

Synthesis of Unsymmetrically Substituted Cyclotrimerenes and the First Example of Cis Configuration around the Ge=Ge Double Bond

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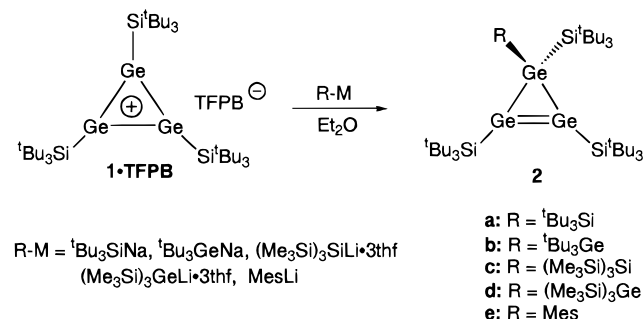
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The chemistry of unsaturated cyclic compounds consisting of Group 14 elements heavier than carbon has developed very rapidly during the past five years.^{1,2} In 1995, we reported the first successful synthesis of cyclotrimerene (R_4Ge_3), analogous to cyclopropene (R_4C_3) that has an unsaturated three-membered ring skeleton, from the reaction of $GeCl_2$ ·dioxane with t -Bu₃SiNa and t -Bu₃GeLi.³ We have subsequently shown that cyclotrimerene is a source of cyclotrimerenium ion (R_3Ge_3)⁺, which has been a long sought free germyl cation with a 2π -electron system.⁴ Shortly thereafter, a cyclotrimerenyl radical was synthesized by the dehalogenation of $ArGeCl$ ($Ar = 2,6$ -Mes₂C₆H₃, Mes = 2,4,6-trimethylphenyl) with potassium graphite (KC₈).⁵ In 1999, both Kira et al. and our group independently reported the synthesis of cyclotrisilene derivatives (R_4Si_3) by the alkali metal (KC₈ or Na) induced condensation of the appropriate halosilanes.^{6,7} The cyclotristannene derivative (R_4Sn_3) was also recently reported.⁸ However, the strategy adopted for the synthesis of unsaturated ring systems of the heavier Group 14 elements was not a general one, and the mechanism for the formation of the unsaturated ring is currently not understood. Here, we report on a versatile and simple method for the synthesis of symmetrically and unsymmetrically substituted cyclotrimerenes. Moreover, we report on the discovery of a cis configuration around the germanium–germanium double bond (Ge=Ge).

Good yields of cyclotrimerenes were obtained from the reactions of tris(tri-*tert*-butylsilyl)cyclotrimerenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**1**·TFPB,^{4b} TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) with the appropriate nu-

Scheme 1



cleophiles. At first we examined the reaction of **1**·TFPB with t -Bu₃SiNa in oxygen-free dry diethyl ether at -78 °C. The reaction mixture immediately turned into a dark-red solution due to the quantitative formation of **2a**³ (Scheme 1). Unsymmetrically substituted cyclotrimerene **2b** was isolated with t -Bu₃GeNa at a 75% yield.⁹ The lithium derivatives, (Me₃Si)₃SiLi and (Me₃-Si)₃GeLi, also reacted readily with **1**·TFPB to produce **2c** (86%) and **2d** (73%).^{9,10} However, a small nucleophile, Ph₃SiLi, produced a complicated mixture. A carbon nucleophile, MesLi, also readily reacted to give mesityl-substituted cyclotrimerene **2e** with an 80% yield.⁹ The present method apparently offers a promising route for the synthesis of new unsaturated ring systems.

The geometry around the Ge=Ge double bond of **2** is quite interesting since the double-bond systems of the heavier Group 14 elements are generally characterized by a trans-bent (or twist) arrangement.¹ However, the present system enables a cis-bent geometry around the Ge=Ge double bond by the steric and electronic effects.

