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Synthesis of highly functionalised dendrimers based on polyhedral silsesquioxane cores †

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A number of dendrimers based on polyhedral silsesquioxane cores have been synthesised and characterised. The new molecules are prepared by repetitive hydrosilation/alkenylation reactions, which provide a facile and high yield route to dendrimers with a high density of branch ends per generation. Judicious choice of hydrosilating agent [$HSiCl_3$, $H(CH_3)SiCl_2$ or $H(CH_3)_2SiCl$] produces dendrimers with varying numbers of chain ends, and alkenylating agents of different lengths produce molecules with different physical properties. The 24-vinyl functionalised dendrimer, **5**, has been characterised using single-crystal X-ray diffraction techniques.

Dendrimers are molecules with a globular structure in which well defined branches radiate from a central core, becoming more branched and crowded as they extend out to the periphery.[1] Since the first successful synthesis of a symmetrical branched dendrimer,[2] this class of polymers has received considerable interest, with possible applications ranging from drug delivery agents, micelle mimics, nanoscale building blocks, high performance polymers and nanoscale reactors.[3] The rigid spheroidal 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,[4–6] where dendrimers have some striking advantages over both homogeneous and heterogeneous catalysts including the possibility of preparing highly active yet recyclable catalysts.

Dendrimers are generally prepared using two approaches; a divergent method where successive dendrimer layers (generations) are added to a core and a convergent method where the arms of the dendrimer are synthesised first and subsequently attached together at a focal point to produce the final molecule. A major drawback with dendrimer synthesis, especially the divergent method, is that it often requires many repetitive steps in order to build the dendrimer outwards leading to multi-step and often low yield preparations. Our goal is to prepare dendrimers that can be used as supports for catalysts, combining a high number of active sites on the exterior of the molecule with the possibility of separating the catalyst from the reaction mixture using ultrafiltration techniques, so taking advantage of the relatively large size of the dendrimers to produce a molecule that combines the advantages of homogeneous and heterogeneous catalysts while minimising the disadvantages of each.

Recently, a large amount of literature has emerged based on the use of pentacyclooctasiloxanes (more commonly known as polyhedral oligomeric silsesquioxanes or POSS, which are molecules of formula $R_8Si_8O_{12}$; R = H, CH_3, vinyl, C_6H_{11}, *etc.*) as building blocks from which polymers can be constructed.[7–9] Polyhedral silsesquioxane molecules are easy to prepare in high yield (some are commercially available through Aldrich) and standard organic manipulations can be applied to functionalise the exterior of the molecules, generally in high yield with retention of the silsesquioxane structure intact. Examples of reactions of POSS species can be found in the recent review by Lichtenhan and references therein.[10] We report here a facile divergent synthetic route to dendrimers using these POSS molecules as the core. These preparative routes produce a high density of functional groups on the exterior of the dendrimer without resorting to repetitive synthesis of large numbers of generations. These molecules have been previously used as core species to produce what can be described as zeroth generation dendrimers, for example, the octopus molecules prepared by Bassindale and Gentle[11,12] and the ferrocene derivatised octasilsesquioxane species of Moràn *et al.*[13] More recently, Hong and co-workers and Feher have reported the use of polyhedral silsesquioxanes as cores for dendrimers, based on functionalising phosphine derivatised dendrimers,[14] and functionalising the rather unstable γ-aminopropyl-derivatised silsesquioxane core[15] respectively.

Results

The synthesis of the dendrimer molecules was accomplished according to Scheme 1, using a similar repetitive hydrosilation/vinylation procedure to those published previously.[16–18] The 24-Cl dendrimer, **2**, can be prepared in quantitative yield (as measured by NMR spectroscopy) *via* the hydrosilation of octavinylsilsesquioxane, **1**, using trichlorosilane. This compound can also be synthesised by the hydrosilation of octahydridosilsesquioxane, using vinyltrichlorosilane, although compound **1** is the preferred starting material as it is extremely simple to synthesise[19] (or it can be obtained from Aldrich); the bulky nature of the silsesquioxane means that the unwanted side reaction, where addition to the vinyl groups occurs in the β-position, is suppressed. Hydrosilation of compound **1** can also be completed with a number of other chlorosilane molecules, including dichloromethylsilane and chlorodimethylsilane, to produce dendrimers such as the 16-Cl and 8-Cl derivatised molecules, **3** and **4**, shown in Fig. 1. This illustrates a method by which we have control over the number of reactive chain ends a dendrimer possesses.

