

Ring Contraction of 1,2-Digermacyclohexa-1,4-diene to (Germacyclopent-3-enyl)germylene

Norihisa Fukaya, Masaaki Ichinohe, Yoshio Kabe, and Akira Sekiguchi*

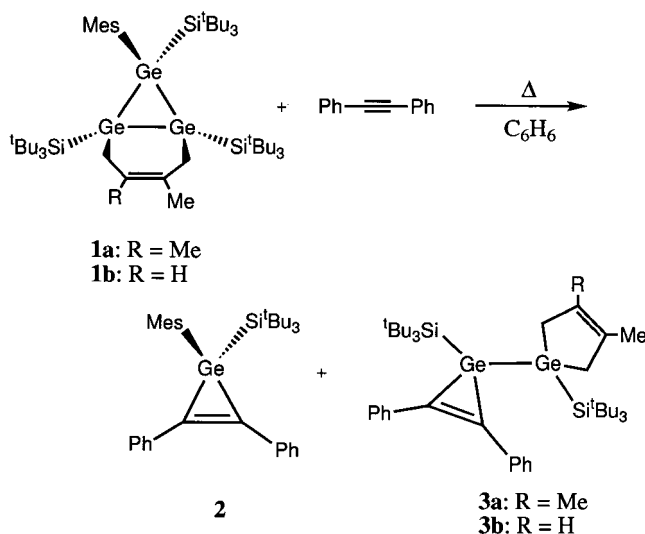
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

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Summary: Thermolysis of *cis,cis*-1,6,7-trigerma-1,6,7-tris(tri-*tert*-butylsilyl)-7-mesityl-3,4-dimethylbicyclo[4.1.0]hept-3-ene (**1a**) and *cis,cis*-1,6,7-trigerma-1,6,7-tris(tri-*tert*-butylsilyl)-7-mesityl-3-methylbicyclo[4.1.0]hept-3-ene (**1b**) at 70 °C in benzene in the presence of diphenylacetylene and triethylsilane yielded products arising from (germacyclopent-3-enyl)germylene, which is formed by the ring contraction of 1,2-digermacyclohexa-1,4-diene. Theoretical calculations on this contraction reaction leading from a six-membered ring with a Ge=Ge double bond to a five-membered ring have also been performed.

The chemistry of unsaturated cyclic compounds containing group 14 elements heavier than carbon is a recent subject of considerable interest.^{1,2} Synthetic methodologies and studies of the structural features of such compounds have developed quickly during the past 5 years.² Ring contraction and expansion reactions of unsaturated cyclic compounds are very important and well-established in organic chemistry; however, such reactions are very rare in the chemistry of heavier group 14 elements.³ Recently, we have succeeded in synthesizing bicyclic 1,6,7-trigerma-bicyclo[4.1.0]hept-3-ene and 1,4,5-trigerma-bicyclo[2.1.0]pent-2-ene derivatives by a cycloaddition reaction of 2,3-dimethyl-1,3-butadiene or isoprene and phenylacetylene to the endocyclic Ge=Ge double bond of mesityl-substituted cyclotrimerene.⁴ We presumed that the present fused bicyclic cyclotrimer-

Scheme 1



manes could be suitable precursors of the unsaturated germanium compounds by the cycloelimination reaction, since the thermal and photochemical generation of digermenes and germylenes from the cyclotrimeranes is well-established.¹ Thus, we examined the thermal reaction of the 1,6,7-trigerma-bicyclo[4.1.0]hept-3-ene derivative in the presence of diphenylacetylene and triethylsilane and found an unprecedented ring contraction of a 1,2-digermacyclohexa-1,4-diene to a (germacyclopent-3-enyl)germylene derivative. We here report the first example of a facile ring contraction of unsaturated cyclic germanium compounds, studied from both the experimental and theoretical points of view.

