Octasilsesquioxane Chemistry II. Hydrosilylation Reaction of Octa(hydrido)silsesquioxane with Unsaturated Substrates and Product Properties

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The hydrosilylation reaction of octa(hydrido)silsesquioxane with ω-halo-1-alkenes and other unsaturated substrates allows attachment of 8 long-chain functionalized alkyls on the cubic Si_8O_{12} skeleton. Pt/C and H_2PtCl_6 have been adopted as the catalysts, the yields being 74-98% for compounds **2-9**. For terminal alkenes, the hydrosilylation follows the anti-Markonikov's rule. The morphological state of **2-9** ranges from viscous liquid to crystalline materials. The pyrolysis results indicate that **7**, a material of hard spherical core and soft flexible shell, may likely act as nanometer-size ball bearings up to more than 400 °C. The X-ray structure of **9** reveals that the molecule is required to possess a center of symmetry crystallographically. The linear arms on **9**, except for two of them, are virtually *all-trans* in conformation, not counting the ω-C-Cl bond.
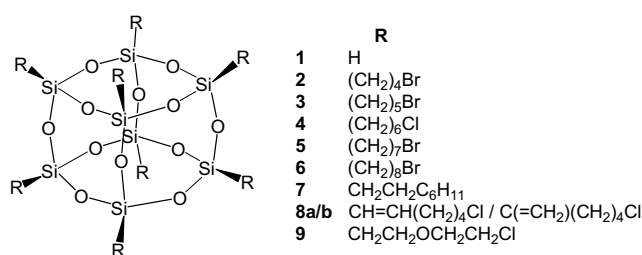
Keywords: Octasilsesquioxane; Hydrosilylation; Nanocomposites; Pyrolysis.

INTRODUCTION

Because of the length scales involved, nanocomposite materials incorporate extensive interfacial interactions that can result in non-linear changes in the composite property.[1] Such changes in the nano region are so great that the rules commonly used to estimate the macroscopic property of composites no longer hold. The nanocomposites then offer potential access to completely new classes of materials with unique properties. One of the more difficult problems with nanocomposites is in developing synthetic and processing approaches that precisely define the volume and shape of individual phases and their periodicity.

Chemists often start from a much reduced domain-size and work at the molecular level, incorporating polymerizable inorganic and organic constituents in the molecule to build organic/inorganic hybrids that combine advantageous properties of disparate components.[2] Silsesquioxanes $(RSiO_{1.5})_n$, derived from, e.g., $RSiCl_3$ or $RSi(OEt)_3$ by hydrolysis/condensation in a sol-gel process, are a class of silicate frameworks where each Si-atom is linked covalently to an organic radical R.[3] Because of the introduction of R, these polymeric/oligomeric species are chemically modified silicates. Physically for instance, they have completely different thermal behaviors from silicates without modification. Structurally, silsesquioxanes consist of tetrahedral silicon atoms, each being a 'T' unit,[4] i.e., connected to three O-atoms and

one R group. The O-atoms are bridges between Si-atoms belonging to different T units, or between Si- and H-atoms. Among many other incompletely condensed silsesquioxanes is also the octa(hydrido)silsesquioxane, H_8-T_8, which is completely condensed with a cubane-shaped structure, is suitable for more structural elaboration.[5] The intention of this work is to produce hybrid nanomolecules from H_8-T_8 via addition of organic moieties, the target being a Si_8O_{12} core carrying 8 functionalities for later use in starburst dendrimers.[6]



	R
1	H
2	$(CH_2)_4Br$
3	$(CH_2)_5Br$
4	$(CH_2)_6Cl$
5	$(CH_2)_7Br$
6	$(CH_2)_8Br$
7	$CH_2CH_2C_6H_{11}$
8a/b	$CH=CH(CH_2)_4Cl$ / $C(=CH_2)(CH_2)_4Cl$
9	$CH_2CH_2OCH_2CH_2Cl$

RESULTS AND DISCUSSION

Attempted synthesis of H_8-T_8 with solid acid route

H_8-T_8 was first synthesized serendipitously in 1958 at <1% yield from $HSiCl_3$.[7] There have been a number of improved preparations since. Agaskar reported a much more reproducible procedure in 1987 and described a purification protocol to yield gram quantities of H_8-T_8, H_{10}-T_{10}, H_{12}-T_{12},

and H_{14}-T_{14}.[8] Our current preparation follows the method reported by Agaskar in 1991,[9] the yield of H_8-T_8 being 17.5% based on $HSiCl_3$. As large amounts of Bronsted acid HCl(aq) and Lewis acid $FeCl_3$(aq) were used in the Agaskar preparation, we thought about the possibility of using a solid acid as a replacement for HCl(aq) and $FeCl_3$(aq), and facilitating the purification steps after condensation. Thus the mixed CH_3OH/ hexane in a round-bottomed flask over acid Amberlite (IR 120) was introduced with hexane-diluted $HSiCl_3$ from a dropping funnel over a long period of time, keeping the mixture under constant stirring. Then the standard Agaskar purification protocol yielded exclusively H_8-T_8, however in just 5.1% yield (Scheme I). According to our own experiences, the utility of solid acid Amberlite has improved many other preparatory methods.[10] But the low yield of H_8-T_8 in this attempt was below expectations. A large percentage of insoluble resinous material was isolated whose ^{1}H NMR spectrum clearly exhibited no proton resonance at all, suggesting the H loss during the sol-gel process of $HSiCl_3$ with addition of acid Amberlite.

