Group-14-Element-Based Hybrid Dendrimers. Synthesis and Characterization of Dendrimers with Alternating Si and Ge Atoms in the Chains

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*Summary: A hybrid dendrimer with alternating Si and Ge atoms in the chains has been synthesized by the divergent growth method using Me(PhMe$_2$Ge)$_2$SiLi as a branching reagent. The structure of the first generation of the hybrid permethylated dendrimer **1G** has been established by X-ray crystallography.*

There is considerable interest in the synthesis as well as the physical and chemical properties of dendrimers.[1] Recently, much attention has been focused on main-group-element-based dendrimers in view of their optical properties and surface functionalization.[2,3] Lambert, Suzuki, and we independently reported polysilane dendrimers with homocatenated chains composed of silicon atoms.[4] A theoretical calculation suggests that Si/Ge copolymers with an ordered sequence have a one-dimensional superlattice structure.[5] Although Si/Ge copolymers have been synthesized by a Wurtz-type coupling reaction, the catenation of Si and Ge atoms is not ordered for synthetic reasons.[6] The coupling reaction of Bu$_2$Ge(SiMe$_2$Cl)$_2$ with sodium is believed to produce copolymers with an ordered SiSiGe sequence.[7] We report here the synthesis of new dendritic molecules with alternating Si and Ge atoms along the dendritic backbone, including the molecular structure of a first-generation hybrid permethylated dendrimer.

As an appropriate building reagent, bis(dimethylphenylgermyl)(methyl)silyllithium (**1**) was prepared by a lithium−mercury exchange reaction of bis[bis-(dimethylphenylgermyl)(methyl)silyl]mercury in diethyl ether at room temperature. In other solvents such as THF or toluene, the reaction produced a complicated product mixture. Silyllithium **1** has diethyl ether molecules coordinated to the lithium atom in toluene-*d$_8$*.[8]

The divergent growth method used to synthesize the dendrimers with alternating Si and Ge atoms in the chains is shown in Scheme 1. The reaction of chlorodimethylphenylgermane with **1**·(Et$_2$O)$_n$ in ether gave the coupled product tris(dimethylphenylgermyl)methylsilane as the initiator core **0G(Ph$_3$)** in quantitative yield as colorless crystals.[9] The initiator core possesses three branching points with phenyl protecting groups. The three phenyl groups of **0G(Ph$_3$)** were readily cleaved by treatment with 3 mol equiv of trifluoromethanesulfonic acid (TfOH) in CH$_2$Cl$_2$ at 0 °C. The resulting deprotected **0G(OTf$_3$)** was subsequently treated with the branching reagent **1**. The product was separated and purified by gel permeation chromatography (GPC) with a recycling system to give the first-generation dendrimer **1G(Ph$_6$)** with alternating Si and Ge atoms in the chains in 12% yield. **1G(Ph$_6$)** has a molecular weight of 1599 and is a colorless, viscous oil. It was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.[10]

The hybrid permethyl-substituted dendrimer has been synthesized by conversion of the six phenyl groups of **1G(Ph$_6$)** into methyl groups as shown in Scheme 2. Thus, **1G(Ph$_6$)** was treated with 6 mol equiv of TfOH in CH$_2$Cl$_2$ at 0 °C to give **1G(OTf$_6$)**. Without isolating **1G(OTf$_6$)**, an excess of ammonium chloride was added to the reaction mixture to yield the hexachloride **1G-**

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(8) Spectroscopic data for **1**·(Et$_2$O)$_n$: ^{1}H NMR (C$_7$D$_8$, 300 MHz) δ 0.68 (s, 3 H), 0.70 (s, 6 H), 0.73 (s, 6 H), 1.09 (t, 36 H, Et$_2$O), 3.27 (q, 24 H, Et$_2$O), 7.18−7.32 (m, 6 H), 7.72−7.78 (m, 4 H); ^{13}C NMR (C$_7$D$_8$, 75.5 MHz) δ −6.9, 0.0, 0.4, 15.2 (Et$_2$O), 65.9 (Et$_2$O), 126.3, 127.4, 134.1, 151.7; ^{29}Si NMR (C$_7$D$_8$, 223 K, 59.6 MHz) δ −100.9 (t, ^1J(^{29}Si−^{6}Li) = 19.7 Hz); ^{6}Li NMR (C$_7$D$_8$, 223 K, 44.2 MHz) δ 0.42.

