

On the Role of *cis,trans*-(*t*-Bu₃SiGeCl)₃ in the Reaction of GeCl₂·dioxane with Tri-*tert*-butylsilylsodium: Evidence for Existence of Digermanylsodium *t*-Bu₃SiGe(Cl)₂Ge(Cl)(Na)Si*t*-Bu₃ and Digermene *t*-Bu₃Si(Cl)Ge=Ge(Cl)Si*t*-Bu₃

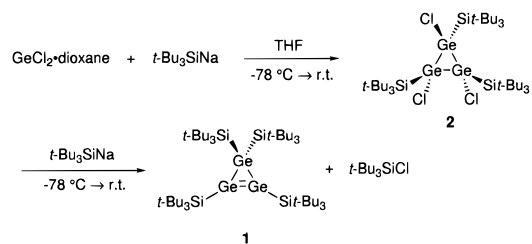
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The chemistry of three-membered ring systems containing Group 14 elements is a subject of considerable interest.¹ Almost all of these compounds have been synthesized by the reductive coupling reaction of R₂EX₂ (E = Si, Ge, Sn; X = halogen) with bulky substituents.¹ However, the most extensively studied saturated three-membered ring compounds have been limited to the type (R₂E)₃.^{1,2} We have already succeeded in the synthesis of an unsaturated germanium three-membered ring compound, cyclotrigermene (**1**), by the reaction of GeCl₂·dioxane with two molar amounts of *t*-Bu₃SiNa.^{3–5} We have also reported the conversion of **1** to the cyclotrigermanium ion, which has been shown to be not only a free germyl cation,⁶ but also a convenient precursor of the unsymmetrically substituted cyclotrigermenes.⁷ Now, the question arises: what species is involved to form **1** in the reaction of GeCl₂·dioxane with *t*-Bu₃SiNa? In this paper, evidence for the formation of digermanylsodium, *t*-Bu₃SiGe(Cl)₂Ge(Cl)(Na)Si*t*-Bu₃ as an initial intermediate which provides *t*-Bu₃Si(Cl)Ge=Ge(Cl)Si*t*-Bu₃ as a reactive intermediate, is presented. We also report the first X-ray structure of a cyclo-

Scheme 1



trigermene derivative, *cis,trans*-(*t*-Bu₃SiGeCl)₃, with reactive chlorine atoms together with its reaction with *t*-Bu₃SiNa to afford **1**.

The reaction of GeCl₂·dioxane and equimolar amount of *t*-Bu₃SiNa in tetrahydrofuran (THF) at -78 °C with subsequent warming to room temperature led to the formation of *cis,trans*-1,2,3-trichloro-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermene (**2**) in 98% yield (Scheme 1).^{8,9} Of the two possible stereoisomers, only one stereoisomer was formed. The *cis,trans* conformation of **2** was established by NMR spectroscopy⁸ and X-ray crystallography,¹⁰ as shown in Figure 1. The chlorine atoms and *t*-Bu₃Si groups occupy pseudoaxial and pseudoequatorial positions, respectively; the angles of the Cl–Ge and Si–Ge bonds to the Ge1–Ge2–Ge3 plane are 74.5–75.6° and 28.5–31.5°, respectively. The Ge–Ge bond length of 2.504 (av) Å is intermediate between that in hexakis(trimethylsilyl)cyclotrigermene (2.460(1) Å)^{4a} and those observed in carbon substituted cyclotrigermenes (2.531–2.590 Å).^{1c,2a,f,h} The Ge–Si bond length (2.460 (av) Å) is significantly longer than that in hexakis(trimethylsilyl)cyclotrigermene (2.388(4) Å),^{4a} probably due to steric repulsion.

Treatment of **2** with two molar amounts of *t*-Bu₃SiNa in THF at -78 °C followed by warming to room temperature cleanly produced **1** together with *t*-Bu₃SiCl (Scheme 1). Thus, compound **2** is an evident precursor of **1**. The reductive dechlorination of **2** by *t*-Bu₃SiNa at first occurs to form a Ge=Ge double bond in the Ge₃ ring, and the fourth *t*-Bu₃Si group is subsequently introduced to give **1**.

