1,3-Digermabicyclo[1.1.0]butane with an Inverted Bridge Ge–Ge σ Bond

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1,3-Digermabicyclo[1.1.0]butane **2** was synthesized as yellow crystals. The molecular structure, ^{13}C NMR and UV–vis spectra, and theoretical calculations have revealed that **2** is a typical long bond isomer, similarly to the silicon congener **1**. Structural comparison between **1** and **2** is achieved.

Metallabicyclo[1.1.0]butanes of heavier group-14 elements have received much attention because of their unique structural characteristics.[1] Theoretical studies have shown that there are two isomers in the metallabicyclobutanes, short-bond (SB) and long-bond (LB) isomers, which differ primarily in the distance between the bridgehead atoms. The LB isomer is expected to have an inverted σ bond resulting from an overlap between back lobes of pertinent hybridized orbitals on the bridgehead atoms, while the SB isomer a typical bent σ bond, as shown in Chart 1.[2]

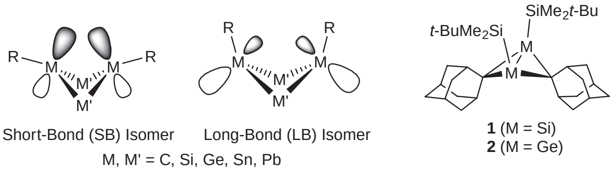
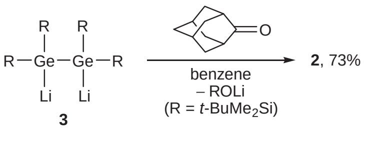


Chart 1.

Recently, we have synthesized 1,3-disilabicyclobutane **1** as the first LB isomer of the metallabicyclobutane having bridgehead heavier group-14 elements.[3] In the present paper, we wish to report the successful synthesis and molecular structure of the first 1,3-digermabicyclo[1.1.0]butane **2** with the LB structure. Although a number of related germanium-containing bicyclobutane derivatives have been reported,[4,5] **2** constitutes the first LB isomer among them.

Digermabicyclobutane **2** was synthesized by using a formal double germa-Peterson reaction[6] of 1,1,2,2-tetrakis(*t*-butyldimethylsilyl)-1,2-dilithiodigermane (**3**) (265 mg, 0.252 mmol) and 2-adamantanone (76 mg, 0.51 mmol) in dry benzene (10 mL) at room temperature, similarly to the synthesis of **1** (eq 1).[3] Recrystallization from diethyl ether gave analytically pure **2** (236 mg, 0.366 mmol) as air-sensitive but thermally stable orange crystals (mp 203.7–205.5 °C) in 73% yield.[7] The structure of **2** was determined by NMR and MS spectroscopy and X-ray crystallography.



(1)

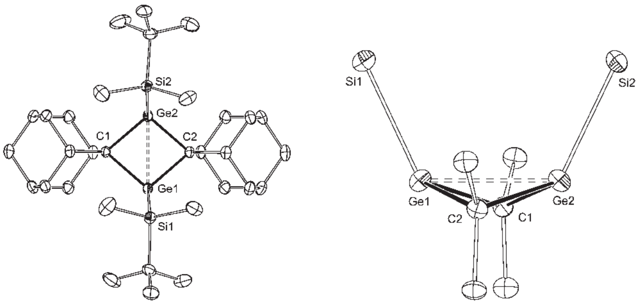
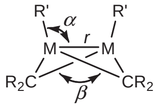


Figure 1. ORTEP drawings of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. (a) Top view. (b) Side view. A part of carbons in adamantylidene and *t*-butyldimethylsilyl moieties are omitted for clarity.

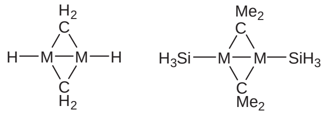
Table 1. Comparison of selected structural parameters and chemical shift of **2** with those of related compounds[a]



Compound	r/Å	α/°	β/°	$\Sigma\varphi$/°[b]	δ_C[c]	ΔE[d]
2	2.5827(3)	115.28(2) 115.89(2)	142.26(9)	332.83(7) 333.88(6)	+135.4	—
1[e]	2.412(1)	118.76(2)	141.1(1)	338.30(7)	+98.3	—
SB-**5**	2.156	165.33	117.28	351.4	+11.4	+20.6
LB-**5**	2.473	92.60	137.59	306.31	+73.4	0.0
SB-**5′**[e]	2.201	152.14	126.74	359.55	+50.8	+11.8
LB-**5′**[e]	2.448	106.93	141.48	324.82	+105.6	0.0
SB-**6**	2.312	107.67	117.03	349.97	+24.7	+33.5
LB-**6**	2.643	90.02	137.52	301.83	+111.7	0.0
LB-**6′**	2.642	103.72	142.68	335.69	+151.7	—

[a]Theoretical calculations of the model compounds were carried out at the B3LYP/6-311+G(d,p) level. [b]The sum of bond angles around bridgehead atoms except for the angles containing the bridge bond. [c]Chemical shift of the bridge carbon nuclei. The values for the model compounds were calculated at the GIAO/B3LYP/6-311G(2df,p)//B3LYP/6-311+G(d,p) level. [d]Calculated relative energy in kcal·mol^{-1} with a zero-point energy. [e]Ref 3.