(9) Spectroscopic data for **0G(Ph$_3$)**: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.32 (s, 3 H), 0.33 (s, 18 H), 7.20−7.26 (br s, 15 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ −9.6, −1.9, 128.1, 128.2, 133.7, 142.6; ^{29}Si NMR (CDCl$_3$, 59.6 MHz) δ −61.6. Anal. Calcd for C$_{25}$H$_{36}$Ge$_3$Si: C, 51.55; H, 6.23. Found: C, 51.68; H, 6.31.

Scheme 1
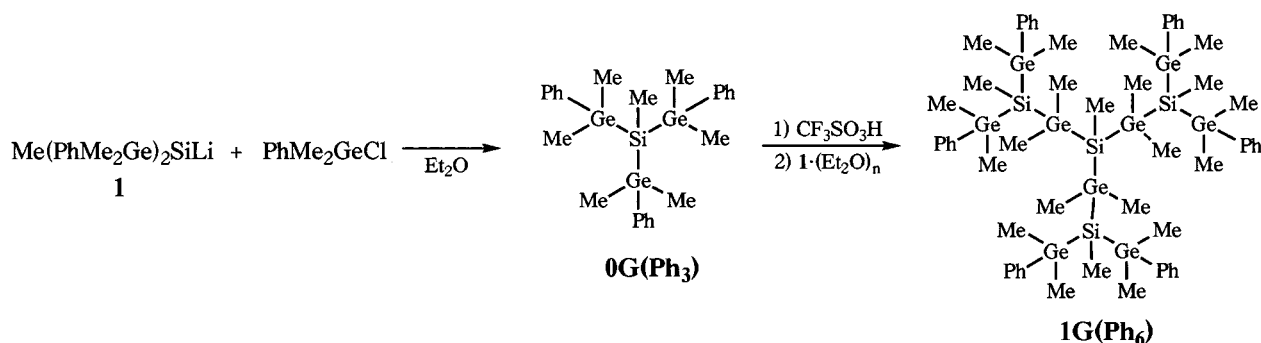
Scheme 2
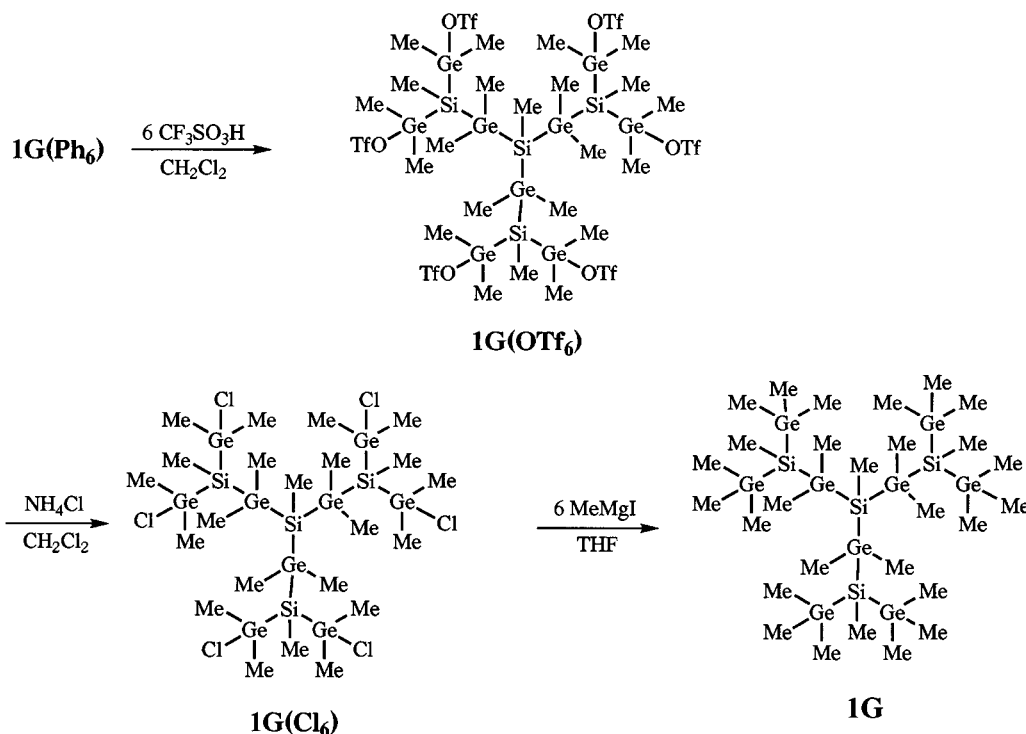
(Cl₆), which was subsequently treated with 6 mol equiv of CH_3MgI in THF to afford the permethylated dendrimer **1G** as colorless crystals in 74% yield based on **1G(Ph₆)**.[11]