The reaction mixture of GeCl₂·dioxane and *t*-Bu₃SiNa afforded a yellow suspension within 10 min at -78 °C, this mixture being monitored by NMR spectroscopy. Two signals at $\delta = 21.9$ and 23.7, assignable to digermanylsodium **4**, *t*-Bu₃SiGe(Cl)₂Ge(Cl)(Na)Si*t*-Bu₃, were observed in the ²⁹Si NMR spectrum (Figure 2 and Scheme 2). The formation of **2** from **4** could be followed by ²⁹Si NMR spectroscopy. The ²⁹Si NMR spectrum was unchanged below -8 °C. However, above -8 °C, new signals at $\delta = 46.3$ and 48.3 due to **2** appeared and grew with a simultaneous decrease of the signals due to **4**. The digermene **4** was quenched by hydrochloric acid at -78 °C to give a protonated product **5a** in

(8) The colorless crystals of GeCl₂·dioxane (73 mg, 0.32 mmol) and *t*-Bu₃SiNa (70 mg, 0.32 mmol) were placed in a glass reaction vessel. After degassing, dry, oxygen-free THF (2 mL) was introduced by vacuum transfer. The reaction mixture was stirred at -78 °C to give a yellow suspension within 10 min and then allowed to warm to room temperature. After evaporation of the solvent, **2** was obtained as pale yellow crystals (95 mg, 98% yield); mp 146 °C dec; ¹H NMR (C₆D₆, δ) 1.379 (s, 54 H), 1.389 (s, 27 H); ¹³C NMR (C₆D₆, δ) 25.8, 26.2, 31.9, 32.0; ²⁹Si NMR (C₆D₆, δ) 46.3, 48.3; MS (EI, 70 eV) 914 – 930 (M⁺) for C₃₆H₈₁Cl₃Ge₃Si₃.

(9) Wiberg et al. briefly described in the footnote of ref **5a** that **2** was initially formed together with [(*t*-Bu₃Si)₂GeCl₂] by the reaction of GeCl₂·dioxane with *t*-Bu₃SiNa, but the characterization of **2** was based only on NMR spectral data. However, their reported NMR spectral data are somewhat different from ours.

(10) The single crystals for X-ray analysis were obtained by the recrystallization from hexane. Crystal data for **2**·(*n*-C₆H₁₄)_{0.5} at 120 K: MF = C₃₉H₈₈Cl₃Ge₃Si₃, MW = 965.48, monoclinic, P2₁/c, *a* = 13.4370(3) Å, *b* = 30.791(1) Å, *c* = 13.6260(5) Å, β = 116.324(2)°, *V* = 5053.0(3) Å³, *Z* = 4, *D*_{calc} = 1.269 g·cm⁻³. The final *R* factor was 0.0487 for 9939 reflections with *I*_o > 2 σ (*I*_o) (*R*_w = 0.1388 for all data, 11335 reflections).

(1) For the reviews on the small ring system of Group 14 elements, see: (a) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 1627. (b) Barrau, J.; Escudé, 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) Nagase, S. *Polyhedron* **1991**, 10, 1299. (e) Sekiguchi, A.; Sakurai, H. *The Chemistry of Inorganic Ring Systems*; Stedel, R., Ed.; Elsevier: New York, 1992; Chapter 7. (f) Escudé, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, 130, 427. (g) Mackay, K. M. *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Patai, S., Ed.; John Wiley & Sons Ltd.: New York, 1995; Chapter 2. (h) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, 39, 275. (i) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 828. (j) Kaftory, M.; Kapon, M.; Botoshansky, M. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Vol. 2, Part 1, Chapter 5. (k) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373.

(2) (a) Masamune, S.; Hanazawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, 104, 6136. (b) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, 25, 4191. (c) Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* **1985**, 26, 1281. (d) Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, 29, 3383. (e) Masamune, S.; Batcheller, S. A.; Park, J.; Davis, W. M.; Yamaguchi, O.; Ohta, Y.; Kabe, Y. *J. Am. Chem. Soc.* **1989**, 111, 1888. (f) Baines, K. M.; Cooke, J. A.; Payne, N. C.; Vittel, J. J. *Organometallics* **1992**, 11, 1408. (g) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514. (h) Weidenbruch, M.; Grimm, F.-T.; Herrndorf, M.; Schäfer, A. *J. Organomet. Chem.* **1988**, 341, 335.

