Synthesis of an Organosilicon Dendrimer Containing 324 Si–H Bonds

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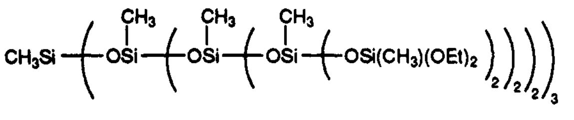
Starting with tetravinylsilane as the core molecule, a succession of alternate Pt-catalyzed hydrosilylations of all vinyl groups with $HSiCl_3$ and vinylations of all of the SiCl groups thus introduced with $CH_2{=}CHMgBr$ in THF provided a divergent synthesis of four generations of polycarbosilane dendrimers in which the Si atoms are linked by CH_2CH_2 groups. The chlorosilane of each generation was reduced with $LiAlH_4$ to the corresponding silicon hydride. The fourth generation hydride **4G-H**, contains 324 Si–H bonds. The crystal structure of the second generation hydride, **2G-H**, is described: space group $P\bar{1}$, $a = 13.907$ Å, $b = 15.682$ Å, $c = 16.414$ Å, $\alpha = 82.76°$, $\beta = 71.76°$, $\gamma = 82.49°$, $Z = 2$, $R = 0.0996$, $R_w = 0.1274$. The high residuals result from the inherently high thermal activity at the ends of the dendrimer arms.

Introduction

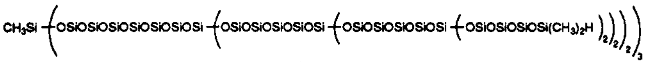
There has been great interest in recent years in polymers with a regular, three-dimensional, treelike structure. Such polymers are called dendrimers or starburst polymers.[1] While most of such polymers are wholly organic, a few organosilicon dendrimers have been prepared. Zhdanov and co-workers[2] reacted CH_3SiCl_3 with $(EtO)_2CH_3SiONa$ and subsequently with $SOCl_2$. By repetitive $(EtO)_2CH_3SiONa$ and $SOCl_2$ reaction steps the synthesis of a dendrimer containing 46 silicon atoms, 1, was effected.



$CH_3Si\left(OSi(CH_3)\left(OSi(CH_3)\left(OSi(CH_3)\left(OSi(CH_3)(OEt)_2\right)_2\right)_2\right)_2\right)_3$

1

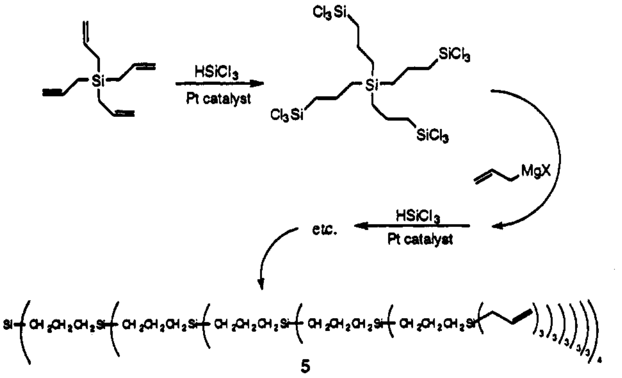
Masamune and co-workers[3] prepared dendritic polysiloxanes that had a "coating" of Si–H groups, 2. Another example of a polysiloxane dendrimer was reported by Mathias and Carothers.[4] In this synthesis $CH_2{=}CHCH_2$-$Si(OSi(CH_3)_2H)_3$ was polymerized by stirring it with a platinum catalyst. Although this reaction has the advantage of being basically a one-pot procedure, the molecular weight distribution and uniformity of branching could not be strictly controlled. A similar polysiloxane, 3, was prepared by Morikawa et al.[5]



$CH_3Si\left(OSiOSiOSiOSiOSiOSiOSi\left(OSiOSiOSiOSi\left(OSiOSiOSiOSi\left(OSiOSiOSiOSi(CH_3)_2H\right)_2\right)_2\right)_2\right)_3$

2 (interior silicon atoms have attached methyl groups)

Scheme 1



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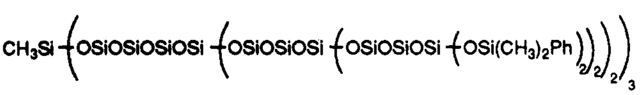

$CH_3Si\left(OSiOSiOSiOSi\left(OSiOSiOSi\left(OSiOSiOSi\left(OSi(CH_3)_2Ph\right)_2\right)_2\right)_2\right)_3$

3 (interior silicon atoms have attached methyl groups)

Carbosilane dendrimers have been reported only recently, while our work was in progress. Using tetraallylsilane as a core, van der Made and van Leeuwen[6] applied hydrosilylation and allylation steps to grow dendrimer 5 (Scheme 1). Roovers et al.[7a,b] carried out a similar synthesis using tetravinylsilane as the core molecule and methyldichlorosilane in the hydrosilylation step. Dendrimers up to the fourth generation were prepared (Scheme 2). In further studies,[7c] dendrimers of this type, which contained 64 and 128 Si–Cl bonds, respectively, in the periphery,

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(1) For reviews see: (a) Tomalia, D. D.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Mekelburger, H.-B.; Jaworek, W.; Vögtle, F. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1571.

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(3) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077.

(4) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(5) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469.

(6) van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400.

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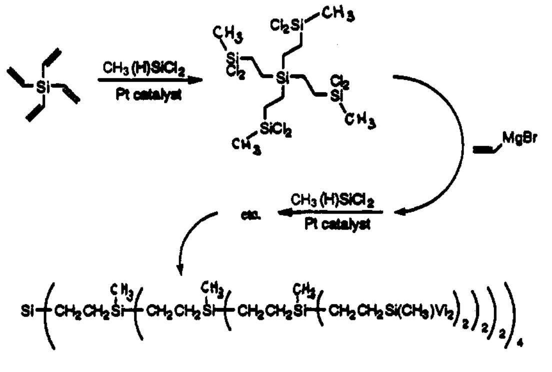
Scheme 2



were treated with monodisperse poly(butadienyl)lithium to give two series of regular star polybutadienes.

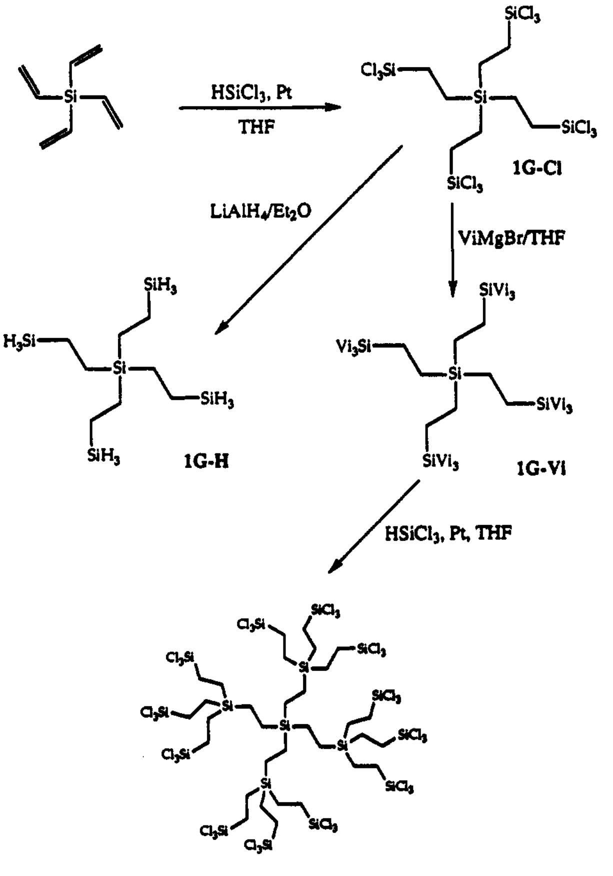
In concept, carbosilane dendrimers, via their pyrolysis in an inert gas stream, should be silicon carbide precursors. Although their synthesis is tedious and expensive, we have tested this concept. We report here our study of the synthesis of a carbosilane dendrimer based on tetravinylsilane as the core molecule and hydrosilylation (with $HSiCl_3$) and vinylation (with $CH_2{=}CHMgBr$) as the growth steps. The final product was a carbosilane star whose periphery contained 324 Si–H bonds after $LiAlH_4$ reduction of the Si–Cl bonds.