The molecular structure of **1G** was confirmed by X-ray diffraction.[12] There are two independent molecules in the unit cell. An ORTEP drawing of **1G** is shown in Figure 1. The Si–Ge bond lengths (2.376(4) – 2.405(4)

Å) are within the normal range of 2.38–2.39 Å.[13] The inner Si–Ge distances (av. 2.40 Å) are somewhat longer than the outermost ones (av. 2.38 Å), probably owing to the steric repulsion of dendritic arms. Although the geometries at the branching points are nearly tetrahedral, the bond angles at the spacer (Si1–Ge1–Si2 = 116.9(2)°, Si1–Ge2–Si3 = 115.2(1)°, Si1–Ge3–Si4 = 114.3(1)°) are apparently expanded. Of particular interest are the conformations of the alternating Si and Ge chains. The importance of the *A* (anti, ~180°), *O* (orthogonal, ~90°), and *G* (gauche, ~60°) conformers in polysilane dendrimers has been recognized by Lambert et al.[4d] As **1G** has 12 chain pathways, Table 1 lists all of the M–M–M–M (M = Si or Ge) conformations based on the torsion angles. There are two types of angles in

(10) Synthesis of **1G(Ph₆)**: To a dichloromethane solution of **0G-(Ph₃)** (193 mg, 0.331 mmol), TfOH (155 mg, 1.03 mmol) was added dropwise under a nitrogen atmosphere at 0 °C. The mixture was stirred for 1 h, and the solvent was replaced by hexane. A diethyl ether solution (5 mL) of **1** (ca. 3 mmol) was added, and then the mixture was stirred for 1 h. After the usual workup, the solvent was evaporated and the components were separated by GPC to give **1G(Ph₆)** (62 mg, 0.040 mmol) as a colorless viscous oil in 12% yield. The low yield of the product is caused by the reaction of silyl triflate with THF to produce unidentified high molecular weight substances: ¹H NMR (CDCl₃, 300 MHz) δ −0.17 (s, 3 H), 0.22 (s, 18 H), 0.32 (s, 9 H), 0.36 (s, 18 H, Ge*Me*MePh), 0.41 (s, 18 H, GeMe*Me*Ph), 7.20−7.28 (m, 30 H); ¹³C NMR (CDCl₃, 75.5 MHz) δ −6.5, −3.8, −1.0, 0.8, 128.1, 128.2, 133.8, 143.1; ²⁹Si NMR (CDCl₃, 59.6 MHz) δ −53.8, −38.1. Anal. Calcd for C₅₈H₉₆Ge₉Si₄: C, 44.68; H, 6.21. Found: C, 45.08; H, 6.50.