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

(4) The reaction of GeCl₂·dioxane with two molar amounts of (Me₃Si)₃GeLi afforded cyclotrigermene, [(Me₃Si)₂Ge]₃, together with tetrachlorocyclotetragermene, [(Me₃Si)₂GeGeCl]₄, see: (a) Mallela, S. P.; Hill, S.; Geanangel, R. A. *Inorg. Chem.* **1997**, 36, 6247. With (Me₃Si)₂SiLi, disilagermirene derivative was formed, see: (b) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 113.

(5) Tetragermatetrahedrane was isolated by the reaction of the same reagents under different conditions, see: (a) Wiberg, N.; Hochmuth, W.; Nöth, H.; Appel, A.; Schmidt-Amelunxen, M. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1333. (b) Wiberg, N. *Coord. Chem. Rev.* **1997**, 163, 217.

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(7) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **1999**, 121, 11587.

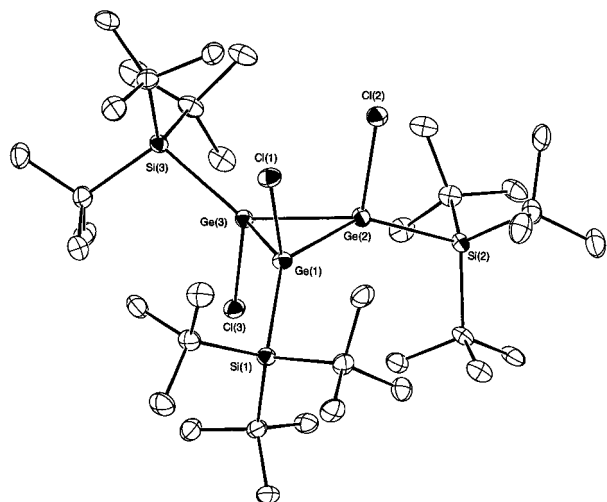


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1–Cl1 2.2120(8), Ge1–Si1 2.4532(9), Ge1–Ge(3) 2.4883(5), Ge1–Ge2 2.5306(4), Ge2–Cl2 2.2237(8), Ge2–Si2 2.4731(8), Ge2–Ge3 2.4931(5), Ge3–Cl3 2.2328(8), Ge3–Si3 2.4547(9). Selected bond angles (deg): Cl1–Ge1–Ge3 104.05(3), Si1–Ge1–Ge3 138.04(3), Cl1–Ge1–Ge2 102.69(2), Si1–Ge1–Ge2 139.77(3), Ge3–Ge1–Ge2 59.56(1), Cl2–Ge2–Ge3 103.12(3), Si2–Ge2–Ge3 134.87(3), Cl2–Ge2–Ge1 101.76(3), Si2–Ge2–Ge1 144.21(3), Ge3–Ge2–Ge1 59.38(1), Cl3–Ge3–Si3 106.43(3), Si3–Ge3–Ge1 135.32(2), Cl3–Ge3–Ge2 102.46(2), Si3–Ge3–Ge2 139.11(2), Ge1–Ge3–Ge2 61.06(1).

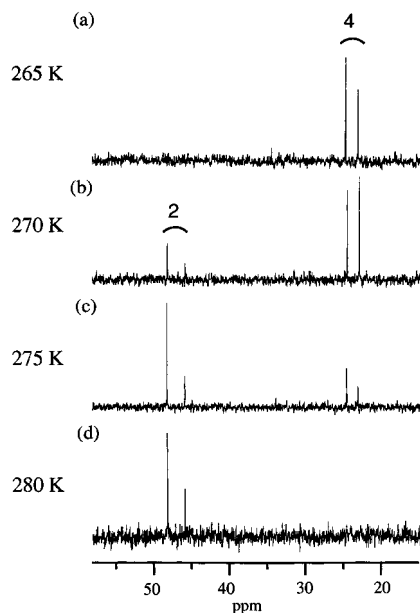


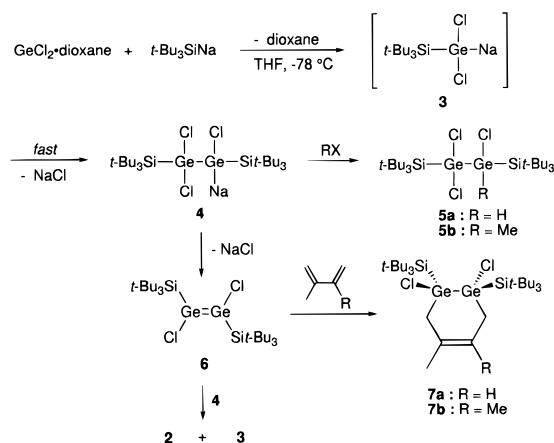
Figure 2. Thermal reaction of digermanylsodium **4** monitored by ^{29}Si NMR spectroscopy in $\text{THF-}d_8$ with increasing temperature.