Results and Discussion

Synthesis. The basic outline for the preparation of the four generations of the carbosilanes is outlined in Schemes 3–6. Tetravinylsilane was the initiator core. There is a limit to the number of layers (or generations) that can be added in a divergent dendrimer synthesis, mainly due to problems of increasing steric congestion as layers accumulate since the vinylation step involves nucleophilic substitution at silicon.

The First Generation (1G). The reactions which led to the first generation dendrimers proceeded cleanly in high yield. Hydrosilylation of tetravinylsilane with trichlorosilane using $H_2PtCl_6{\cdot}6H_2O$ as catalyst gave **1G-Cl**, while $LiAlH_4$ (LAH) reduction and vinylation of **1G-Cl** provided **1G-H** and **1G-Vi**, respectively (Scheme 3).

Scheme 3



A major problem in carrying out a hydrosilylation of an unsymmetrically substituted olefin is controlling the regioselectivity of the Si–H addition. In the reaction of a terminal olefin, $R'CH{=}CH_2$, with a silane, R_3SiH, the α adduct, $R_3SiCH(R')CH_3$, and the β-adduct, $R_3SiCH_2CH_2R'$, can be formed. Often both isomers, with one predominating, are formed. In the $Si(CH{=}CH_2)_4/4HSiCl_3$ reaction the desired product was the all-β adduct, $Si(CH_2CH_2SiCl_3)_4$. The reaction, carried out without a solvent, gave a white solid product. According to its ^1H NMR spectrum (four sets of multiplets centered at δ 0.82, 1.0, 1.25, and 1.3 ppm), a mixture of isomers rather than the desired all-β product (two multiplets expected) had been formed.

Although the presence of both $SiCH_2CH_2SiCl_3$ and $SiCH(CH_3)SiCl_3$ units in the hydrosilylation product should not affect further growth chemistry in a major way, it was desired to have only $SiCH_2CH_2SiCl_3$ units in order to generate a dendrimer of maximum symmetry. Musolf and Speier[8] had reported that in the presence of tetrahydrofuran, trichlorosilane added to styrene to give only $Cl_3SiCH_2CH_2Ph$. Following this lead, we found that use of THF as a solvent in the $Si(CH{=}CH_2)_4/HSiCl_3$ ($H_2PtCl_6{\cdot}6H_2O$) reaction completely suppressed formation of the α-isomer unit. The product, **1G-Cl**, a white solid, was obtained in nearly quantitative yield. Its ^1H NMR spectrum showed only two multiplets at δ 0.85 and 1.25 ppm.

Treatment of **1G-Cl** with LAH in diethyl ether gave **1G-H** in 84% yield as a colorless, distillable liquid. The chemical environments of the CH_2 groups in $Si(CH_2CH_2SiH_3)_4$ are very similar, and in its ^1H NMR spectrum the resonance due to both CH_2 groups is a singlet at δ 0.63 ppm. Its major ^{29}Si NMR resonance (−53.6 ppm) is in the region characteristic for $RSiH_3$ compounds.[9]

$Si[CH_2CH_2Si(CH{=}CH_2)_3]_4$, **1G-Vi**, was prepared in good yield by reaction of **1G-Cl** with $CH_2{=}CHMgBr$ in THF,[10] for 1 day at reflux. This provided the starting material for the next generation.

The Second Generation (2G). The preparation of **2G-Cl** using the procedure that was successful in the synthesis of **1G-Cl** gave an impure product, according to the ^1H NMR spectrum of the white solid obtained. Purification by recrystallization was unsuccessful. Satisfactory results were obtained when the Karstedt catalyst (the $[(CH_3)_2(CH_2{=}CH)Si]_2O/H_2PtCl_6{\cdot}6H_2O$ reaction product)[11] was used instead of $H_2PtCl_6{\cdot}6H_2O$ in a reaction of an excess

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[9] (9) Harris, R. K.; Kennedy, J. D.; McFarlane, W. *NMR and the* Periodic Table; Harris, R. K., Mann, B. E., Eds., Academic: London, 1978; Chapter 10a.3. See also the papers of Schmidbaur and co-workers, e.g.: Schmidbaur, H.; Dörzbach, C. *Z. Naturforsch.* **1987**, *42b*, 1088. Schmidbaur, H.; Ebenhöch, J. *Z. Naturforsch.* **1987**, *42b*, 1543. Schmidbaur, H.; Zech, J. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 5.

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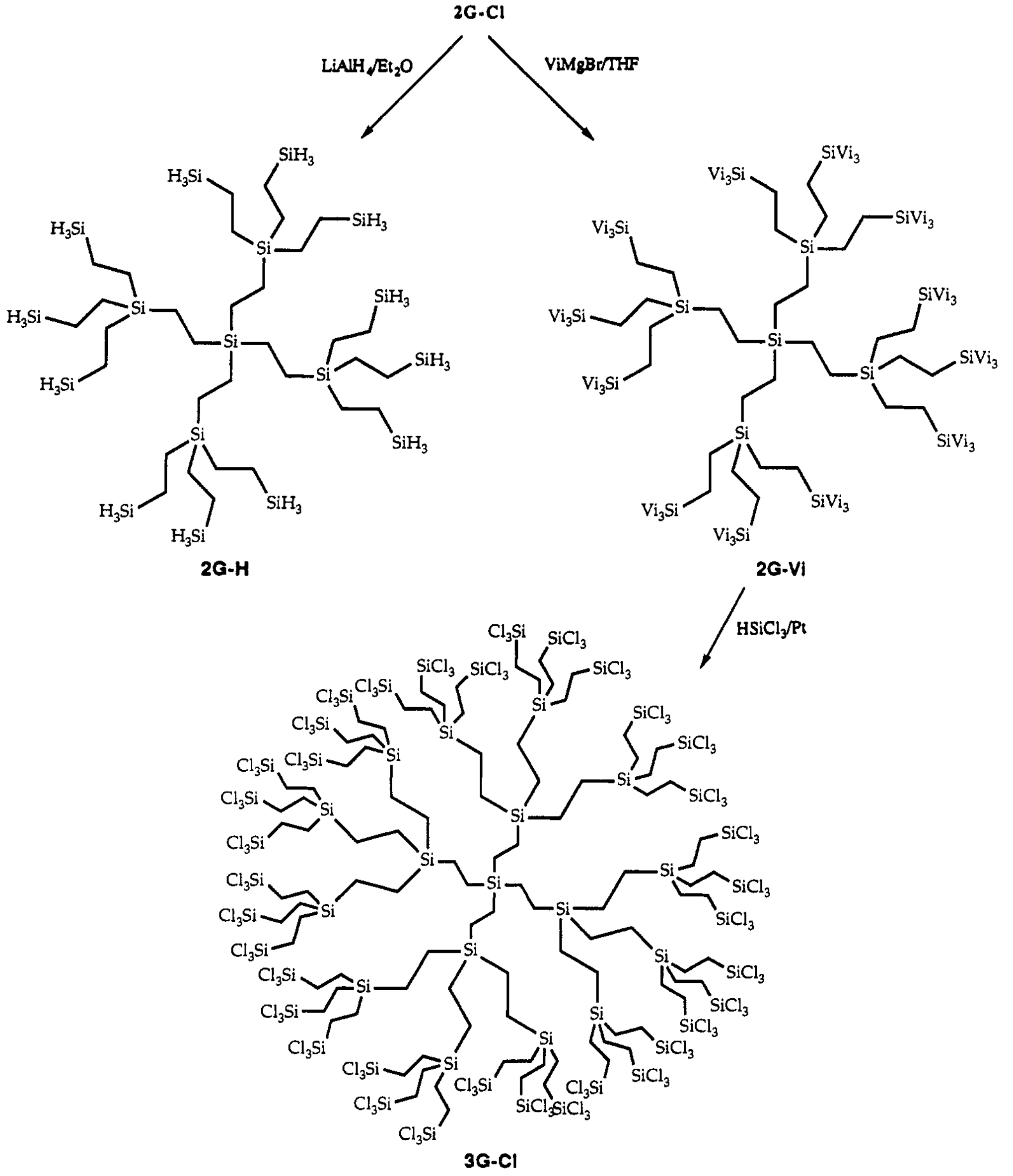
[11] (11) Karstedt, B. D. U.S. Patent 3, 775, 452 (1973).

