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Silsesquioxanes: Part I: A key intermediate in the building of molecular composite materials[1]

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Abstract

A high yield synthesis for octakis(hydrodimethylsiloxy)octasilsesquioxane, $[Si_8O_{12}](OSi(CH_3)_2H)_8$, a key building block for making new molecular composites, and highly functionalised silsesquioxanes, is reported. The X-ray crystal structure confirms the existence of a perfect symmetrical core consisting of a Si_8O_{12} cube, with $OSi(CH_3)_2H$ attachments protruding from each corner of the cube. The highly reactive Si–H groups are readily transformed into other functionalised organic substituents making this silsesquioxane a key starting reagent in building molecular composites. In addition, hydrosilylation of allyl bromide to the title compound is carried out for the first time and compared to an analogous reaction with T_8H_8. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Octasilsesquioxane; Si_8O_{12} cube; X-ray structure

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1. Introduction

Silsesquioxanes are a class of three-dimensional oligomeric organosiliceous compounds of the general formula $(RSiO_{1.5})n$, where *n is* an even number and R can be any of a large number of groups (typically methyl, halogen, vinyl or phenyl). Silsesquioxanes exhibit structures having polyhedral frameworks with varying degrees of symmetry, with the silicon atoms on corners and oxygen atoms interspersed between them in a tetrahedral configuration. In the last few years, silsesquioxanes have begun to show promise as new materials in understanding the surface chemistry on heterogeneous silica particles.

Recently, these novel compounds have been used as well-defined molecular models for silica surfaces [1], and as ligands for main group [2] or transition metal catalysts on silica surfaces [3–5]. Their potential to mimic silica surfaces stems from the close similarity of silsesquioxanes to highly siliceous clusters that possess the structural and electronic features of hydroxylated silica surfaces.

Aside from their key application as homogeneous surface mimics of heterogeneous silica surfaces, silsesquioxanes have found widespread use in sol-gel polymerization [6], as models of zeolite activity [7], as alternatives for SiO_2 thin films [8], as liquid crystal polymers [9], in hair fixatives [10] and in the studies of supported catalysts [11].

Greater exploitation of these unique compounds has in the past been severely restricted by limitations in their synthesis. Synthetic routes to silsesquioxanes generally involve hydrolysis/condensation of trifunctional

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[1] This paper is dedicated to Professor M.I. Bruce on the occasion of his 60th birthday. It is always good to cheerfully reflect upon the start of one's own research career, and acknowledge your mentor, upon such a happy and memorable occasions.

