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The First Three-Membered Unsaturated Rings Consisting of Different Heavier Group 14 Elements: 1-Disilagermirene with a Si═Si Double Bond and Its Isomerization to a 2-Disilagermirene with a Si═Ge Double Bond

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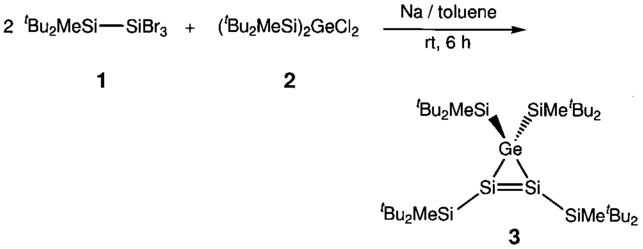
The chemistry of highly strained three-membered rings consisting of heavier group 14 elements has attracted considerable attention because of their unique structures.[1] Following the discovery of stable cyclotrimetallanes $(R_2M)_3$ (M = Si,[2] Ge,[3] Sn[4]), great progress has been made during the last two decades concerning their synthesis, structural characterization and reactivity. There are only four examples for the mixed compounds, consisting of two different heavier group 14 elements: digermasilirane synthesized by Baines,[5] two disilagermiranes by Stalke[6] and Watanabe,[7] and distannagermirane prepared by Escudié.[8] Cyclotrimetallenes (R_4M_3) with endocyclic metal−metal double bonds have been prepared quite recently: cyclotrigermenes were synthesized in 1995 by our group,[9] cyclotrisilenes were reported by Kira[10] and our group[11] in 1999, and cyclotristannene was prepared by Wiberg[12] in 1999. Mixed cyclotrimetallenes, consisting of two different group 14 elements, were still unknown, although one can expect very interesting and unusual properties of such molecules. Here we report the synthesis, full characterization and molecular structure of the first mixed cyclotrimetallene, 1-disilagermirene **3**, as well as its photochemical and thermal isomerization to a stable 2-disilagermirene **4**.

Scheme 1



The reaction of 2,2,2-tribromo-1,1-di(*tert*-butyl)-1-methyldisilane **1** and dichlorobis[di-*tert*-butyl(methyl)silyl]germane **2** with excess sodium in toluene at room temperature produced a dark-red reaction mixture, which contains tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene **3** as a major product (Scheme 1).[13]

1-Disilagermirene **3** was isolated as hexagonal ruby crystals by recrystallization from hexane. The 1-disilagermirene **3** is a very air- and moisture-sensitive compound and the red solution of **3** immediately decolorized upon exposure to air. ${}^1H$- and ${}^{13}C$ NMR spectra correspond well to a symmetrical structure for **3**, showing only two sets of signals for methyl- and *tert*-butyl groups, whereas the ${}^{29}Si$ NMR spectrum revealed three resonances: +18.7, +25.6, and +92.2 ppm, of which the first two belong to the silyl-substituents, and the last one is characteristic of the Si═Si double bond.

The molecular structure of **3** was determined by X-ray crystallography (Figure 1).[14] The three-membered ring represents an almost isosceles triangle with bond angles of 52.71(3), 63.76(3), and 63.53(3)°. The silicon−silicon double bond length of **3** is 2.146(1) Å, which is rather short compared with other Si═Si bond distances reported thus far (2.138−2.289 Å).[1i,15] The average bond length between germanium and the two silicon atoms in the ring is 2.417(1) Å, which is intermediate between the endocyclic Ge−Ge bond length of 2.522(4) Å in cyclotrigermene[9] and the Si−Si bond length of 2.358(3) Å in cyclotrisilene.[11] The geometry around the Si═Si double bond is not planar but *trans*-bent,[16] as was determined by the sum of the bond angles of the unsaturated silicon atoms (357.4° for Si1 and 356.9° for Si2), with a torsional angle Si3−Si1−Si2−Si4 of 37.0°

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(1) For the reviews on three-membered ring systems and doubly-bonded compounds consisting of group 14 elements, see: (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (c) Sekiguchi, A.; Sakurai, H. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Chapter 7, Elsevier (**1992**). (d) Tsumuraya, T.; Kabe, Y.; Ando, W. *J. Organomet. Chem.* **1994**, *482*, 131. (e) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (f) Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479. (g) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (h) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (i) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Vol. 2, Part 1, Chapter 5. (j) Sekiguchi, A.; Nagase, S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Vol. 2, Part 1, Chapter 3. (k) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373.

