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Synthesis and characterisation of silanol-functionalised dendrimers†

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A number of carbosilane dendrimers derivatised on their external surface by silanol groups have been synthesized and characterised. The new molecules are prepared by repetitive hydrosilation/alkenylation reactions, and then careful hydrolysis of Si–Cl groups in one of two ways produces dendrimers with external Si–OH groups. Various molecules with three, four and eight vinyl groups were used as the starting molecules to produce dendrimers of different sizes. The first-generation dendrimer based on a tetravinylsilane core has been characterised by single crystal X-ray diffraction.

Introduction

Since the first successful synthesis of a symmetrical branched dendrimer[1] this class of molecule has received considerable interest, with possible applications ranging from drug delivery agents, micelle mimics, nanoscale building blocks, high performance polymers and nanoscale reactors.[2] The unusual architecture of these molecules leads to properties such as low intrinsic viscosity, high solubility and miscibility, and high reactivity (from the presence of many chain ends). An alternative application that has achieved some attention is that of catalysis,[3–5] where dendrimers have some striking advantages over both homogeneous and heterogeneous catalysts. Homogeneous catalysts have a number of benefits over other types of catalysts (for example, faster kinetics, accessibility of the metal centre, *etc*.). However, a large drawback is that they are often difficult to separate from the reaction mixture. Heterogeneous catalysts on the other hand are easy to separate from the reaction stream, but have the disadvantage that the catalytic sites are often inaccessible and that mass transport problems can decrease the activity of the catalysts. Dendritic catalysts lie at the interface between homogeneous and heterogeneous systems in that their size (>25 Å diameter) and their high shape persistence in solution (*i.e.* no reptation) will allow them to be separated from a solvent stream using ultrafiltration methods while their spheroidal shape will allow precise control over the number and location of the catalytic sites.

This paper reports the synthesis and characterisation of new silanol-functionalised dendrimers. Our goal in preparing these molecules is to use them as mimics for silica surfaces by attaching catalytically active metal atoms to the silanol group. Silica is a well known support for many types of catalytically active centre, and recently Thomas and co-workers[6] have elegantly shown that organometallic chemistry can be used to 'graft' or 'tether' catalytic sites onto the inside surfaces of a mesoporous silica. This procedure has successfully been used in a number of ways, many of which are reviewed in the recent publication by Clark and MacQuarrie.[7] In addition, Feher *et al.*[8] have prepared a number of incompletely condensed polyhedral oligomeric silsesquioxane molecules made up of seven silicon atoms at the corners of a cube, the last vertex being vacant. Three silanol groups point towards the empty corner of the cube and a number of metal atoms can then be tethered through these groups to produce catalytically active molecules. Van Santen and co-workers[9] have shown that capping the empty corner of the cube with titanium produces a species that is active for the epoxidation of a number of unsaturated hydrocarbons and, moreover, that none of the titanium is lost during the reaction. The silanol-functionalised dendrimers reported in this paper are related to these other types of silica mimics by having Si–OH units available at their surfaces for reaction with other species.

Results and discussion

Carbosilane dendrimer cores were synthesized according to the methods described previously,[10–12] including some of our own previously published work in this area,[13] using a repetitive procedure where hydrosilation of the exterior vinyl groups is followed by reaction with vinylmagnesium bromide. Once the required size of vinyl-derivatised dendrimer has been reached, hydrosilation with $H(CH_3)_2SiCl$ in the presence of Karstedt's catalyst (a platinum–divinylsiloxane complex) produces the monochlorosilane derivative regiospecifically on the terminal carbon of the vinyl group. Two methods were then used to synthesize the silanol-functionalised dendrimers (see Scheme 1). Method one involves the simple hydrolysis of the chloro group using water. To prevent condensation between the dendrimers this was accomplished with water as a fairly dilute solution in aniline. This method is successful for the first-generation dendrimers, although there are complications for the larger dendrimers leading to impure products. The second method involves the reduction of Si–Cl to Si–H using $LiAlH_4$ and subsequent catalytic hydrolysis to Si–OH using water over palladium supported on carbon.[14] This method is very clean and reasonably high yielding, and even though it involves an extra synthetic step produces comparable purity and yields to the first method, especially for the preparation of the larger silanol-functionalised dendrimers reported here where it is the method of choice. The methodology works equally well for dendrimers based on silane, cyclosiloxane and polyhedral oligomeric silsesquioxane cores.