The vinylation of **2** using vinylmagnesium bromide produces the 24-vinyl dendrimer, **5**, in 81% yield. Compound **5** can then be used as a starting material for the subsequent preparation of the second generation dendrimer by hydrosilation with trichlorosilane (to produce the 72-Cl dendrimer **6**) and by a repeat of the vinylation reaction to produce the 72-vinyl dendrimer **7**, although the yield from this last reaction is reduced (to 21%)

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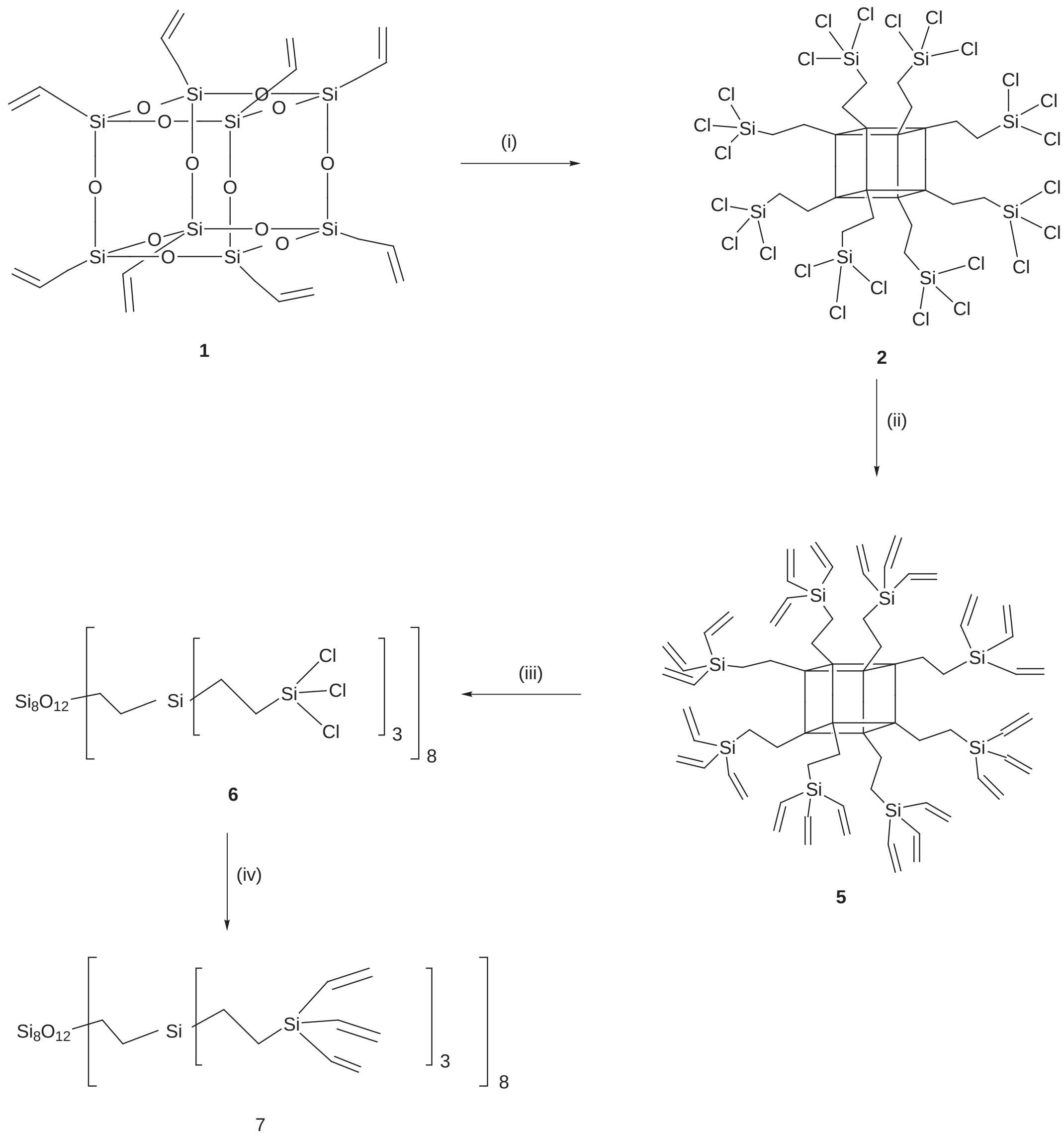
† *Supplementary data available*: experimental details and characterisation for compounds **2**–**11**. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/2767/, otherwise available from BLDSC (No. SUP 57403, 8 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).



