J|A|C|S
COMMUNICATIONS

2,4-Disila-1-germatricyclo[2.1.0.0^{2,5}]pentane: A New Type of Cage Compound of Group 14 Elements with an Extremely Long Ge−C Bridge Bond and an “Umbrella”-Type Configuration of a Ge Atom

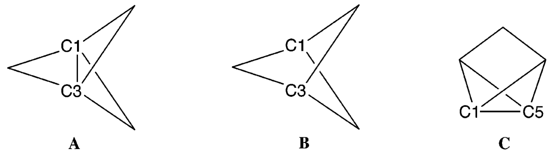
Vladimir Ya. Lee, Masaaki Ichinohe, and Akira Sekiguchi*

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

Received April 22, 2002

The nature of the chemical bond is one of the most fundamental concepts in organic chemistry. The so-called “non-classical” structures, which do not follow the normal, classical presentation of the chemical bond (from such viewpoints as valency, hybridization, and geometry), are among the greatest challenges for both experimental and theoretical chemists. One of the most fascinating findings in the field of such unusual “non-classical” molecules was the discovery of highly strained [1.1.1]propellanes (Chart 1, **A**).[1]

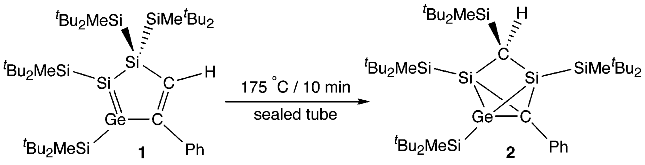
Chart 1



These compounds exhibited a very long C1−C3 bridging bond distance with an inverted tetrahedral geometry of both bridgehead carbon atoms, which was reasonably explained by the biradical character of this bond.[1] Bicyclo[1.1.1]pentanes (Chart 1, **B**) showed a very short C1−C3 nonbonding distance, which was taken as evidence for the existence of an interbridgehead 1,3-nonbonding interaction.[2,3] In sharp contrast to [1.1.1]propellanes, tricyclo-[2.1.0.0^{2,5}]pentanes (Chart 1, **C**) are well-known to have a very short C1−C5 bridge bond distance.[4] In this work we report the synthesis of a very unusual compound, 2,4-disila-1-germatricyclo-[2.1.0.0^{2,5}]pentane; it formally has a **C**-type skeleton, but its structural and chemical properties actually match the [1.1.1]-propellane properties rather than the real tricyclo[2.1.0.0^{2,5}]pentane ones.

We have found that thermolysis of the silole **1**[5] (50 mg) in a sealed evacuated tube without solvent at 175 °C for 10 min quickly, cleanly, and quantitatively resulted in the formation of the unexpected isomeric compound 1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-5-phenyl-2,4-disila-1-germatricyclo[2.1.0.0^{2,5}]pentane **2** (Scheme 1).[6,7] Compound **2**, representing a new type of cage compound of group 14 elements, was isolated by recrystallization from hexane as very air-sensitive yellow plate crystals. In the ^{29}Si NMR spectrum of **2**, four signals were observed in a ratio of 2:1:2:1; −28.0 (endocylic Si atoms), 8.9 (Si-substituent connected to C atom), 16.9 (Si-substituents connected to endocyclic Si atoms), 34.1 (Si-substituent connected to Ge atom). The most informative for the characterization of the cage compound was the ^{13}C NMR spectrum: the resonance of the bridgehead C atom is strongly shifted downfield and appeared at +60.8 ppm,[8] which is quite unusual for the C atom in a three-membered ring system.

Scheme 1



The crystal structure of compound **2** was determined by X-ray analysis, as shown in Figure 1.[9] The tricyclic skeleton incorporates the two fused three-membered rings comprising all different group 14 elements: C, Si, and Ge. Although the skeletal bond lengths are somewhat elongated compared with the normal values, the most unusual one is an extremely long Ge−C bridging bond of 2.242(3) Å, which greatly exceeds the normal value of 1.95 Å by 15%.[10,11] The second unusual structural peculiarity is the geometry of the Ge atom, representing the first example of an inverted tetrahedral geometry, which is also known as an “umbrella”-type configuration.[12] The geometry of C atom at the bridging position is also largely distorted, and the four atoms (C1, Si1, Si2, and C3) are arranged in the nearly same plane (a sum of the bond angle around C1 atom: 356.8°). These surprising structural features, the long Ge−C bridge bond and “umbrella” configuration of the Ge