The dendrimers **1**–**6** were prepared successfully in this way and were characterised using ^{13}C and ^{1}H NMR, and CHN microanalysis. The first-generation dendrimer **1** was also unambiguously characterised by single-crystal X-ray diffraction. The

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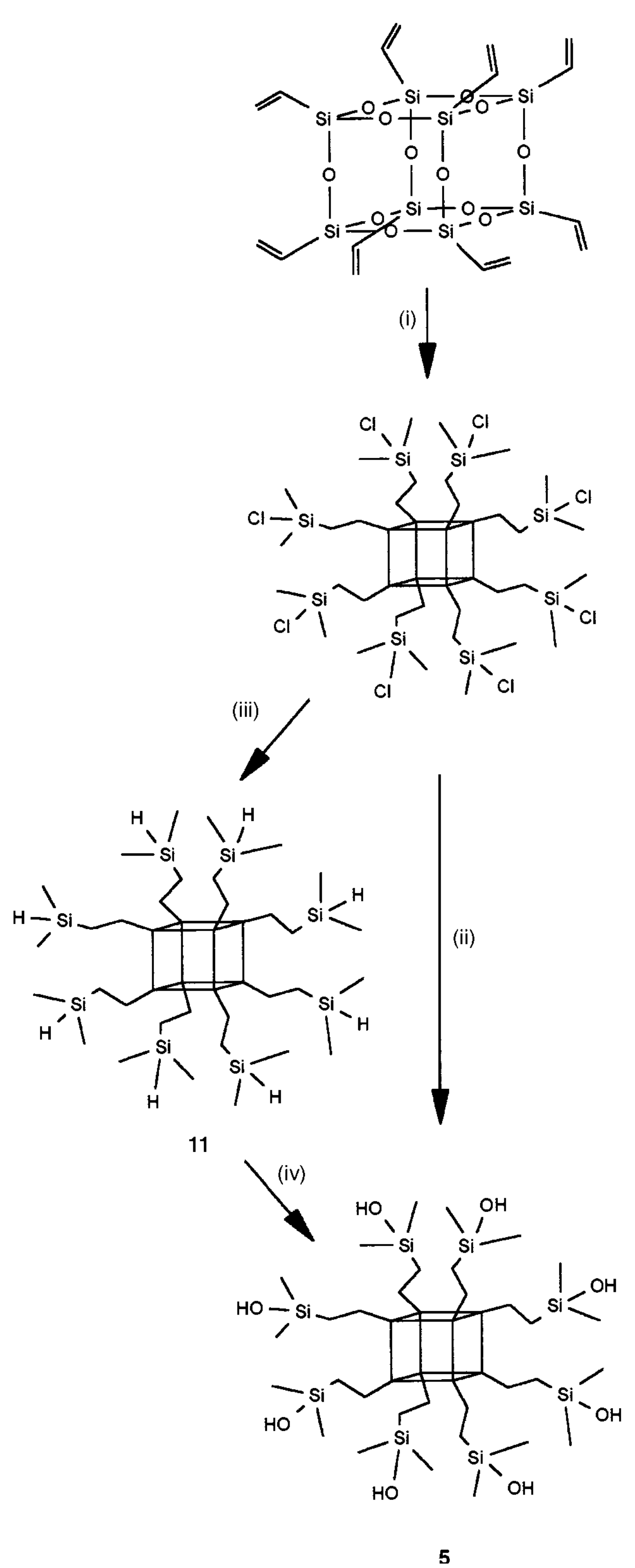
† *Supplementary data available*: detailed synthetic procedures for compounds **1**–**12**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/2183/, otherwise available from BLDSC (No. SUP 57564, 8 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).