(11) Spectroscopic data for **1G**: ¹H NMR (CDCl₃, 300 MHz) δ 0.23 (s, 54 H), 0.30 (s, 9 H), 0.40 (s, 18 H), 0.46 (s, 3 H); ¹³C NMR (CDCl₃, 75.5 MHz) δ −8.0, −3.3, 0.13, 0.33; ²⁹Si NMR (CDCl₃, 59.6 MHz) δ −55.1, −39.9. Anal. Calcd for C₂₈H₈₄Ge₉Si₄: C, 28.34; H, 7.13. Found: C, 28.54; H, 7.04.

(12) Crystallographic data for **1G**: C₂₈H₈₄Ge₉Si₄, fw 1186.6, monoclinic, $P2_1/c$, a = 19.196(1) Å, b = 23.975(1) Å, c = 24.784(1) Å, β = 106.065(1)°, V = 10960.76(1) Å³, Z = 8, D = 1.439 g/cm³, T = 180 K. The final R factor converged at 0.054 (R_w = 0.058) for 14 780 reflections with $I > 3\sigma(I)$.

(13) For the mean Si–Ge distances reported for Me₃Si–GePh₃ (2.384(1) Å) and Ph₃Si–GeMe₃ (2.394(1) Å), see: (a) Párkányi, L.; Hernandez, C.; Pannell, K. H. *J. Organomet. Chem.* **1986**, *301*, 145. (b) Pannell, K. H.; Kapoor, R. N.; Raptis, R.; Párkányi, L.; Fülöp, V. *J. Organomet. Chem.* **1990**, *384*, 41.
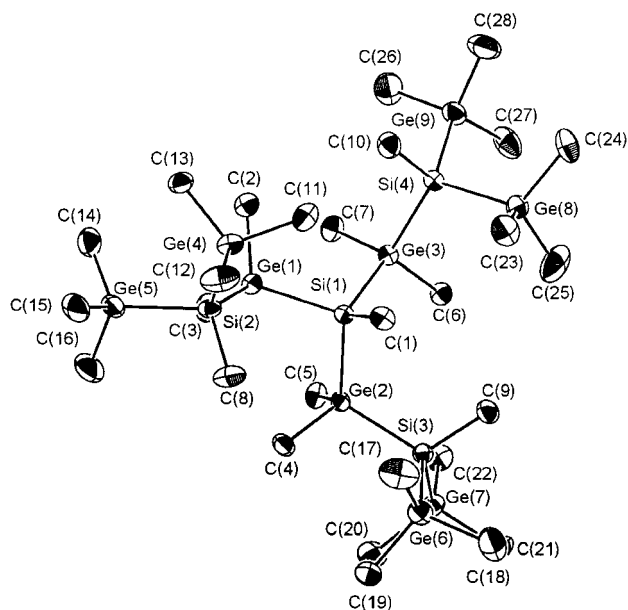
Figure 1. An ORTEP representation of the X-ray molecular crystal structure of **1G** (hydrogen atoms are omitted for clarity). Selected torsion angles (deg): Si1−Ge1−Si2−Ge4 87.5(2), Si1−Ge1−Si2−Ge5 156.0(2), Si1−Ge2−Si3−Ge6 95.5(2), Si1−Ge2−Si3−Ge7 143.9(2), Si1−Ge3−Si4−Ge8 73.6(2), Si1−Ge3−Si4−Ge9 165.0(2), Ge1−Si1−Ge2−Si3 161.5(2), Ge1−Si1−Ge3−Si4 90.1(2), Ge2−Si1−Ge1−Si2 87.5(2), Ge2−Si1−Ge3−Si4 152.4(2), Ge3−Si1−Ge1−Si2 155.0(2), Ge3−Si1−Ge2−Si3 80.7(2). Selected bond distances (Å): Si1−C1 1.889(11), Si1−Ge1 2.405(4), Si1−Ge2 2.393(3), Si1−Ge3 2.401(3), Si2−Ge1 2.391(3), Si2−Ge4 2.388(3), Si2−Ge5 2.386(4), Si3−Ge2 2.402(4), Si3−Ge6 2.378(4), Si3−Ge7 2.384(3), Si4−Ge3 2.394(3), Si4−Ge8 2.387(4), Si4−Ge9 2.381(4).