An X-ray crystallographic analysis of **2c** established the exact structure, as shown in Figure 1.¹¹ The three-membered ring is almost an isosceles triangle with bond angles of 62.9(1)°, 63.3(1)°, and 53.8(1)°. The geometry around the Ge=Ge double bond is not planar, as determined by the torsional angles of Si7–Ge3–Ge2–Ge1 and Si6–Ge2–Ge3–Ge1, which are 167.5(2)° and 175.6(2)°, respectively. This shows that the Ge=Ge double bond

(9) The mass spectrum of **2** showed no molecular ion peaks, but the ion peaks attributable to the cyclotrimerenium ion by loss of the substituent attached to saturated germanium atom. **2b**: dark red crystals; mp 125–127 °C dec; ¹H NMR (C₆D₆) δ 1.39 (s, 54 H), 1.51 (s, 27 H), 1.57 (s, 27 H); ¹³C NMR (C₆D₆) δ 26.1, 28.4, 31.5, 32.3, 34.5, 34.9; ²⁹Si NMR (C₆D₆) δ 36.5, 49.9; MS (EI, 70 eV) 809–824 (M⁺ – Ge^tBu₃) for C₃₆H₈₁Ge₃Si₃. Anal. Calcd for C₃₆H₁₀₈Ge₄Si₃: C, 54.39; H, 10.27. Found: C, 54.49; H, 10.02. **2d**: dark red crystals; mp 153–155 °C dec; ¹H NMR (C₆D₆) δ 0.53 (s, 27 H), 1.39 (s, 54 H), 1.45 (s, 27 H); ¹³C NMR (C₆D₆) δ 6.7, 26.0, 27.3, 32.4, 34.0; ²⁹Si NMR (C₆D₆) δ –0.5, 26.4, 49.5; MS (EI, 70 eV) 809–824 (M⁺ – Ge(SiMe₃)₃) for C₃₆H₈₁Ge₃Si₃. Anal. Calcd for C₄₅H₁₀₈Ge₄Si₆: C, 48.77; H, 9.82. Found: C, 48.47; H, 9.54. **2e**: orange crystals; mp 142–145 °C; ¹H NMR (C₆D₆) δ 1.38 (s, 54 H), 1.39 (s, 27 H), 2.04 (s, 3 H), 2.97 (s, 6 H), 6.79 (s, 2 H); ¹³C NMR (C₆D₆) δ 20.9, 25.9, 27.3, 28.1, 32.3, 33.0, 128.6, 136.7, 147.0, 148.8; ²⁹Si NMR (C₆D₆) δ 20.7, 49.4; MS (EI, 70 eV) 729–742 (M⁺ – Si^tBu₃) for C₃₃H₆₆Ge₃Si₂. The structure of **2e** was also characterized by X-ray crystallography.

(10) Typically, **2c** was synthesized by the following procedure. The dry degassed Et₂O was introduced by vacuum transfer to a mixture of **1**·TFPB (71 mg, 0.042 mmol) and (Me₃Si)₃SiLi·3thf (20 mg, 0.042 mmol). The reaction mixture was stirred for 3 min at -100 °C. Slow warming to room temperature afforded a red solution. The solvent was removed under vacuum and the residue extracted with hexane and filtered. After evaporation of hexane, a red solid of **2c** was isolated (38 mg, 86%); mp 148–150 °C dec; ¹H NMR (C₆D₆) δ 0.52 (s, 27 H), 1.40 (s, 54 H), 1.45 (s, 27 H); ¹³C NMR (C₆D₆) δ 6.3, 26.1, 27.2, 32.4, 34.0; ²⁹Si NMR (C₆D₆) δ –87.9, –6.5, 28.1, 50.4; MS (EI, 70 eV) 857–871 (M⁺ – Si^tBu₃) for C₃₃H₈₁Ge₃Si₆, 809–824 (M⁺ – Si(SiMe₃)₃) for C₃₆H₈₁Ge₃Si₃. Anal. Calcd for C₄₅H₁₀₈Ge₃Si₇: C, 50.81; H, 10.23. Found: C, 50.62; H, 9.94.

