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A higher yielding route for T_8 silsesquioxane cages and X-ray crystal structures of some novel spherosilicates

Alan R. Bassindale,[a] Zhihua Liu,[a] Iain A. MacKinnon,[b] Peter G. Taylor,[a] Yuxing Yang,[a] Mark E. Light,[c] Peter N. Horton[c] and Michael B. Hursthouse[c]
[a] *Department of Chemistry, Open University, Walton Hall, Milton Keynes, UK MK7 6AA. E-mail: p.g.taylor@open.ac.uk*
[b] *Dow Corning Ltd., Barry, UK CF63 2YL*
[c] *EPSRC National Crystallography Service, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

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The synthesis of T_8 silsesquioxane cages from trialkoxysilanes using tetra *n*-butylammonium fluoride is described. The yields are in the range 20–95%, which is a great improvement on other literature routes. This methodology enables a wide range of functionalised T_8 cages to be prepared. The X-ray crystal structures of three new T_8 cages, octacyclopentylsilsesquioxane, octaisobutylsilsesquioxane and octa(4-carboxymethyl-3,3-dimethylbutyl)-silsesquioxane are also reported.

Introduction

Spherosilicate silsesquioxane cages, and in particular the octasilsesquioxanes, known as T_8, have been used extensively as scaffolds for the development of liquid crystals,[1,2] biocompatible materials,[3] catalysts[4,5] and dendrimers.[6] Unfortunately preparative yields of spherosilicates are often low because of the ordered geometry required for cage formation. High yields of functionalised T_8 cages can be obtained by hydrosilylation of the corresponding octahydrosilsesquioxane, however, this route is limited by the poor yields (10–15%) of the starting cage obtained in the scarce water hydrolysis.[7,8] Functionalised cages can be obtained by the controlled hydrolysis of the corresponding trichloro or trialkoxysilane, but again the yields are low. Hydrolysis of cyclohexyltrichlorosilane in acetone–water gave yields of the corresponding T_8 cage around 20%[9–11] and acid catalysed hydrolysis of 3-aminopropyltriethoxysilane in methanol gave the cage in about 30% yield.[6] In view of the importance of such compounds as the starting point for the development of a wide range of novel materials, we have examined alternative hydrolytic routes that may lead to a wide range of functionalised cages in good yield.

Results and discussion

Previous studies have shown that hydrolysis of chlorosilanes leads to the formation of substantial amounts of hydrochloric acid, which, as well as catalysing the formation of cages, also enhances the formation of resin and probably leads to further breakdown of the cage once formed. To avoid such uncontrolled build up of catalytic species we focused on the hydrolysis of trialkoxysilanes. The first reported synthesis of an octasilsesquioxane cage from an alkoxysilane was in 1955 by Sprung and Guenther, who hydrolysed methyltriethoxysilane in benzene using hydrochloric acid as the catalyst.[12] They obtained the corresponding T_8 compound in about 1% yield, along with the T_6 cage. They found that the yield of the cages depended upon the amount of water, the time for reaction, the catalyst and the solvent system.[13] Subsequent hydrolyses of trialkoxysilanes to give cages have used predominantly acid catalysis in an organic solvent. Table 1 shows some typical examples of acid catalysis and the optimum conditions, however, the yields are generally quite poor.

Sprung and Guenther also showed that the yield of the octaphenylsilsesquioxane cage was improved on moving from acid catalysis in isobutyl methyl ketone to base catalysis using tetraethylammonium hydroxide.[14] Tetrabutylammonium fluoride has been shown to act as a good base in aldol condensations and thus may catalyse the hydrolysis of alkoxysilanes.[15] Since tetrabutylammonium fluoride contains 5% water, which is difficult to remove from the salt even in THF solution, we decided to use this as our source of water in the hydrolysis.

Table 2 shows the results of our hydrolysis of trialkoxysilanes in THF using tetrabutylammonium fluoride as the catalyst.

Clearly the use of tetrabutylammonium fluoride leads to very good yields of the T_8 cages, up to 95%. Reasonable yields are obtained with a range of substituents on the silicon, from primary alkyl and secondary alkyl to phenyl. A number of functionalities are tolerated in this reaction, such as the 4-carboxymethyl-3,3-dimethylbutyl which we are using as a core for developing dendrimers.