a quantitative yield.¹¹ With iodomethane, a methylated product **5b** was quantitatively obtained.¹¹

Above -8°C , the digermenoid **4** undergoes selective β -elimination to give the digermene intermediate, $t\text{-Bu}_3\text{Si}(\text{Cl})\text{Ge}=\text{Ge}(\text{Cl})\text{Si}t\text{-Bu}_3$ (**6**), which is not isolable but can be trapped (Scheme

(11) All of the new products obtained here showed the satisfactory spectral and analytical data.

Scheme 2



2). In the presence of an excess amount of isoprene, a THF solution of **4** was allowed to warm to room temperature to afford the 1,2-digermacyclohex-4-ene derivative **7a** (45%)¹¹ as a single stereoisomer together with **2** (24%). With 2,3-dimethyl-1,3-butadiene, **7b** (41%)^{11,12} was obtained along with **2** (8%). In both cases, none of the germacyclopent-3-ene derivative was formed, indicating that α -elimination to generate a germylene intermediate is not involved.

Thus, it is reasonable to assume the following mechanism for the reaction of $\text{GeCl}_2\cdot\text{dioxane}$ with $t\text{-Bu}_3\text{SiNa}$. At first, the insertion of GeCl_2 into the Si–Na bond occurred to form $t\text{-Bu}_3\text{SiGe}(\text{Cl})_2\text{Na}$ (**3**), which underwent bimolecular self-condensation even at -78°C to afford **4**, stable at low temperature (Scheme 2).¹³ Second, above -8°C , thermal decomposition of **4** occurred to produce **6** as a transient intermediate.¹⁴ Finally, intermediately formed digermene **6** consumed because of the reaction with the digermenoid **4**, followed by cyclization with formation of **2** and dichlorogermylsodium **3**.¹⁵ The resulting **3** was transformed into the final product **2**. Thus, cyclotrigermane **2** is exclusively produced in the absence of a trapping reagent.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **2** and **7b**, experimental procedure and spectral data of **5a**, **5b**, **7a**, and **7b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Crystal data for **7b** at 120 K: MF = $\text{C}_{30}\text{H}_{64}\text{Cl}_2\text{Ge}_2\text{Si}_2$, MW = 697.07, monoclinic, $P2_1/c$, $a = 13.2170(3)\text{Å}$, $b = 16.9900(3)\text{Å}$, $c = 17.4050(3)\text{Å}$, $\beta = 111.787(1)^\circ$, $V = 3629.2(1)\text{Å}^3$, $Z = 4$, $D_{\text{calcd}} = 1.276\text{ g}\cdot\text{cm}^{-3}$. The final R factor was 0.0324 for 8175 reflections with $I_o > 2\sigma(I_o)$ ($R_w = 0.0894$ for all data, 8660 reflections).

(13) Tamao et al. have reported the reactivities of an alkoxysilyllithium named “silylenoid”, which undergoes bimolecular self-condensation to give disilyanyllithium, see: (a) Tamao, K.; Kawachi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 818. (b) Kawachi, A.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 945.

(14) One of the reviewers has pointed out the possibility of α -elimination in **4** with formation of germylene $t\text{-Bu}_3\text{Si}(\text{Cl})\text{Ge}$: and **3** followed by condensation of the germylene on **6** giving **2**. However, this possibility is unlikely, because none of the germacyclopent-3-ene derivative is formed in the presence of isoprene or 2,3-dimethyl-1,3-butadiene.

(15) The addition of Grignard reagents and RLi to $\text{Ge}=\text{Ge}$ and $\text{Ge}=\text{Si}$ has a precedent, see: Dixon, C. E.; Netherton, M. R.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 10365.