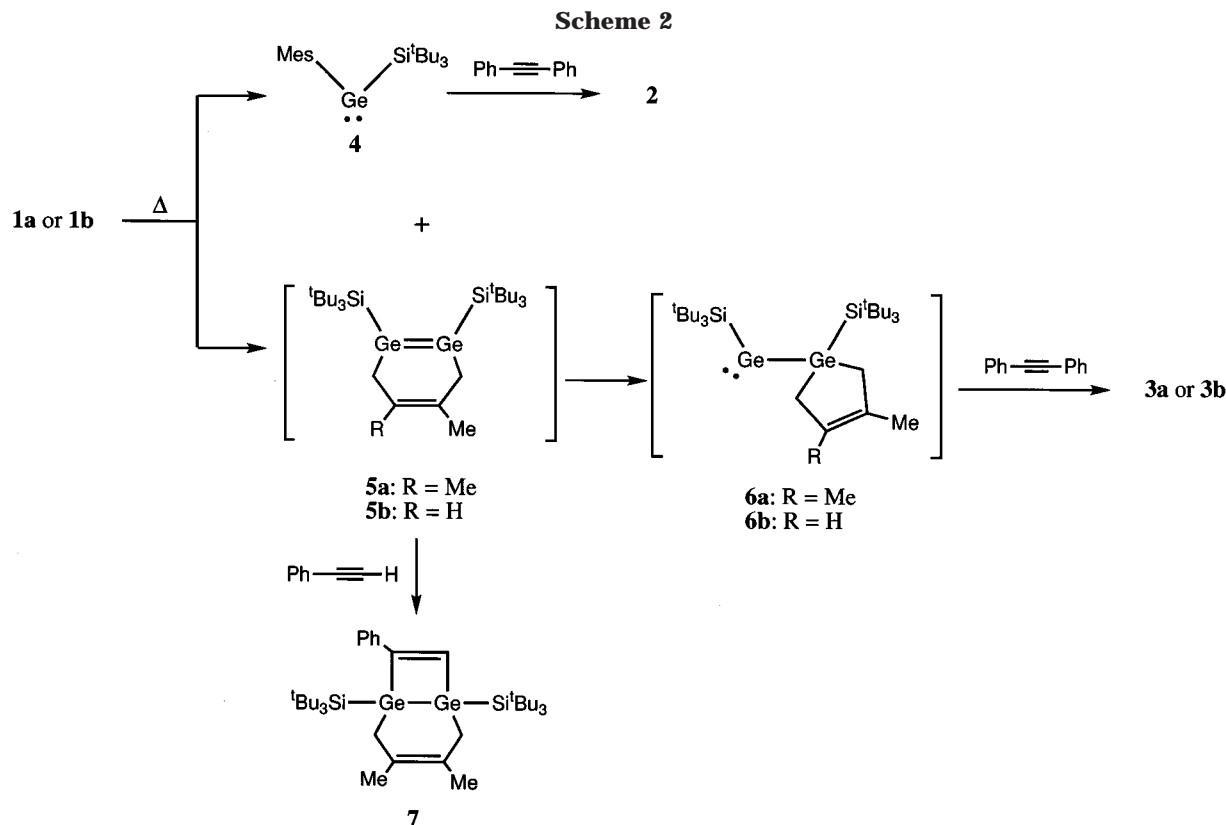
Thermolysis of a benzene solution of 1,6,7-trigerma-bicyclo[4.1.0]hept-3-ene (**1a**)⁴ for 6 h at 70 °C in a sealed tube in the presence of diphenylacetylene afforded colorless crystals of the germacyclopentene derivative **2** in 82% yield and pale yellow crystals of the germacyclopentylgermacyclopentene derivative **3a** in 53% yield (Scheme 1).⁵ Thermolysis of **1b** with diphenylacetylene also gave **2** (88%) and **3b** (58%). However, no evidence for the [2 + 2] reaction of the 1,2-digermacyclohexa-1,4-diene species **5** with diphenylacetylene to form the 1,6-digerma-bicyclo[4.2.0]octa-3,7-diene derivative was found. Interestingly, thermal reaction of **1a** in the presence of phenylacetylene proceeded in a different way to give colorless crystals of 3,4-dimethyl-7-phenyl-1,6-bis[tris(tri-*tert*-butylsilyl)]-1,6-digerma-bicyclo[4.2.0]octa-3,7-diene (**7**) in 77% yield, arising from [2 + 2] cycloaddition of **5a** with phenylacetylene.⁶

(4) Fukaya, N.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3881.