Scheme I
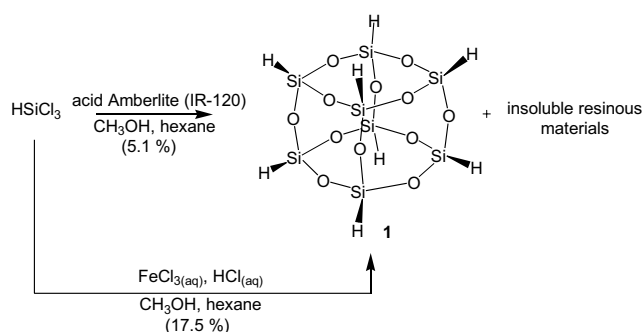
Hydrosilylation on H_8-T_8 with alkenes

Among the principal objectives of this work is one directed towards the synthesis of novel, stable, polyhedral silsesquioxanes carrying various Si-R substituents. The direct condensation of $RSiCl_3$ to form R_8-T_8 in a sol-gel process[11] involves both a monomer $RSiCl_3$ synthesis and a sol-gel procedure. For each different sol-gel preparation, there are different issues of side reactions and tedious optimizations. And hence modification on an existing Si_8O_{12} skeleton without breaking apart the core is more commonly adopted. In the literature, vinyl$_8$-T_8,[12] Ph_8-T_8,[13] and H_8-T_8 all have been synthesized to serve as an intermediate and subject to modification to yield R_8-T_8.

In order to functionalize organic/inorganic nanocomposites, currently one of our attempts is to attach long-chain ω-halogenated functionality to all of the Si-atoms on cubic

silsesquioxanes, and we have carried out experiments on H_8-T_8 employing the hydrosilylation reaction, which is an important reaction in Si chemistry, converting Si-H bond to Si-C bond by 1,2-addition of the Si-H moiety onto an unsaturated C-C bond.[14] In this manuscript, we report the reaction of H_8-T_8 and a series of ω-halogenated terminal alkenes to produce new octa(ω-halo-alkyl)silsesquioxanes. The hydrosilylation reaction has been found to proceed with retention of the Si_8O_{12} skeleton. Pt/C and H_2PtCl_6 have been adopted as the catalysts[15] with various ω-halo-1-alkenes as the unsaturated substrates (Scheme II): 4-bromo-1-butene, 5-bromo-1-pentene, 6-chloro-1-hexene, 7-bromo-1-heptene, and 8-bromo-1-octene; together with other unsaturated substrates: vinylcyclohexane, 6-chloro-1-hexyne, and 2-chloro-ethyl-vinylether. The reactions of the last three substrates are shown as examples in Scheme III. The hydrosilylation was carried out with excess unsaturated substrates at reflux. The yields were excellent following the anti-Markonikov's rule for alkenes and the purification very simple. The reaction was monitored by ^{1}H NMR spectroscopy, noting the disappearance of resonance at δ 4.19, and the emergence of appropriate peaks due to expected products. The products **2-9** were analyzed spectroscopically with good elemental analysis data. The morphological state of **2-9** ranges from viscous liquid to crystalline materials (Table 1). The viscous nature of liquids with increasing carbon length attached to the Si_8O_{12} framework was particularly observed.

Scheme II
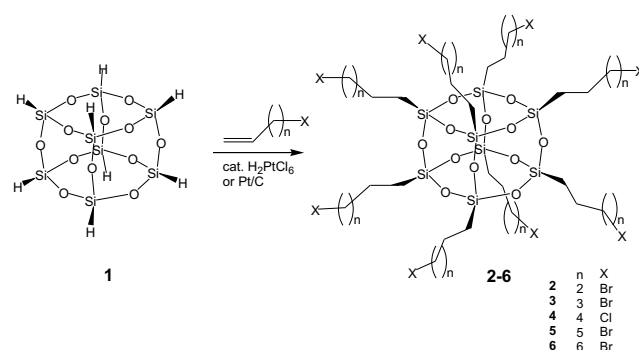
The comparison between Pt/C and H_2PtCl_6 as the hydrosilylation catalysts is as follows. It was found that the latter, homogeneous in nature, effectively hydrosilylated all the unsaturated substrates listed earlier, whereas the former was selective towards that of ω-halo-1-alkenes. There was no reaction when Pt/C was adopted as catalyst in the cases of vinylcyclohexane, 6-chloro-1-hexyne, and 2-chloroethyl-