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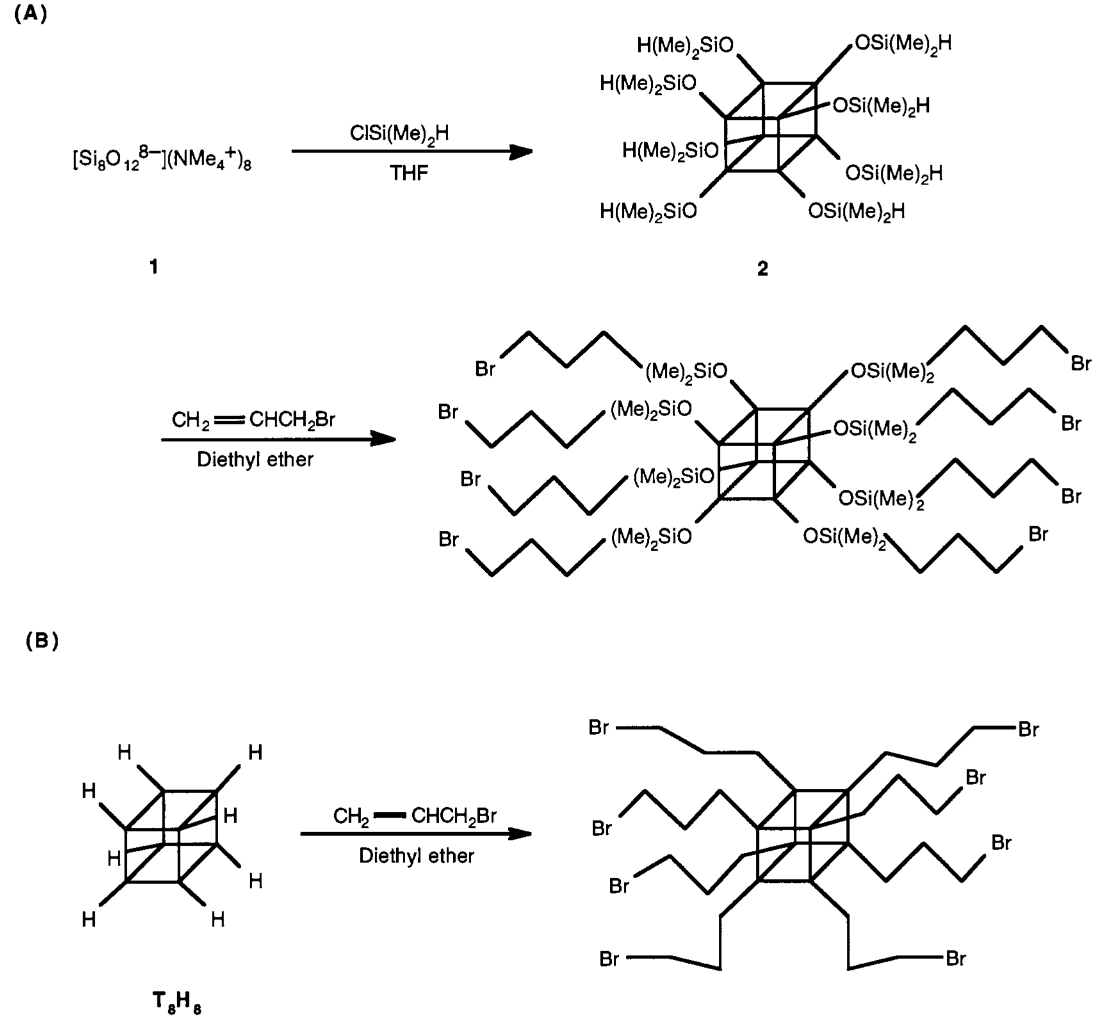

Scheme 1.

monomers, $RSiX_3$ [12,13]. Unfortunately, most of these routes employ multistep procedures using a large excess of silane, long reaction times and even then such routes only result in very low yields of the desired products. Exploitation of the resulting silsesquioxanes has, therefore, been severely limited in the past. Recently however, silsesquioxanes have attracted renewed interest, largely because new synthetic strategies have not only drastically reduced reaction times and the number of steps involved, but have also significantly improved the product yield.

Hasegawa and Motojima [14] reported a quick and facile method for synthesising tetramethylammonium silicate, octa-anion, $[Si_8O_{12}^{8-}]((CH_3)_4N^+)_8$. The octa-anion is formed by the treatment of tetraethylorthosilicate with tetramethylammonium ions (or other similar organic quaternary ammonium ions containing at least three methyl groups) in mixed organic solvents. A further one-step procedure introduces hydrodimethylsiloxy groups to each corner of the octasilsesquioxanes cubic core structure in high yield [15]. The resultant octasilsesquioxane is stable in moist air, providing an alternative route in derivatisation of new organolithic macromolecular materials.

The objective of this research was the preparation of octakis(hydrodimethylsiloxy) octasilsesquioxane and its subsequent hydrosilylation with a variety of nucleophiles; in this paper allyl bromide derivatives are reported. Comparisons of the octakis(hydrodimethylsiloxy)octasilsesquioxane coupled to allyl bromide and T_8H_8 coupled to allyl bromide are investigated (see Scheme 1).

2. Experimental

Allyl bromide, chlorodimethylsilane, dimethylformamide, hexachloroplatinic acid, tetramethylammonium hydroxide (10% aqueous solution), and tetraethylorthosilicate (Aldrich) were used as supplied. Hexane was treated with concentrated sulphuric acid and nitric acid, dried over $MgSO_4$ prior to distillation and stored over 4 Å molecular sieves. Methanol was purified by drying with CaH_2 and distilling under nitrogen. Diethyl ether and tetrahydrofuran were purified by distilling over sodium wire with benzophenone until a violet colour develops indicating the formation of a ketyl radical.