Scheme 1 General synthetic scheme for silanol dendrimer preparation. Reagents and conditions: (i) $HSi(CH_3)_2Cl$–H_2PtCl_6 (see ref. 13); (ii) water, aniline in diethyl ether, 25 °C, 12 h; (iii) $LiAlH_4$–diethyl ether, 25 °C, 15 h; (iv) water, Pd/C in 1,4-dioxane, 25 °C, 12 h.

intermediate silane (*i.e.* Si–H) functionalised dendrimers, **7**–**12**, were also isolated and characterised by ^{13}C and ^{1}H NMR, and CHN microanalysis. For all these compounds, infrared spectroscopy showed a strong band at around 2120 cm^{-1}, which is the Si–H stretching vibration. This strong absorption together with the volume of H_2 produced during the course of the reaction are useful indicators that can be used to follow the progress of the catalytic hydrolysis to silanol-functionalised dendrimers. Details of the synthesis and characterisation of dendrimers **1**–**12** can be found in the Supplementary data. Of course, given the already demonstrated utility of the hydrosilation reaction in the preparation of dendrimers, these Si–H functionalised dendrimers should be themselves excellent synthetic platforms on which many new functionalised dendrimers could be based.

Surprisingly, upon standing for 6 months in air the dendrimers show very little evidence for intermolecular condensation. The solubility of the dendrimers in methanol is similar to that of the freshly prepared samples and the CHN analysis results are within experimental error of those obtained originally.

The crystal structure of dendrimer **1** (Fig. 1) confirms the molecular structure of the compound, and also that the synthetic procedure produces the expected functional transformations. As expected, the dendrimers pack in the solid state so that they are held together through the hydrogen bonds between silanol groups from different molecules. This produces ‘channels’ in the structure lined by oxygen atoms as well as regions that only contain the van der Waals interactions between the methylene and methyl hydrogens. This can be most clearly seen in the view of the structure parallel to the crystallographic *b* axis shown in Fig. 2.

The successful synthesis and characterisation of these new dendrimers offers us the opportunity to use these molecules as mimics for silica surfaces by attaching chemical species to the external surfaces in the same way as that accomplished for silica surfaces, mesoporous silica and polyhedral oligomeric silsesquioxanes. Coupled with improved ultrafiltration techniques currently being developed, this may lead to a completely new class of homogeneous catalyst that can more easily be separated out of solution. The dendrimers based on polyhedral silsesquioxane cores are especially attractive for catalytic applications as they have a fairly high density of external sites that are all accessible for derivatisation. Further work aimed at functionalising the exterior surface of these molecules with catalytically active groups is currently underway.

The dendrimers prepared in this work are monosilanols (*i.e.* there is only one hydroxyl group per silicon). However, the work of Roesky and co-workers[15] has shown that sterically hindered molecules, such as these dendrimers, can also be used to make di- and tri-silanols. We are also exploring the possibilities that the synthetic methods reported by Roesky can be applied to dendrimers of the type reported here.

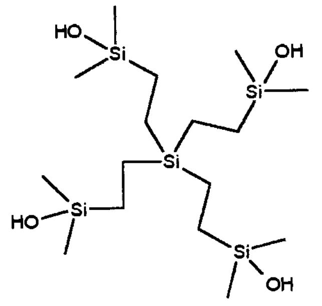
Experimental

All manipulations were carried out under an atmosphere of argon. Solvents were dried according to established procedures. The starting materials for many of these syntheses have been reported in a previous paper.[13] The buffer solution contained $NaH_2PO_4 \cdot H_2O$ (4.7 mmol l^{-1}) and NaOH (4 mmol l^{-1}).

The ^{1}H NMR spectra were recorded at 300.13 MHz and ^{13}C NMR spectra at 75.47 MHz on a Bruker AM300 spectrometer operating in the Fourier transform mode with, for ^{13}C spectra, noise proton decoupling. FTIR Spectra were recorded on a Perkin-Elmer 1710 spectrometer. Chemical analysis was accomplished by the University of St. Andrews Microanalysis service.