Scheme III
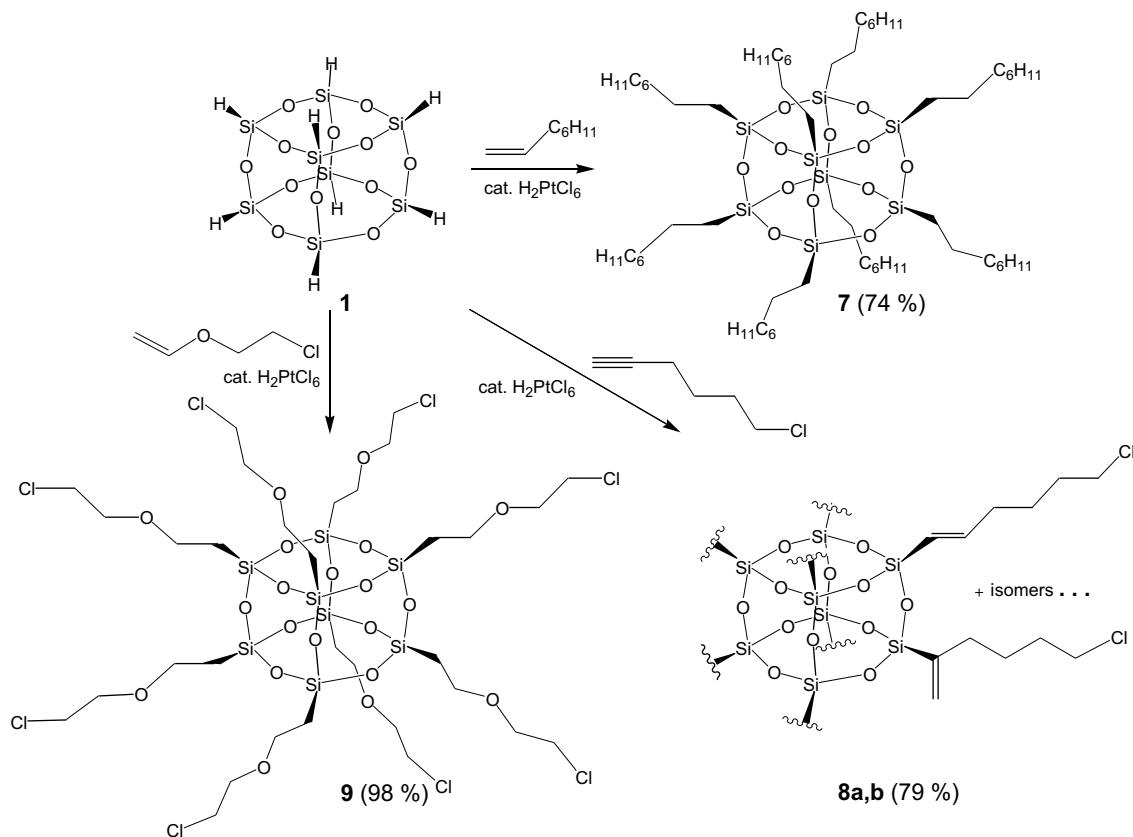
vinylether to produce **7-9** (see Table 1, entries 6-8). Compared to Pt/C, H_2PtCl_6 has been judged to be more applicable overall, and its effectiveness at very low concentration has been quite remarkable. The production of **2-9** involves 8

steps of hydrosilylation reactions on a single Si_8O_{12} skeleton; the yields ranging 74% - 98% suggest almost complete conversion for each step. The generally accepted reaction mechanism based on fundamental transition metal reactions in-

Table 1. Preparation and Properties of R_8-T_8

Entry	Product	Catalyst, Solvent	Yield	Physical state[a]	M+
1	**2**	H_2PtCl_6, neat	88	Brown liquid	1504.0
		Pt/C, neat	90		
2	**3**	H_2PtCl_6, neat	98	White solids	1617.3
		Pt/C, neat	99		
5	**4**	H_2PtCl_6, neat	98	Colorless liquid	1373.2
		Pt/C, neat	86		
4	**5**	H_2PtCl_6, toluene	90	Brown liquid	1841.4
		Pt/C, toluene	74		
5	**6**	H_2PtCl_6, neat	96	Brown liquid	1952.2
		Pt/C, neat	88		
6	**7**	H_2PtCl_6, hexane	74	White micro crystals	1306.7
		Pt/C, hexane	[b]		
7	**8a, b**	H_2PtCl_6, toluene	79	Light brown liquid	1357.1
		Pt/C, toluene	[b]		
8	**9**	H_2PtCl_6, neat	98	Colorless crystals	1275.1
		Pt/C, neat	[b]		

[a] At room temperature. All liquids are highly viscous. [b] No reaction.

cludes oxidative addition of Si-H bond on Pt, olefin coordination, migratory 1,2-insertion of hydride, and reductive elimination, that is, the 'Chalk-Harod' mechanism[16] as further extended by Speier.[17] The regioselectivity favoring linear products in the cases of ω-halo-1-alkenes as substrates is attributable to steric bulkiness of the Si_8O_{12} core.

Compounds **2-9**, prepared under nitrogen atmosphere, are stable under air. The ^{1}H NMR taken before and after exposing them to air for 2 h gave no differential observation. Overall the Pt-catalyzed hydrosilylation reaction of H_8-T_8 provides convenient access to ω-halo-functionalized cubic silsesquioxanes.

In the case of vinylcyclohexane (Table 1, entry 6), the steric energy of cyclohexane groups caused a relatively lower yield of **7**. In the case of 6-chloro-1-hexyne (Table 1, entry 7), the products **8a,b** were found to be a mixture of isomers, attributed to α- and β-additions. Gentle and Bassindale reported that β-addition and side reactions can be suppressed if the steric bulkiness on the γ-position of the unsaturated substrates increases.[18] In the case of 2-chloroethylvinylether (Table 1, entry 8), the ether functionality might also have caused a slight decrease on the yield of **9** (*cf*. yields of **3**, **4**).

