

## SILSESQUIOXANE CHEMISTRY III. CARBOSILANE DENDRIMERS BASED ON A CUBIC Si<sub>8</sub>O<sub>12</sub> CORE

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### ABSTRACT

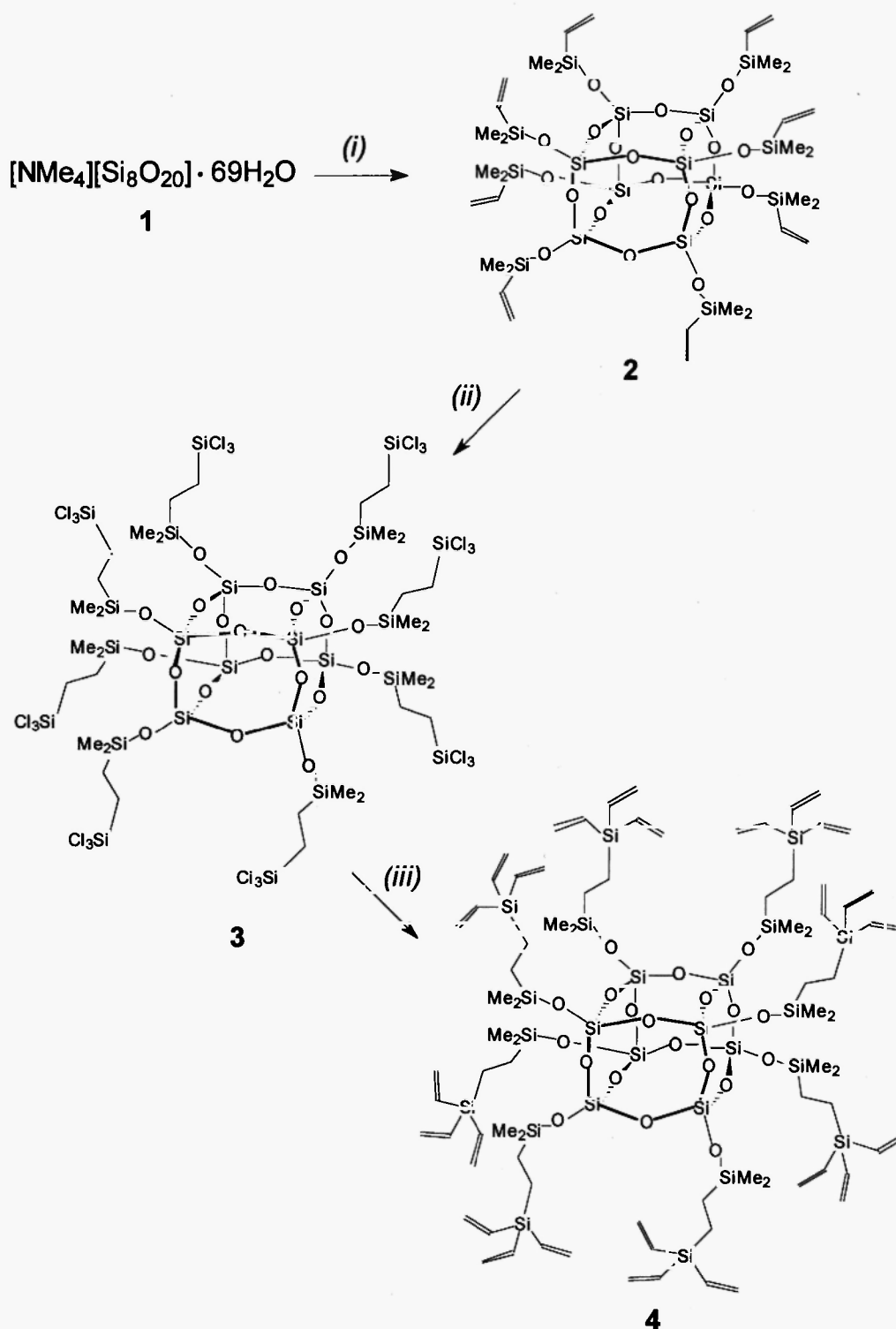
The preparation and characterization of carbosilane dendrimers based on a central Si<sub>8</sub>O<sub>12</sub> silsesquioxane cube is reported. The synthesis starts with the readily available precursor [NMe<sub>4</sub>]<sub>8</sub>[Si<sub>8</sub>O<sub>20</sub>]-69H<sub>2</sub>O (**1**) and uses consecutive hydrosilylation/vinylation steps.