(2) Masamune, S.; Hanzawa, W.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(3) Masamune, S.; Hanzawa, W.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6137.

(4) Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630.

(5) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419.

(6) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 113.

(7) Suzuki, H.; Okabe, K.; Uchida, S.; Watanabe, H.; Goto, M. *J. Organomet. Chem.* **1996**, *509*, 177.

(8) Chaubon, M.-A.; Escudié, J.; Ranaivonjatovo, H.; Satgé, J. *Chem. Commun.* **1996**, 2621.

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

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

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

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

(13) Compound **3** was synthesized by the following procedure: a mixture of ${}^tBu_2MeSi-SiBr_3$ (**1**) (1.45 g, 3.41 mmol) and $({}^tBu_2MeSi)_2GeCl_2$ (**2**) (0.74 g, 1.62 mmol) in dry, oxygen-free toluene (10 mL) was added to a fine sodium suspension (0.76 g, 33.3 mmol) in toluene (10 mL) at room temperature under vigorous stirring. Reaction progress was monitored by GC by the disappearance of **1**, and reaction was finished in 6 h. Excess sodium and inorganic salts were filtered off and solvent was evaporated in a vacuum. Recrystallization of the residue from hexane at −30 °C gave **3** as ruby hexagonal crystals (0.36 g, 29 %); mp 205−207 °C.; ${}^1H$ NMR (C_6D_6, δ) 0.46 (s, 6 H), 0.49 (s, 6 H), 1.22 (s, 36 H), 1.28 (s, 36 H); ${}^{13}C$ NMR (C_6D_6, δ) −4.5, -2.2, 22.2, 23.6, 30.0, 31.0; ${}^{29}Si$ NMR (C_6D_6, δ) 18.7, 25.6, 92.2; MS (EI, 70 eV) 758 (M^+, 0.1), 701 ($M^+ - {}^tBu$, 0.05), 601 ($M^+ - SiMe{}^tBu_2$, 2.6), 73 (100); UV/vis (hexane) λ_{max}/nm (ϵ) 230 (33440), 259 (18220), 308 (6300), 469 (1890); Anal. Calcd for $C_{36}H_{84}GeSi_6$: C, 57.03; H, 11.17. Found: C, 57.42; H, 10.75.

(14) Crystal data for **3** at 150 K: MF = $C_{36}H_{84}GeSi_6$, MW = 758.16, monoclinic, $P2_1/c$, $a = 24.131(1)$ Å, $b = 11.6630(6)$ Å, $c = 17.760(1)$ Å, $\beta = 110.362(4)°$, $V = 4686.0(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.075$ g·cm^{-3}. The final R factor was 0.0589 for 7920 reflections with $I_o > 2\sigma(I_o)$ ($R_w = 0.1691$ for all data, 10779 reflections). GOF = 1.044.

(15) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.

(16) The geometry around the metal−metal double bond in cyclotrimetallenes depends on the nature of the metal and the substituents. Thus, tetrakis(tri-*tert*-butylsilyl)cyclotrigermene[9] and tetrakis(tri-*tert*-butylsilyl)cyclotristannene[12] have a planar configuration, tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene[11] exhibits a *trans*-bent structure, whereas 1,2,3-tris(tri-*tert*-butylsilyl)-3-[tris(trimethylsilyl)silyl] cyclotrigermene reveals a *cis*-bent geometry around the Ge═Ge double bond, see: Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Takagi, N, Nagase, S. *J. Am. Chem. Soc.* **1999**, *121*, 11587.