Pyrolysis of compounds 3, 7, and 9

Polysiloxanes, and a few of the octa(alkyl)silsesquioxanes have already received attention as precursors to ceramics and special glasses, for example, to silicon carbide, silicon oxycarbide and silicon oxynitride glasses. Out of the new R_8-T_8 compounds, only **3**, **7**, and **9** are solid samples whose thermolysis under normal conditions has been carried out in order to evaluate their relative thermal stability and possible ceramics-making potential. Fig. 1 shows the results of a thermogravimetric analysis study.

The three selected compounds are reasonably stable. All of them remain at constant weight below 350 °C, with the temperature of 10% weight loss occurring at 381, 442, and 338 °C, for **3**, **7**, and **9**, respectively, compound **7** being the most stable. Both **3** and **7** have single step weight loss whereas **9** shows more than one step as reasonably expected from its ether linkages. The bromosilsesquioxane **3** is also seen thermally more stable than the chlorosilsesquioxane **9**. The high thermal stability of **7** is attributed to its branching arms that carry one cyclohexyl group as the end group each (many more cyclic atoms on **7** relative to that on **3** and **9**). Compound **7** is likely a much better material consisting of hard spherical cores and soft flexible shells that may act as nanometer-size ball bearings at above 400 ºC. It has been conceived that at high temperatures, mineralization takes

place. This degradation process involves the cleavage of many organic (and inorganic) bonds, leading to the escape of pyrolyzed small molecules before the formation of inorganic black glasses. The total weight loss of **7** and **9** exceeds 80% and is thus greater than the organic fraction of the materials, indicative of decomposition and rearrangement under the formation of larger siloxane structures and/or silicon oxycarbide.[19]

X-ray crystal structure of 9

Compounds **3**, **7**, and **9** exist as solid microcrystals, out of which crystals suitable for X-ray diffraction studies were grown successfully for **9**, from ether and from hexane/acetone. Single crystal X-ray structure analysis revealed clearly the molecular connectivity of **9**, as shown in Fig. 2. The molecule is required crystallographically to possess a center of symmetry. The linear arms, except that extending from Si3, are virtually *all-trans* in conformation till ω-C-Cl. The arm extending from Si2 exhibits a disorder in the terminal region, the disorder being common in the X-ray structure study of silsesquioxanes. The structural parameters of the core Si_8O_{12} are normal, similar to those found in the structures deposited in the Cambridge Structural Databases. On average of 9 published structures[20] with an R-factor less than 0.10, the core Si-O bond length is 1.616 ± 0.007 Å, and the core ∠O-Si-O bond angle is $149.0 \pm 4.3º$.

EXPERIMENTAL SECTION

General

All manipulations were performed under an atmosphere of pre-purified nitrogen with standard Schlenk techniques, using a double-fold vacuum line. Most of the solvents
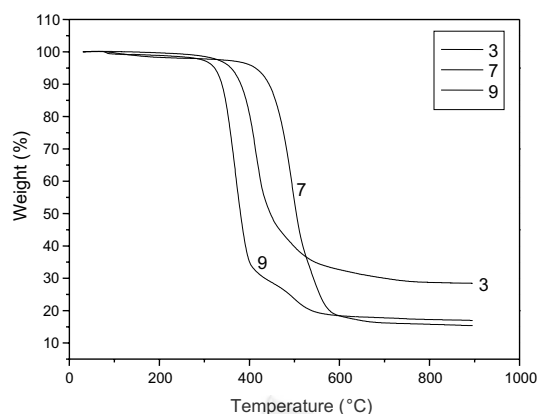

Fig. 1. Thermogravimetric analysis for **3**, **7**, and **9**.

used were distilled from appropriate drying agents.[21] IR spectra were recorded in CH_2Cl_2, using CaF_2 optics on a Perkin-Elmer 882 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on Bruker AC 200/AC 300 spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonance of $CDCl_3$ (^1H, δ 7.24; ^{13}C, δ 77.0), C_6D_6
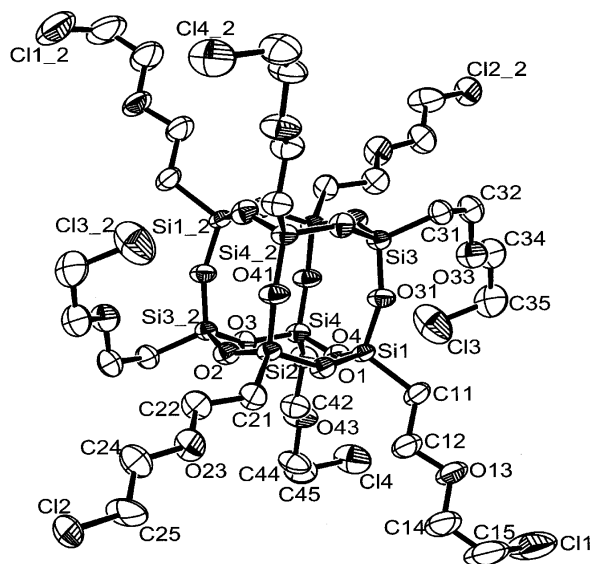