(1) (a) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (b) Mackay, K. M. *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Patai, S., Ed.; Wiley: New York, 1995; Chapter 2. (c) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (d) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (e) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (f) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (g) Escudé, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113.

(2) (a) Cyclotrimeranes: Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025. (b) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **1999**, *121*, 11587. Cyclotetrasilenes: (c) Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1996**, *118*, 10303. (d) Wiberg, N.; Auner, H.; Nöth, H.; Knizek, J.; Polborn, K. *Angew. Chem., Int. Ed.* **1998**, *36*, 2869. Cyclotrisilenes: (e) Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 886. (f) Ichinohe, M.; Matsuno, T.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2194. Disilagermirenes: (g) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, J. *Am. Chem. Soc.* **2000**, *122*, 9034. Spiropentasiladiene: (h) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504. Chalcogenatetrasilacyclopentenes: (i) Grybat, A.; Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2010. Cyclostannene: (j) Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikvar, W. *Eur. J. Inorg. Chem.* **1999**, 1211. Disilagermacyclopentadiene: (k) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604.

(3) Isomerization of a 4-silamethylenecyclopropene derivative to a silacyclobutadiene derivative was reported; see: (a) Sakamoto, K.; Ogasawara, J.; Sakurai, H.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 3405. (b) Veszprémi, T.; Takahashi, M.; Ogasawara, J.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 2408.



The formation of products **2** and **3** clearly shows the existence of intermediate germynes **4** and **6** during the thermolysis of **1** (Scheme 2). It seems that the 1,2-digermacyclohexa-1,4-diene **5**, which could be initially formed by the cycloelimination of **1**, does not undergo [2 + 2] cycloaddition with diphenylacetylene, probably because of steric reasons. Alternatively, the resulting **5** undergoes a ring contraction to give the germylene **6**, which then reacts with diphenylacetylene to form compound **3**.

The molecular structure of **3b** was unambiguously characterized by X-ray crystallography, as shown in

(5) Procedure of thermolysis of **1a** in the presence of diphenylacetylene. The yellow crystals of **1a** (50 mg, 0.049 mmol) and diphenylacetylene (40 mg, 0.22 mmol) were placed in a reaction tube with a magnetic stirrer. Dry degassed benzene (0.6 mL) was introduced by vacuum transfer, and then the tube was sealed. The mixture was heated for 6 h at 70 °C. The solvent was removed in vacuo, and the resulting residue was separated by gel permeation chromatography to give **2** (23 mg, 82%) and **3a** (21 mg, 53%). **2**: colorless crystals; mp 145–148 °C; ¹H NMR (C₆D₆, δ) 1.25 (s, 27 H), 2.06 (s, 3 H), 2.85 (s, 6 H), 6.72 (s, 2 H), 7.02 (t, *J* = 7 Hz, 2 H), 7.16 (t, *J* = 7 Hz, 4 H), 7.68 (d, *J* = 7 Hz, 4 H); ¹³C NMR (C₆D₆, δ) 21.0, 25.1, 26.5, 31.8, 127.1, 128.4, 128.5, 128.7, 136.4, 137.8, 142.5, 143.4, 148.9; ²⁹Si NMR (C₆D₆, δ) 25.3. Anal. Calcd for C₃₅H₄₈GeSi: C, 73.82; H, 8.50. Found: C, 73.35; H, 8.48. **3a**: pale yellow crystals; mp 194–197 °C; ¹H NMR (C₆D₆, δ) 1.13 (s, 27 H), 1.25 (s, 27 H), 1.87 (s, 6 H), 2.34 (d, *J* = 17 Hz, 2 H), 2.40 (d, *J* = 17 Hz, 2 H), 7.05 (t, *J* = 7 Hz, 2 H), 7.24 (t, *J* = 7 Hz, 4 H), 7.92 (d, *J* = 7 Hz, 4 H); ¹³C NMR (C₆D₆, δ) 19.8, 24.7 (2C), 31.9, 32.1, 32.4, 127.6, 128.5, 130.2, 132.4, 135.3, 144.0; ²⁹Si NMR (C₆D₆, δ) 27.7, 36.5. Anal. Calcd for C₄₄H₇₄Ge₂Si₂: C, 65.70; H, 9.27. Found: C, 65.32; H, 9.14.