Representative synthetic procedures (compounds 1, 5 and 11)

Tetrakis[2-(hydroxydimethylsilyl)ethyl]silane 1. *From tetrakis-[2-(chlorodimethylsilyl)ethyl]silane.* A solution of tetrakis[2-(chlorodimethylsilyl)ethyl]silane (3.82 g, 7.3 mmol) in diethyl ether (50 ml) was added dropwise to a mixture of aniline (2.79 g, 30 mmol) and water (0.54 g, 30 mmol) in diethyl ether (100 ml). The solution was stirred at room temperature overnight. Diethyl ether (50 ml) was added and the anilinium salt removed by filtration. The filtrate was concentrated *in vacuo* and



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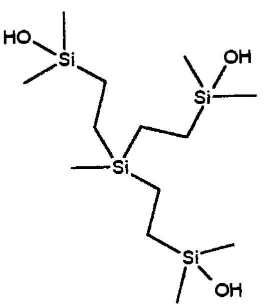

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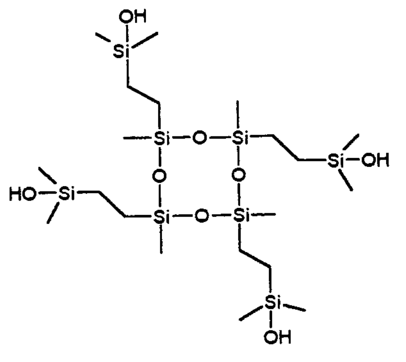

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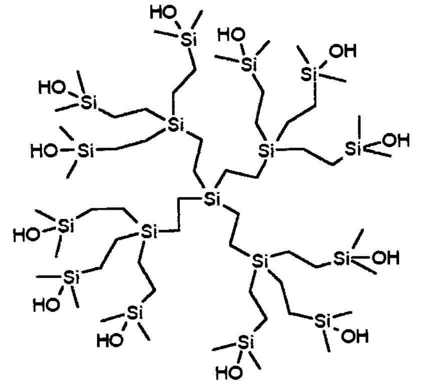

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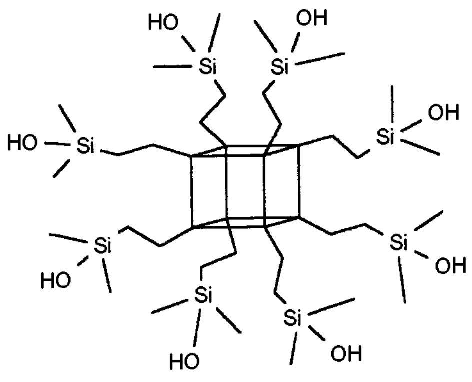

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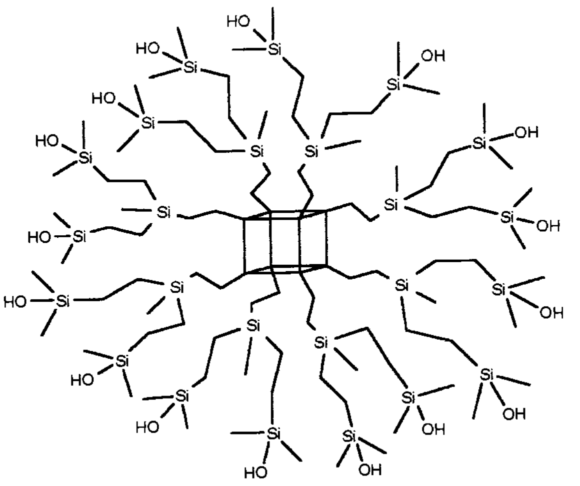

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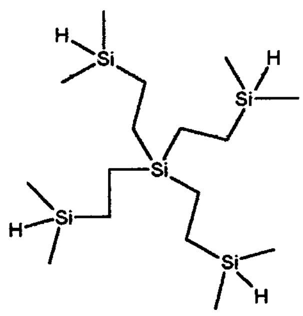
the residue crystallised from diethyl ether–hexane. Compound **1** was obtained by filtration as a white solid (2.07 g, 64%).