NMR spectra were recorded on Varian Gemini-200 MHz NMR spectrometer. All chemical shifts are reported in units of δ (ppm) in deuterated solvent ($CDCl_3$) at $\delta = 7.260$ ppm for ^1H- and $\delta = 77.00$ for ^{13}C-NMR. ^{29}Si-NMR were carried out on a Jeol-60 MHz spectrometer with Telmac software using D_2O deuterated solvent and tetramethylsilane as external standard. Infrared spectra were recorded in pressed KBr pellets on a Nicolet 750 Magna FTIR spectrometer. Elemental analyses were obtained from the microanalytical service of the Department of Chemistry at the University of Queensland.

2.1. Preparation of octakis(tetramethylammonium)octasilsesquioxane (1)

In preparing tetramethylammonium silicates, the $[SiO_2]$ present in solution must be 1.0 M with the molar ratios of tetramethylammonium ion to SiO_2 to water being 1:1:10, respectively. A solution of tetramethylammonium silicate (20 ml) was prepared by adding 4.48 ml of tetraethoxysilicate to 10 ml of a 2.0 M tetramethylammonium hydroxide pentahydrate solution in methanol, and adding 1.8 ml of water whilst stirring vigorously. Further methanol was introduced into the reaction vessel to bring the total volume of methanol to 20 ml, and stirring was maintained for 24 h. The resulting colourless solution was then concentrated and cooled to below 5°C, filtered and dried to give a white solid (7.16 g, 79%). ^{29}Si-NMR (D_2O) δ: -103.9 ppm.

2.2. Preparation of octakis(hydrodimethylsiloxy)octasilsesquioxane (2)

Tetramethylammonium silicate (20 ml) was added dropwise to a stirred mixture of chlorodimethylsilane (100 ml, 1.46 mol) and tetrahydrofuran (50 ml) under a slow continuous nitrogen purge. HCl gas generated from the reaction mixture was purged into a bubbler filled with CaO suspended in water. The reaction mixture was allowed to stir overnight to ascertain that all sites were fully reacted (by ^1H-NMR). The solvent was removed in vacuo, and the resultant crude material recrystallised from THF/hexane to produce colourless crystals of 2 (9.95 g, 87%). ^1H-NMR ($CDCl_3$ at 7.246 ppm) δ: 0.1 (s, $C\underline{H}_3$–Si), 4.7 (septuplet, Si–$\underline{H}$). ^{13}C-NMR ($CDC1_3$ at 77.00 ppm) δ: 0.85 ($\underline{C}H_3$–Si). ^{29}Si-NMR (D_2O) δ: -0.8, -103.9 ppm. IR (KBr, cm^{-1}) 2967 (s), 2126 (m), 1260 (s), 1070 (s). Anal. Calcd. for $C_{16}H_{56}O_{20}Si_{16}$: C, 18.87; H, 5.55. Found: C, 18.95; H, 5.49.

*2.3. Reaction of **2** with allyl bromide*

To a stirred solution of 2 (9.9 g, 9.7 mmol) in anhydrous diethyl ether (15 ml) and three drops of a 1% solution of H_2PtCl_6 in dimethylformamide was slowly added allylbromide (9.43 g, 0.078 mmol) over a period of 6 h. The mixture was allowed to reflux until ^1H-NMR showed the disappearance of allyl and Si–H peaks and the subsequent appearance of propyl groups attached to the silsesquioxane core. The mixture was then cooled, filtered through a celite bed, washed with methanol and dried in vacuo to give a white solid (9.6 g, 49.7% yield. ^1H-NMR ($CDCl_3$ at 7.246 ppm) δ: 0.1 (s, $C\underline{H}_3$–Si), 0.6 (m, $C\underline{H}_2$–Si), 1.7 (m, $C\underline{H}_2CH_2$–Si), 4.1 (tr, $BrC\underline{H}_2CH_2CH_2$–Si). ^{13}C-NMR ($CDCl_3$ at 77.00 ppm) δ: 0.30 ($\underline{C}H_3$–Si), 14.0 ($\underline{C}H_2$–Si), 22.55 ($\underline{C}H_2CH_2$–Si), 66.98 ($Br\underline{C}H_2CH_2CH_2$–Si). ^{29}Si-NMR (D_2O) δ: 10.7, -106.9 ppm. IR (KBr, cm^{-1}) 2963 (s), 1265 (s), 1081 (s), 794 (m).