(6) Spectroscopic data for **7**: mp 179–182 °C; ¹H NMR (C₆D₆, δ) 1.19 (s, 27 H), 1.30 (s, 27 H), 1.88 (s, 3 H), 2.04 (s, 3 H), 2.11–2.18 (m, 2 H), 2.32–2.41 (m, 1 H), 2.69–2.74 (m, 1 H), 7.00 (t, *J* = 9 Hz, 2 H), 7.12 (t, *J* = 9 Hz, 1 H), 7.25 (s, 1 H), 7.32 (d, *J* = 9 Hz, 2 H); ¹³C NMR (C₆D₆, δ) 22.1, 22.5, 24.5, 24.6, 30.6, 31.5, 31.8, 31.9, 123.1, 125.5, 126.4, 126.7, 128.1, 146.1, 151.4, 170.3; ²⁹Si NMR (C₆D₆, δ) 27.9, 29.7. Anal. Calcd for C₃₈H₇₀Ge₂Si₂: C, 62.67; H, 9.69. Found: C, 63.16; H, 9.32. Crystal data for **7**·0.5(toluene) at 120 K: molecular formula C₃₈H₇₀Ge₂Si₂·0.5C₇H₈, mol wt 774.37, triclinic, *a* = 9.3000(8) Å, *b* = 12.303(1) Å, *c* = 19.992(1) Å, α = 75.719(5)°, β = 85.135(5)°, γ = 74.544(4)°, *V* = 2136.1(3) Å³, space group *PI*, *Z* = 2, *D*_{calc} = 1.204 g/cm³. The final *R* factor was 0.0499 (*R*_w = 0.1301 for all data) for 9484 reflections with *I* > 2σ(*I*). GOF = 1.042.

Figure 1.⁷ The five-membered ring is nearly planar (sum of interior angles 538.9°). Although the Ge–C bond lengths of the three-membered ring (1.980(3) and 1.985(3) Å) slightly exceed the upper limit of literature values of germacyclopropenes (typically 1.88–1.94 Å), the C=C double bond (1.328(5) Å) is relatively short (typically 1.33–1.39 Å).⁸ The Ge–Ge bond (2.4922(5) Å) and Ge–Si bonds (2.449(1) and 2.439(1) Å) are elongated by the steric repulsion.


To confirm the formation of the germylene **6**, we have also examined thermolysis of **1** in the presence of triethylsilane, which can react exclusively with the divalent species. Thus, thermolysis of **1a** with an excess of triethylsilane for 6 h at 70 °C yielded (tri-*tert*-butylsilyl)(triethylsilyl)(mesityl)germane (**8**) in 86% yield and digermene derivative **9** in 83% yield (Scheme 3).⁹ These compounds appear to be derived from the insertion of the resulting germylene **4** and (germacyclopentenyl)germylene **6a** into the Si–H bond of triethylsilane, respectively.

Baines et al. reported the facile digermene-to-germylgermylene and gemasilene-to-silylgermylene rearrangements by 1,2-mesityl shifts of tetramesityldigermene

(7) Single crystals of **3b** were obtained by recrystallization from hexane. Crystal data for **3b** at 120 K: molecular formula C₄₃H₇₂Ge₂Si₂, mol wt 790.37, monoclinic, *a* = 14.6250(8) Å, *b* = 14.6190(7) Å, *c* = 20.1150(11) Å, β = 91.077(4)°, *V* = 4299.9(4) Å³, space group *P2*₁/*n*, *Z* = 4, *D*_{calc} = 1.221 g/cm³. The final *R* factor was 0.0559 (*R*_w = 0.1631 for all data) for 10 018 reflections with *I* > 2σ(*I*). GOF = 1.091. The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELXL-97 program. The position of the carbon atom of the methyl group attached to the C=C double bond of the five-membered ring is disordered between the C40 and C41 atoms, and the molecular structure with the largest occupancy (70%, C43 bonded to C40) is shown in Figure 1.