From tetrakis[2-(dimethylsilyl)ethyl]silane. A solution of tetrakis[2-(dimethylsilyl)ethyl]silane (0.3 g, 0.79 mmol) in 1,4-dioxane (15 ml) was added dropwise to a suspension of 5% palladium on charcoal (0.1 g) in a mixture of dioxane (5 ml) and buffer solution (0.5 ml). After the addition the solution was stirred at room temperature overnight, then filtered on Celite (THF as eluent) and the filtrate concentrated *in vacuo*. The residue (0.34 g) was crystallised from diethyl ether–hexane affording compound **1** as a white solid (0.32 g, 91%) mp 129 °C (Found: C, 44.11 ; H, 10.43. $C_{16}H_{44}O_4Si_5$ requires C, 43.58 ; H, 10.06%). ^1H NMR (CD_3OD): δ 0.27 (s, Si-CH_3, 48 H), 0.70 (m, CH_2, 32 H) and 5.07 (s, -OH, 8 H). ^{13}C NMR (CD_3OD): −0.84 (Si-CH_3), 3.38 (CH_2) and 11.06 (CH_2). IR (KBr, disc): 3270vs, 2959m, 2910m, 1407m, 1250s, 1127s, 1068m, 868vs and 764s.

1,3,5,7,9,11,13,15-Octakis[2-(hydroxydimethylsilyl)ethyl]-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 5. A solution of 1,3,5,7,9,11,13,15-octakis[2-(dimethylsilyl)ethyl]pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane **11** (0.36 g, 0.32 mmol) in 1,4-dioxane (25 ml) was added dropwise to a suspension of 10% palladium on charcoal (0.1 g) in a mixture of dioxane (5 ml) and a buffer solution (0.7 ml). After the addition the solution was stirred at room temperature overnight. The solution was filtered on Celite (THF as eluent) and the filtrate concentrated *in vacuo*. The viscous oil (0.48 g) was crystallised from ethyl acetate to give compound **5** as a white solid (0.26 g, 65%) (Found: C, 30.79 ; H, 6.89. $C_8H_{22}O_5Si_4$ requires C, 30.93 ; H, 7.14%). ^1H NMR (CD_3OD): δ 0.29 (s br, Si-CH_3, 48 H), 0.81 (m, CH_2, 32 H) and 5.08 (s, -OH, 8 H). ^{13}C NMR (CD_3OD): δ −1.61 (Si-CH_3), 6.09 (CH_2) and 9.70 (CH_2). IR (KBr, disc): 3316vs, 2958m, 2895m, 1408m, 1253s, 1143vs, 868s, 757m, 632m, 536m and 470m.



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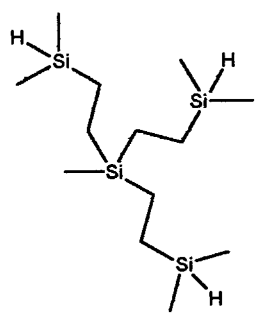

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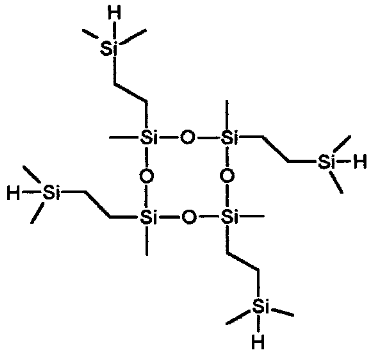

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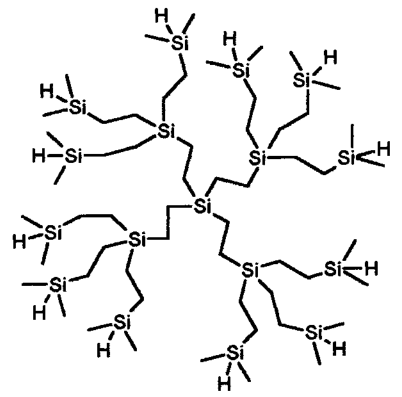