Scheme 1 Synthetic scheme for the production of 24-Cl dendrimer, **2**, 24-vinyl dendrimer, **5**, 72-Cl dendrimer, **6** and the 72-vinyl dendrimer **7**. (i) $HSiCl_3$, Speier's catalyst, Et_2O, reflux, 8 h; (ii) $CH_2CHMgBr$, THF, 80 °C, 24 h; (iii) $HSiCl_3$, Speier's catalyst, Et_2O, reflux, 8 h; (iv) $CH_2CHMgBr$, THF, 80 °C, 18 h

compared to the lower generations. All molecules have been characterised spectroscopically and the 24-vinyl dendrimer, **5**, has also been partially characterised using single-crystal X-ray diffraction, although because of extensive disorder of the carbon atoms at the periphery of the dendrimer, only a partial structure refinement was possible. Fig. 2 shows the results of this diffraction study. Taken in conjugation with the spectroscopic and analytical data reported in this paper, the diffraction experiment confirms the molecular structure of **5** as the defect-free 24-vinyl functionalised dendrimer.

The 24-Cl dendrimer, **2**, can also be reacted with allylmagnesium bromide to produce the 24-allyl dendrimer, **8**. This reaction occurs in high yield and the crude product is almost pure (within the detection limit of ^1H NMR spectroscopy). All of the chloro-functionalised dendrimers undergo similar alkenylation reactions, all in relatively high yield, to produce dendrimers with varying numbers of chain ends. For example, the 16-Cl dendrimer **3** also undergoes this reaction under similar conditions to produce molecule **9**.

Discussion

Dendrimers synthesised using the divergent method start with a core, representing the zeroth generation, possessing one or more reactive sites. The number of monomer units that can be added to the next generation of dendrimer depends on the number of reactive sites on the core and how many monomers can be added to each reactive site (their valency). For previous carbosilane dendrimers the maximum number of reactive sites on the core is four (using tetravinylsilane or tetraallylsilane),[16–18] and on successive hydrosilation/vinylation reactions involving the trivalent $SiCl_3$ unit as the reactive site a branching progression of 4→12→36→108 occurs for the zeroth, first, second and third generation dendrimers respectively. Utilising the octafunctionality of a polyhedral oligomeric silsesquioxane core we get a progression of 8→24→72→216 for the same generations, providing a route to silane dendrimers with a high density of exterior functionalised sites with fewer steps than previously published methods. Other examples of using core and branching units of high multiplicity to form dendrimers with a large number of chain ends can be found in the review by Tomalia and Hurst.[20] Dendrimers with polyhedral silsesquioxane cores will also approach their De Gennes limit (the size where surface congestion becomes too great for further defect-free generations to be added) in fewer generations than those prepared with other cores. These molecules will also be more spherically symmetric for the lower generation numbers than other dendrimers because the spatial constraints imposed by eight dendrimer arms are greater than those of other core molecules.