Fig. 2. Molecular structure of **9** with H-atoms, C25', and Cl2' omitted for clarity. Selected bond lengths: Si1-O1 1.627(3), Si1-O4 1.616(4), Si1-O31 1.605(3), Si2-O1 1.614(3), Si2-O2 1.608(4), Si2-O41 1.618(3), Si3-O2 1.613(3), Si3-O3 1.631(3), Si3-O31 1.605(3), Si4-O3 1.621(3), Si4-O4 1.619(4), Si4-O41 1.614(3) Å; Si1-C11 1.842(5), Si2-C21 1.846(5), Si3-C31 1.841(5), Si4-C41 1.837(5) Å; bond angles: O1-Si1-O4 108.42(19), O1-Si1-O31 108.79(18), O1-Si1-C11 109.01(20), O4-Si1-O31 109.52(18), O4-Si1-C11 111.64(23), O31-Si1-C11 109.42(23), O1-Si2-O2 109.50(18), O1-Si2-O41 108.45(18), O1-Si2-C21 107.96(20), O2-Si2-O41 108.83(18), O2-Si2-C21 109.98(23), O41-Si2-C21 112.09(24), O2-Si3-O3 108.32(18), O2-Si3-O31 109.44(19), O2-Si3-C31 110.53(21), O3-Si3-O31 107.69(18), O3-Si3-C31 108.74(21), O31-Si3-C31 112.01(21), O3-Si4-O4 108.45(18), O3-Si4-O41 109.97(18), O3-Si4-C41 109.67(22), O4-Si4-O41 110.14(20), O4-Si4-C41 111.28(22), O41-Si4-C41 107.33(21)°; consecutive torsion angles: Si1-C11-C12-O13-C14-C15-Cl1 -175.6°, -177.2°, -179.1°, -49.8°; Si2-C21-C22-O23-C24-C25-Cl2 176.7°, -174.1°, 159.0°, 155.0°; Si3-C31-C32-O33-C34-C35-Cl3 -52.4°, 169.6°, 178.5°, 62.8°; Si4-C41-C42-O43-C44-C45-Cl4 178.9°, 177.3°, -179.7°, 63.8°.

(^1H, δ 7.15), and d-acetone (^1H, δ 2.04). High resolution FAB-mass spectra were collected on a JEOL JMS-700 double focusing mass spectrometer with a resolution of 8000 (5% valley definition). For FAB-mass spectra, the source accelerating voltage was operated 10 kV with a Xe gun, using 3-nitrobenzyl alcohol as matrix. Micro-analytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer, independently operated by the Institute of Chemistry, Academia Sinica. Thermal gravimetric analyses were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer where measurements were performed at a rate of 10 °C/min under air/nitrogen. The melting points were determined on a Fargo melting point apparatus and the values were uncorrected. Reagents/chemicals were obtained from commercial sources, e.g. Aldrich and Fluka, and used without further purification. Acid Amberlite (IR-120) was regenerated after use by washing with concentrated aqueous HCl, water, and methanol.

Synthesis of H_8-T_8, 1

(a) With Agaskar procedure

$FeCl_3$ (anhydrous, 50 g) was taken in a round-bottomed flask, and concentrated aqueous HCl (20 mL) was added followed by CH_3OH (40 mL). Hexane (350 mL) was added, and the mixture was stirred. A solution of $HSiCl_3$ (20 mL, 0.2 mol) in hexane (150 mL) was added dropwise over a period of 9 h. After an additional 30 min of stirring, the upper hexane layer was transferred to another round-bottomed flask along with a suspended yellow solid. K_2CO_3 (14 g) and $CaCl_2$ (10 g) were added to the flask and the contents stirred overnight. The mixture was filtered, and the filtrate volume was reduced by evaporation until it was about 20 mL. ^1H NMR (C_6D_6) showed that these crystals were a mixture of H_8-T_8 and H_{10}-T_{10} with singlets at δ 4.19 and 4.23, respectively. H_{10}-T_{10} was eliminated by further washings of the mixture with hexane to give a yield of **1** as 17.5%. **1**: ^1H NMR (C_6D_6): δ 4.19 (s, 8H). MS (FAB): 425.4 (M^+).

(b) With attempted Amberlite procedure

A mixture of CH_3OH (30 mL) and hexane (150 mL) were put in a 500 mL round-bottomed flask containing acid Amberlite (IR 120, 50 g). While stirring, a 10-fold hexane diluted $HSiCl_3$ (4.0 mL, 0.040 mol) was added from a dropping funnel over a period of 6 h and then stirred overnight. The hexane layer was removed and put into a mixture of K_2CO_3 (14 g) and $CaCl_2$ (10 g) and vigorously stirred for 5 h. The filtrate was evaporated until it was less than 7 mL in volume. White microcrystals of **1** were exclusively collected in 5.1%

yield.

Hydrosilylation reaction of H_8-T_8 with 4-bromo-1-butene

H_8-T_8 (0.25 g, 5.7×10^{-4} mol) and 4-bromo-1-butene (2.0 mL, 1.9×10^{-2} mol) were put in a 5.0 mL flask. Five drops of 0.1 M H_2PtCl_6 in *i*-PrOH were added, and the mixture heated at reflux for 10 h. Excess reactant was removed under vacuum to give a brown viscous liquid {Br(CH$_2$)$_4$}$_8$-T_8 **2**. Yield = 88%. **2**: ^{1}H NMR (CDCl$_3$): δ 0.62 (b, SiCH$_2$, 2H); 1.53 (b, CH$_2$, 2H); 1.83 (b, CH$_2$, 2H); 3.38 (b, CH$_2$Br, 2H). ^{13}C NMR (CDCl$_3$): δ 10.90 (CH$_2$); 21.35 (CH$_2$); 33.52 (CH$_2$). MS (FAB): 1504.04 (M$^+$, parent ion).