2.4. Preparation of hydridosilsesquioxane, T_8H_8

The T_8H_8 precursor was prepared by standard literature methods [16,17].

2.5. Reaction of T_8H_8 with allyl bromide

To a stirred solution of T_8H_8 (500 mg, 1.2 mmol) in anhydrous THF (20 ml) containing three drops of a 1% solution of H_2PtCl_6 in THF, was slowly added allylbromide (0.78 ml, 1.1 g, 9.6 mmol) over a period of 6 h. The mixture was allowed to reflux until ^1H-NMR showed the disappearance of allyl and Si–H peaks and the subsequent appearance of propyl groups attached to the T_8H_8 core. When hydrosilylation was adjudged to be complete, the reaction was allowed to cool, the moisture filtered through a celite bed, and washed with methanol before drying in vacuo to give a white solid product (934 mg, 57.0% yield). ^1H-NMR ($CDCl_3$ at 7.246 ppm) δ: 0.1 (s, $C\underline{H}_3$–Si), 0.55 (m, $C\underline{H}_2$–Si), 1.6 (m, $C\underline{H}_2CH_2$–Si), 4.0 (tr, $BrC\underline{H}_2CH_2CH_2$–Si). ^{13}C-NMR ($CDC1_3$ at 77.00 ppm) δ: 0.15 ($\underline{C}H_3$–Si), 12.7 ($\underline{C}H_2$–Si), 23.7 ($\underline{C}H_2CH_2$–Si), 66.06 ($Br\underline{C}H_2CH_2CH_2$–Si). IR (KBr, cm^{-1}) 2958 (s), 1260 (s), 1079 (s).

*2.6. Structure determination for **2***

The colourless crystals used for the X-ray study were grown by slow vapour diffusion of hexane into a solution of octakis(hydrodimethylsiloxy)octasilsesquioxane in tetrahydrofuran over a period of several days. The crystals were mounted in a thin walled glass capillary and were sealed as a precaution against moisture. A room temperature four-circle diffractometer data set was measured($2\theta_{max} = 50°$; $2\theta/\theta$ scan mode; monochromatic Mo–K_α radiation, $\lambda = 0.71073$ Å; T ca. 295 K) encompassing the range $h = -13$ to $+6$ yielding 7824 reflections, merging to 1604 unique after Gaussian absorption correction, R_{int} being 0.074, with 447 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement. Anisotropic thermal parameters were refined for all non-hydrogen atoms and fragments thereof, $(x, y, z, U_{\text{iso}})_{\text{H}}$ being included constrained at estimated values. In the present space group, one of the silicon atoms (Si(11)) was modelled over a set of sites disposed about the crystallographic 3-axis separated by 0.56(8) Å, associated methyl groups being similarly disordered; methyl groups associated with Si(21) were also modelled as disordered over sites whose occupancies were set at 0.5 after trial refinement. Conventional residuals R, Rw (statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^2(I_{\text{diff}})$ were 0.041, 0.038 at convergence. The molecule is a conventional $(\text{SiOSiO}_{(3/2)})_8$ centrosymmetric cubane array, disposed about the 3-axis of the space group with one of the peripheral silicon atoms, and all peripheral methyl atoms disordered. A projection of the $(\text{SiOSiO}_{(3/2)})_8$ core is given in Fig. 1; the highly disordered methyl array is omitted here for clarity although deposited in the supplement. Computation used the Xtal 3.4 program system [18].

Crystal data for 2: $C_{16}H_{56}O_{20}Si_{16}$, $M = 1018.06$, Rhombohedral, space group $R\bar{3}$ (C_{3i}^2, No. 148), $a = 11.142(3)$ Å, $\alpha = 95.23(2)°$ Å, $V = 1364.8$ Å^3. D_{calc} ($Z = 1$ f.u.) $= 1.238$ g cm^{-3}; $F(000) = 536$. $\mu_{\text{Mo}} = 4.3$ cm^{-1}; specimen (capillary) $= 0.42 \times 0.30 \times 0.30$ mm; $A^*_{\text{min,max}} = 1.11, 1.14$.