The use of octafunctional polyhedral oligomeric silsesqui-

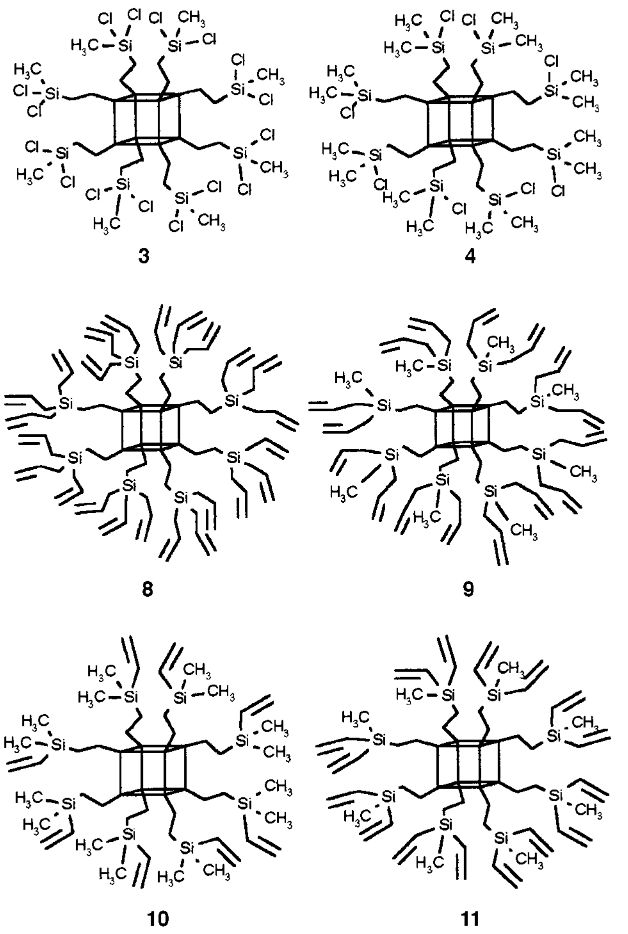


Fig. 1 Molecular structures of compounds **3**, **4**, **8**, **9**, **10** and **11**. The cubic silsesquioxane core is shown as lines linking the silicon atoms. The oxygen atoms would be near the centres of these lines

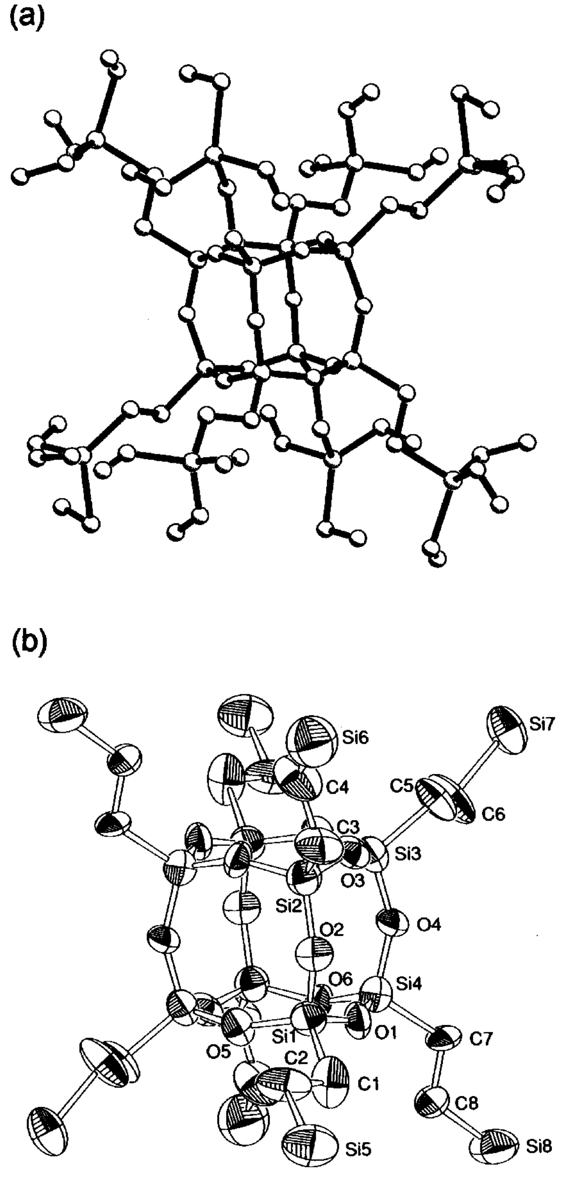


Fig. 2 (a) Ball and stick and (b) thermal ellipsoid representations of the crystal structure of the 24-vinyl dendrimer, **5**. For clarity, the disordered vinyl groups are not shown on the thermal ellipsoid plot

oxane cores provides an easy route to highly functional dendrimer molecules. They may also be advantageous in tuning the properties of the dendrimer to suit the environment in which a particular application will occur. For example, much of the interest in polyhedral silsesquioxane molecules in polymer chemistry is in their use as 'hard blocks' to modify the thermal and mechanical stability of materials.[10] The use of POSS molecules in dendrimers should have a similar effect, leading to dendrimers with different properties from those based on, for example, tetravinylsilane cores. The properties of the dendrimer can also be altered by changing the length of the carbon chain between branching silicon atoms by using different alkenyl Grignard reagents in the alkenylation step. This will have a marked effect on the physical characteristics of the molecules, especially, of course, their size and the number of generations that can be synthesised before surface congestion becomes the size-limiting factor. It will almost certainly play an important role in any catalytic utility of these molecules, affecting, for example, the selectivity of a catalyst. The effect of the chain length on the physical properties of the dendrimers can be seen clearly by noting the difference in appearance of the 24-vinyl dendrimer, which is a crystalline solid, and the 24-allyl dendrimer, which is a viscous liquid. Similar variations in physical properties have been reported for other carbosilane dendrimers, where varying the length of alkenylating agents from C_2 to C_{10} produced dendrimers varying markedly in physical properties.[21]