Hydrosilylation reaction of H_8-T_8 with 5-bromo-1-pentene

H_8-T_8 (0.25 g, 5.7×10^{-4} mol), Pt/C (5 mg) [or alternatively 8 drops of 0.1 M H_2PtCl_6 in *i*-PrOH], and 5-bromo-1-pentene (1.5 mL, 1.3×10^{-2} mol) were heated at reflux for 17 h [in the case of H_2PtCl_6, 7 h]. A small amount of ether was then added and filtered over celite. The solution was vacuum-dried to afford a white solid {Br(CH$_2$)$_5$}$_8$-T_8 **3**. Yield = 98% [in the case of H_2PtCl_6, 100%]. **3**: M.p. 67.9 °C. ^{1}H NMR (CDCl$_3$): δ 0.59-0.64 (t, SiCH$_2$, 2H); 1.42-1.45 (m, CH$_2$, 4H); 1.80-1.84 (m, CH$_2$, 2H); 3.36-3.40 (t, CH$_2$Br, 2H). ^{13}C NMR (CDCl$_3$): δ 11.75 (SiCH$_2$); 22.04 (CH$_2$); 30.99 (CH$_2$); 32.40 (CH$_2$); 33.78 (CH$_2$Br). IR (CH$_2$Cl$_2$): 3688.7, 1447.4, 1118.9 cm^{-1}. MS (FAB): 1617.3 (M$^+$, parent ion). Elem. Anal. Calcd. for C$_{40}$H$_{80}$O$_{12}$Si$_8$Br$_8$: C 29.73%, H 4.96%; Found: C 29.79%, H 5.0%.

Hydrosilylation reaction of H_8-T_8 with 6-chloro-1-hexene

H_8-T_8 (0.25 g, 5.7×10^{-4} mol) and 6-chloro-1-hexene (1.20 mL, 9.0×10^{-3} mol) were put in a 5.0 mL flask. Eight drops of 0.1 M H_2PtCl_6 in *i*-PrOH were added and the mixture heated at reflux for 10 h. Excess reactant was removed under vacuum to give a clear colorless viscous liquid {Cl(CH$_2$)$_6$}$_8$-T_8 **4**. Yield = 98%. **4**: ^{1}H NMR (CDCl$_3$): δ 0.56-0.61 (t, SiCH$_2$, 2H); 1.31-1.39 (m, CH$_2$, 6H); 1.68-1.76 (m, CH$_2$, 2H); 3.48-3.52 (t, CH$_2$Cl, 2H). ^{13}C NMR (CDCl$_3$): δ 11.80 (SiCH$_2$); 22.60 (CH$_2$); 26.50 (CH$_2$); 31.79 (CH$_2$); 32.48 (CH$_2$); 45.08 (CH$_2$Cl). IR (CH$_2$Cl$_2$): 3688.7, 1447.4, 1117.2 cm^{-1}. MS (FAB): 1373.2 (M$^+$, parent ion). Elem. Anal. Calcd. for C$_{48}$H$_{96}$O$_{12}$Si$_8$Cl$_8$: C 41.89, H 6.9; Found: C 41.72, H 6.82.

Hydrosilylation reaction of H_8-T_8 with 7-bromo-1-heptene

H_8-T_8 (0.125 g, 2.89×10^{-4} mol) in toluene (3.0 mL) and 7-bromo-1-heptene (1.0 mL, 6.5×10^{-3} mol) were put in a 5.0 mL flask. Eight drops of 0.1 M H_2PtCl_6 *i*-PrOH were added and the mixture heated at reflux for 16 h. Toluene and excess reactant were removed under vacuum to give a clear colorless viscous liquid {Br(CH$_2$)$_7$}$_8$-T_8 **5**. Yield = 90%. **5**: ^{1}H NMR (CDCl$_3$): δ 0.58 (b, SiCH$_2$, 2H); 1.30-1.37 (m, CH$_2$, 8H); 1.78 (b, CH$_2$, 2H); 3.36 (b, CH$_2$Br, 2H). ^{13}C NMR (CDCl$_3$): δ 11.87 (CH$_2$); 22.64 (CH$_2$); 28.03 (CH$_2$); 28.40 (CH$_2$); 32.38 (CH$_2$); 32.78 (CH$_2$); 33.97 (CH$_2$). IR (CH$_2$Cl$_2$): 3685.2, 1449.0, 1118.3 cm^{-1}. MS (FAB): 1841.41 (M$^+$, parent ion). Elem. Anal. Calcd. for C$_{56}$H$_{112}$O$_{12}$Si$_8$Br$_8$: C 36.43%, H 6.13%; Found C 35.45%, H 5.84%.