### INTRODUCTION

Functionalized silsesquioxanes bearing a cube-like Si<sub>8</sub>O<sub>12</sub> central core are highly promising building blocks in the design of new materials [1-5] and novel polymers [6-8]. Another type of silicon-containing molecules which offer a variety of interesting possible applications are carbosilane dendrimers [9-13]. It thus appeared to be an interesting synthetic goal to combine these two exciting areas of silicon chemistry, i.e. to prepare and study carbosilane dendrimers based on a central Si<sub>8</sub>O<sub>12</sub> silsesquioxane cube. A recent publication by Morris et al. [14] in which a closely related series of such compounds is described prompts us to report our initial results in this field.

### PREPARATIVE RESULTS

Scheme 1 illustrates the synthesis of the dendritic silsesquioxane molecules **3** and **4**. The silsesquioxane-type tetramethylammonium octasilicate [NMe<sub>4</sub>]<sub>8</sub>[Si<sub>8</sub>O<sub>20</sub>]-69H<sub>2</sub>O (**1**) was chosen as a suitable starting material. This compound is easily accessible by reacting colloidal SiO<sub>2</sub> with aqueous tetramethylammonium hydroxide [15-18]. Despite the high water content it can be converted into neutral octasubstituted silsesquioxanes by treatment with various chlorosilanes or siloxanes [15,17,19,20]. The use of vinyl- or allylchlorosilanes allows the introduction of olefinic functional groups which are a prerequisite for the construction of dendrimers *via* hydrosilylation/olefination sequences. An improvement of the literature preparation [20] enabled us to prepare the octasubstituted dimethyl(vinyl)siloxy derivative **2** in 96% isolated yield. A gas chromatographic analysis confirmed the presence of a single product. The subsequent hydrosilylation of **2** with HSiCl<sub>3</sub> is sluggish in the presence of catalytic amounts of H<sub>2</sub>PtCl<sub>6</sub>, but it was found that good results can be obtained by using Karstedt's catalyst. The hydrosilylation product **3** was isolated in 95% yield as a crystalline white solid, which was readily characterized by elemental analysis and spectroscopic data (IR, <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR). Despite the presence of 24 Si-Cl bonds in the molecule, compound **3** appears to be moderately air-stable. Crystalline **3** can be briefly handled in air without noticeable decomposition. The first generation trichlorosilane dendrimer **3** can be converted into the corresponding 24-vinyl dendrimer **4** by treatment with excess vinylmagnesium bromide in THF solution. Compound **4** too has been characterized by elemental analysis and its spectroscopic data. These initial results clearly show that the use of the cubic Si<sub>8</sub>O<sub>12</sub> core allows the straightforward preparation of nearly spherical carbosilane dendrimers with a large number of functional groups on the outside.



**Scheme 1. Preparation of the vinyl dendrimer 4**

(i)  $\text{ClSiMe}_2(\text{CH}=\text{CH}_2)/\text{DMF}$ , r.t.; (ii)  $\text{HSiCl}_3/\text{Karstedt catalyst}$ ; (iii)  $(\text{H}_2\text{C}=\text{CH})\text{MgBr}/\text{THF}$

## EXPERIMENTAL

The preparations of **3** and **4** were carried out under purified nitrogen using standard Schlenk-line techniques. THF was dried over sodium/benzophenone and freshly distilled under nitrogen prior to use. IR spectra: Perkin Elmer FTIR-2000 spectrometer. NMR spectra: Bruker DPX 400. Elemental analyses: Microanalytical Laboratory of the Chemistry Department, Otto-von-Guericke-Universität Magdeburg. The starting material **1** was prepared according to the literature procedure [15].  $\text{HSiCl}_3$  and Karstedt's catalyst were obtained commercially and used as received.

*Improved preparation of  $\text{Si}_8\text{O}_{12}[\text{OSiMe}_2(\text{CH}=\text{CH}_2)]_8$ , (**2**).*

10.0 g (4.2 mmol) of finely ground **1** are added in small portions to a stirred and cooled (5 °C) mixture of 50 ml (44.7 g, 0.37 mol)  $\text{ClSiMe}_2(\text{CH}=\text{CH}_2)$ , 100 ml DMF, and 50 ml heptane. The resulting solution is stirred for 1 h at room temperature and then poured onto 200 g of crushed ice. The heptane phase is separated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and evaporated to dryness to afford 4.95 g (96%) of pure (GC analysis) **2**. M.p. 186-190 °C. Analytical and spectroscopic data were identical with those reported in the literature [20].