Scheme 4



of HSiCl$_3$ with **1G-Vi** in THF solution. The ^{1}H NMR spectrum of the white solid product showed the presence of significantly fewer impurities. The interior CH$_2$CH$_2$ protons gave a singlet at δ 0.5 ppm in the ^{1}H NMR spectrum, while the SiCH$_2$CH$_2$SiCl$_3$ protons gave two multiplets at δ 0.85 and 1.25 ppm. The impurities present in only minor amount did not interfere in the isolation of pure products in the subsequent reduction and vinylation of **2G-Cl**.

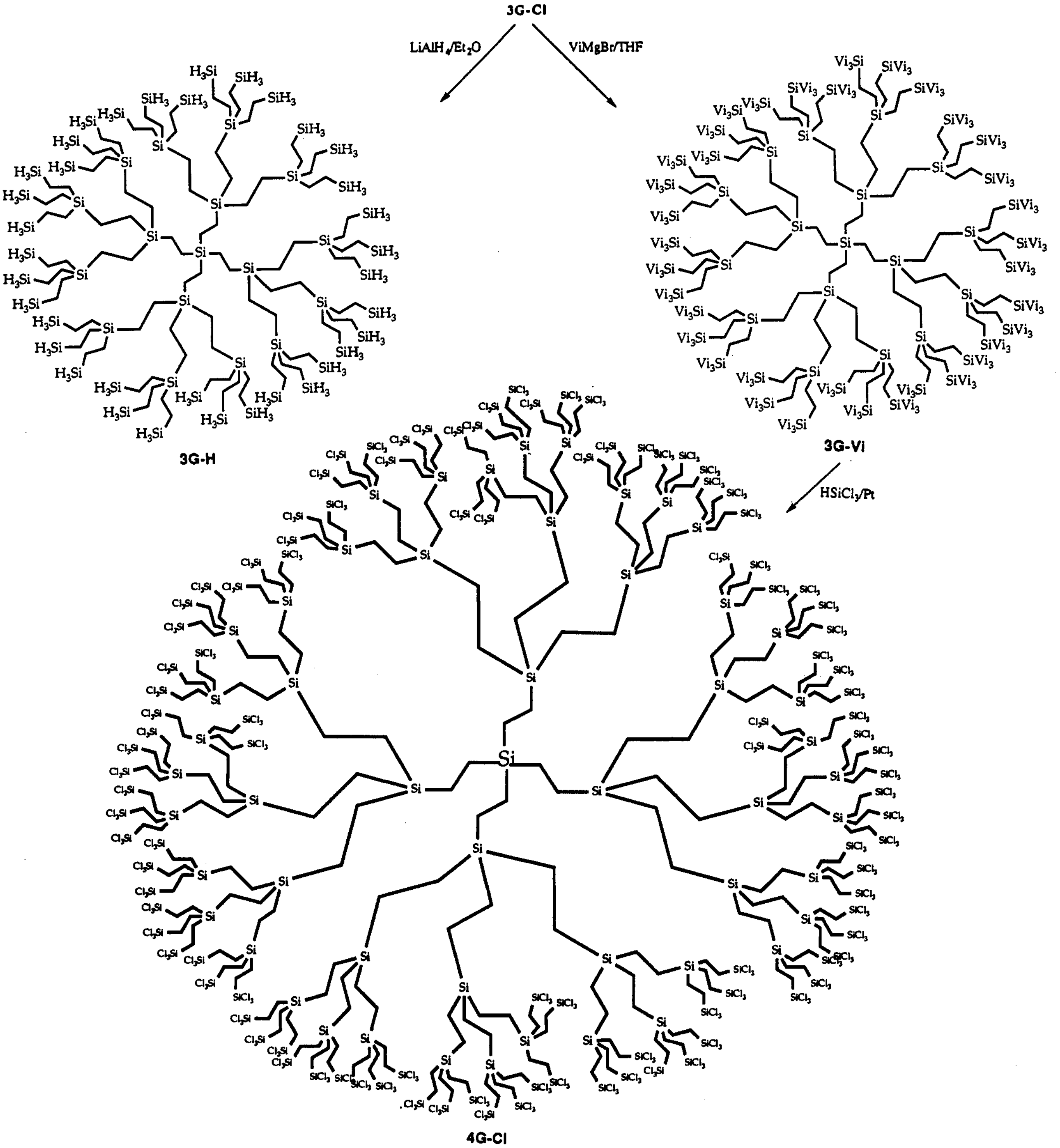
The LAH reduction of **2G-Cl** gave **2G-H** in 90% yield as an analytically and spectroscopically pure white, crystalline solid, mp 48–49 °C. Its molecular weight, measured by vapor pressure osmometry (VPO) in CHCl$_3$, was 976 (*vs* 962 calculated). Single crystals of **2G-H** were grown in pentane at −23 °C and an X-ray diffraction study was carried out.

Atomic coordinates and equivalent isotropic displacement coefficients for **2G-H** are given in Table 1. Figure 1 is a PLUTO drawing which shows the molecular structure and numbering scheme in which all atoms are shown isotropically for clarity. An ORTEP plot has been deposited with the supplementary material. Figure 2 is a second PLUTO drawing which allows comparison of the conformation of the arms. The thermal motions associated with each dendritic arm increase with distance from the central silicon atom. The thermal parameters are internally consistent for chemically equivalent atoms and appear physically correct. However, these large thermal motions of the peripheral atoms result in a chemically large range of C–C and C–Si bond distances at the ends of the arms. These effects are likely compounded by unknown contributions of disorder as well. Thus, this structure should be viewed as a picture of connectivity and spatial arrangement without taking literally individual bond distances. Table 2 presents the averaged bond distances for chemically equivalent atoms in the structure. The superscript numbers on the atom labels show how far removed an atom is from the central silicon atom. Thus, C^2–Si^3 represents the chemically equivalent bonds C(2)–Si(2), C(4)–Si(3), C(6)–Si(4), and C(8)–Si(5).