10.1021/ja001551s CCC: $19.00

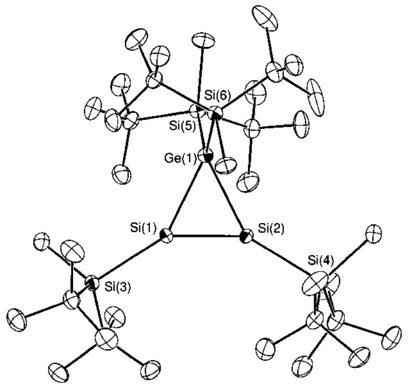
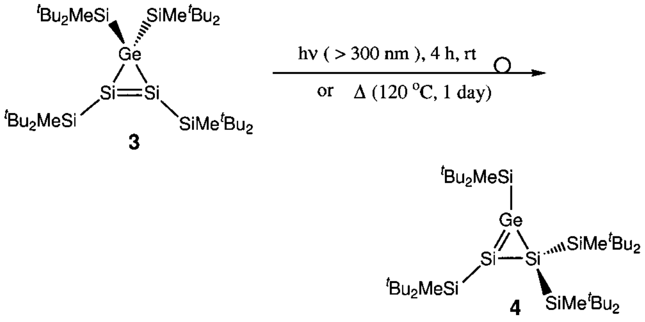


Figure 1. ORTEP drawing of **3**. Hydrogen atoms are omitted for the clarity. Selected bond lengths (Å): Si(1)−Si(2) 2.146(1), Ge(1)−Si(1) 2.415(1), Ge(1)−Si(2) 2.420(1), Ge(1)−Si(5) 2.435(1), Ge(1)−Si(6) 2.432(1), Si(1)−Si(3) 2.361(1), Si(2)−Si(4) 2.367 (1). Selected bond angles (deg): Ge(1)−Si(1)-Si(2) 63.76(3), Ge(1)−Si(2)−Si(1) 63.53(3), Si(1)−Ge(1)−Si(2) 52.71(3), Si(5)−Ge(1)−Si(6) 123.33(3). Selected torsion angle (deg): Si(3)−Si(1)−Si(2)−Si(4) 37.0(2).

Scheme 2



(2). One of the possible reasons for such twisting of the Si═Si double bond may be the eclipsed conformation of the two ᵗBu₂-MeSi substituents connected to the unsaturated silicon atoms.

Photolysis of the deuteriobenzene solution of **3** with a high-pressure Hg-lamp ($\lambda > 300$ nm) for 4 h caused a migration of the silyl substituent with the formation of an endocyclic Si═Ge double bond system (Scheme 2). The reaction proceeds quite cleanly and the 2-disilagermirene **4** was formed almost quantitatively. This is the first example of a stable germasilene reported to date.[17]

The 2-disilagermirene **4** was isolated as scarlet plate crystals from the hexane solution and appeared to be extremely thermally stable with a melting point of 194−196 °C.[18] ^{1}H- and ^{13}C NMR spectra of **4** are more complicated than those of **3**, because the 2-disilagermirene **4** has lost the C_{2v} symmetry of the 1-disilagermirene **3**. Thus, the ^{1}H NMR spectrum of **4** showed three resonances for three types of methyl groups and four resonances for four non-equivalent *tert*-butyl groups, whereas the ^{13}C NMR spectrum showed three sets of signals both for methyl and *tert*-butyl groups. The ^{29}Si NMR spectrum showed five signals, of which three belong to the silyl substituents, +39.5, +27.8, and +6.9; the endocyclic double-bonded Si atom exhibits a downfield resonance at +99.3, and the endocyclic saturated Si atom has an upfield resonance at −120.1 ppm.