The two types of dendrimer reported here, chloro- and vinyl-functionalised, are ideal platforms on which to build synthetic strategies aimed at the preparation of new supported catalysts and we are continuing our research in order both to optimise the synthetic conditions for their synthesis and to utilise the molecules as catalyst supports. The high reactivity of the $SiCl_3$ groups towards nucleophiles, and vinyl chain ends towards addition reactions, should allow facile derivatisation of these dendrimers with useful catalytic functionality.

Experimental

All manipulations were carried out under an atmosphere of argon. Solvents were dried according to established procedures. Compound **1** was synthesised according to reported methods.[16] Proton NMR spectra were recorded at 300.13 MHz, ^{13}C NMR spectra at 75.47 MHz and ^{29}Si NMR spectra at 59.63 MHz on a Bruker AM300 spectrometer operating in the Fourier-transform mode with, for ^{13}C spectra, noise proton decoupling: reference $Si(CH_3)_4$. The FTIR spectra were recorded on a Perkin-Elmer 1710 spectrometer. Chemical analysis was accomplished by the University of St. Andrews Microanalysis service. Example synthetic procedures follow. Complete methods can be found in SUP 57403.

Syntheses

1,3,5,7,9,11,13,15-Octakis[2-(trichlorosilyl)ethyl]pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 2. The compounds $HSiCl_3$ (6 ml, 59.3 mmol) and $H_2[PtCl_6]$ (0.1 mol L^{-1} in Pr^iOH, 10 drops) were added to a solution of octavinylpentacyclooctasiloxane **1** (1.0 g, 1.58 mmol) in diethyl ether (50 ml). The resulting mixture was heated at reflux for 8 h and at 20 °C for 15 h. The solvent was removed *in vacuo* to give 2.65 g (97.8%) of **2** as a white solid. Compound **2** can also be synthesised by adding $H_2[PtCl_6]$ (0.1 mol L^{-1} in Pr^{i}OH, 2 drops) to a solution of octahydridopentacyclooctasiloxane[22] (0.15 g, 0.35 mmol) and vinyltrichlorosilane (9 ml, 70 mmol). The resulting mixture was heated at reflux for 22 h. The solvent was removed *in vacuo* to give 0.77 g (100%) of **2** as a white solid. ^{1}H NMR ($CDCl_3$): δ 0.95 (m, CH_2, 16 H), 1.45 (m, CH_2, 16 H). ^{13}C NMR ($CDCl_3$): δ 3.41 (O_3SiCH_2), 16.77 (CH_2SiCl_3). ^{29}Si NMR ($CDCl_3$): δ 12.82 ($SiCl_3$), −67.48 (O_3SiC).

1,3,5,7,9,11,13,15-Octakis[2-(trivinylsilyl)ethyl]pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 5. Vinylmagnesium bromide (1 M in THF, 45 ml) was added to a solution of **2** (2.65 g, 1.54 mmol) in THF (40 ml). The resulting solution was stirred at room temperature for 17 h. Ammonium chloride (1 M in H_2O, 50 ml) was added and the solution was extracted with diethyl ether (2 × 80 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue (2.33 g) was loaded onto a column of silica gel and eluted with 95:5 hexane–diethyl ether to afford compound **5** (1.90 g, 81%) (Found: C, 50.7; H, 6.9. $C_{64}H_{104}O_{12}Si_{16}$ requires C, 50.8; H, 7.1%). ^{1}H NMR ($CDCl_3$): δ 0.62 (m, CH_2, 16 H), 0.76 (m, CH_2, 16 H), 5.78 (dd, $^3J_{HH} = 7.4$, $^3J_{HH} = 16.8$ Hz, SiCH, 24 H), 6.08–6.21 (m, $CH{=}CH_2$, 48 H). ^{13}C NMR ($CDCl_3$): δ 4.13 (CH_2Si). 4.34 (O_3SiCH_2), 134.32 ($CH{=}CH_2$), 134.66 ($CH{=}CH_2$). ^{29}Si NMR ($CDCl_3$): δ −18.2 [$Si(CH{=}CH_2)_3$], −67.48 (O_3SiC). IR/cm^{-1} (KBr disc): 3050m, 2945m, 1593m (C=C), 1404s, 1263m, 1116vs (SiOSi), 1009s, 955s, 710s, 595s, 470m.