Reaction of **2G-Cl** with an excess of CH$_2$=CHMgBr in THF at reflux gave **2G-Vi**, a white semisolid in 77% yield.

The Third Generation (3G). Heating **2G-Vi** with an excess of HSiCl$_3$ in THF in the presence of the Karstedt catalyst resulted in formation of a thick, oily product which ^{1}H NMR spectroscopy showed to be grossly impure.

Scheme 5

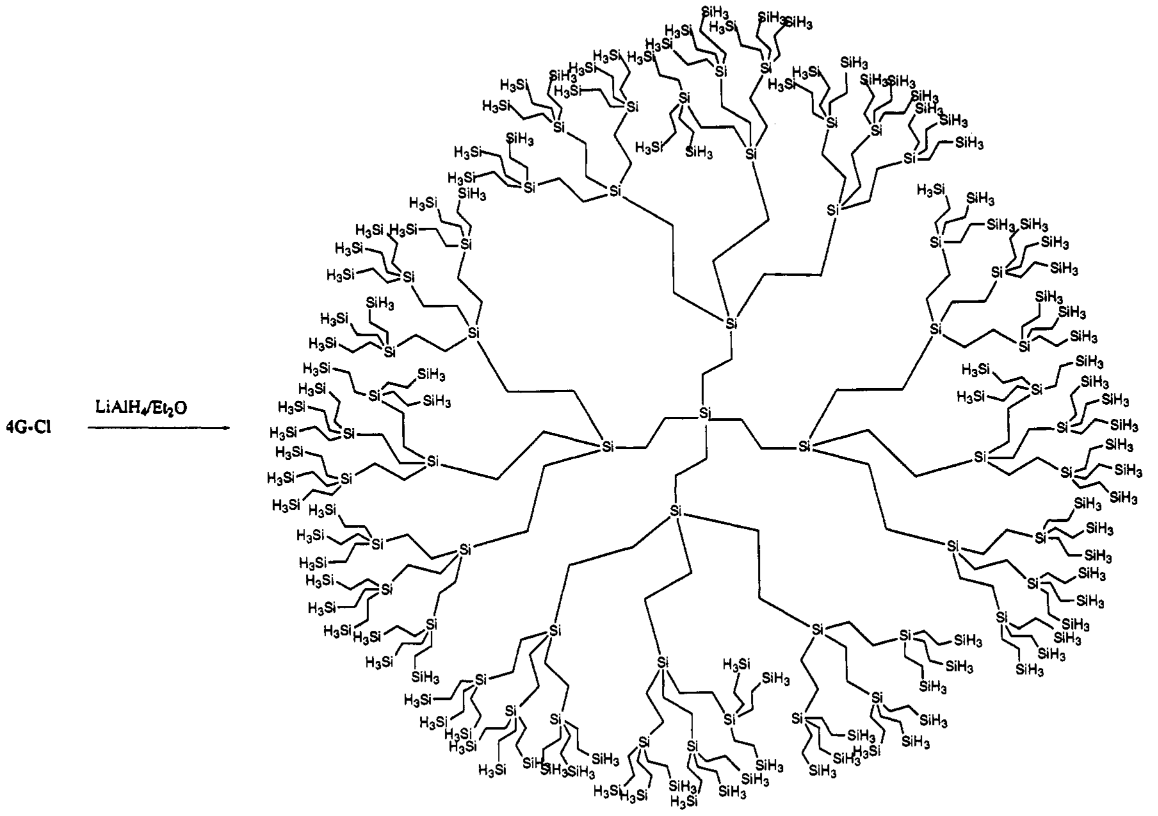


Further work showed that replacement of the THF solvent with diethyl ether completely suppressed formation of the impurities. Furthermore, in the presence of Et_2O, $HSiCl_3$ underwent β-addition, giving only $SiCH_2CH_2SiCl_3$ branches. The **3G-Cl** product was a pale yellow powder. Its ^1H NMR spectrum showed two broad singlets at δ 0.35 and 0.5 ppm due to the interior CH_2CH_2 protons and two multiplets centered at δ 0.80 and 1.25 ppm, representing the exterior CH_2CH_2 groups. Its LAH reduction gave **3G-H** as a thick, colorless oil. The calculated molecular weight of **3G-H**, $C_{104}H_{316}Si_{53}$, is 3056.2. VPO gave a measured molecular weight of 3153. As expected, the ^{29}Si NMR spectrum showed 4 resonances: the core Si atom at 9.34 ppm; the next further out Si atoms at 9.58 ppm; the Si atoms in the next layer at 8.71 ppm, and the outermost $\mathit{Si}H_3$ silicon atoms at −53.5 ppm. Assignments were made on the basis of peak intensities. The 9.34 ppm core Si signal is a barely visible shoulder on the 9.58 ppm peak.

As before, reaction of **3G-Cl** with an excess of $CH_2=CHMgBr$ in THF gave **3G-Vi**, a white semisolid, in 36% yield. The crude product yield was 90%, but large losses occurred in its chromatographic purification.

The Fourth Generation (4G). Attempted preparation of **4G-Cl** by hydrosilylation of **3G-Vi** using the procedure that was successful in the synthesis of **3G-Cl** resulted in only partial reaction according to the ^1H NMR spectrum of the powder product obtained. Most likely, steric congestion in the periphery hindered complete reaction

Scheme 6



and, therefore, more forcing reaction conditions were applied. When the Et_2O solution of **3G-Vi**, an excess of $HSiCl_3$, and the Karstedt catalyst were sealed in a thick-walled Pyrex tube and heated at 140 °C for 45 h, complete hydrosilylation of all vinyl groups was accomplished, according to the ^1H NMR spectrum of the brittle, pale yellow solid product. LAH reduction of the latter gave **4G-H**, a hard, clear, colorless solid, $C_{320}H_{964}Si_{161}$ (mol wt 9336.99), whose molecular weight was measured by VPO to be 9432. NMR spectroscopy at the **4G** stage is less useful in structure determination since the resonances in the ^1H, ^{13}C, and ^{29}Si NMR spectra now were quite broad. In the ^{29}Si NMR spectrum of **4G-H** the *Si*H_3 signal is readily apparent at −53.3 ppm, but all other Si resonances had merged into a broad feature centered at 8.8 ppm. The **4G-H** molecule contains 324 Si–H bonds.

Pyrolysis Studies. The ceramic residue yields obtained on pyrolysis of the **nG-H** compounds in argon to 950 °C (TGA experiments) increased with increasing molecular complexity: **1G-H**, 1%; **2G-H**, 35%; **3G-H**, 66%; **4G-H**, 72%. In preceramic polymer chemistry, ceramic residue yields greater than 60% generally are considered satisfactory, although higher yields (>75%) are preferred.[12] Thus **3G-H** and **4G-H**, in principle, would be satisfactory preceramic materials. However, in practice, their utility is nil in view of the preparative procedure required. It seemed worthwhile to examine the potential utility of **1G-H**, whose preparation is relatively simple, as a pyrolytic SiC precursor. Since its pyrolysis (TGA) gave only a 1% ceramic residue yield, this low molecular weight compound must be converted to material of higher molecular weight by an appropriate cross-linking procedure.