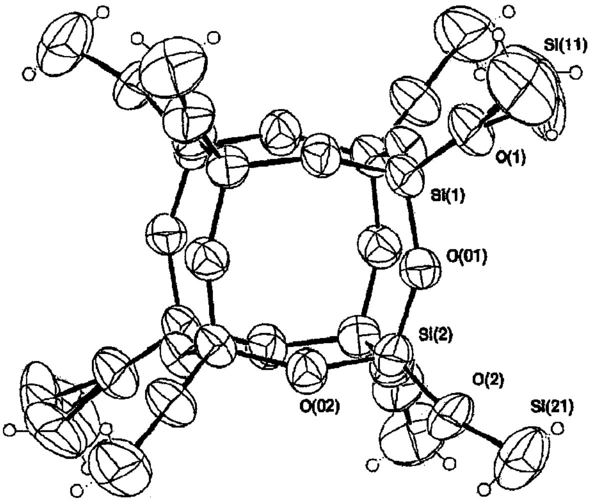

Fig. 1. Molecular projection of **2**, oblique to the 3-axis, showing 20% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Methyl groups, all of which are disordered, are omitted for clarity.

3. Results and discussion

Hydridosilsesquioxanes are among the most interesting materials in the silsesquioxane family, primarily because they possess reactive Si–H functional groups around a cage-like core consisting of Si–O–Si linkages and have a molecular formula $(\text{HSiO}_{1.5})n$, where $n = 8$–20. Hydridosilsesquioxanes are excellent precursors, as the Si–H functionalities can be modified to incorporate a host of organic functional groups suitable for copolymerization, thermolysis, photochemical irradiation and solubility in selected media.

The synthesis of the octakis(hydrodimethylsiloxy)octasilsesquioxane was accomplished by a two step process as shown in Scheme 1(A), loosely based on work by Hoebbel et al. [19]. The octasilsesquioxane anion **1**, was first prepared by mixing tetraethylorthosilicate with tetramethylammonium silicate in methanol/water solution. Charaterisation by ^{29}Si-NMR spectroscopy reveals a peak at -103.9 ppm corresponding to the $\text{Si(OSi)}_3(\text{O}^-)$ unit or Q^3.

Octakis(hydrodimethylsiloxy)octasilsesquioxane **2**, was then prepared by reacting the freshly prepared octasilsesquioxane anion **1** with chlorodimethylsilane in freshly distilled tetrahydrofuran [Scheme 1(A)]. Dropwise addition of the octasilsesquioxane anion to the silane allows greater temperature control in the reaction mixture and prevents hydrochloric acid fumes from accumulating to the critical levels capable of disrupting the Si–O bond framework inherent to the silsesquioxane core. ^{29}Si-NMR analysis reveals a peak at -100.9 and -103.9 ppm corresponding to the $\text{Si(OSi)}_3(\text{O}^-)$ unit or Q^3 and a single peak at $\delta = -0.8$ ppm belonging to the Si(Me)_2–H groups [15]. No evidence of breakdown products due to hydrochloric acid was observed in the ^{29}Si-NMR spectrum.

3.1. Crystal structure determination

Colourless crystals of **2** were obtained by slow diffusion of hexane into a saturated THF solution, and were submitted for structure determination. The crystal structure of octakis(hydrodimethylsiloxy)octasilsesquioxane (**2**) with atomic labelling and 20% thermal ellipsoids for the non-hydrogen atoms is shown in Fig. 1 (methyl groups are omitted for clarity). Atomic coordinates, bond lengths and angles for **2** are given in Tables 1–3, respectively. The molecule crystallises in the space group $R\bar{3}$, with Si(11) and methyl groups C(1n) disordered and with Si(11) displaced off the 3-fold axis to make Si–O–Si ca. 164° and not 180°. The non-equivalent position of the octakis(hydrodimethylsiloxy)octasilsesquioxane is confirmed by the considerable variation in the bond lengths of the Si–C from 1.60 to 1.85 Å, whereas the conventional range is 1.81 to 1.85 Å (Table 2).