Hydrosilylation reaction of H_8-T_8 with 8-bromo-1-octene

8-Bromo-1-octene (1.5 mL, 8.9×10^{-3} mol) was added to a 5.0 mL flask containing H_8-T_8 (0.25 g, 5.7×10^{-4} mol). Eight drops of 0.1 M H_2PtCl_6 in *i*-PrOH were added and the mixture heated at reflux for 10 h before vacuum-removal of excess reactant to give a light brown viscous liquid {Br(CH$_2$)$_8$}$_8$-T_8 **6**. Yield = 96%. **6**: ^{1}H NMR (CHCl$_3$): δ 0.55 (b, SiCH$_2$, 2H); 1.27 (b, CH$_2$, 10H); 1.78 (b, CH$_2$, 2H); 3.35 (b, CH$_2$Br, 2H). ^{13}C NMR (CDCl$_3$): δ 11.80, 22.60, 28.10, 28.58, 29.00, 32.40, 32.73 & 33.83 (all CH$_2$). MS (FAB): 1952.2 (M$^+$, parent ion). Elem. Anal. Calcd. for C$_{64}$H$_{128}$O$_{12}$Si$_8$Br$_8$: C 39.37%, H 6.56%; Found C 39.26%, H 6.49%.

Hydrosilylation reaction of H_8-T_8 with vinylcyclohexane

To a solution of H_8-T_8 (0.25 g, 5.7×10^{-4} mol) in hexane (10.0 mL) in a 25 mL flask was added vinylcyclohexane (1.80 mL, 1.3×10^{-2} mol). Ten drops of 0.1 M H_2PtCl_6 in *i*-PrOH were added and the mixture heated at reflux for 3 d. The solvent and excess vinylcyclohexane were removed under vacuum to give a white solid {C$_6$H$_{11}$(CH$_2$)$_2$}$_8$-T_8 **7**, which was purified by washing with CH$_3$OH. Yield = 74%. **7**: ^{1}H NMR (CDCl$_3$): δ 0.54 (b, SiCH$_2$, 2H); 0.79 (b, CH$_2$, 2H); 1.13 (b, C$_6$H$_{11}$, 6H); 1.61 (b, C$_6$H$_{11}$, 5H). ^{13}C NMR (CDCl$_3$): δ 9.08 (SiCH$_2$); 30.20 (CH$_2$C$_6$H$_{11}$); 26.39, 26.80, 32.94, 39.94 (all C$_6$H$_{11}$). MS (FAB): 1306.7 (M$^+$, parent ion). Elem. Anal. Calcd. for C$_{64}$H$_{120}$O$_{12}$Si$_8$: C 58.96%, H 9.27%, Found C 59.52%, H 9.60.

Hydrosilylation reaction of H_8-T_8 with 6-chloro-1-hexyne

To a solution of H_8-T_8 (0.25 g, 5.7×10^{-4} mol) in toluene (4.0 mL) in a 10 mL flask was added 6-chloro-1-hexyne (1.40 mL, 1.20×10^{-2} mol). Six drops of 0.1 M H_2PtCl_6 in *i*-PrOH were added and the mixture heated at reflux for 8 h to give brown viscous liquid {Cl(CH$_2$)$_4$CH=CH}$_n$-{Cl(CH$_2$)$_4$C=CH$_2$}$_{(8-n)}$-

Hydrosilylation of Octa(hydrido)silsesquioxane

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T$_8$ **8a,b** (isomeric α and β hydrosilylated products which were not further isolated). **8a,b**: ^{1}H NMR (CDCl$_3$): δ 1.53 (b, SiCH$_2$, 2H); 1.69 (b, CH$_2$, 2H); 2.17 (b, CH$_2$, 2H); 3.46 (b, CH$_2$, 4H); 5.41 (d, CH, 1H); 6.36 (d, CH, 1H); 5.68 (b, CH$_2$, 2H). MS (FAB): 1357.1 (M$^+$, parent ions for isomers).

Hydrosilylation reaction of H$_8$-T$_8$ with 2-chloroethyl-vinylether

2-Chloroethylvinylether (2.0 mL, 1.9 × 10^{-2} mol) was added to a 5.0 mL flask containing H$_8$-T$_8$ (0.25 g, 5.7 × 10^{-4} mol). Eight drops of 0.1 M H$_2$PtCl$_6$ in *i*-PrOH were added and the mixture heated at reflux overnight before vacuum-removal of excess reactant to give off-white microcrystals which were washed with hexane {Cl(CH$_2$)$_2$O(CH$_2$)$_2$}$_8$-T$_8$ **9**. Yield = 98%. **9**: ^{1}H NMR (CHCl$_3$): δ 1.06 (t, SiCH$_2$, 2H); 3.55-3.67 (m, CH$_2$OCH$_2$CH$_2$Cl, 6H). ^{13}C NMR (CDCl$_3$): δ 13.99, 42.94, 66.65, & 70.38 (all CH$_2$). MS (FAB): 1275.1 (M$^+$, parent ion). Elem. Anal. Calcd. for C$_{32}$H$_{64}$O$_{20}$Si$_8$Cl$_8$: C 30.01%, H 4.98%; Found C 29.75%, H 4.91%.