1G representing *A* (the anti angles fall in the range 143.9−165.2°) and *O* (the orthogonal angles 73.6−95.5°).[14] The chains are divided into four *OAOO*, *AOAO*, *AAOO*, and *AAOA* conformation pathways.[15] Dendrimer **1G** has no G conformer in the range of 49−61°, whereas the all-Si structure with the same skeleton with the core Si−H has a host of *G* conformations.[4d] However, the reason the Me's bring about such a profound change in the molecular conformations is unclear at this moment.

The UV spectrum of **1G** in 3-methylpentane at 300 K shows the $\sigma-\sigma^*$ band of the Si−Ge chains at 271 nm ($\epsilon = 50\,700$ M^{-1} cm^{-1}). By lowering the temperature,

Table 1. Conformation of 1G

Si/Ge chain	conformation[a]
Ge4−Si2−Ge1−Si1−Ge3−Si4−Ge8	*O, A, O, O*
Ge4−Si2−Ge1−Si1−Ge3−Si4−Ge9	*O, A, O, A*
Ge5−Si2−Ge1−Si1−Ge3−Si4−Ge8	*A, A, O, O*
Ge5−Si2−Ge1−Si1−Ge3−Si4−Ge9	*A, A, O, A*
Ge4−Si2−Ge1−Si1−Ge2−Si3−Ge6	*O, O, A, O*
Ge4−Si2−Ge1−Si1−Ge2−Si3−Ge7	*O, O, A, A*
Ge5−Si2−Ge1−Si1−Ge2−Si3−Ge6	*A, O, A, O*
Ge5−Si2−Ge1−Si1−Ge2−Si3−Ge7	*A, O, A, A*
Ge6−Si3−Ge2−Si1−Ge3−Si4−Ge8	*O, O, A, O*
Ge6−Si3−Ge2−Si1−Ge3−Si4−Ge9	*O, O, A, A*
Ge7−Si3−Ge2−Si1−Ge3−Si4−Ge8	*A, O, A, O*
Ge7−Si3−Ge2−Si1−Ge3−Si4−Ge9	*A, O, A, A*

[a] *A* and *O* are torsion angles of the M−M−M−M (M = Si or Ge) unit in the range of 143.9−165.2° and 73.6−95.5°, respectively.

this absorption band gradually shifts to the shorter wavelength; 269 nm at 250 K, 268 nm at 150 K, and 267 nm at 77 K. In addition, a new absorption band with a maximum at 243 nm appears by lowering the temperature.[16]

The UV spectrum of **1G(Ph₆)** exhibits the absorption bands at 235 ($\epsilon = 70\,000$ M^{-1} cm^{-1}) and 276 nm ($\epsilon = 61\,900$ M^{-1} cm^{-1}) at room temperature.

The growth of larger generation and applications of the hybrid dendrimers based on their optical properties and their surface chemistry are in progress.

Supporting Information Available: Tables giving the details of the X-ray structure determination, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles, figures of an ORTEP diagram, the NMR and UV spectra of **1G(Ph₆)** and the permethylated dendrimer **1G**, variable-temperature UV spectra of **1G**, and a GPC trace of the **1G(Ph₆)** reaction mixture, and synthetic procedure of **1G** (26 pages). Ordering information is given on any current masthead page.

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(14) The first publication which used the label *O* for the orthogonal conformer is the report by Michl et al., see: Albinsson, B.; Michl, J. *J. Am. Chem. Soc.* **1995**, *117*, 7, 6378.

(15) The closest comparison with **1G** is with the typical values of 92° and 165° obtained for a single crystal of Si₁₆Me₃₂, see: Shafiee, F.; Haller, K. J.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 5478.

(16) The *O* conformation seems to break the σ-conjugation of Si and Ge chains due to less overlap of the Si−Ge σ-bond orbitals. Indeed, a new absorption band at 243 nm appeared by lowering the temperature. The absorption band at 271 nm may be due to the $\sigma-\sigma^*$ transition of the longest chain (Ge(SiGe)₃), whereas the band at 243 nm may be due to that of a shorter chain.