In some cases other cages were formed alongside the T_8 cage. For example, reaction of octylytriethoxysilane led to formation of 65% T_8 together with 27% T_{10}. The precise yield of T_8 cage clearly depended upon the nature of the carbon adjacent to the silicon, with secondary substrates yielding the greatest amount of T_8 cage. As the steric effect of the alkyl groups got smaller, so the proportion of T_{10} and T_{12} increased. For

Table 1 Typical yields of T_8 cages from the acid catalysed hydrolysis of trialkoxysilanes

Trialkoxysilane	Catalyst	Solvent	Time	Yield (%)	Ref.
$MeSi(OEt)_3$	HCl	Benzene	>2 hours	–	12,13,30
$EtSi(OEt)_3/EtSiCl_3$	HCl	Benzene	>2 hours	1	31
$VinylSi(OEt)_3$	HCl	—	Several days	–	19
$C_6H_5Si(OEt)_3$	HCl	Acetone–H_2O	5 months	4	29
$HS(CH_2)_3Si(OMe)_3$	HCl	Methanol	5 weeks	17	32,33
$ClCH_2Si(OMe)_3$	HCl	Methanol	5 weeks	25	32,33
$H_2N(CH_2)_3Si(OEt)_3$	HCl	Methanol	6 weeks	30	6

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Table 2 Yields of T_8 silsesquioxane cages obtained from treatment of the corresponding trialkoxysilane with tetrabutylammonium fluoride

Functionality R in $RSi(OEt)_3$	Yield of T_8 cage (%)	Other T cages present	^{29}Si NMR chemical shift of T_8 cage silicon
Hexyl	44	T_{10}	−66.6
Octyl	65	T_{10}	−66.6
4-Carboxymethyl-3,3-dimethylbutyl	20	T_{10}	−65.9
Isobutyl	26	T_{10}	−67.9
Cyclopentyl	95	–	−66.6
Cyclohexyl	84	–	−68.7
Phenyl	49	T_{12}	(CPMAS) −76.82, −80.40
2-Bicycloheptyl	56	–	−68.7
Methyl	0	–	–
Vinyl	1	T_{10}, T_{12}	–
Allyl	3	T_{10}, T_{12}	–
tert-Butyl	0	–	–

example, vinyltriethoxysilane gave virtually no T_8 cage (1%) but did allow the isolation of 11% T_{10} and 25% T_{12} cage. In most of these reactions whilst the yield of the T_8 cage may only be modest the total yield of cage compound is usually quite high. Reaction of methyltriethoxysilane gave a white solid precipitate which could not be further separated or analysed because of its poor solubility. Thus the sterically less demanding methyl group may either have led to resin or larger cages that proved to be insoluble. Tertiary alkyl groups such as *tert*-butyltriethoxysilane also gave insoluble products possibly due to the high steric demand of placing eight *tert*-butyl groups around a T_8 cage. This may perhaps favour the formation of T_6, however, no such product was isolated in these reactions.

All reactions were carried out using a 2 : 1 ratio of trialkoxysilane to tetrabutylammonium fluoride. Since the tetrabutylammonium fluoride contains 5% water the molar ratio of water to triethoxysilane is about 3 : 2, matching the stoichiometry of the reaction.

$$8\,RSi(OEt)_3 + 12\,H_2O = R_8Si_8O_{12} + 24\,EtOH$$

The proportion of water is critical. Following the reaction by ^{29}Si NMR and increasing the amount of water in the tetrabutylammonium fluoride solution led to a slower rate of reaction with a decrease in the yield of T_8 and the formation of partial cage compounds and silanols. If the water is removed from the tetrabutylammonium fluoride solution,[16] ^{29}Si NMR showed the presence of fluorosilanes such as $RSiF_3$, $RSiF_4^-$ and $RSiF_6^{2-}$. The role of the fluoride ion as base was confirmed by repeating the reaction with tetrabutylammonium chloride in THF containing 5% water, which gave no reaction. We found that the yield of T_8 silsesquioxane cage was to some extent dependent upon the solvent employed, some trialkoxysilanes giving higher yields in acetone and others in chloroform. The use of added THF as the solvent (the tetrabutylammonium fluoride solution is supplied in THF) did not improve the yield substantially and the use of methanol as the solvent always led to a lower yield.

One of the reasons why it is difficult to dry tetrabutylammonium fluoride solution is because the fluoride ion hydrogen bonds with the water to give $(H–O \cdots H \cdots F)^-$ species. Thus, we believe that the fluoride ion acts as a general base enabling hydroxide ion to attack the triethoxysilane to form the silanol.

Further interaction of a fluoride ion with the hydrogen of the silanol leads to an increase in its nucleophilicity leading to Si–O–Si bond formation.

Free fluoride ion is never formed as such during the reaction since there is always sufficient ethanol to form $(Et–O \cdots H \cdots F)^-$ species. However, if the reaction is left for two or three days penta-coordinate alkyltetrafluorosilanes and hexacoordinate alkylpentafluorosilanes are observed in the ^{29}Si NMR.