The Harrod dehydrogenative coupling reaction of $RSiH_3$ compounds[13] (eq 1) seemed quite appropriate for this purpose. In earlier work we had applied this reaction to

$$n\mathrm{RSiH}_3 \xrightarrow{(\eta^5\text{-}C_5H_5)_2M(CH_3)_2\ (M = Ti, Zr)} nH_2 + (\mathrm{RSiH})_n \qquad (1)$$

the crosslinking of poly(methylsilane), $[(CH_3SiH)_x(CH_3Si)_y(CH_2SiH_2)_z]_n$ ($x \gg y,z$) with good advantage.[14] An excellent preceramic material resulted whose pyrolysis in an argon stream gave near stoichiometric silicon carbide in high yield. Zirconocene-derived catalysts proved to be the best in this application: $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_n$, $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$, and $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_9\text{-}n)_2$.

Our crosslinking experiments to date have been troubled by the formation of insoluble products. For instance, treatment of **1G-H** in toluene with *in situ*-formed $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_9\text{-}n)_2$[15] for 6 h at room temperature gave a clear yellow solution whose evaporation at reduced pressure, with heating to 60 °C, gave a yellow-orange solid that now was insoluble in all common organic solvents. Its bulk pyrolysis in argon to 1500 °C gave a gray ceramic residue in 80% yield. Elemental analysis of this solid allowed calculation of a nominal composition of 1 SiC + 0.27 C which is equivalent, in weight %, to 93% SiC and 7% carbon. Powder X-ray diffraction showed the presence of β-SiC.

A soluble, cross-linked product from **1G-H** could not be obtained by this procedure. Apparently, further cross-

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
Si(1)	4658(2)	7381(2)	1021(2)	63(1)
Si(2)	6718(3)	8913(2)	−1317(2)	81(2)
Si(3)	6701(3)	6841(3)	2781(2)	88(2)
Si(4)	1661(3)	7561(3)	3251(3)	107(2)
Si(5)	3401(4)	6217(3)	−828(3)	109(2)
Si(21)	4228(4)	9776(4)	−2603(3)	143(3)
Si(22)	9151(4)	8472(5)	−3860(3)	212(4)
Si(23)	8207(4)	10416(3)	99(3)	132(3)
Si(31)	6602(6)	4239(4)	4376(4)	211(5)
Si(32)	9604(4)	7337(4)	641(4)	162(3)
Si(33)	6081(6)	8311(4)	5145(4)	211(5)
Si(41)	2800(5)	8980(5)	4947(4)	211(4)
Si(42)	−861(4)	9463(4)	2690(4)	162(3)
Si(43)	−88(7)	5194(7)	3766(7)	297(7)
Si(51)	6392(5)	5837(4)	−2982(4)	190(4)
Si(52)	1225(5)	7349(7)	−2332(5)	267(6)
Si(53)	1537(7)	4273(5)	1063(5)	243(6)
C(1)	5250(8)	8296(7)	267(6)	72(5)
C(2)	6186(8)	8029(7)	−493(7)	78(6)
C(3)	5514(8)	6833(7)	1624(6)	66(5)
C(4)	5713(8)	7352(7)	2264(7)	76(6)
C(5)	3456(8)	7823(7)	1797(7)	70(5)
C(6)	2824(9)	7145(7)	2450(8)	98(7)
C(7)	4383(8)	6585(7)	383(7)	77(6)
C(8)	3657(9)	6957(7)	−153(8)	90(6)
C(21)	5702(10)	9545(9)	−1743(8)	108(7)
C(22)	5139(11)	9045(9)	−2147(9)	115(8)
C(23)	7727(10)	8419(9)	−2210(8)	122(8)
C(24)	8195(13)	8978(13)	−2967(11)	194(13)
C(25)	7151(12)	9730(10)	−817(10)	133(9)
C(26)	7839(14)	9518(10)	−362(11)	154(11)
C(31)	6332(12)	5781(9)	3297(9)	116(8)
C(32)	6910(16)	5276(11)	3814(11)	182(13)
C(33)	7977(11)	6675(10)	1944(10)	124(9)
C(34)	8309(11)	7423(11)	1337(10)	148(11)
C(35)	6821(12)	7527(9)	3580(9)	122(9)
C(36)	5943(15)	7635(11)	4334(11)	163(12)
C(41)	1942(15)	8222(22)	3982(14)	279(22)
C(42)	2561(18)	8249(21)	4254(18)	292(25)
C(43)	967(12)	6606(13)	3846(11)	202(13)
C(44)	552(13)	6033(13)	3262(12)	188(13)
C(45)	867(10)	8319(9)	2691(8)	110(7)
C(46)	−176(13)	8683(13)	3220(10)	171(12)
C(51)	4573(16)	5743(11)	−1585(13)	171(15)
C(52)	5237(16)	6359(12)	−2178(13)	175(14)
C(53)	2500(17)	6918(16)	−1432(14)	202(16)
C(54)	2012(19)	6506(17)	−1757(16)	271(22)
C(55)	2793(18)	5308(14)	−148(15)	213(20)
C(56)	2100(21)	5173(20)	452(17)	282(24)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

linking occurs on solvent removal. Various strategies to remove Zr catalyst still present were ineffective. It may be noted that similar problems of insolubility were encountered by other workers when the formation of soluble polymers was sought by the $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ZrH_2]_2$-catalyzed dehydrogenative coupling of *p*-$H_3SiC_6H_4SiH_3$.[16]

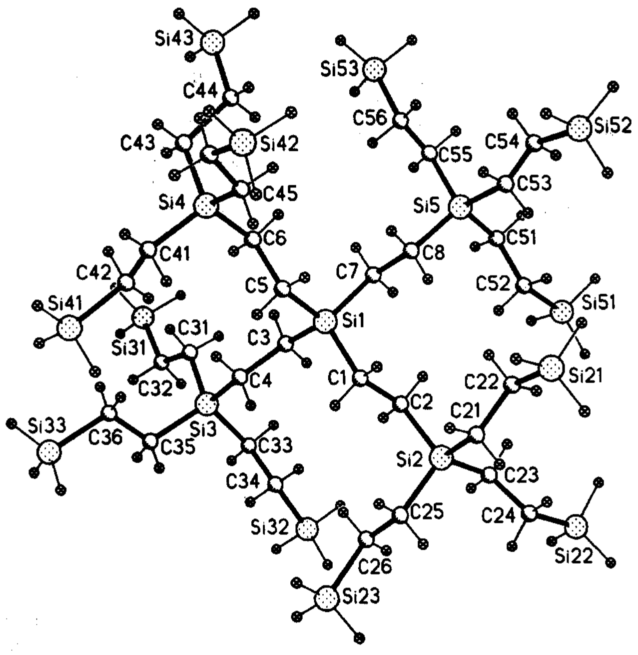

Figure 1. Molecular structure of 2G-H.