*$\text{Si}_8\text{O}_{12}[\text{OSiMe}_2(\text{CH}_2\text{CH}_2\text{SiCl}_3)]_8$ , (**3**).*

5.0 g (4.1 mmol) **2** are dissolved in 7 ml (9.4 g, 69 mmol) of neat  $\text{HSiCl}_3$  and 20  $\mu\text{l}$  of a xylene solution (2.1 - 2.4% Pt) of Karstedt's catalyst are added. After heating to reflux for 15 h the excess of trichlorosilane is distilled off to give 8.93 g (95%) **3** as a crystalline white solid. M.p. 74.5 - 75 °C.  $\text{C}_{32}\text{H}_{80}\text{Si}_{24}\text{O}_{20}\text{Cl}_{24}$  (2309.9) calcd.: C, 16.64; H, 3.49%. Found: C, 16.33; H, 3.62%. IR (KBr):  $\nu = 2962 \text{ m}, 2928 \text{ w}, 2896 \text{ w}, 1412 \text{ w}, 1394 \text{ w}, 1258 \text{ s}, 1144 \text{ vs}, 1100 \text{ vs br}, 855 \text{ vs}, 814 \text{ s}, 759 \text{ vs}, 726 \text{ s}, 701 \text{ m}, 628 \text{ m}, 563 \text{ vs}, 423 \text{ s cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.33 (m, 16 H,  $\text{CH}_2$ ), 0.79 (m, 16 H,  $\text{CH}_2$ ), 0.21 (s, 48 H,  $\text{SiMe}_2$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  16.8 (s,  $\text{CH}_2$ ), 8.7 (s,  $\text{CH}_2$ ), -0.8 (s,  $\text{SiMe}_2$ ) ppm.  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 13.1 (s,s,  $\text{SiMe}_2$  and  $\text{SiCl}_3$ ), -109.0 (s,  $\text{Si}_8\text{O}_{12}$ ) ppm.

*$\text{Si}_8\text{O}_{12}[\text{OSiMe}_2(\text{CH}_2\text{CH}_2\text{Si}(\text{CH}=\text{CH}_2)_3)]_8$ , (**4**).*

100 ml of a 1M solution of vinylmagnesium bromide in THF are added dropwise to a stirred solution of **3** (7.0 g, 3.0 mmol) in 70 ml THF and the mixture is stirred at reflux temperature for 10 h. After removal of the solvent *in vacuo*, 100 ml of a 1M aqueous solution of  $\text{NH}_4\text{Cl}$  are added to the residue and the mixture is extracted with diethylether (4 x 80 ml). The combined extracts are washed with aqueous  $\text{NH}_4\text{Cl}$  and dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of the filtered solution to dryness affords 5.0 g (78%) of **4** as a low-melting white solid.  $\text{C}_{80}\text{H}_{152}\text{Si}_{24}\text{O}_{20}$  (2108.1) calcd.: C, 45.58; H, 7.27%. Found: C, 44.18; H, 7.15%. IR (KBr):  $\nu = 3050 \text{ s}$  ( $\nu$  CH vinyl), 3009 m ( $\nu$  CH vinyl), 2960 s ( $\nu_{\text{as}} \text{CH}_3$ ), 2913 s ( $\nu_{\text{as}} \text{CH}_2$ ), 2884 s ( $\nu_{\text{s}} \text{CH}_3$ ), 2793 ( $\nu_{\text{s}} \text{CH}_2$ ), 1592 ( $\nu$  C=C vinyl), 1461 w, 1455 w, 1404 s ( $\delta$   $\text{CH}_2=\text{}$ ), 1253 vs ( $\delta_{\text{s}} \text{CH}_3$ ), 1158 s sh, 1089 vs ( $\nu_{\text{as}} \text{O-Si-O}$ ), 1009 vs (trans CH wag.), 954 vs (vinyl  $\text{CH}_2$  wag.), 842 vs ( $\nu$  Si-C), 813 vs sh (Si- $\text{CH}_3$  rock.), 727 vs, 658 m, 624 m, 551 s ( $\delta$  O-Si-O), 459  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.09 (m, 16 H,  $\text{CH}=\text{CH}_2$ ), 5.79 (m, 8 H,  $\text{CH}=\text{CH}_2$ ), 0.68 (m, 16 H,  $\text{SiCH}_2$ ), 0.55 (m, 16 H,  $\text{SiCH}_2$ ), 0.13 (m, 48 H,  $\text{SiMe}_2$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  134.6 (s,  $\text{CH}=\text{CH}_2$ ), 134.5 (s,  $\text{CH}=\text{CH}_2$ ), 9.5 (s,  $\text{CH}_2$ ), 3.8 (s,  $\text{CH}_2$ ), -0.9 (s,  $\text{SiMe}_2$ ) ppm.

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