We believe that silsesquioxane cages are an inevitable consequence of trialkoxysilane hydrolysis, providing the hydrolysis is carried out in a gentle fashion that enables selective Si–O bond formation. The corollary of this is that silsesquioxane cages represent islands of stability rather than the product of serendipitous linking of Si–O units. The relative stability of T_8, T_{10} and T_{12} cages depends upon the size of the alkyl group such that different distributions of cages are obtained.

Table 3 Selected bond distances (Å) and bond angles (°) of octacyclopentylsilsesquioxane, **1**

Si(1)–O(1)	1.618(3)	O(1)–Si(2)–O(2)	109.12(14)
Si(1)–O(5)	1.624(3)	O(1)–Si(2)–O(6)	108.67(14)
Si(1)–O(4)	1.630(3)	O(2)–Si(2)–O(6)	108.61(14)
Si(2)–O(1)	1.617(3)	O(1)–Si(1)–C(1)	108.48(17)
Si(2)–O(2)	1.628(3)	O(4)–Si(1)–C(1)	111.37(16)
Si(2)–O(6)	1.629(3)	O(5)–Si(1)–C(1)	109.95(16)
O(1)–Si(1)–O(5)	108.76(14)	O(1)–Si(2)–C(6)	110.06(16)
O(1)–Si(1)–O(4)	109.59(14)	O(2)–Si(2)–C(6)	111.64(16)
O(5)–Si(1)–O(4)	108.65(14)	O(6)–Si(2)–C(6)	108.68(16)

Table 2 also lists the ^{29}Si NMR chemical shifts of the T_8 cages prepared. They are all in the expected region around −67 ppm for sp^3 carbons attached to silicon and −79 ppm for sp^2 carbons attached to silicon.[17] Figs. 1–3 show the X-ray crystal structures of octacyclopentylsilsesquioxane, **1**, octaisobutylsilsesquioxane, **2** and octa(4-carboxymethyl-3,3-dimethylbutyl)-silsesquioxane, **3**. Tables 3–6 list the crystallographic data for these compounds, including relevant bond lengths (Å) and bond angles (°).

Octacyclopentylsilsesquioxane, **1**, crystallises with half a molecule in the asymmetric unit that completes *via* a centre of

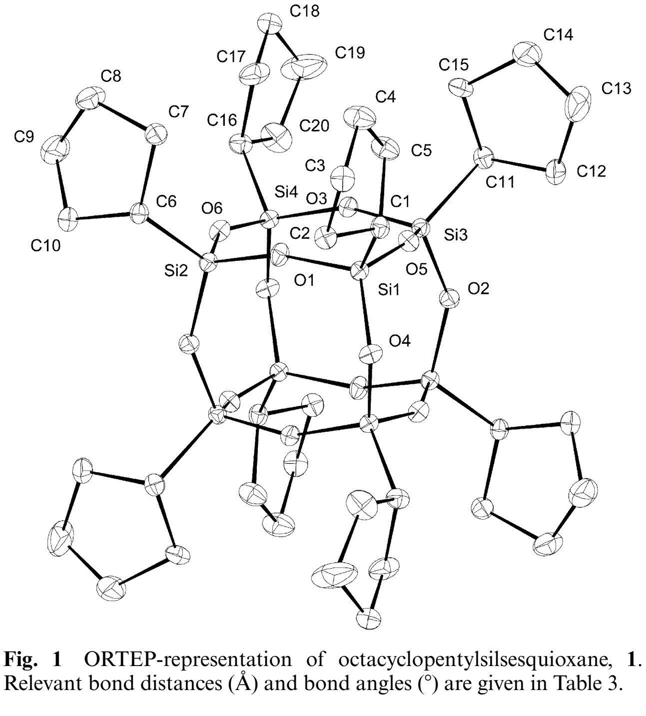

Fig. 1 ORTEP-representation of octacyclopentylsilsesquioxane, **1**. Relevant bond distances (Å) and bond angles (°) are given in Table 3.

Table 4 Selected bond distances (Å) and bond angles (°) of octaisobutylsilsesquioxane, **2**

O(1)–Si(1)	1.614(5)	O(2)–Si(1)–O(1)	108.5(2)
O(2)–Si(1)	1.611(5)	O(2)–Si(1)–O(6)	108.3(2)
O(2)–Si(4)	1.618(4)	O(1)–Si(1)–O(6)	109.6(2)
O(3)–Si(4)	1.616(4)	O(6)–Si(2)–O(4)	108.2(2)
O(6)–Si(1)	1.620(4)	O(2)–Si(1)–C(1)	112.9(3)
Si(1)–O(2)–Si(4)	153.3(3)	O(1)–Si(1)–C(1)	108.5(3)
Si(4)–O(3)–Si(3)	151.9(3)	O(6)–Si(1)–C(1)	109.1(3)
Si(2)–O(6)–Si(1)	152.1(3)	O(3)–Si(3)–C(9)	108.8(3)