X-ray structure analysis of 9

Diffraction intensities were measured with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every 60 min, showed no significant decrease in intensity during data collection. Data were corrected for Lorentz-polarization and absorption (empirical ψ corrections). The structure was solved by direct methods MULTAN.[22] Calculations and full matrix least-squares refinements were performed utilizing the NRCVAX program package.[23] Disorders were found in that 2 extra atomic positions were also included in the final molecular structure: Cl2 with occupancy 0.75 and Cl2' 0.25, C25 with occupancy 0.50 and C25' with 0.50. All non-H atoms were refined with anisotropic thermal parameters with hydrogen atoms fixed (C-H = 1.00 Å). Scattering factor curves of Cl, Si, O, C, and H were taken from the International Tables.[24] Crystal data of **9**: C$_{32}$H$_{64}$Cl$_8$O$_{20}$Si$_8$, FW 1277.16; Triclinic P -1, a 8.9592(13), b 12.4123(19), c 13.1479(12) Å, α 99.719 (11), β 95.264(11), γ 84.052(12)°; V = 1429.2(3) Å^3; Z = 1; F(000) 664; D$_{calc}$ 1.477 g/cm^3; λ 0.7107 Å; μ 0.63 mm^{-1}; 2θ max 50.0°; Nonius CAD4 data; -10 < h < 10, 0 < k < 14; -15 < l < 15; crystal size 0.21 × 0.24 × 0.40 mm; transmission factors 0.483-0.868; T = 298 K; No. of refined atoms 36; No. of calculated atoms 32; No. of refined parameters 325; No. of unique reflections 5038; No. of observed reflections 3618 [I > 2.0 σ(I)]; R = 0.076; R$_w$ = 0.106; Goodness of fit = 1.76; (Δ/σ)$_{max}$ = 0.0001; (D-map)$_{max}$ = 1.050 e/Å^3; Minimizing function = Σ(w||F$_o$| - |F$_c$||^2); Weighting scheme = counting statistics plus a weight modifier 0.05. Final fractional coordinates of non-H atoms are given in Table 2, selected structural parameters in the caption of Fig. 2.

Table 2. Final Fractional Coordinates of Non-hydrogen Atoms of **9**

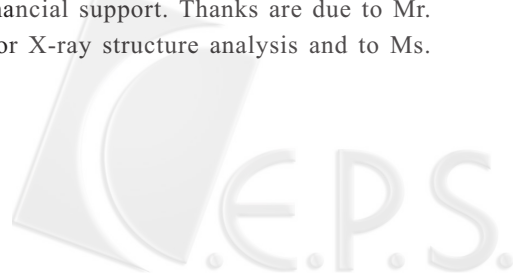| Atom	x	y	z	Biso
Si1	0.62559(15)	0.55395(10)	0.83948(9)	2.75(5)
Si2	0.54165(15)	0.32253(9)	0.85134(8)	2.69(5)
Si3	0.76642(14)	0.57978(10)	1.07048(9)	2.65(5)
Si4	0.31717(15)	0.65225(10)	0.91708(9)	2.94(6)
C11	0.8684(5)	0.6944(3)	0.3933(2)	15.18(28)
C12	0.3547(3)	-0.2486(2)	0.5220(2)	5.88(10)[a]
C12'	0.4982(35)	-0.2238(21)	0.5585(16)	23.21(55)[b]
C13	0.5945(3)	0.8754(2)	0.9093(2)	9.43(14)
C14	-0.0278(3)	1.0540(2)	0.6430(2)	7.91(12)
O1	0.6027(4)	0.4237(2)	0.8097(2)	3.3(1)
O2	0.3644(4)	0.3476(3)	0.8654(2)	3.4(1)
O3	0.2236(4)	0.5452(2)	0.9043(2)	3.4(1)
O4	0.4618(4)	0.6213(3)	0.8490(3)	3.7(2)
O13	0.7809(6)	0.5792(4)	0.5633(3)	6.2(2)
O23	0.5092(5)	0.0252(3)	0.6659(3)	5.3(2)
O31	0.7224(4)	0.5747(3)	0.9488(2)	3.5(1)
O33	0.8732(5)	0.7939(3)	1.0333(3)	5.0(2)
O41	0.6289(4)	0.3105(3)	0.9627(2)	3.8(1)
O43	0.0332(5)	0.8462(3)	0.7482(3)	5.1(2)
C11	0.7280(7)	0.5949(4)	0.7390(4)	4.1(2)
C12	0.6865(9)	0.5476(6)	0.6314(4)	6.4(4)
C14	0.7394(13)	0.5396(8)	0.4599(5)	9.2(5)
C15	0.8292(14)	0.5664(8)	0.3883(5)	9.8(6)
C21	0.5759(7)	0.1981(4)	0.7546(4)	4.3(2)
C22	0.4720(7)	0.1114(4)	0.7477(4)	4.5(2)
C24	0.4097(9)	-0.0567(6)	0.6452(6)	6.6(4)
C25	0.4088(36)	-0.1219(18)	0.5472(18)	8.0(15)[c]
C25'	0.4817(19)	-0.1436(17)	0.5698(17)	4.7(8)[d]
C31	0.9494(6)	0.6353(4)	1.1099(4)	3.6(2)
C32	0.9440(7)	0.7597(5)	1.1236(4)	4.5(3)
C34	0.8382(8)	0.9090(5)	1.0440(5)	5.5(3)
C35	0.7683(10)	0.9363(5)	0.9444(6)	6.6(4)
C41	0.1949(6)	0.7672(4)	0.8748(4)	3.8(2)
C42	0.1258(7)	0.7495(4)	0.7657(4)	4.4(2)
C44	-0.0294(8)	0.8350(5)	0.6441(5)	5.7(3)
C45	-0.1230(8)	0.9358(6)	0.6285(5)	6.3(3)

[a] C12: occupancy factor = 0.75. [b] C12': occupancy factor = 0.25. [c] C25: occupancy factor = 0.50. [d] C25': occupancy factor = 0.50.

Ping-You Lin for high resolution FAB mass measurements.

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