(11) Crystal data for **2c** at 120 K: MF = C₄₅H₁₀₈Ge₃Si₇, MW = 1063.78, orthorhombic, P2₁2₁2₁ (No. 19), $a = 12.4420(6)$ Å, $b = 18.6350(7)$ Å, $c = 28.370(1)$ Å, $V = 6577.8(5)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.074$ g·cm^{–3}. The final R factor was 0.064 for 7281 reflections with $I_o > 3\sigma(I_o)$ ($R_w = 0.142$ for all data, 8618 reflections).

(1) For the reviews of R₂M=MR₂ (M = Si, Ge, Sn), see: (a) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (b) Barrau, J.; Escudie, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (c) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (d) Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (e) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157. (f) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (g) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (h) Raabe, G.; Michl, J. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; Part 2, Chapter 17. (i) Sakurai, H. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Vol. 2, Part 1, Chapter 15. (j) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373.

(2) For cyclotetrasilene derivatives, see: (a) Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1996**, *118*, 10303. (b) Iwamoto, T.; Kira, M. *Chem. Lett.* **1998**, 277. (c) Wiberg, N.; Auer, H.; Nöth, H.; Knizek, J.; Polborn, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2869.

(3) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025.

(4) (a) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60. (b) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045.

(5) Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *Chem. Commun.* **1997**, 1595.

(6) Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 886.

(7) Ichinohe, M.; Matsuno, T.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2194.

(8) Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikvar, W. *Eur. J. Inorg. Chem.* **1999**, 1211.

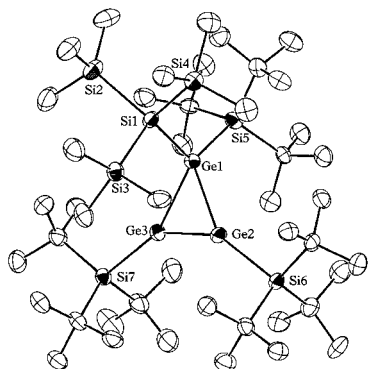


Figure 1. ORTEP drawing of **2c**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1–Ge2 2.507(2), Ge1–Ge3 2.498(2), Ge2–Ge3 2.264(2), Ge1–Si1 2.510(3), Ge1–Si5 2.510(3), Ge2–Si6 2.462(3), Ge3–Si7 2.438(3). Selected bond angles (deg): Ge2–Ge1–Ge3 53.8(1), Ge1–Ge2–Ge3 62.9(1), Ge1–Ge3–Ge2 63.3(1), Si1–Ge1–Si5 119.7(1). Selected torsion angles (deg): Si7–Ge3–Ge2–Ge1 167.5 (2), Si6–Ge2–Ge3–Ge1 175.6(2), Si6–Ge2–Ge3–Si7 8.1(2).

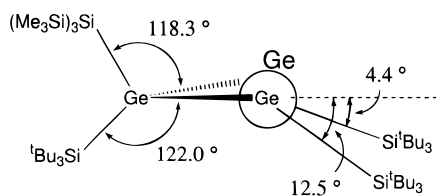


Figure 2. Schematic representation of **2c** (side view).

has a cis-bent geometry with folding angles of 12.5° for the Ge3 atom and 4.4° for the Ge2 atom (Figure 2). On the other hand, tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**2a**) has a planar Ge=Ge double bond.³ The Ge=Ge bond length of **2c** is 2.264(2) Å, and Ge–Ge bond lengths are 2.507(2) and 2.498(2) Å. The bond lengths of Ge1–Si1 (2.510(3) Å) and Ge1–Si5 (2.510(3) Å), which are attached to saturated germanium atom, are stretched significantly, as a result of the steric congestion. The bond lengths of Ge2–Si6 and Ge3–Si7, which are attached to the Ge=Ge double bond, are 2.462(3) and 2.438(3) Å, respectively. These are somewhat elongated relative to the normal one (2.38–2.39 Å).¹²

The cis-bent Ge=Ge double bond in **2c** is not due to the influence of the crystal packing, as shown by the perspective view of the crystal packing diagram. In addition, the crystal structure of **2c** can also be reproduced by *ab initio* calculations.^{13,14} The optimized structure of **2c** shows that the cis folding angles are

(12) The mean Si–Ge distances reported for $\text{Me}_3\text{Si–GePh}_3$ (2.384(1) Å) and $\text{Ph}_3\text{Si–GeMe}_3$ (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.

