to Schemes 2 and 3 afforded the new silsesquioxane vinyl monomer $Cy_7Si_7O_9(OSiMe_2CH{=}CH_2)_3$ (**7**) in 86% yield.

Colorless crystalline **7** is air stable and soluble in hydrocarbon solvents including pentane and hexane. The compound has been fully characterized by its analytical and spectroscopic data as well as an X-ray crystal structure determination (Table 1). Fig. 3 shows the monomeric molecule containing three $-OSiMe_2(CH{=}CH_2)$ functional groups. Related vinyl-substituted silsesquioxanes have previously been reported for *closo*-silsesquioxane cages [8]. Typical examples include among others the cube-like compounds $Si_8O_{12}(CH{=}CH_2)_8$ (**9**) [18] and $Si_8O_{12}[OSiMe_2(CH{=}CH_2)]_8$ (**10**) [19]. Such polyfunctionalized vinyl silsesquioxanes readily undergo hydrosilylation [20], hydrophosphination [21] and epoxidation reactions [22] and thus offer a great synthetic potential as building blocks for the preparation of dendrimers, polyphosphines, and polyepoxides based on the polyhedral Si–O cores. Compound **7** is the first example of a related tris(vinyl) derivative based on the incompletely condensed silsesquioxane cage of **1**.



Scheme 2. Preparation of the Me_2Si-bridged silsesquioxane derivative **5**.

4. Conclusions

Silylation reactions performed on silsesquioxanes are a valuable method of derivatizing these Si/O cage com-

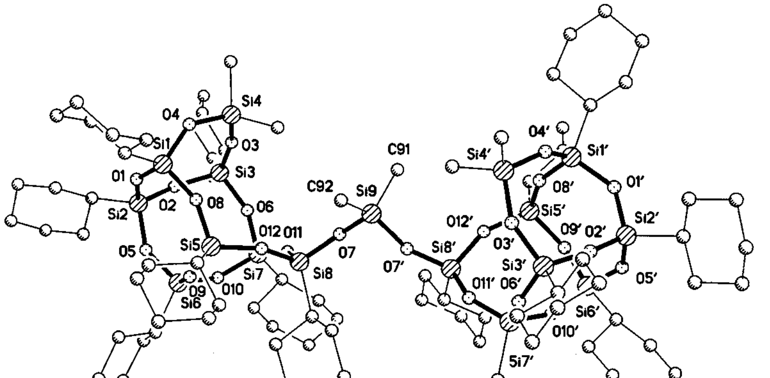
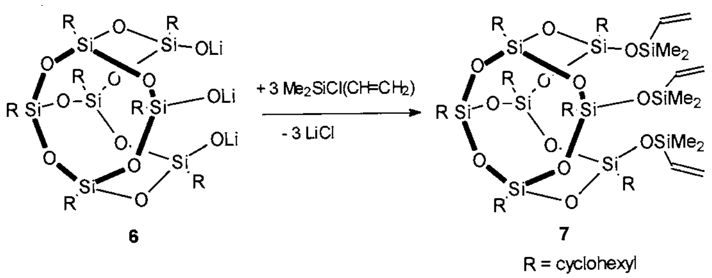


Fig. 2. Structure of **5** in the crystal. Selected interatomic distances (pm) and bond angles (°): Si(1)–O(4) 162.1(2), Si(4)–O(4) 164.0(2), Si(4)–O(3) 162.4(2), Si(3)–O(3) 161.6(2), Si(8)–O(7) 161.5(2), Si(9)–O(7) 163.1(2), Si(1)–O(4)–Si(4) 137.3(1), O(4)–Si(4)–O(3) 108.9(1), Si(3)–O(3)–Si(4) 163.1(1), Si(8)–O(7)–Si(9) 149.2(1), O(7)–Si(9)–O(7′) 108.0(1).



Scheme 3. Preparation of the silsesquioxane vinyl monomer **7**.

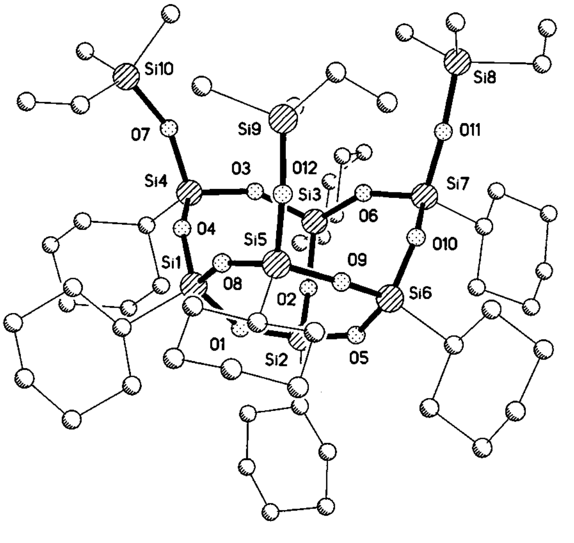


Fig. 3. Structure of **7** in the crystal. Selected interatomic distances (pm) and bond angles (°): Si(4)–O(7) 161.3(4), Si(10)–O(7) 163.3(4), Si(5)–O(12) 161.7(4), Si(9)–O(12) 160.6(5), Si(7)–O(11) 161.9(4), Si(8)–O(11) 162.4(4), Si–C(vinyl) 188(3), Si(4)–O(7)–Si(10) 155.1(3), Si(5)–O(12)–Si(9) 148.9(3), Si(7)–O(11)–Si(8) 158.9(3)

pounds. Previous studies by Feher et al. had already shown that trimethylsilylation of polyfunctional silsesquioxanes can be used to modify the reactivity by selectively blocking one or more silanol functions [5,11]. An extension of this work using the difunctional reagent Me_2SiCl_2 afforded a rare example of a bis(silsesquioxane) derivative. The recently discovered lithium silsesquioxane reagent $Cy_7Si_7O_9(OLi)_3$ (**6**) has been shown to be an excellent precursor for the synthesis of functionalized silsesquioxanes, as exemplified by the preparation of the silsesquioxane vinyl monomer $Cy_7Si_7O_9(OSiMe_2CH{=}CH_2)_3$ (**7**).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 141717 (**3**), CCDC 141718 (**5**), and CCDC 141719 (**7**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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