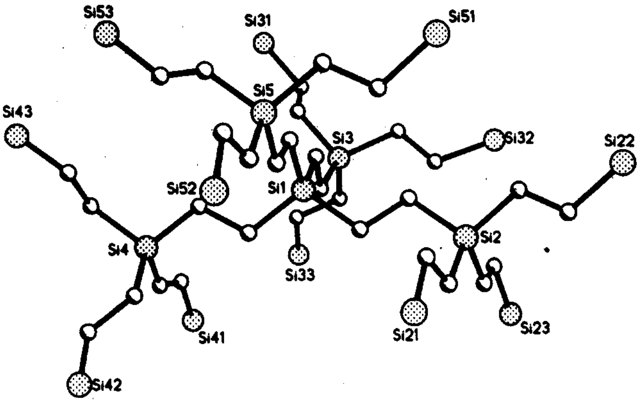

Figure 2. Side view of the molecular structure of 2G-H.

Table 2. Averaged Bond Distances for the Organosilicon Dendrimer 2G-H

	bond distances (Å)		
atoms[a]	averaged bond	shortest bond	longest bond
Si^0–C^1	1.862(14)	1.841	1.872
C^1–C^2	1.543(18)	1.517	1.555
C^2–Si^3	1.854(19)	1.838	1.877
Si^3–C^4	1.866(41)	1.822	1.977
C^4–C^5	1.40(16)	1.094	1.660
C^5–Si^6	1.825(75)	1.667	1.946

[a] Superscripts denote how far removed from the central silicon the atoms involved in bonding are; see text for complete explanation. Numbers in parentheses are standard deviations from the mean.

Experimental Section

General Comments. All reactions were carried out in an inert atmosphere unless otherwise noted. Solvents were purified by established procedures. IR spectra were measured on a Perkin-Elmer 1600 FTIR spectrophotometer and NMR spectra in $CDCl_3$ solution on a Bruker-250 or a Varian 300 instrument. VPO molecular weights were determined using a Wescan Model 233 molecular weight apparatus. Triphenylphosphine was used as a standard; all measurements were carried out with $CHCl_3$ solutions. Thermogravimetric analysis (TGA) of samples was performed using a Perkin-Elmer TGS-2 system under a 100 mL/min argon flow. Samples were heated from 50–950 °C at 10 °C/min. Bulk pyrolyses were carried out using a Lindberg Model 59545 single zone tube furnace equipped with a mullite tube, Eurotherm Model E5 controller, and a carbon pyrolysis boat supported on a 6-in alumina tube dee.

Chloroplatinic acid (CPA) solution was prepared as a 0.1 M solution in *i*-PrOH. The Karstedt catalyst was obtained from Hüls America as a 5% solution in xylene. Tetravinylsilane and trichlorosilane were commercial products and were distilled before use. Vinyl bromide was purchased from Matheson and condensed

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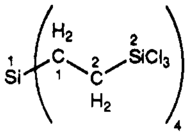
(16) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863.

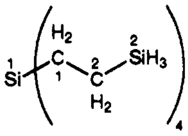
into a graduated cylinder which was cooled in dry ice/acetone prior to use.

Preparation of 1G-Cl. A 50-mL round-bottomed flask equipped with a reflux condenser, a stir-bar, and a septum was charged with 2.0 g (14.7 mmol) of $Si(CH{=}CH_2)_4$, $HSiCl_3$ (12.1 g, 89 mmol), 10 mL of THF, and five drops of CPA solution. The resulting mixture was stirred for 30 min at room temperature and subsequently for 10 h at 65 °C. Volatiles were removed at reduced pressure to leave 10 g (~100%) of 1G-Cl as a white solid.



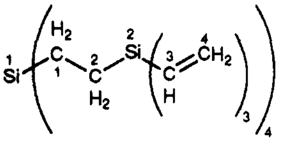
	C(1)	C(2)	Si(1)	Si(2)
^1H	0.82–0.89 (m)	1.2–1.3 (m)		
^{13}C	2.00	17.1		
^{29}Si			11.2	12.4

Preparation of 1G-H. A solution of 1G-Cl (20.0 g, 29.5 mmol) in 75 mL of Et_2O was cannulated slowly into an ice-cooled suspension of LAH (6.7 g, 177 mmol) in 500 mL of Et_2O. The mixture was stirred overnight at room temperature and then was filtered through Celite. The filtrate was added cautiously to 400 mL of ice-cooled 2 N HCl. The aqueous layer was extracted twice with Et_2O and the combined organic layers were washed twice with H_2O and once with saturated aqueous NaCl. The organic layer was dried over anhydrous $MgSO_4$ and filtered through a pad of silica gel. Most of the volatiles were removed using a rotary evaporator and the residual liquid was distilled at reduced pressure to give 6.54 g (84%) of 1G-H, a clear, colorless liquid: bp 66–67 °C/0.3 Torr; IR (cm^{-1}, neat) 2918 (s), 2892 (s), 2145 (vs, Si-H), 1408 (m), 1137 (s), 1068 (m), 920 (br s), 716 (br s); ^1H NMR (ppm) 0.63 (s, 16H, C(1) and C(2)), 3.53 (s) with weak satellites due to J_{Si-H} = 192 Hz (12 H, Si(2)); ^{13}C NMR (ppm) 1.0 (C(1)), 7.0 (C(2)); ^{29}Si NMR (ppm) 8.4 (Si(1)), −53.6 (Si(2), q, J_{Si-H} = 192 Hz; mol wt (VPO) 275 (calcd 264); mass spectrum (*m/z*) 264 (M^+), 205, 177, 147, 89. Anal. Calcd for $C_8H_{28}Si_5$: C, 36.33; H, 10.59. Found: C, 36.43; H, 10.65.



1G-H

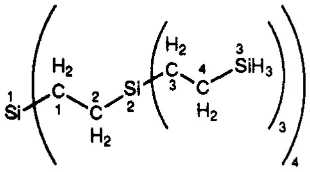
Preparation of 1G-Vi. A 500-mL three-necked, round-bottomed flask was equipped with an addition funnel, a stir-bar, a dry ice condenser, and a septum. Magnesium turnings (6.6 g, 0.27 g atom) were added to the flask and covered with THF. A small amount of vinyl bromide (3 mL) was added, along with a crystal of iodine. After the reaction had commenced, 60 mL of THF was added and then a solution of 21 mL (0.30 mol) of vinyl bromide in 20 mL of THF was added dropwise, at a rate sufficient to maintain a gentle reflux. After the addition had been completed, the $CH_2{=}CHMgBr$ solution was refluxed for 30 min. After the solution had cooled to room temperature, a solution of 1G-Cl (10.0 g, 15 mmol) in 50 mL of THF was added dropwise at a rate sufficient to maintain a moderate reflux. After completion of the addition, the reaction mixture was heated at reflux for 24 h. The mixture was cooled to room temperature and then poured into ice-cold saturated aqueous NH_4Cl. The aqueous layer was extracted twice with Et_2O, and the combined organic layers were washed twice with water and once with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. The volatile components were removed on the rotary evaporator, leaving 9.7 g of a yellow oil. A 1.0-g aliquot was chromatographed on silica gel with 3:500 v/v EtOAc/hexane as eluent. The product, 1G-Vi, was obtained as a clear, colorless oil (0.55 g, 63%): IR (cm^{-1}, neat) 3049 (m), 3007 (s), 2967 (m), 2944 (m), 1591 (s, C=C), 1403 (s), 1129 (m), 1008 (s), 953 (s), 726 (s); ^1H NMR (ppm) 0.47–0.55 (mult, 16H, C(1) and C(2)), 5.69–5.77 (mult, 12H, C(3)), 6.03–6.17 (mult, 24H, C(4)); ^{13}C NMR (ppm) 2.60 (C(1)), 4.85 (C(2)), 134.5 and 134.6 (C(3) and C(4)); ^{29}Si NMR (ppm) −18.3 (Si(2)), 10.5 (Si(1)). Anal. Calcd for $C_{32}H_{52}Si_5$: C, 66.64; H, 9.02. Found: C, 67.07; H, 9.18.