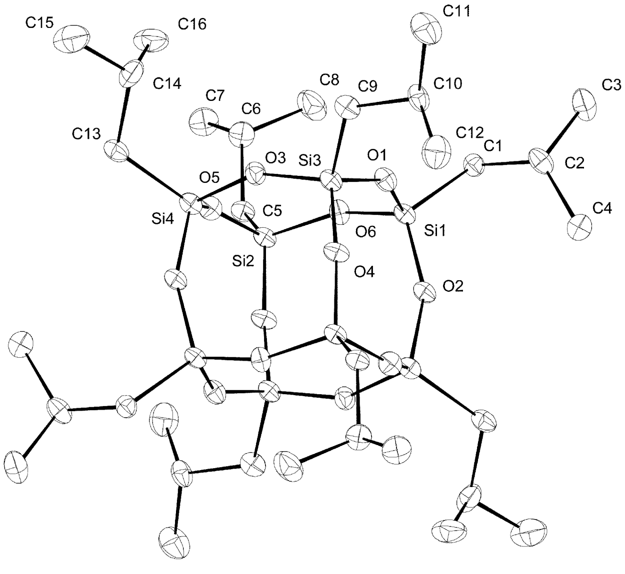

Fig. 2 ORTEP-representation of octaisobutylsilsesquioxane, **2**. Relevant bond distances (Å) and bond angles (°) are given in Table 4.

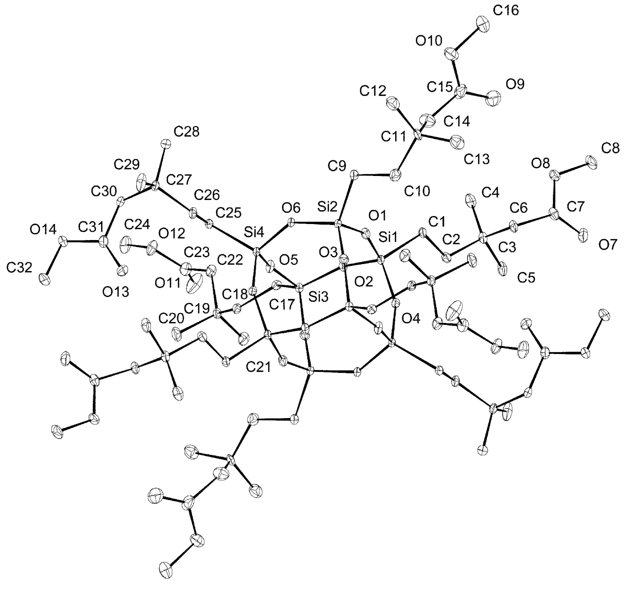

Fig. 3 ORTEP-representation of octa(4-carboxymethyl-3,3-dimethylbutyl)silsesquioxane, **3**. Relevant bond distances (Å) and bond angles (°) are given in Table 5.

inversion. It has the least distorted cage with the O–Si–O angles in the range 108.61(14)–109.59(14)°, the O–Si–C angles in the range 108.48(17)–111.64(16)° and the Si–O and Si–C bond lengths in the ranges 1.615(3)–1.630(3) Å and 1.838(4)–1.841(4) Å. This may be a reflection of very little or no steric hinderence between the cyclopentane rings that arrange in a "paddle wheel" like configuration.

Octaisobutylsilsesquioxane, **2**, also crystallises with half a molecule in the asymmetric unit that completes *via* a centre of inversion. It has only a slightly distorted cage with the O–Si–O angles in the range 108.1(2)–109.6(2)°, the O–Si–C angles in the range 107.6(3)–113.1(3)° and the Si–O and Si–C bond lengths in the ranges 1.611(5)–1.622(5) Å and 1.825(7)–1.838(7) Å.

Table 5 Selected bond distances (Å) and bond angles (°) of octa-(4-carboxymethyl-3, 3-dimethylbutyl)silsesquioxane, **3**

O(1)–Si(1)	1.614(2)	O(2)–Si(2)–O(1)	108.56(11)
O(1)–Si(2)	1.617(2)	O(2)–Si(2)–O(6)	108.99(10)
O(2)–Si(2)	1.611(2)	O(1)–Si(2)–O(6)	108.58(11)
O(2)–Si(3)	1.625(2)	O(1)–Si(1)–C(1)	108.38(12)
O(3)–Si(3)	1.625(2)	O(4)–Si(1)–C(1)	110.06(12)
O(3)–Si(1)	1.632(2)	O(3)–Si(1)–C(1)	111.79(12)
O(1)–Si(1)–O(4)	109.18(11)	O(5)–Si(4)–C(25)	111.19(12)
O(1)–Si(1)–O(3)	108.85(11)	O(4)–Si(4)–C(25)	111.00(12)
O(4)–Si(1)–O(3)	108.54(10)	O(6)–Si(4)–C(25)	108.54(12)