(8) (a) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Y. T.; Antipin, M. Y.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27. (b) Ando, W.; Ohgaki, H.; Kabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 659. (c) Tokitoh, N.; Kishikawa, K.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 827.

Table 1. Relative Energies (in kcal/mol) of the Digermenes, the Corresponding Germylgermylene Isomers, and the Transition States at the B3LYP/6-31G* Level Calculations

Reaction	Digermene	Transition State	Germylgermylene
$\text{H}_2\text{Ge}=\text{GeH}_2 \longrightarrow \text{H}\ddot{\text{G}}\text{e}-\text{GeH}_3$	0.0	9.5	1.7
$\text{Me(H)Ge}=\text{GeH}_2 \longrightarrow \text{H}\ddot{\text{G}}\text{e}-\text{Ge(H)}_2\text{Me}$	0.0	19.8	2.8
	0.0	8.1	-3.2

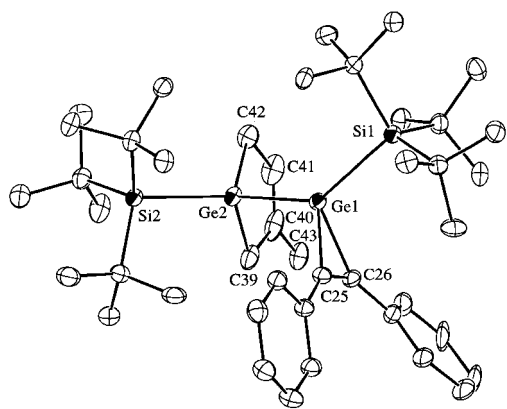


Figure 1. Molecular structure of **3b** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity). Selected bond distances (Å): Ge1–Ge2 = 2.4922(5), Ge1–Si1 = 2.449(1), Ge2–Si2 = 2.439(1), Ge1–C25 = 1.980(3), Ge1–C26 = 1.985(3), C25–C26 = 1.328(5). Selected bond angles (deg): C25–Ge1–C26 = 39.2(1), C26–C25–Ge1 = 70.7(2), C25–C26–Ge1 = 70.2(2), Si1–Ge1–Ge2 = 134.0(0), Si2–Ge2–Ge1 = 121.6(0), C39–Ge2–C42 = 91.3(1).

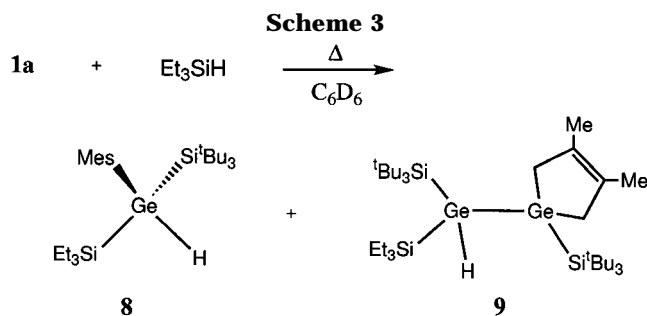
and tetramesitylgermasilene, respectively.^{10,11} Since the present system is quite interesting from the viewpoint of the unusual contraction reaction leading from a six-membered ring with a Ge=Ge double bond to a five-membered ring, we have performed theoretical calculations on this system.¹² Barriers to isomerization of the three prototype digermenes, $\text{H}_2\text{Ge}=\text{GeH}_2$, $\text{Me(H)Ge}=\text{GeH}_2$, and the parent 1,2-digermacyclohexa-1,4-diene, to the corresponding germylgermylenes have been determined by DFT calculations at the B3LYP level with