Table 1
Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	x/a	y/b	z/c	U_{eq} Å^2
Si(1)	0.1522(1)	$x+1$	x	0.1258(6)
O(1)	0.2428(3)	$x+1$	x	0.170(2)
Si(11)[a]	0.314(7)	1.314(5)	0.348(3)	0.30(2)
C(11)[a]	0.41(1)	1.434(7)	0.312(5)	0.45(5)
C(12)[a]	0.318(5)	1.258(5)	0.481(3)	0.53(5)
Si(2)	0.2004(1)	0.8958(1)	0.0562(2)	0.1256(9)
O(2)	0.3167(3)	0.8339(4)	0.0878(4)	0.174(2)
Si(21)	0.4451(3)	0.8081(3)	0.1299(3)	0.261(2)
C(21)[b]	0.539(2)	0.727(3)	0.070(2)	0.52(3)
C(22)[b]	0.531(2)	0.939(2)	0.224(2)	0.46(2)
C(21′)[b]	0.474(3)	0.740(4)	0.251(3)	0.64(3)
C(22′)[b]	0.523(2)	0.813(3)	0.009(3)	0.50(3)
O(01)	0.2123(3)	1.0285(3)	0.1233(3)	0.130(2)
O(02)	0.0865(3)	0.8176(3)	0.0968(3)	0.134(2)

[a] Site occupancy factor 0.333.
[b] Site occupancy factor 0.50.

Due to the interest of these materials as core initiators for building macromolecular organolithic materials (e.g. dendrimer chemistry), it was decided to couple specific functional groups to the core molecules that will target subsequent chemistry. In addition to the functionalisation of T_8H_8 with specific groups (in this case, allyl bromide), a silsesquioxane core containing dimethylsiloxy spacers at each corner of the cubic core was prepared. The addition of dimethylsiloxy units increases the radial geometry of the silicalike core, yet as with T_8H_8, the terminal species at each corner still contains an Si–H reactive group. Hydrosilylation of unsaturated organic molecules to the Si–H vertices of **2** and T_8H_8, produce inorganic-organic, core-shell materials, that are finding widespread applications in polymeric composites. The ability to control and vary the size of the core is critical for optimising material performance.

Table 2
Bond distances (Å) for **2**

Bond distances	(Å)
Si(1)–O(1)	1.582(3)
Si(1)–O(01)	1.605(4)
O(1)–Si(11)	1.48(5)
Si(11)–C(11)	1.7(1)
Si(11)–C(12)	1.66(6)
Si(11)···Si(11)	0.56(8)
Si(2)–O(2)	1.550(4)
Si(2)–O(01)	1.583(4)
Si(2)–O(02)	1.596(4)
O(2)–Si(21)	1.525(5)
Si(21)–C(21)	1.60(3)
Si(21)–C(22)	1.85(2)
Si(21)-C(21′)	1.63(4)
Si(21)–C(22′)	1.68(3)

Table 3
Bond angles (°) of **2**

Bond angles	(°)
O(1)–Si(1)–O(01)	109.6(2)
O(01)–Si(1)–O(01)[a]	109.4(2)
Si(1)–O(1)–Si(11)	167(2)
O(1)–Si(11)–C(11)	115(3)
O(1)–Si(1)–C(12)	118(4)
C(11)–Si(11)–C(12)	126(4)
O(2)–Si(2)–O(01)	110.1(2)
O(2)–Si(2)–O(02)	109.3(2)
O(0l)–Si(2)–O(02)	109.8(2)
Si(2)–O(2)–Si(21)	164.5(3)
O(2)–Si(21)–C(21)	132.8(9)
O(2)–Si(21)–C(22)	112.0(8)
O(2)–Si(21)–C(21′)	121(1)
O(2)–Si(21)–C(22′)	106(1)
C(21)–Si(21)–C(22)	109(1)
C(21′)–Si(21)–C(22′)	128(2)
Si(1)–O(0l)–Si(2)	148.5(2)
Si(2)–O(02)–Si(2)[b]	148.5(3)

Symmetry operations: [a] y−1, $1+z$, x.
[b] $-z$, $1-x$, $1-y$.