Octa(4-carboxymethyl-3,3-dimethylbutyl)silsesquioxane, **3**, crystallises with two half molecules in the asymmetric unit that complete *via* a centre of inversion. The O–Si–O angles are in the range 107.91(12)–109.61(10)°, the O–Si–C angles are in the range 107.17(12)–111.79(12)° and the Si–O and Si–C bond lengths are in the ranges 1.611(2)–1.632(2) Å and 1.825(3)–1.836(3) Å. This is probably the most distorted of the cages due to the larger steric bulk of the ligands, however, the distortion is not great. However, all the data of the cores of the three crystals are in the normal range of octasilsesquioxanes: Si–O bond (1.55–1.65 Å) (av. = 1.60 Å); Si–O–Si angle (145–152°) (av. = 148.5°); O–Si–O angle (107–112°) (av. = 109°).[18–27]

Conclusions

In conclusion, we have developed a route that leads to T_8 silsesquioxane cages in much greater yields than previously reported. The treatment of trialkoxysilanes with a THF solution of tetrabutylammonium fluoride provides a mild method of hydrolysis and we are at present examining the mechanism in greater detail and the selectivity of cage formation.

Experimental

Melting points were determined on an Electrothermal Digital melting point apparatus and are uncorrected. Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates or as KBr discs on a Nicolet 205 FT-IR spectrometer. NMR spectra were recorded as solutions in deuteriochloroform with tetramethylsilane as internal standard on a Jeol Lamda 300 NMR spectrometer or a JEOL EX 400 NMR spectrometer (*J* values are given in Hz). MALDI TOF mass spectra were carried out by the University of Southampton using 2,5-dihydroxybenzoic acid as a matrix and dichloromethane as the solvent.

Synthesis of octahexylsilsesquioxane, octaoctylsilsesquioxane, octa(4-carboxymethyl-3,3-dimethylbutyl)silsesquioxane, octaisobutylsilsesquioxane and octaphenylsilsesquioxane

These compounds were prepared using a standard method in chloroform. The trialkoxysilane (1.750×10^{-3} mol) and NBu_4F (1.0 ml, 1 M in THF, 1.0×10^{-3} mol) were mixed together in CH_2Cl_2 (40 ml) and stirred for 1 day at room temperature. Removal of CH_2Cl_2 under vacuum gave the crude product.

Octahexylsilsesquioxane.[7] This was obtained in 44% yield after purification using column chromatography (SiO_2–hexane).

Octaoctylsilsesquioxane.[7,28] This was obtained in 65% yield after purification using column chromatography (SiO_2–hexane).

Octa(4-carboxymethyl-3,3-dimethylbutyl)silsesquioxane, 3. This was obtained in 19% yield after purification using column chromatography (SiO_2–hexane–CH_2Cl_2). Recrystallisation

Table 6 Crystallographic data for compounds **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{40}H_{72}O_{12}Si_8$	$C_{64}H_{120}O_{28}Si_8$	$C_{32}H_{72}O_{12}Si_8$
M_r	969.70	1562.32	873.62
T/K	120(2)	120(2)	120(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.9936(6)	14.3683(3)	9.9881(13)
b/Å	10.1401(8)	18.0913(4)	10.8183(14)
c/Å	12.1205(8)	18.3397(4)	10.9540(18)
α/°	98.333(6)	106.2590(10)	96.541(8)
β/°	92.328(5)	109.9200(10)	91.269(7)
γ/°	95.545(2)	101.9080(10)	99.439(7)
V/Å^3	1207.73(14)	4055.20(15)	1159.0(3)
Z	1	2	2
μ/mm^{-1}	0.279	0.207	0.283
Reflections collected	15579	30226	10942
Independent reflections (R_{int})	4219 (0.0769)	13466 (0.0645)	3921 (0.2177)
Goodness-of-fit on F^2	1.049	0.975	0.968
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0562$, $wR2 = 0.1382$	$R1 = 0.0495$, $wR2 = 0.1000$	$R1 = 0.0841$, $wR2 = 0.1572$
R indices (all data)	$R1 = 0.1009$, $wR2 = 0.1558$	$R1 = 0.0996$, $wR2 = 0.1162$	$R1 = 0.2189$, $wR2 = 0.2024$
Largest diff. peak and hole/e Å^{-3}	0.797 and −0.385	0.541 and −0.335	0.445 and −0.403