(9) Spectroscopic data for **8** and **9**: **8**: colorless oil; ¹H NMR (C_6D_6 , δ) 0.84–0.90 (m, 6 H), 0.95–0.98 (m, 9 H), 1.23 (s, 27 H), 2.10 (s, 3 H), 2.55 (s, 3 H), 2.65 (s, 3 H), 4.23 (s, 1 H), 6.78 (s, 1 H), 6.87 (s, 1 H); ¹³C NMR (C_6D_6 , δ) 6.8, 8.5, 21.0, 24.8, 27.5 (2C), 31.8, 128.2, 129.7, 136.8, 137.9, 142.8, 143.9; ²⁹Si NMR (C_6D_6 , δ) 4.6, 28.1. Anal. Calcd for $\text{C}_{27}\text{H}_{54}\text{GeSi}_2$: C, 63.90; H, 10.72. Found: C, 63.56; H, 10.44. **9**: colorless solid; mp 96–99 °C; ¹H NMR (C_6D_6 , δ) 1.05–1.09 (m, 6 H), 1.13–1.18 (m, 9 H), 1.29 (s, 27 H), 1.30 (s, 27 H), 1.78 (s, 6 H), 2.49 (d, J = 17 Hz, 2 H), 2.60 (d, J = 17 Hz, 2 H), 3.29 (s, 1 H); ¹³C NMR (C_6D_6 , δ) 8.2, 8.9, 19.4 (2C), 24.3, 26.0, 32.0, 32.4, 32.7, 36.9, 131.9, 132.3; ²⁹Si NMR (C_6D_6 , δ) 9.1, 25.5, 40.2. Anal. Calcd for $\text{C}_{36}\text{H}_{80}\text{Ge}_2\text{Si}_3$: C, 58.24; H, 10.86. Found: C, 58.04; H, 10.54.

(10) (a) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487. (b) Baines, K. M.; Cooke, J. A.; Vittal, J. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1484.

(11) Baines, K. M.; Cooke, J. A.; Dixon, C. E.; Liu, H. W.; Netherton, M. R. *Organometallics* **1994**, *13*, 631.

(12) A theoretical calculation on the isomerization of $\text{H}_2\text{Ge}=\text{GeH}_2$ to $\text{H}\ddot{\text{G}}\text{e}-\text{GeH}_3$ at the CCSD(T)/ANO level has been reported; see: Grev, R. S.; Schaefer, H. F., III. *Organometallics* **1992**, *11*, 3489.



the 6-31G* basis set (Table 1). In $\text{H}_2\text{Ge}=\text{GeH}_2$, digermene-to-germylgermylene isomerization is endothermic by 1.7 kcal mol⁻¹ with a barrier of 9.5 kcal mol⁻¹. For $\text{Me(H)Ge}=\text{GeH}_2$, the isomerization barrier (19.8 kcal mol⁻¹) is much higher than that of $\text{H}_2\text{Ge}=\text{GeH}_2$, although the energy difference between $\text{Me(H)Ge}=\text{GeH}_2$ and $\text{H}\ddot{\text{G}}\text{e}-\text{Ge(H)}_2\text{Me}$ (2.8 kcal mol⁻¹ endothermic) is similar to that of $\text{H}_2\text{Ge}=\text{GeH}_2$ and $\text{H}\ddot{\text{G}}\text{e}-\text{GeH}_3$. This result suggests that alkyl groups are much more reluctant to migrate than hydrogen atoms. However, the isomerization of the parent 1,2-digermacyclohexa-1,4-diene to (germacyclopent-3-enyl)germylene is 3.2 kcal mol⁻¹ exothermic, and the barrier is only 8.1 kcal mol⁻¹, in sharp contrast to the Me group migration. Thus, this theoretical study shows that the ring contraction of 1,2-digermacyclohexa-1,4-diene is the favored reaction both kinetically and thermodynamically.¹³

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Supporting Information Available: Tables giving the details of the X-ray structure determination, and bond angles and figures giving thermal ellipsoid plots for **3b** and **7** and figures and tables giving the calculated geometrical parameters of the transition state structure for the cyclic digermene and IRC results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) The migratory aptitude of silyl groups would be much larger than that of H and alkyl, as reported in disilene–silylene isomerization calculated by Nagase et al.; see: Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 1320. However, the migration of the ^tBu₃Si group in the real molecule was not observed due to steric reasons.