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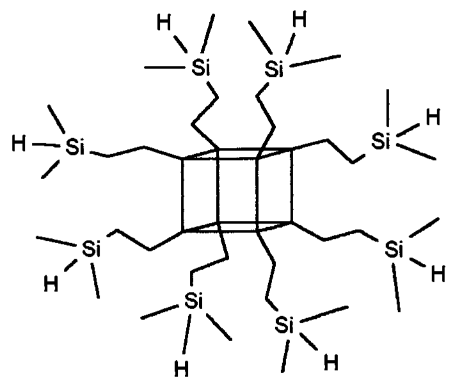

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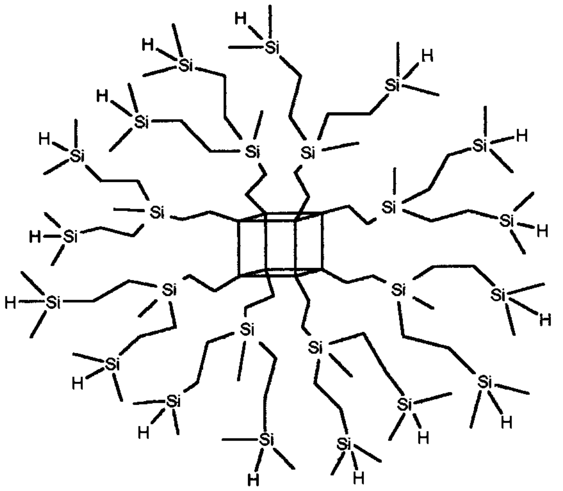

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1,3,5,7,9,11,13,15-Octakis[2-(dimethylsilyl)ethyl]pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 11. A solution of 1,3,5,7, 9, 11, 13,15-octakis[2-(chlorodimethylsilyl)ethyl]pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (see ref. 13; 2.20 g, 1.58 mmol) in diethyl ether (100 ml) was added dropwise to a suspension of $LiAlH_4$ (0.26 g, 6.8 mmol) in diethyl ether (80 ml). After additional stirring at room temperature for 15 h the solution was filtered on Celite. The filtrate was cautiously added to a mixture of hydrogen chloride (1 M in water, 100 ml) and ice. The organic layer was washed with brine (2 × 40 ml), dried over $MgSO_4$ and concentrated. The residue (1.74 g) was recrystallised from acetone–ethanol affording compound **11** as a white solid (1.07 g, 61%), mp 147 °C (Found: C, 34.09; H, 8.21. $C_8H_{22}O_3Si_4$ requires C, 34.49; H, 7.96%). ^{1}H NMR ($CDCl_3$): δ 0.09 (d, $^3J_{HH}$ = 3.6 Hz, Si-CH_3, 48 H), 0.63 (m, CH_2, 32 H) and 3.87 (m, Si-H, 8 H). ^{13}C NMR ($CDCl_3$): δ −4.80 (Si-CH_3), 5.06 (CH_2) and 5.68 (CH_2). IR (KBr, disc): 2959m, 2923m, 2111vs (Si–H), 1407m, 1250s, 1145s, 1111vs, 888s, 836m, 806m, 720m, 625m, 545m and 470m.

Spectroscopic data for other compounds 2–4, 6–10 and 12. Where no microanalysis results are given, NMR spectroscopy indicates that a small amount of solvent is trapped in the dendrimer. This is not an uncommon problem in dendrimer chemistry, especially for higher generations.

Compound **2**: ^{1}H NMR (CD_3OD) δ 0.14 (s, Si-CH_3, 3 H), 0.27 (s, Si-CH_3, 16 H), 0.66 (m, CH_2, 12 H) and 5.06 (s, OH, 3 H); ^{13}C NMR (CD_3OD) δ −4.94 (Si-CH_3), 0.42 (Si-CH_3), 6.44 (CH_2) and 12.24 (CH_2).