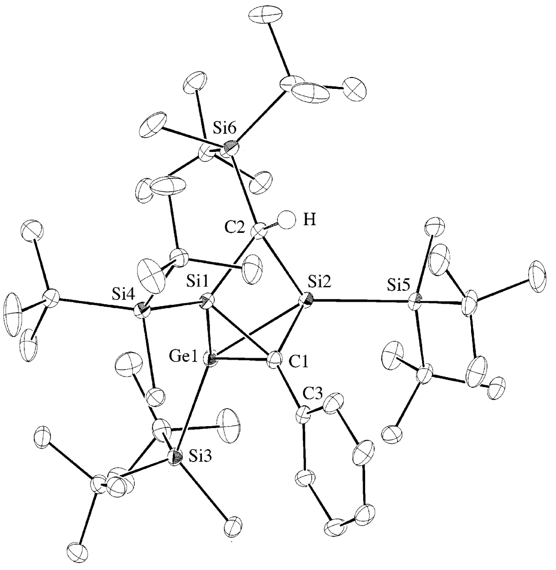


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1−C1 = 2.242(3), Ge1−Si1 = 2.3664(8), Ge1−Si2 = 2.3999(8), Si1−C1 = 1.877(3), Si1−C2 = 1.931(3), Si2−C2 = 1.928(3), Si2−C1 = 1.873(3); Selected bond angles (deg): Si2−Ge1−C1 = 47.43(7), Ge1−C1−Si2 = 70.71(9), C1−Si2−Ge1 = 61.85(8), Ge1−C1−Si1 = 69.48(9), C1−Si1−Ge1 = 62.54(8), Si1−Ge1−C1 = 47.98(7), Si1−C2−Si2 = 83.03(10).

---

* To whom correspondence should be addressed. E-mail: sekiguch@staff.chem.tsukuba.ac.jp.

10.1021/ja020574z CCC: $22.00 © 2002 American Chemical Society

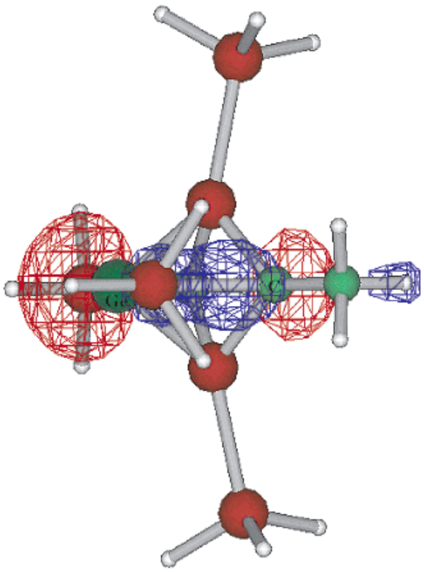


Figure 2. HOMO (σ-orbital of Ge−C bridging bond) of the model compound (H_3Si-substituents on the C, Si, Ge atoms and H_3C-substituent on the bridgehead C atom).

atom, were perfectly reproduced by DFT calculations at the B3LYP/6-31G(d) level on both H- and H_3Si-substituted model cage compounds. In sharp contrast, the same level calculations on the parent tricyclo[2.1.0.0^{2,5}]pentane, containing only carbon skeletal atoms, showed the typical skeleton for tricyclopentanes with the normal tetrahedral geometry of the bridgehead carbon atoms and with a very short C−C bridge bond length of 1.452 Å, comparable with the experimental values of 1.41−1.51 Å.[1c] The most appropriate interpretation of all the experimental data is that the Ge−C bridge bond has a singlet biradical character with sp^2-type hybridization of both the Ge and C atoms. Such a suggestion can explain the highly downfield-shifted resonance of the bridgehead C atom and its almost planar geometry. Indeed, the NBO analysis (B3LYP/6-31G(d)) showed a Ge−C bond order of 0.63 (Wiberg bond index) with both of the Ge and C atoms having $sp^{2.2}$ hybridization. On the other hand, NBO analysis clearly demonstrated that the Ge−C bridging σ-bond is formed by almost pure p-orbitals (92% p-character and 8% s-character for Ge atom, 98% p-character and 2% s-character for C atom), which is fully consistent with our understanding of the biradical character of the Ge−C bond. Indeed, an appreciable part of the electron density would be located outside the Ge−C bond, as depicted in Figure 2.[13]

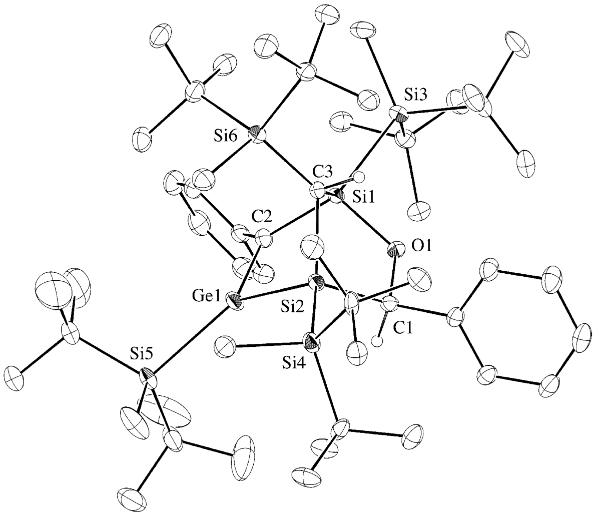
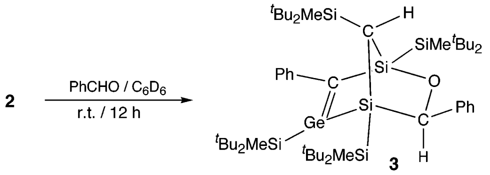


Figure 3. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1−C2 = 1.859(3), Ge1−Si2 = 2.4212(9), Si1−C2 = 1.890(3), Si2−C1 = 1.981(3), Si1−O1 = 1.681(2), C1−O1 = 1.449(3), Si1−C3 = 1.925(3), Si2−C3 = 1.936(3).