Molecular structure of **2**[9] is shown in Figure 1 and selected structural parameters are summarized in Table 1. The bridge Ge1–Ge2 bond distance r [2.5827(3) Å] is much longer than the Ge–Ge bonds of a known digermirane $H_2C[Ge(2,6\text{-}Et_2C_6H_3)_2]_2$ (**4**) [2.379(1) Å][10] and $Me_3Ge–GePh_3$ [2.419(1) Å].[11] Bridgehead germanium atoms in **2** have an inverted-tetrahedral configuration as shown in Figure 1b. The bridgehead germanium atoms in **2** are much more pyramidalized than the bridgehead silicon atoms in **1**. The sums of three bond angles around Ge atoms ($\Sigma\varphi$), except for the angles containing bridge bond, are 332.83(7)° for Ge1 and 333.88(6)° for Ge2, while that for **1** was 338.30(7)°.[3] The Ge1–Ge2–Si2 and Si1–Ge1–



5 (M = Si)
6 (M = Ge)

5′ (M = Si)
6′ (M = Ge)

Chart 2.

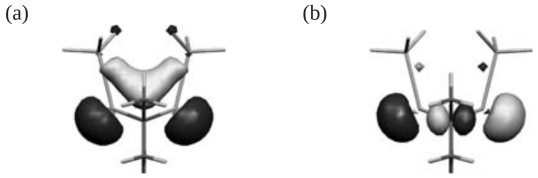


Figure 2. Frontier Kohn–Sham orbitals for LB-**6′** at the B3LYP/6-311++G(d,p)//B3LYP/6-311+G(d,p) level. (a) HOMO. (b) LUMO.

Ge2 angles (α) are 115.28(2) and 115.89(2)°, respectively. The four-membered ring of **2** is folded with an interflap angle β between two Ge_2C ring planes of 142.26(9)°. Four atoms, Si1, Ge1, Ge2, and Si2, in **2** are arranged to be almost planar with the dihedral angle Si1–Ge1–Ge2–Si2 of 2.99(3)°. These structural characteristics of **2** in the solid state are quite similar to those of **1**, suggesting **2** is an LB isomer.

To disclose the structural details of **2**, we carried out DFT calculations for four model compounds, parent 1,3-digermabicyclobutane (**6**), 1,3-disilyl-2,2,4,4-tetramethyl-1,3-digermabicyclobutane (**6′**), and their silicon congeners **5** and **5′**[3] at the B3LYP/6-311+G(d,p) level (Chart 2).[12] The results are summarized in Table 1.

Similarly to the parent 1,3-disilabicyclobutane **5**, 1,3-digermabicyclobutane **6** was found to show two local minima with the structural characteristics of LB (LB-**6**) and SB (SB-**6**) isomers. The energetic preference of LB-**6** over SB-**6** is much larger than that of LB-**5** over SB-**5**. LB-**6** is 33.0 kcal·mol^{-1} more stable than SB-**6**, while LB-**5** is 20.6 kcal·mol^{-1} more stable than SB-**5**.[13] For **6′**, only a long bond isomer (LB-**6′**) having structural parameters similar to LB-**6** was found at the same level. The structural parameters of **2** are in good accord with those of LB-**6′**.

The frontier orbitals of LB-**6′** are characterized by the high-lying HOMO [σ(Ge–Ge)] and low-lying LUMO [σ^*(Ge–Ge)] resulting from an overlap between the back lobes on the bridgehead germanium atoms as shown in Figure 2. Both the σ and σ^* orbital levels of LB-**6′** (−5.65 and −2.57 eV) are slightly lower in energy than those of LB-**5′** (−5.56 and −2.41 eV) and the σ–σ^* energy gap of LB-**6′** (3.08 eV) is slightly smaller than that of LB-**5′** (3.15 eV).

Similarly to **1**, **2** shows a clear absorption band at a visible region; λ_{max}/nm (ε) in *n*-hexane, 440 nm (9800).[14] The band assignable to the σ(Ge–Ge) $\rightarrow$ σ^*(Ge–Ge) transition is slightly red-shifted and more intense than the σ(Si–Si) $\rightarrow$ σ^*(Si–Si) transition band in **1** [420 nm (6500)].[17]

The ^{13}C chemical shift of the ring carbon in **2** (δ_C +135.4) is close to that in LB-**6′** (δ_C +151.7) being consistent with the LB structure of **2** in solution.[18]

In summary, 1,3-digermabicyclo[1.1.0]butane **2** is a long bond isomer similarly to the silicon congener **1**. The HOMO–LUMO gap of **2** is slightly smaller than that of **1**.