from a mixture of chloroform and acetone gave a crystal suitable for X ray diffraction. ν_{max} (Neat)/cm^{-1}: 2968, 2871, 2263, 1782, 1461, 1439, 1343, 1305, 1246, 1105, 912, 801, 741 and 697; δ_H (300 MHz, $CDCl_3$): 0.52 (16H, m, $SiCH_2$), 0.91 (48H, s, $C(CH_3)_2$), 1.36 (16H, m, $\mathrm{SiCH_2C}\mathit{H}_2$), 2.18 (16H, s, CH_2COO), 3.57 (24H, s, OCH_3); δ_C (75.5 MHz, $CDCl_3$): 6.05 ($SiCH_2$), 26.48 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$), 33.80 ($\mathit{C}\mathrm{(CH_3)_2}$), 35.31 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 44.95 ($\mathit{C}\mathrm{H_2COO}$), 51.05 ($OCH_3$), 172.71 ($\mathrm{CH_2}\mathit{C}\mathrm{OO}$); δ_{Si} (79.3 MHz, $CDCl_3$): −65.91; m/z (MALDI-TOF) ($C_{80}H_{150}O_{35}Si_{10}$ + Na^+): (found) 1584.96; (calc.) 1585.32.

Octaisobutylsilsesquioxane, 2. This was obtained in 26% yield after purification using column chromatography (SiO_2–hexane). Recrystallisation from a mixture of dichloromethane and acetone gave a crystal suitable for X ray diffraction. Mp 268 °C; ν_{max} (Nujol)/cm^{-1}: 2732, 2627, 1417, 1328, 1231, 1120, 1046, 964, 845, 756 and 697; δ_H (300 MHz, $CDCl_3$): 0.59 (16H, d, $J = 6.96$, $\mathrm{SiC}\mathit{H}_2\mathrm{CH}$), 0.93 (48H, d, $J = 6.60$, CH_3), 1.79 (8H, m, $\mathrm{C}\mathit{H}\mathrm{CH_2}$); δ_C (75.5 MHz, $CDCl_3$): 22.60 ($\mathrm{Si}\mathit{C}\mathrm{H_2CH}$), 23.95 ($\mathit{C}\mathrm{HCH_2}$), 25.78 ($CH_3$); m/z (MALDI-TOF) ($C_{32}H_{72}O_{12}Si_8$ + H^+): (found) 873.24 (100%), 874.21 (76%), 875.23 (48%), 876.19 (22%), 877.24 (15%); (calc.) 873 (100%), 874 (77%), 875 (58%), 876 (28%), 877 (12%).

Octaphenylsilsesquioxane[29]. This was obtained in 49% yield after purification using column chromatography (SiO_2–hexane).

Synthesis of octacyclopentylsilsesquioxane and octacyclohexylsilsesquioxane

These compounds were prepared using a standard method in acetone. The trialkoxysilane (4.53 mmol) was dissolved in acetone (20 ml), then NBu_4F (2.46 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature for 24 h, which gave a white solid.

Octacyclopentylsilsesquioxane, 1. This was obtained by filtration in 95% yield. Recrystallisation from a mixture of dichloromethane and acetone gave a crystal suitable for X ray diffraction; mp < 400° (decomp.); ν_{max} (Nujol)/cm^{-1} 2726, 1323, 1249, 1110, 949, 914 and 723; δ_H (300 MHz; $CDCl_3$): 1.70 (16H, m, vbr, CH_2) 1.44 (48H, m, vbr, CH_2), 0.88 (8H, m, vbr, CH); δ_C (75.5 MHz; $CDCl_3$): 27.28 (CH_2), 26.99 (CH_2) and 22.25 (CH); δ_{Si} (79.3 MHz; $CDCl_3$): −66.55.

Octacyclohexylsilsesquioxane.[9–11] This was obtained by filtration in 84% yield.

Synthesis of octa(2-bicycloheptyl)silsesquioxane

A mixture of *exo*- and *endo*-5-(bicycloheptenyl)triethoxysilane was purchased from Gelest and purified by column chromatography (SiO_2–CH_2Cl_2) to give pure samples of *exo*- and *endo*-5-(bicycloheptenyl)triethoxysilane.