As one would expect, **2** exhibited an enhanced reactivity. Thus, it easily undergoes reaction with benzaldehyde at room temperature to form a rather unusual product: norbornene with an endocyclic Ge=C double bond (1.859(3) Å), 1,4,5,7-tetrakis(di-*tert*-butyl-(methyl)silyl)-3,6-diphenyl-2-oxa-1,4-disila-5-germabicyclo[2.2.1]-hept-5-ene **3** in 73% yield (Scheme 2 and Figure 3).[14,15]

Scheme 2



Supporting Information Available: Experimental procedure and spectral data of **3**, tables of crystallographic data including atomic positional and thermal parameters for **2** and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For the reviews on [1.1.1]propellanes, see: (a) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975. (b) Kaszynski, P.; Michl, J. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley & Sons Ltd.: New York, 1995; Vol. 2, Chapter 13. (c) Levin, M. D.; Kaszynski, P.; Michl, J. *Chem. Rev.* **2000**, *100*, 169.

(2) For the reviews on bicyclo[1.1.1]pentanes, see ref 1c.

(3) The heavier analogues of the compounds **A** and **B** were reported only for the case of tin. For [1.1.1]pentastannapropellane derivative, see: (a) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454. For bicyclo-[1.1.1]pentastannane derivative, see: (b) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839. For 1,3-disilabicyclo[1.1.0]butane derivative with a long Si−Si bridge bond, see: (c) Iwamoto, T.; Yin, D.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2001**, *123*, 12730.

(4) For the reviews on tricyclo[2.1.0.0$^{2.5}$]pentanes, see: (a) Dowd, P.; Irngartinger, H. *Chem. Rev.* **1989**, *89*, 985. (b) See ref 1c.

(5) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604.

(6) Spectral data for **2**: yellow crystals; mp 197−198 °C; ^1H NMR (C_6D_6, δ) 0.07 (s, 6 H), 0.27 (s, 3 H), 0.56 (s, 3 H), 1.15 (s, 36 H), 1.26 (s, 18 H), 1.31 (s, 18 H), 1.91 (s, 1 H), 6.99 (t, $J = 7.3$ Hz, 1 H, ArH), 7.17 (t, $J = 7.3$ Hz, 2H, ArH), 7.68 (d, $J = 7.3$ Hz, 2H, ArH); ^{13}C NMR (C_6D_6, δ) −4.7, −2.6, −1.4, 20.6, 21.80, 21.83, 23.2, 30.4, 30.5, 30.7, 38.6 (*C*H), 60.8 (*C*Ph), 123.2, 127.0, 134.3, 144.7; ^{29}Si NMR (C_6D_6, δ) −28.0 (2 Si), 8.9, 16.9 (2 Si), 34.1; Anal. Calcd for $C_{44}H_{90}GeSi_6$: C, 61.43; H, 10.54. Found: C, 61.14; H, 10.24.

(7) The mechanism for the formation of cage compound **2** is not evident at this point, although it seems clear that the process of the two σ-bonds breaking and the two new σ-bonds forming should be involved in the reaction pathway. Apparently the reaction scheme may consist of several consecutive valence isomerization−cycloaddition steps.

(8) The ^{13}C NMR chemical shifts of the bridging carbon atoms bearing phenyl substituents in the organic tricyclo[2.1.0.0$^{2.5}$]pentanes are around +30 ppm (see ref 1c, p 187).

(9) For the crystal data of **2**, see the Supporting Information.

(10) Baines, K. M.; Stibbs, W. *Coord. Chem. Rev.* **1995**, *145*, 157.

(11) Such structural features closely resemble the structure of [1.1.1]propellane rather than the real tricyclo[2.1.0. 0$^{2.5}$]pentanes in organic chemistry, which have an unusually short C−C bridging bond (see refs 1c, 4).

(12) For the review on the inverted geometries at carbon atom, see: Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379.

(13) Indeed, the electron occupancy of the Ge−C bond is only 1.78 (B3LYP/6-31G(d)), quite parallel to the case of [1.1.1]propellanes, for which the electron occupancy of the central C−C bridge bond was calculated to be 1.83 (ref 1b, p 779).

(14) For the spectral and crystal data of **3**, see the Supporting Information.

(15) Compound **3** is a product of [4 + 2] cycloaddition reaction of PhCHO and 2,5-disila-3-germacyclopenta-2,4-diene, which may result from isomerization of **2**. [1.1.1]propellanes undergo a quite similar isomerization to form the corresponding 1,3-diene systems: 1,2-dimethylenecyclopropanes (see ref 1b, p 779).

JA020574Z