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References and Notes

1 T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902; M. Driess, H. Grützmacher, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828; A. Sekiguchi, S. Nagase, in *The Chemistry of Organic Silicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, John Wiley & Sons, New York, **1998**, Vol. 2, Chap. 3.

2 G. Parkin, *Chem. Rev.* **1993**, *93*, 887; H. Grützmacher, F. Breher, *Angew. Chem., Int. Ed.* **2002**, *41*, 4006; F. Breher, *Coord. Chem. Rev.* **2007**, *251*, 1007; For theoretical studies on germabicyclobutanes, see: S. Nagase, M. Nakano, *J. Chem. Soc., Chem. Commun.* **1988**, 1077; R. Koch, T. Bruhn, M. Weidenbruch, *J. Mol. Struct. (THEOCHEM)* **2005**, *714*, 109.

3 T. Iwamoto, D. Yin, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2001**, *123*, 12730.

4 V. Y. Lee, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2002**, *124*, 9962.

5 For compounds with an inverted-tetrahedral configuration, see: A. F. Richards, M. Brynda, M. M. Olmstead, P. P. Power, *Organometallics* **2004**, *23*, 2841; A. F. Richards, M. Brynda, P. P. Power, *Organometallics* **2004**, *23*, 4009.

6 D. Bravo-Zhivotovskii, I. Zharov, M. Kapon, Y. Apeloig, *J. Chem. Soc., Chem. Commun.* **1995**, 1625.

7 **2**: yellow-orange crystals; mp 203.7–205.5 °C; ^1H NMR (C_6D_6, δ) 0.44 (s, 12H, $SiCH_3$), 1.30 (s, 18H, *t*-Bu), 1.72–2.46 (m, 28H, adamantylidene); ^{13}C NMR (C_6D_6, δ) –0.2 (CH_3), 20.3 ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$), 29.5, 39.8, 42.5, 43.5, 44.7, 45.4, 135.4 (ring carbon); ^{29}Si NMR (C_6D_6, δ) 11.1; UV–vis (*n*-hexane) λ_{max}/nm ($\varepsilon/10^3$) 325 (4.0) 440 (9.8); MS (EI, 70 eV) m/z (%) 646 (76, M^+), 589 (51), 531 (16), 474 (6), 73 (100); HRMS m/z calcd for $C_{32}H_{58}Ge_2Si_2$, 646.2501; found, 646.2503. For experimental details including synthesis of **3**, see Supporting Information.[8]

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 Single crystals of $\mathbf{2}\cdot 0.5(C_6H_6)$ suitable for X-ray analysis was obtained by recrystallization from a mixed solvent (hexane: benzene = 1:1). Crystallographic data for $\mathbf{2}\cdot 0.5(C_6H_6)$ have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 680574.

10 T. Tsumuraya, S. Sato, W. Ando, *Organometallics* **1990**, *9*, 2061.

11 L. Párkányi, A. Kalman, S. Sharma, D. M. Nolen, K. H. Pannel, *Inorg. Chem.* **1994**, *33*, 180.

12 Details for the DFT calculations, see Supporting Information.[8]

13 The greater relative stability of LB isomer to SB isomer of parent bicyclo[1.1.0]tetragermane than parent bicyclotetrasilane has been predicted theoretically by Nagase et al.[2]

14 The absorption maximum of **2** is far red-shifted compared to those of $Me_3GeGeMe_3$ [λ_{max} 193.7 nm (ε 16000)],[15] (t-$BuMe_2SiMe_2Ge)_2$ (229 nm)[16] and digermirane **4** (300 nm (ε 17400)).[10]

15 M. Okano, K. Mochida, *Chem. Lett.* **1990**, 701.

16 H. K. Sharma, F. Cervantes-Lee, L. Párkányi, K. H. Pannel, *Organometallics* **1996**, *15*, 429.

17 TD-DFT calculations for LB-**5′** and LB-**6′** at the B3LYP/6-311++G(d,p) level confirmed the assignment, while the relative oscillator strengths (f) of the transition bands between **1** and **2** were not reproduced by the calculations. The theoretical absorption bands with the lowest excitation energy are: λ_{max} = 395 nm, $f = 0.204$ for LB-**5′** and λ_{max} = 409 nm, $f = 0.188$ and LB-**6′**.

18 Remarkable difference of the ^{13}C NMR chemical shift between SB and LB isomers provides a good index to distinguish the isomers.[3]