Endo-5-(Bicycloheptenyl)triethoxysilane was obtained in 32% yield; δ_H (300 MHz, $CDCl_3$): 1.10 (1H, m, $\mathrm{SiCHC}\mathit{H}$), 1.20 (11H, m, $\mathrm{OCH_2C}\mathit{H}_3$ + $\mathrm{SiCHC}\mathit{H}_2$), 1.35 (1H, m, $\mathrm{SiCHCH_2C}\mathit{H}$), 1.84 (1H, m, SiCH), 2.85 (1H, m, $\mathrm{SiCHCHC}\mathit{H}_2$), 3.00 (1H, m, $\mathrm{SiCHCHC}\mathit{H}_2$), 3.80 (6H, q, $J = 6.96$, OCH_2), 5.99 (2H, m, CH=CH); δ_C (75.5 MHz, $CDCl_3$): 18.56 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 21.05 (SiCH), 27.19 ($\mathrm{SiCH}\mathit{C}\mathrm{H_2}$), 42.42 ($\mathrm{SiCH}\mathit{C}\mathrm{H}$), 44.47 ($\mathrm{SiCHCH_2}\mathit{C}\mathrm{H}$), 51.08 ($\mathrm{SiCHCH}\mathit{C}\mathrm{H_2}$), 58.54 ($OCH_2$), 134.91 (CH=CH), 135.57 (CH=CH); δ_{Si} (79.3 MHz, $CDCl_3$): −47.09.

Exo-5-(Bicycloheptenyl)triethoxysilane was obtained in 51% yield; δ_H (300 MHz, $CDCl_3$): 0.44 (1H, m, SiCH), 1.10 (3H, m, $\mathrm{SiCHC}\mathit{H}$ + $\mathrm{SiCHC}\mathit{H}_2$), 1.20 (9H, t, $J = 6.96$, $\mathrm{OCH_2C}\mathit{H}_3$), 1.30 (1H, m, $\mathrm{SiCHCH_2C}\mathit{H}$), 2.89 (2H, m, $\mathrm{SiCHCHC}\mathit{H}_2$), 3.88 (6H, q, $J = 6.96$, OCH_2), 5.90 (1H, m, CH=CH), 6.08 (1H, m, CH=CH); δ_C (75.5 MHz, $CDCl_3$): 18.32 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 20.26 (SiCH), 26.25 ($\mathrm{SiCH}\mathit{C}\mathrm{H_2}$), 42.44 ($\mathrm{SiCH}\mathit{C}\mathrm{H}$), 42.79 ($\mathrm{SiCHCH_2}\mathit{C}\mathrm{H}$), 46.98 ($\mathrm{SiCHCH}\mathit{C}\mathrm{H_2}$), 58.50 ($OCH_2$), 133.72 (CH=CH), 137.73 (CH=CH); δ_{Si} (79.3 MHz, $CDCl_3$): −46.46.

Octa(*endo*-2-bicycloheptyl)silsesquioxane. *Endo*-5-(Bicycloheptenyl)triethoxysilane (0.3055 g, 1.192×10^{-3} mol) and NBu_4F (0.595 ml, 1 M in THF, 5.95×10^{-4} mol) were mixed together in CH_2Cl_2 (50 ml) and stirred for 1 day at room temperature. After the removal of CH_2Cl_2 under vacuum, the product was purified by column chromatography (SiO_2–hexane) to give octa(*endo*-2-bicycloheptyl)silsesquioxane in 55.5% yield (0.096 g); δ_H (300 MHz, $CDCl_3$): 1.03 (2H, m, $\mathrm{SiCHC}\mathit{H}_2$), 1.29 (1H, m, $\mathrm{SiCHCH_2C}\mathit{H}$), 1.80 (1H, m, SiCH), 2.83 (1H, m, $\mathrm{SiCHCHC}\mathit{H}_2$), 2.93 (1H, m, $\mathrm{SiCHCHC}\mathit{H}_2$), 5.90 (2H, m, CH=CH); δ_C (75.5 MHz, $CDCl_3$): 21.45 (SiCH), 26.80 ($\mathrm{SiCH}\mathit{C}\mathrm{H_2}$), 42.44 ($\mathrm{SiCH}\mathit{C}\mathrm{H}$), 44.27 ($\mathrm{SiCHCH_2}\mathit{C}\mathrm{H}$), 50.69 ($\mathrm{SiCHCH}\mathit{C}\mathrm{H_2}$), 133.78 (CH=CH), 135.64 (CH=CH); δ_{Si} (79.3 MHz, $CDCl_3$): −68.72.

Octa(*exo*-2-bicycloheptyl)silsesquioxane. *Exo*-5-(Bicycloheptenyl)triethoxysilane (0.2620 g, 1.002×10^{-3} mol) and NBu_4F (0.52 ml, 1 M in THF, 5.2×10^{-4} mol) were mixed together in CH_2Cl_2 (50 ml) and stirred for 1 day at room temperature. After the removal of CH_2Cl_2 under vacuum, the product was purified by column chromatography (SiO_2–hexane) to give octa(*exo*-2-bicycloheptyl)silsesquioxane in 47.4% yield (0.069 g); δ_H (300 MHz, $CDCl_3$): 0.45 (1H, m, SiCH), 1.23 (2H, m, SiCHCH_2), 1.77 (1H, m, SiCHCH$_2$CH); δ_C (75.5 MHz, CDCl$_3$): 21.29 (SiCH), 26.39 (SiCHCH$_2$), 42.28 (SiCHCH), 42.79 (SiCHCH$_2$$C$H), 46.93 (SiCHCH$CH_2$), 133.97 (CH=CH), 137.61 (CH=CH); δ_{Si} (79.3 MHz, CDCl$_3$): −66.93.