Hydrosilylation of allyl bromide to the core molecule (**2**) was carried out by refluxing reactants together in dry diethyl ether. The disappearance of the allyl and Si–H peaks in the ^{1}H-NMR confirmed the reaction went to completion (alternatively, the absence of the $\nu_{\text{Si–H}}$ absorption band in the IR spectrum at 2126 cm^{-1} may be used). The corresponding Si–H resonance in the ^{29}Si-NMR spectrum ($\delta = -0.8$ ppm) also disappears. The resultant white solid product had a yield of 49.7%. Final characterisation was accomplished by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy as well as IR spectroscopy. The three propyl groups (α, β, γ, to the terminal silicon atom), associated with hydrosilylation of an allyl derivative, were clearly seen in the ^{13}C-NMR (α-CH$_2$ at 14.0, β-CH$_2$ at 22.55, and γ-CH$_2$ at 66.98 ppm). The ^{1}H-NMR spectrum supports the characterisation (α-CH$_2$ at 0.6, β-CH$_2$ at 1.7, and γ-CH$_2$ at 4.1 ppm). In addition, the ^{29}Si-NMR spectrum of the final product displays signals for Q- and M- type silicon atoms [20] with chemical shifts in the expected region of the spectrum [21], which agrees with a totally symmetrical and substituted structure. This means that the resonance at -106.9 ppm is assigned to the Q-type silicon atoms of the [Si_8O_{12}] framework and the resonance at 10.7 ppm is assigned to the M(CH$_2$)$_3$Br group [22]. Most hydrosilylations produce two products, α (minor product, –SiCH(CH$_3$)CH$_2$–) and β (major product, –Si(CH$_2$)$_3$–) which are typically of the order 10–20% and 80–90%, respectively. Significantly, no evidence by NMR spectroscopy was observed for the minor α isomer after hydrosilylation, affirming only one isomer is isolated from each reaction. Bassindale and Gentle [23] have reported vinyl/H exchange on the silicon atom may possibly be occuring. Such vinyl/H exchange will form an additional product which would be an octopus dimer in which two silsesquioxane cores are joined by an ethylene linkage bridging the two cores together. Both NMR and GPC do not reveal the presence of such a product, although in the NMR spectra, any possible resonances are obscured behind those of the main addition product.

To compare the above hydrosilylation reaction, an analogous hydrosilylation reaction was performed on the cubic hydridosilsesquioxane [$Si_8H_8O_{12}$ or T_8H_8]. T_8H_8 was initially prepared using a modified method of Agaskar's [13] by the controlled hydrolysis of $HSiCl_3$. Good yields of around 16% using purified hexane as solvent were obtained with sodium dodecyl sulphate as the surfactant. A single peak in both ^1H- and ^{29}Si-NMR spectra at $\delta = 4.27$ and -84.7 ppm, respectively, indicates pure T_8H_8. Interestingly, a recent paper by Crivello and Malik reports a modified procedure which gives yields of 23%, the highest reported yield for the synthesis of T_8H_8 to date [24].

Similarly to the octakis(hydrodimethylsiloxy)octasilsesquioxane **2**, the T_8H_8 core was successfully hydrosilylated with allyl bromide in good yield (57.0%). The reaction was monitored using NMR and IR spectroscopy as described for the analogous reaction using **2** [Scheme 1(B)]. Again, no α-isomer is observed after hydrosilylation.

The T_8H_8 molecule is essentially a small, compact core, where the sequential addition of bulkier substituents (in this case, allyl bromide), is subject to spatial and orientational constraints imposed by the core. This is even more so for the hydrodimethylsiloxy octasilsesquioxane functionalised core (**2**), where the presence of $SiO(Me)_2$ groups increases both steric and orientational effects.

The unique cube-shaped molecules, which were once thought to be a novelty and of no practical importance, are quickly becoming a major driving force in the search for improved composite materials. The innate nature of the silsesquioxane framework to act as a model surface for heterogeneous silica systems has secured a role for such materials in evaluating complex phenomena on surfaces well into the next century.

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[20] In siloxane chemistry, the symbols M, D, T, and Q represent $R_3SiO_{0.5}$, $R_2Si(O_{0.5})_2$, $RSi(O_{0.5})_3$, and $Si(O_{0.5})_4$ units, respectively. Superscripts are used to designate functional groups on the silicon other than Me, otherwise Me is understood.

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