Silylacetylene dendrimers: synthesis and characterization

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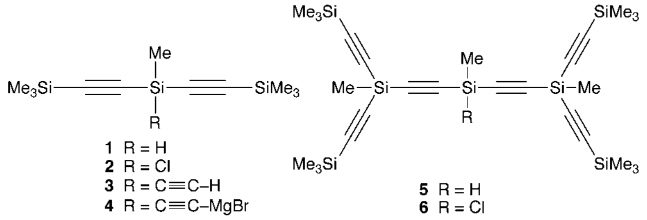
Received (in Cambridge, UK) 25th June 1999, Accepted 5th August 1999

The first silylacetylene dendrimers (1G and 2G) with alternating silicon–acetylene units [(SiC≡C)$_n$] have been synthesized and characterized by spectroscopic methods; the X-ray structure of 1G is reported.

Nanochemistry is a rapidly expanding field that is concerned with the synthesis, characterization and properties of structures of nanosize dimensions.[1] Dendrimers with a regular, three-dimensional, tree-like structure have attracted much attention as well-defined nanosize compounds. In the past 10 years, there has been increasing interest in the synthesis and properties of dendritic molecules.[2] Phenylacetylene dendrimers and related compounds are well known as a class of dendrimers containing acetylene units.[3] However, there are no published studies on dendrimers with alternating E (E = CR, SiR *etc.*) and carbon–carbon triple bonds [(EC≡C)$_n$], due to the instability of polyacetylene derivatives.[4] We report here the structurally defined nanoscale synthesis of the first silylacetylene dendrimers with alternating silicon–acetylene units [(SiC≡C)$_n$] up to the second generation with 22 silicon atoms and 21 acetylene units.

All of the previously characterized silicon-containing dendrimers, *e.g.* carbosilane dendrimers,[5] siloxane dendrimers[6] and polysilane dendrimers,[7] have been made solely by the divergent method. However, the divergent method is not suitable for silylacetylene dendrimers due to the problem of the deprotection step. Thus, we have applied a convergent method for the unprecedented synthesis of silylacetylene dendrimers.

The preparation of the silylacetylene dendrimers starts with the synthesis of the chlorosilanes **2** and **6**.† First, MeHSiCl$_2$ was reacted with (trimethysilyl)ethynylmagnesium bromide in Et$_2$O to give diyne **1** in 76% yield. Then, the Si–H moiety of **1** was converted to a Si–Cl moiety (**2**) using catalytic PdCl$_2$ in CCl$_4$ (85%). Next, **2** was reacted with ethynylmagnesium bromide to yield triyne **3** in 87% yield. After treatment of ethylmagnesium bromide with **3**, the resulting Grignard reagent **4** was added to MeHSiCl$_2$ to produce hexayne derivative **5** in 79% yield. Finally, the Si–H moiety of **5** was converted to a Si–Cl moiety (**6**) in CCl$_4$ using benzoyl peroxide (BPO) (52% yield).

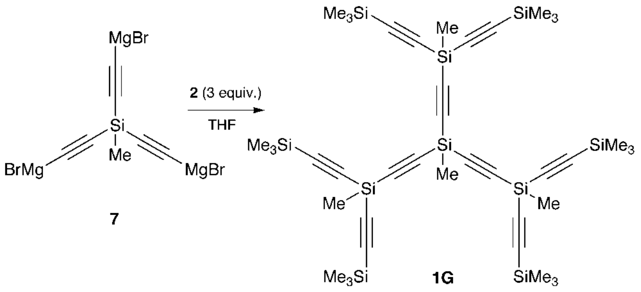


1 R = H
2 R = Cl
3 R = C≡C–H
4 R = C≡C–MgBr

5 R = H
6 R = Cl

As a core part, triyne Grignard reagent **7** was prepared from triethynylmethylsilane[8] with 3 equiv. of ethylmagnesium bromide in THF. Species **1G** was isolated as colorless crystals by the reaction of **7** with 3 equiv. of dendron **2** in THF (48% yield, Scheme 1). Crystallization from benzene afforded fine crystals of **1G** containing three molecules of benzene. However, these crystals quickly become opaque when removed from the mother liquor.