Crystallography. X-Ray crystallographic data for all structures were collected on a Bruker Nonius KappaCCD area detector diffractometer with a rotating anode following standard procedures.

CCDC reference numbers 206049–206051.

See http://www.rsc.org/suppdata/dt/b3/b302950f/ for crystallographic data in CIF or other electronic format.

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References

1 I. M. Saez and J. W. Goodby, *Liq. Cryst.*, 1999, **26**, 1101.
2 R. Elsaber, G. H. Mehl, J. W. Goodby and D. J. Photinos, *Chem. Commun.*, 2000, 851.
3 F. J. Feher, K. D. Wydham, M. A. Sciadone and Y. Hamuro, *Chem. Commun.*, 1998, 1469.
4 F. J. Feher, *J. Am. Chem. Soc.*, 1986, **108**, 3850.
5 F. J. Feher and R. L. Blanski, *J. Chem. Soc., Chem. Commun.*, 1990, 1614.
6 F. J. Feher and K. D. Wyndham, *Chem. Commun.*, 1998, 323.
7 A. R. Bassindale and T. E. Gentle, *J. Mater. Chem*, 1993, **12**, 1319.
8 P. A. Agaskar, *Inorg. Chem.*, 1991, **30**, 2707.
9 J. F. Brown and L. H. Vogt, *J. Am. Chem. Soc.*, 1965, **87**, 4313.
10 H. Behbehani, B. J. Brisdon, M. F. Mahon and K. C. Molloy, *J. Organomet. Chem.*, 1994, **469**, 19.
11 F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 174.
12 M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, 1955, **77**, 3996.
13 M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, 1955, **20**, 6045.
14 M. M. Sprung and F. O. Guenther, *J. Polym. Sci.*, 1958, **XXVIII**, 17.
15 R. J. Chambers and A. Marfat, *J. Heterocycl. Chem.*, 1995, **32**, 1401.
16 D. P. Cox, J. Terpinski and W. Lawrynowicz, *J. Org. Chem.*, 1984, **49**, 3216.
17 E. Rikowski and H. C. Marsmann, *Polyhedron*, 1997, **16**, 3357.
18 U. Dittmar, B. J. Hendan, U. Florke and H. C. Marsmann, *J. Organomet. Chem.*, 1995, **489**, 185.
19 C. Bonhomme, P. Toledano, J. Maquet, J. Livage and L. Bonhomme-Coury, *J. Chem. Soc., Dalton Trans.*, 1997, 1617.
20 M. Unno, A. Suto, K. Takada and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 215.
21 M. Unno, K. Takada and H. Matsumoto, *Chem. Lett.*, 1998, 489.
22 S. Lucke, K. Stoppek-Langner, J. K. Kuchinke and B. Krebs, *J. Organomet. Chem.*, 1999, **584**, 11.
23 A. Provatas, M. Luft, J. C. Mu, A. H. White, J. G. Matisons and S. B. W. Ram, *J. Organomet. Chem.*, 1998, **565**, 159.
24 P. A. Jaffres and R. E. Morris, *J. Chem. Soc., Dalton Trans.*, 1998, 2767.
25 N. V. Podberezskaya, I. A. Baidina, V. I. Alekseev, S. V. Borisov and T. N. Martynova, *J. Struct. Chem. (Engl. Transl.)*, 1981, **22**, 737.
26 N. V. Podberezskaya, S. A. Magarill, I. A. Baidina, S. V. Borisov, L. E. Gorsh, A. N. Kanev and T. N. Martynova, *J. Struct. Chem. (Engl. Transl.)*, 1982, **23**, 422.
27 I. Richter, C. Burschka and R. Tacke, *J. Organomet. Chem.*, 2002, **646**, 200.
28 C. Bolln, A. Tsuchida, H. Frey and R. Mulhaupt, *Chem. Mater.*, 1997, 1475.
29 J. F. Brown, *J. Am. Chem. Soc.*, 1965, **87**, 4317.
30 L. H. Vogt and J. F. Brown, *Inorg. Chem.*, 1963, 189.
31 M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, 1955, **77**, 3996.
32 P. Braunstein, J. R. Galsworthy, B. J. Hendan and H. C. Marsmann, *J. Organomet. Chem.*, 1998, **551**, 125.
33 U. Dittmar, B. J. Hendan, U. Florke and H. C. Marsmann, *J. Organomet. Chem.*, 1995, **489**, 185.