1G-Vi

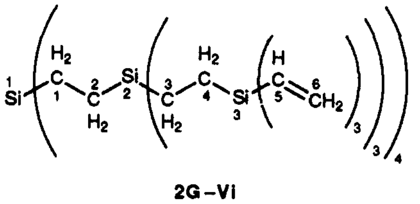
Preparation of 2G-Cl. The procedure used in the preparation of 1G-Cl was used in the reaction of 1.0 g (1.73 mmol) of 1G-Vi with $HSiCl_3$ (3.2 mL, 32 mmol) in 3.5 mL of THF, except that two drops of the xylene solution of the Karstedt catalyst was used. The reaction mixture was stirred and heated at 50 °C for 2 h. Volatiles were removed at reduced pressure to leave 2G-Cl as a white, oily solid (3.7 g, 97%). ^1H NMR (250 MHz, $CDCl_3$) δ 0.48 (s, 16 H), 0.7–0.9 (m, 24 H), 1.2–1.4 (m, 24 H). There were small amounts of impurities present as indicated by the ^1H NMR spectrum, but they did not interfere in subsequent steps.

Preparation of 2G-H. The same procedure that was used in the preparation of 1G-H was used in the reaction of 1.45 g (0.66 mmol) of 2G-Cl in 15 mL of Et_2O with 0.56 g (15 mmol) of LAH in 50 mL of Et_2O. The same workup procedure yielded a cloudy oil which was dissolved in hexane and filtered through a pad of Florisil. Removal of volatiles at reduced pressure left 2G-H as a crystalline, white solid (0.57 g, 90%): mp 48–49 °C; IR (cm^{-1}, $CDCl_3$) 2890 (s), 2790 (m), 2142 (s, Si-H), 1407 (s), 1133 (s), 1066 (m), 920 (s); ^1H NMR (ppm) 0.38 (s, 16H, C(1) and C(2)), 0.62 (s, 48H, C(3) and C(4)), 3.53 with weak satellites due to J_{Si-H} = 191 Hz (s, 36H, Si(3)); ^{13}C NMR (ppm) −0.92, 2.55, 3.42, 6.94 (C(1–4), peaks too close to each other to assign); ^{29}Si NMR (ppm) −53.6 (Si(3), q, J_{Si-H} = 191 Hz), 8.5 (Si(2)), 9.7 (Si(1)). Anal. Calcd for $C_{32}H_{100}Si_{17}$: C, 39.93; H, 10.47. Found: C, 39.97; H, 10.41. Mol wt (VPO) 976 (calcd 962).



2G-H

Preparation of 2G-Vi. The Grignard procedure used was identical to that used in the preparation of 1G-Vi in the reaction of 2.19 g of Mg turnings (0.09 g atom), 8 mL of vinyl bromide (113 mmol), and 3.66 g (1.66 mmol) of 2G-Cl in THF. The same workup left a yellow oil which was taken up in hexane and filtered through a pad of Florisil. Removal of volatiles left 2.61 g of an off-white semisolid. A portion of the latter (1.0 g) was chromatographed on silica gel using first hexane and then 100:1 v/v hexane/EtOAc as eluents to yield 2G-Vi as a white semisolid (0.91 g, 77%): ^1H NMR (ppm) 0.30 (s, 16H, C(1) and C(2)), 0.4–0.6 (mult, 48H, C(3) and C(4)), 5.70–5.78 (mult, 36H, C(5)), 6.03–6.17 (mult, 72H, C(6)); ^{13}C NMR (ppm) 2.0 (broad), 4.54



2G-Vi

Table 3. Crystal Data for the Organosilicon Dendrimer 2G-H

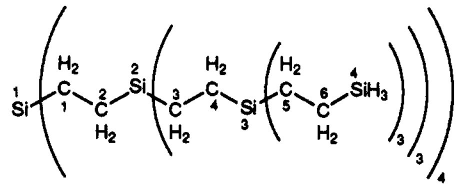
(a) Crystal Parameters			
formula	$C_{32}H_{100}Si_{17}$	γ, deg	82.49(3)
formula weight	962.7	V, Å^3	3356.0(19)
cryst system	triclinic	Z	2
space group	$P\bar{1}$	D(calc), Mg m^{-3}	0.952
a, Å	13.907(4)	μ(Mo Kα), mm^{-1}	0.340
b, Å	15.682(5)	temp, K	240
c, Å	16.414(5)	cryst size, mm	0.34 × 0.38 × 0.41
α, deg	82.76(3)	cryst color	colorless
β, deg	71.76(3)		
(b) Data Collection			
diffractometer	Siemens P4	decay	~?%
monochromator	oriented graphite	octants collcd	±14,±16,+17
radiation	Mo Kα	no. of rflns collcd	9058
wavelength, Å	0.71073	no. of independt rflns	8693
2θ limits, deg	$4 < 2\theta < 45$	no. of independt rflns, $F_o \geq 3\sigma(F_o)$	3445 $F_o \geq 4\sigma(F_o)$
std rflns	3 std/197 rflns	T(max)/T(min)	N/A
(c) Refinement			
$R(F)$,[a] %	9.96	Δ/σ(max)	0.068
$R_w(F)$,[b] %	12.74	$\Delta(\rho)$, e Å^{-3}	0.47
GOF	1.94	N_o/N_v	7.8

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w^{-1} = \sigma^2 F_o + gF_o^2$.

(C(1–4)); ^{29}Si NMR (ppm) −18.3 (Si(3)), 9.1 (Si(1)), 10.4 (Si(2)). Anal. Calcd for $C_{104}H_{172}Si_{17}$: C, 65.75; H, 9.12. Found: C, 65.95; H, 9.07.

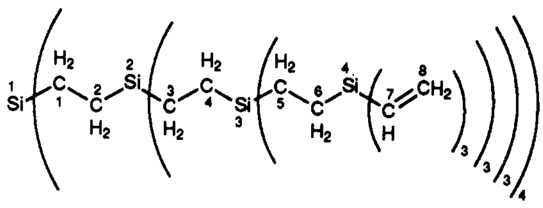
Preparation of 3G-Cl. A solution of **2G-Vi** (1.0 g, 0.53 mmol) and 2.9 mL (29 mmol) of $HSiCl_3$ in 3.2 mL of Et_2O to which two drops of the Karstedt catalyst solution had been added was heated at reflux in a 60 °C oil bath for 15 h. Removal of volatiles at reduced pressure left **3G-Cl** as a pale yellow, crusty solid (3.23 g, 91%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.35 (broad s, 16 H), 0.50 (broad s, 48 H), 0.70–0.90 (m, 72 H), 1.1–1.4 (m, 72 H). There were also small amounts of impurities present as indicated by the ^{1}H NMR spectrum.