The molecular structure of **1G**·3C$_6$H$_6$ and the packing of the molecule in the crystal's unit cell are shown in Figs. 1 and 2, respectively.‡ There are three independent molecules in the unit cell, and the crystal structure possesses a crystallographic three-fold axis. Unlike previously reported dendrimers, **1G** has a nearly planar structure due to the rigid linear acetylene units, with a diameter of about 2 nm. The two molecules of **1G** lie in an alternating fashion to produce layers, in which the dendritic arms of these two molecules are arranged to give a staggered conformation through the core Si–Me bond. The benzene molecules fill spaces between the layers. The C–C triple bond



Scheme 1

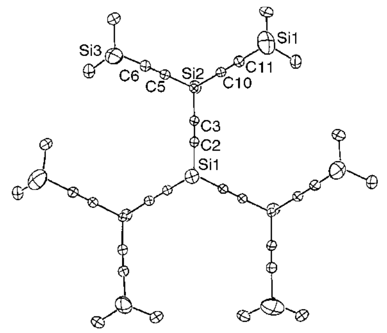


Fig. 1 Structure of **1G**·3C$_6$H$_6$ (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°) are: Si1–C2 1.831(5), Si2–C3 1.835(5), Si2–C5 1.827(5), Si2–C10 1.828(5), Si3–C6 1.851(5), Si4–C11 1.849(5), C2–C3 1.205(6), C5–C6 1.208 (7), C10–C11 1.211(7); Si1–C2–C3 178.3(5), Si2–C3–C2 177.3(4), Si2–C5–C6 177.5(5), Si2–C10–C11 178.3(5), Si3–C6–C5 179.7(5), Si4–C11–C10 179.7(5).

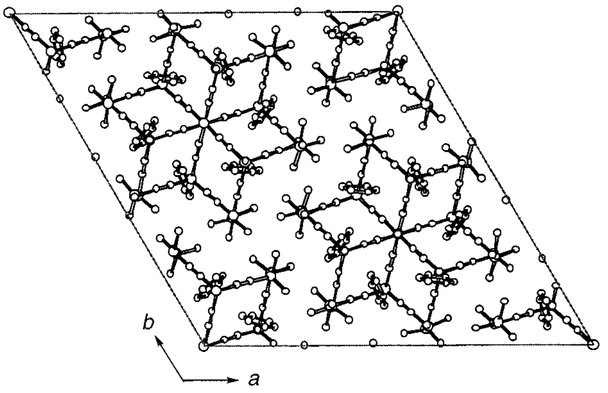
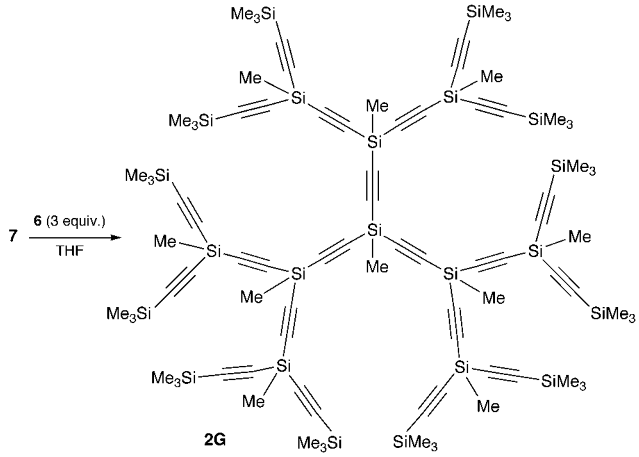


Fig. 2 Perspective view of **1G**·3C$_6$H$_6$ from the direction of the *c* axis.



Scheme 2

lengths are 1.205(6)–1.211(7) Å [av 1.208(7) Å], and the Si–C (sp) single bond lengths are 1.827(5)–1.851(5) Å [av. 1.837(5)Å]. The bond angles of the acetylene units [Si–C(sp)–C(sp)] are almost linear {177.3(4)–179.7(5)° [av. 178.5(5)°]}.

Dendrimer **2G** was obtained as a colorless glassy solid by the reaction of **7** with 3 equiv. of dendron **6** in THF (18% yield, Scheme 2).§ The structure of **2G** was characterized by NMR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. The MALDI-TOF mass spectrum showed an intense ion peak at 1836.8 (M + Na$^+$), in agreement with the formula $C_{88}H_{138}Si_{22}$ + Na$^+$. In the ^{29}Si NMR spectrum, four sets of signals were observed at δ −68.3, −66.5, −66.3 and −17.4. The signal appearing at δ −17.4 is assignable to the terminal trimethylsilyl groups. The other three signals at higher field are assignable to triethynyl-substituted silicon atoms. The ^{13}C NMR showed eight resonances of sp carbon atoms; δ 108.3 (3 C) and 108.6 (3 C) for the innermost acetylene carbons, δ 107.6 (6 C) and 110.1 (6 C) for the middle acetylene carbons, and δ 106.22 (6 C), 106.23 (6 C) 117.3 (6 C), and 117.4 (6 C) for the outermost acetylene carbons. Assignments of these ^{13}C resonances were made on the basis of peak intensities. Four sets of methyl groups were also found in the ^{13}C NMR spectrum; the core SiMe at δ −0.2 (1 C), the adjacent branched SiMe at δ −0.3 (3 C), the next adjacent branched SiMe at δ 1.0 (6 C), and the peripheral SiMe$_3$ at δ −0.55 (18 C) and −0.53 (18 C). The outermost two (trimethylsilyl)ethynyl groups are diastereotopic.