Compound **3** (Found: C, 37.18 H, 8.75. Calc: C, 36.99; H, 8.69%): ^{1}H NMR (CD_3OD) δ 0.25 (s, CH_3), 0.27–0.28 (d, CH_3) and 0.66–0.73 (m, CH_2); ^{13}C NMR (CD_3OD) δ −3.25 (m, CH_3), −1.1 (m, CH_3), 9.53 (s, CH_2) and 10.02 (s, CH_2).

Compound **4**: ^{1}H NMR (CD_3OD) δ 0.28 (s, Si-CH_3, 72 H),

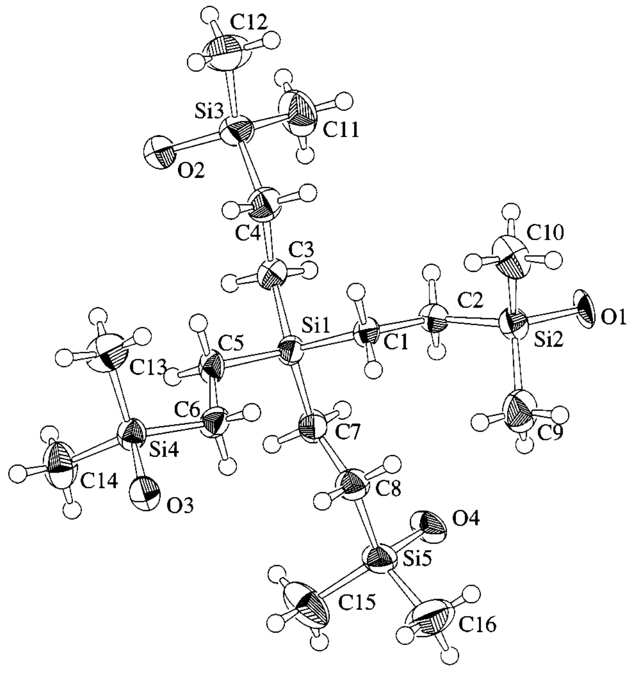

Fig. 1 Thermal ellipsoid plot of the crystal structure of compound **1** (ellipsoids at 50% probability).

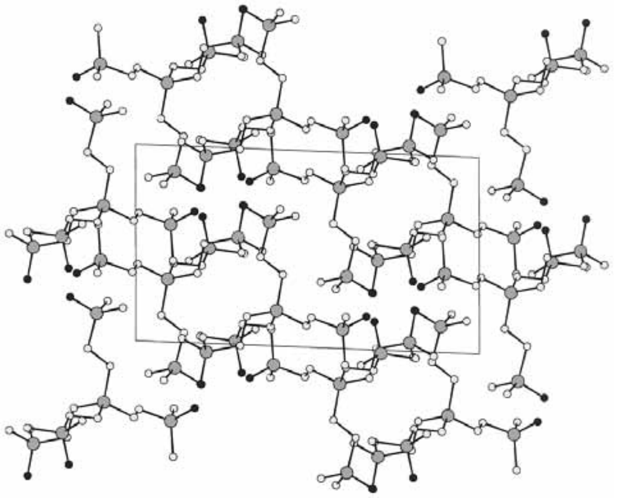

Fig. 2 Packing diagram of compound **1** viewed parallel to the crystallographic *b* axis. Oxygen atoms are shown as black spheres, silicon and carbon atoms as large and small grey spheres respectively.

0.64–0.75 (m, Si-CH_2CH_2SiCH_2CH_2Si, 64 H) and 5.05 (m, Si-OH, 12 H); ^{13}C NMR (CD_3OD) δ 0.78 (Si-CH_3), 4.66 (CH_2), 5.30 (CH_2), 5.83 (CH_2) and 12.53 (CH_2).