(13) The calculations were carried out at the Hartree–Fock level (DZ+d (exponent 0.246) for Ge, DZ for Si, and STO-2G for C and H) with effective core potentials on Ge and Si (Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, 82, 284), using the Gaussian 98 program.

8.8° and 5.8° for Ge3 and Ge2 atoms, respectively, and the torsional angles are 171.2° for Si7–Ge3–Ge2–Ge1 and 174.2° for Si6–Ge2–Ge3–Ge1. No energy minimum was found for the trans-bent form. Thus, the cis-bent geometry of **2c** is apparently caused by the steric and/or electronic effects of the substituents at the saturated germanium atom in the three-membered ring, and not by a crystal packing force.

The double-bond systems of the heavier Group 14 elements, in particular, digermenes and distannenes, show marked trans-folding of the substituents. For example, trans-bent angles of $35\text{--}47^\circ$ have been calculated for $\text{H}_2\text{Ge=GeH}_2$,¹⁵ which have been corroborated by experimental results.¹⁶ However, the introduction of electropositive substituents, such as R_3Si groups, leads to rather small trans-bent angles.¹⁷ We have achieved the unprecedented cis-bent Ge=Ge double bond by the introduction of electropositive and bulky substituents to the skeleton of cyclotrigermene.

It is quite interesting to see which substituents will be removed by the oxidation of unsymmetrically substituted cyclotrigermenes with $\text{Ph}_3\text{C}^+\text{BAR}_4$. The reaction of **2c** with $\text{Ph}_3\text{C}^+\text{TFPB}$ in benzene at room temperature led to the exclusive formation of **1·TFPB** with an 80% yield. The elimination of the tris-(trimethylsilyl)silyl group occurred selectively to form **1·TFPB**, probably due to the stability of the resulting $(t\text{-Bu}_3\text{SiGe})_3^+$ and $(\text{Me}_3\text{Si})_3\text{Si}^+$ species. The reactions of **2d** and **2e** with $\text{Ph}_3\text{C}^+\text{TFPB}$ also exclusively produced **1·TFPB**.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **2c** (PDF) and optimized structural parameters by the computational calculation (PDF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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(14) For example, the optimized bond lengths (Å) and angles (deg) of the central three-membered ring are 2.542 (Ge1–Ge2), 2.532 (Ge1–Ge3), 2.257 (Ge2–Ge3), 52.8 (Ge2–Ge1–Ge3), 63.4 (Ge1–Ge2–Ge3), and 63.8 (Ge1–Ge3–Ge2).

(15) (a) Trinquier, G.; Malrieu, J. P.; Rivière, P. *J. Am. Chem. Soc.* **1982**, 104, 4529. (b) Nagase, S.; Kudo, T. *J. Mol. Struct. (THEOCHEM)* **1983**, 103, 35. (c) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387. (d) Trinquier, G. *J. Am. Chem. Soc.* **1990**, 112, 2130. (e) Grev, R. S.; Schaefer, H. F., III; Baines, K. M. *J. Am. Chem. Soc.* **1990**, 112, 9458. (f) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, 112, 1039. (g) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, 114, 9559. (h) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, 116, 3667.

(16) For crystal structures of digermenes, see: (a) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, 25, 4191. (b) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. (c) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387. (d) Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamune, S. *J. Am. Chem. Soc.* **1990**, 112, 9394. (d) Weidenbruch, M.; Stürmann, M.; Kilian, H.; Pohl, S.; Saak, W. *Chem. Ber.* **1997**, 130, 735.

(17) Kira, M.; Iwamoto, T.; Maruyama, T.; Kabuto, C.; Sakurai, H. *Organometallics* **1996**, 15, 3767.