The polyyne dendrimers (**1G** and **2G**) are thermally stable up to 200 °C. However, they are highly sensitive to both acidic and alkaline conditions, and the Si–C(sp) bonds are easily cleaved. In the UV-VIS spectrum of **2G**, two absorption bands are observed at 210 (ε = 28900) and 219 nm (ε = 15300), whose intensities are about three times larger than those of **1G**, at 210 (ε = 10700) and 219 nm (ε = 5200).

This work was supported by Grants-in-Aid for Scientific Research (Nos. 09239101, 10304051, 1113321, 11166209) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) fund.

Notes and references

† A THF solution of ethylmagnesium bromide (30 ml, 24 mmol) was added to triethynylmethylsilane (0.91 g, 7.7 mmol) in THF (10 ml) to produce the Grignard reagent of the triyne. Bis(trimethylsilylethynyl)methylchlorosilane **2** (6.00 g, 25 mmol) in THF (30 ml) was added to the THF solution of the resulting Grignard reagent **7**, and the mixture was stirred overnight. Usual workup followed by Kugelrohr distillation gave **1G** as colorless crystals (180–190 °C/0.2 mmHg). Yield 48% (3.05 g), mp 115–118 °C; δ_H(300 MHz, CDCl$_3$) 0.18 (s, 54H, CH$_3$), 0.47 (s, 9H, CH$_3$), 0.52 (s, 3H, CH$_3$); δ_C(75.5 MHz, CDCl$_3$) −0.4 (CH$_3$), 0.5 (CH$_3$), 1.0 (CH$_3$), 105.5 (C), 106.9 (C), 109.4 (C), 117.0 (C); δ_{Si}(59.6 MHz, CDCl$_3$) −69.0, −67.3, −17.4 [calc. (MALDI): 850.8 (M + Na$^+$), found: 850.8].

‡ *Crystal data* for **1G**·3 C_6H_6: $C_{40}H_{66}Si_{10}\cdot 3C_6H_6$, M = 1062.17, trigonal, a = 31.061(1), c = 12.566(1) Å, V = 10499.3(3) Å^3, T = 180 K, space group = $P3$, Z = 6, ρ_{calc} = 1.008 g cm^{-3}. Diffraction data were collected on a Mac Science DIP2030K Image Plate Diffractometer employing graphite-monochromatized Mo–Kα radiation (λ = 0.71073 Å). The final R factor was 0.054 (R_w = 0.051) for 7207 reflections with $I > 3\sigma(I)$. Single crystals of **1G**·3 C_6H_6 were obtained by crystallization from benzene, mounted in a glass capilary tube and transferred to the cold gas stream of the diffractometer. The structure was solved by the direct method and refined by the full-matrix least-squares method. CCDC 182/1363. See http://www.rsc.org/suppdata/cc/1999/1799/ for crystallographic data in .cif format.

§ *Spectral data* for **2G**: δ_H(500 MHz, C_6D_6) 0.029 (s, 54H, CH$_3$), 0.034 (s, 54H, CH$_3$), 0.10 (s, 9H, CH$_3$), 0.23 (s, 3H, CH$_3$), 0.41 (s, 18H, CH$_3$); δ_C(125 MHz, C_6D_6) −0.55 (CH$_3$), −0.53 (CH$_3$), −0.3 (CH$_3$), −0.2 (CH$_3$), 1.0 (CH$_3$), 106.22 (C), 106.23 (C), 107.6 (C), 108.3 (C), 108.6 (C), 110.1 (C), 117.3 (C), 117.4 (C); δ_{Si}(59.6 MHz, C_6D_6) −68.3, −66.5, −66.3, −17.4; [calc. (MALDI): 1836.9 (M + Na$^+$), found 1836.8].

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Communication 9/05107D