Preparation of 3G-H. A solution of 3.26 g (0.48 mmol) of **3G-Cl** in 20 mL of Et_2O was added slowly to an ice-cooled suspension of LAH (0.98 g, 26 mmol) in 50 mL of Et_2O in the usual way. The mixture was stirred overnight at room temperature. The usual workup gave a cloudy oil which was dissolved in hexane and filtered through a pad of Florisil. Removal of volatiles at reduced pressure left a clear, colorless, thick oil (0.39 g, 27%): IR (cm^{-1}, neat) 2895 (s), 2146 (s, Si-H), 1407 (m), 1134, (m), 1067 (m), 920 (m), 718 (br); ^{1}H NMR (ppm) 0.36 (s, 16H, C(1) and C(2)), 0.42 (s, 48H, C(3) and C(4)), 0.64 (s, 144H, C(5) and C(6)), 3.56 (s) with weak satellites due to J_{Si-H} = 192 Hz (108 H, Si(4); ^{13}C NMR (ppm) sharp peaks at −0.78, 2.67, 3.69, 6.98 (probably correspond to C(3–6)); C(1) and C(2) peaks are most likely buried; ^{29}Si NMR (ppm) −53.5 (Si(4), q, J_{Si-H} = 192 Hz), 8.71 (Si(3)), 9.34 (Si(1)), 9.58 (Si(2)). Anal. Calcd for $C_{104}H_{316}Si_{53}$: C, 40.87; H, 10.42. Found: C, 41.24; H, 10.21. Mol wt (VPO) 3153 (calcd 3056).



3G-H

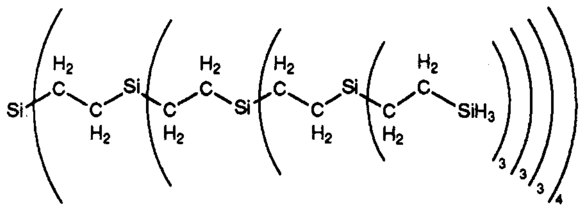
Preparation of 3G-Vi. The usual Grignard procedure was used in the reaction of $CH_2{=}CHMgBr$ (from 3.65 g (0.15 g atom) of Mg and 11.5 mL of vinyl bromide in THF) with 6.46 g (0.95 mmol) of **3G-Cl**. The usual workup gave 5.03 g (90% crude yield) of a crusty, yellow-brown solid. A 1.52-g portion of this material was chromatographed on silica gel using first 100:1 v/v hexane/EtAOc and then 100:3 v/v hexane/EtOAc as eluents. **3G-Vi** was obtained as a sticky, white solid (0.61 g, 36%): ^{1}H NMR (ppm) 0.41 (shoulder), 0.44–0.60 (s, 208H total), 5.67–5.77 (mult, 108H), 6.01–6.12 (mult, 216H); ^{13}C NMR (ppm) 2.6, 5.2, small indistinct peaks between 2.6 and 5.2 (C(1–6)), 134.6 (C(7) and C(8)); ^{29}Si NMR (ppm) −18.2 (Si(4)), 8.1 (Si(2)), 10.4 (Si(3)). The signal due to the central Si was too weak to be observed; it was expected at about 9 ppm. Anal. Calcd for $C_{320}H_{532}Si_{53}$: C, 65.50; H, 9.14. Found: C, 64.68; H, 9.13.



3G-Vi

Preparation of 4G-Cl. A thick-walled Pyrex ampoule was charged with 0.40 g (0.068 mmol) of **3G-Vi**, 0.89 mL (8.8 mmol) of $HSiCl_3$, 2 mL of Et_2O, and two drops of Karstedt catalyst solution. The ampoule was cooled in a liquid nitrogen Dewar flask and sealed under vacuum. (A large excess of $HSiCl_3$ should be avoided since dangerous pressures can develop). The sealed ampoule was heated in an oil bath at 140 °C for 45 h. Subsequently, the ampoule was cooled and opened. The volatiles were removed from the yellow solution under reduced pressure, leaving **4G-Cl** as a brittle, pale yellow solid (1.31 g, 94%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.0–2.0 (broad).

Preparation of 4G-H. A solution of 1.31 g (0.064 mmol) of **4G-Cl** in 25 mL of Et_2O was added slowly to an ice-cooled suspension of LAH (0.42 g, 11 mmol) in 50 mL of Et_2O. The mixture was stirred at room temperature for 4 days and then was filtered through a pad of Celite. The filtrate was added cautiously to 75 mL of an ice-cooled 2 N HCl solution. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed twice with distilled water and once with saturated aqueous NaCl and then were dried over anhydrous $MgSO_4$. The residue left after removal of volatiles at reduced pressure was diluted with hexane and the resulting solution was filtered through a pad of Florisil. Removal of solvent left **4G-H** as a hard, clear solid (0.35 g, 50%): IR (cm^{-1}, $CDCl_3$) 2891 (s), 2144 (s), 1456 (m), 1135 (m), 1064 (m), 920 (s); ^{1}H NMR (ppm) 0.43 (s, broad), 0.63 (s, broad), 3.56 (s, with satellites due to J_{Si-H} = 192 Hz); ^{13}C NMR (ppm) −0.7, 7.1, broad peak at 3.9; ^{29}Si NMR (ppm) −53.3 (q, J_{Si-H} = 192 Hz), 8.8 (broad). Anal. Calcd for $C_{320}H_{964}Si_{161}$: C, 41.16; H, 10.41. Found: C, 41.38; H, 10.08. Mol wt (VPO) 9432 (calcd 9337).



4G-H

Cross-Linking of 1G-H with in Situ-Generated $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_9\text{-}n)_2$. A 10-mL round-bottomed flask was charged with 26 mg (0.089 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and 2 mL of toluene. The flask was cooled in an ice bath and 100 μL of 1.80 M $n\text{-}C_4H_9Li$ in hexane was injected by syringe. The resulting orange-yellow solution was cannulated into 100 mL of toluene in a 300 mL Schlenk flask which was cooled in an ice bath. **1G-H** (2.0 g, 7.6 mmol) was injected by syringe. The resulting clear yellow solution was stirred at room temperature for 6 h. Volatiles were removed at reduced pressure with heating to 60 °C, leaving 2.0 g of a yellow-orange solid that was not soluble in common organic solvents whose ceramic residue yield (TGA) was 82%. A portion (0.54 g) of this solid was heated in a tube furnace to 1500 °C (5 °C/min, 2 h hold). Gray solid chunks (0.43 g, 80% mass recovery) resulted. Anal. Found: C, 35.18; Si, 64.52, from which a nominal composition of 1 SiC + 0.27 C is calculated.

Crystallographic Analysis of 2G-H. Crystallographic data for **2G-H** are collected in Table 3. Preliminary photographic characterization showed 1 Laue. The *E*-statistics indicated *P*1 as an appropriate space group choice. The crystal was well shaped, the absorption coefficient was low (0.340 mm^{-1}), and azimuthal ψ scans showed no significant intensity variations. An absorption correction was therefore considered unnecessary.

The structure was solved by direct methods and completed by difference Fourier synthesis. The non-hydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were treated as idealized, updated isotropic contributions with Si–H bond distances at 1.32 Å. Computations were made with the SHELXTL PLUS (4.27) program library (G. Sheldrick, Siemens, Madison, WI).

The high residuals associated with the structure result from the inherently high thermal activity at the ends of the dendrimer arms.

Acknowledgment. The M.I.T. authors are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: Figure showing ORTEP drawing of **2G-H**, tables of bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates, and B_{iso} (6 pages). Ordering information is given on any current masthead page.

OM940104G