Compound **6**: ^{1}H NMR (CD_3OD) δ 0.25 (s, Si-CH_3, 24 H), 0.28 (s, Si-CH_3, 96 H), 0.60–0.70 (m, CH_2, 96 H) and 5.08 (s, Si-OH, 16 H); ^{13}C NMR (CD_3OD) δ 0.78 (Si-CH_3), 1.40 (Si-CH_3), 6.51 (CH_2), 6.77 (CH_2), 7.02 (CH_2) and 12.31 (CH_2).

Compound **7**: ^{1}H NMR ($CDCl_3$) δ 0.10 (d, $^3J_{HH} = 3.6$ Hz, Si-CH_3, 24 H), 0.50 (m, CH_2CH_2, 16 H) and 3.87 (m, Si-H, 4 H); ^{13}C NMR ($CDCl_3$) δ −4.60 (Si-CH_3), 3.63 (CH_2) and 6.42 (CH_2).

Compound **9** (Found: C, 40.96; H, 9.7. Calc. C, 41.03; H, 9.64%): ^{1}H NMR ($CDCl_3$) δ 3.8–3.9 (m, SiH, 1 H), 0.4–0.6 (m, CH_2, 4H) and 0–0.1 (m, CH_3); ^{13}C NMR ($CDCl_3$) δ 9.764 (m, CH_2), 5.466 (m, CH_2), −1.557 (m, CH_3) and −4.968 (m, CH_3).

Compound **10**: ^{1}H NMR ($CDCl_3$) δ 0.08 (d, $^3J_{HH} = 3.6$ Hz, Si-CH_3, 72 H), 0.49 (m, Si-CH_2CH_2SiCH_2CH_2Si, 64 H) and 3.86 (m, Si-H, 12 H); ^{13}C NMR ($CDCl_3$) δ −4.77 (Si-CH_3), 5.06 (CH_2) and 5.68 (CH_2).

Compound **12**: ^{1}H NMR ($CDCl_3$) δ − 0.04 (s, Si-CH_3, 24 H), 0.08 (d, $^3J_{HH} = 3.6$ Hz, Si-CH_3, 96 H), 0.45–0.50 (m, CH_2, 96 H) and 3.85 (m, Si–H, 16 H); ^{13}C NMR ($CDCl_3$) δ −6.46 (Si-CH_3), −4.77 (Si-CH_3), 4.25 (CH_2), 4.53 (CH_2), 5.33 (CH_2) and 6.33 (CH_2).

Single crystal X-ray diffraction

Single crystal X-ray diffraction data for compound **1**, $C_{16}H_{44}O_4Si_5$ ($M = 444.98$), recrystallised from a 50 : 50 diethyl ether–hexane mixture, crystal size 0.4 × 0.4 × 0.1 mm, were collected on a Rigaku AFC7S four circle diffractometer employing Mo-Kα radiation at 220 K. The molecule crystallises in monoclinic space group $P2_1/n$ (no. 14) with lattice parameters $a = 10.00(2)$, $b = 15.94(2)$, $c = 17.49(1)$ Å, $\beta = 92.4(1)°$, $V = 2785(7)$ Å^3 with $Z = 4$, $\mu = 2.71$ mm^{-1}. The diffraction from the crystal was relatively weak and the reflections were rather irregularly shaped, this presumably accounts for the rather poor precision on the final unit cell refinement. The crystal showed almost no diffraction above 2θ 40°, but the final full-matrix least-squares refinement against F was successfully completed with $R(F) = 0.038$, R'(F) of 0.047 and goodness of fit of 2.4 against 2016 unique reflections ($R_{int} = 0.02$), of which 1521 were observed [$I > 3\sigma(I)$]. The silicon, carbon and oxygen atoms were refined with anisotropic thermal displacement parameters. The hydrogen atoms on the methylene units of the dendrimer arms were placed in geometrically reasonable positions.

CCDC reference number 186/1475.

See http://www.rsc.org/suppdata/dt/1999/2183/ for crystallographic files in .cif format.

Acknowledgements

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