1,3,5,7,9,11,13,15-Octakis{2-{tris[2-(trichlorosilyl)ethyl]silyl}-ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 6. The compounds $HSiCl_3$ (13 ml, 0.128 mol) and $H_2[PtCl_6]$ (0.1 mol L^{-1} in Pr^{i}OH, 15 drops) were added to a solution of **5** (1.8 g, 1.58 mmol) in diethyl ether (50 ml). The resulting mixture was heated at reflux for 27 h. The solvent was removed *in vacuo* to yield 4.97 g (88%) of **6** as a white solid. ^{13}C NMR ($CDCl_3$): δ 1.04 (CH_2Si), 1.99 [$CHSi(CH_2)_3$], 4.27 (O_3SiCH_2), 17.22 (CH_2SiCl_3). ^{29}Si NMR ($CDCl_3$): δ 12.31 ($SiCl_3$), 11.02 (CH_2Si), −67.02 (O_3Si).

1,3,5,7,9,11,13,15-Octakis{2-{tris[2-(trivinylsilyl)ethyl]silyl}-ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane 7. Vinylmagnesium bromide (1 M in THF, 80 ml) was added to a solution of **6** (4.68 g, 1.03 mmol) in THF (50 ml). The resulting solution was stirred at room temperature for 16 h and refluxed for 2 h. Ammonium chloride (1 M in H_2O, 50 ml) was added and the solution was extracted with diethyl ether (2 × 80 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue (4.63 g) was loaded onto a column of silica gel and eluted with 95:5 hexane–diethyl ether to afford compound **7** (0.89 g, 21%). ^{13}C NMR ($CDCl_3$): δ 2.55 (br, CH_2CH_2), 4.86 (br, CH_2CH_2), 134.55 (br, $CH{=}CH_2$). ^{29}Si NMR ($CDCl_3$): δ 10.45 (CH_2SiCH_2), −18.25 ($CH_2SiCH{=}CH_2$), −66.59 (O_3Si).

Crystal structure determination of compound 5

Crystal data. $C_{64}H_{104}O_{12}Si_{16}$, $M = 1522.9$, monoclinic, $a = 13.731(1)$, $b = 13.869(1)$, $c = 23.37(1)$ Å and $\beta = 94.36(5)°$, $U = 4437(4)$ Å^3, $T = 220$ K, space group $P2_1/c$ (no. 14), $Z = 2$, μ(Mo-Kα) = 2.68 mm^{-1}, 2309 unique reflections measured. The crystal showed essentially no diffraction beyond 2θ 30° and so only a partial structure refinement could be accomplished, but agreement values of $R(F^2) = 0.17$, $R'(F^2)$ of 0.25 and goodness of fit of 2.9 were obtained for a full-matrix least-squares refinement against 2309 reflections, of which 1325 were observed according to the criterion $I > 3\sigma(I)$. The paucity of data is presumably due to the intrinsic high levels of thermal motion and/or disorder at the periphery of the dendrimer. These problems are highlighted by the large thermal displacement factors associated with all the atoms. The silicon and oxygen and the eight methylene carbon atoms were refined with anisotropic thermal displacement parameters, and the other carbon atoms isotropically. The carbon atoms of the vinyl groups were located in Fourier-difference maps, but the quality of the crystal data is such that we were unable to refine their positions without bond distance and angle restraints. There is evidence in the Fourier-difference maps for a number of alternative positions for the terminal vinyl carbon (*i.e.* there may be some disorder of the vinyl groups), but these could not be modelled satisfactorily. The experiment does, however, confirm the basic connectivity of compound **5**.

CCDC reference number 186/1059.

See http://www.rsc.org/suppdata/dt/1998/2767/ for crystallographic files in .cif format.

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