The molecular structure of **4** was established by X-ray crystallography, which revealed the triangle structure composed of one saturated silicon atom, one unsaturated silicon and one unsaturated germanium atoms. Unfortunately, accurate determination of bond lengths and angles in the three-membered ring was impossible because of significant disorder in the positions of double-bonded Si and Ge atoms. Nevertheless, it was possible to determine the geometry around the Si═Ge double bond, which also has the *trans*-bent configuration with a torsion angle of 40.3(5)°.

The isomerization of **3** to **4** can also be performed under thermal conditions. Thus, thermolysis of the solution of **3** in mesitylene at 120 °C in a sealed NMR tube cleanly produced 2-disilagermirene **4** in 1 day. Thermal reaction of **3** produced an equilibrium mixture of **3** (~2%) and **4** (~98%), from which it is roughly estimated that **4** is more stable than **3** by ~3 kcal/mol.

Ab initio molecular orbital and density functional calculations were carried out for the model H$_3$Si-substituted 1-disilagermirene **5** and 2-disilagermirene **6** at the MP2/DZd and B3LYP/DZd levels.[19] The Si═Si double bond length in **5** was calculated to be 2.105 (MP2) and 2.107 Å (B3LYP), which correspond well to the experimental value of 2.146 Å, and the Si═Ge double bond length in **6** was predicted to be 2.180 (MP2) and 2.178 Å (B3LYP), which are closer to the Si═Si than the Ge═Ge double bond length.[20] It was also found that **6** is more stable than **5** by 3.9 (MP2) and 2.3 (B3LYP) kcal/mol. These values are in good agreement with the experimentally estimated value of ~3 kcal/mol.[19] The geometries around the Si═Si and Si═Ge double bonds were calculated to be planar for **5** and **6**, although they are *trans*-bent in **3** and **4** according to the X-ray data. However, introduction of the real substituents led to a *trans*-bent configuration; the bend angle was 18.5° at the HF/DZd level for 1-disilagermirene **3**.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **3**, optimized structural parameters of H$_3$Si-substituted 1-disilagermirene **5** and 2-disilagermirene **6** at the MP2/DZd level by the computational calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] The only example of a germasilene reported to date is tetramesitylgermasilene, but this compound is unstable and can survive only at low temperature, see: Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487.

[18] Spectral data for **4**: scarlet plate crystals; mp 194−196 °C.; ^{1}H NMR (C$_6$D$_6$, δ) 0.43 (s, 6 H), 0.48 (s, 3 H), 0.53 (s, 3 H), 1.20 (s, 18 H), 1.22 (s, 18 H), 1.29 (s, 18 H), 1.30 (s, 18 H); ^{13}C NMR (C$_6$D$_6$, δ) −4.6, −3.9, −2.2, 22.2, 22.8, 23.4, 29.9, 30.0, 31.3; ^{29}Si NMR (C$_6$D$_6$, δ) −120.1, 6.9, 27.8, 39.5, 99.3; MS (EI, 70 eV) 758 (M$^+$, 3.2), 701 (M$^+$ − ᵗBu, 1.5), 601 (M$^+$ − SiMeᵗBu$_2$, 31.6), 73 (100); UV/vis (hexane) λ_{max}/nm (ϵ) 235 (58100), 263 (27000), 301 (11600), 395 (1600), 467 (4200); Anal. Calcd for C$_{36}$H$_{84}$GeSi$_6$: C, 57.03; H, 11.17. Found: C, 56.53; H, 10.84.

[19] The calculations were carried out with effective core potentials and double-ζ (DZ) basis sets on Si and Ge (Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284) augmented by d-type polarization functions (d exponent 0.45 (Si), 0.246 (Ge)) and 3-21G on H, using the Gaussian 98 program. For the calculations of **3**, STO-2G was used for C and H.

[20] Typical values for a Si═Si double bond length range from 2.138 to 2.289 Å,[1i,15] whereas Ge═Ge double bond lengths lie in the range 2.213−2.347 Å.[1e]