12730 *J. Am. Chem. Soc.* **2001,** *123,* 12730−12731

The First 1,3-Disilabicyclo[1.1.0]butane with Long-Bridge Silicon−Silicon Bond

Takeaki Iwamoto, Dongzhu Yin, Chizuko Kabuto, and Mitsuo Kira*

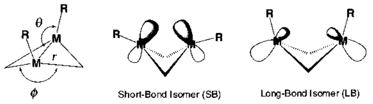
Department of Chemistry
Graduate School of Science, Tohoku University
Aoba-ku, Sendai, 980-8578, Japan

Received July 9, 2001

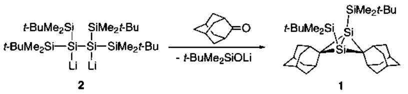
The unique structures and reactivities of metallabicyclo[1.1.0]-butanes containing heavy main group elements have been the focus of experimental and theoretical studies.[1−3] As revealed by the theoretical calculations, one of the most interesting features of metallabicyclo[1.1.0]butanes[3] as well as bicyclo[1.1.0]butanes[4] should be the existence of the bond-stretch isomers, which differ primarily in the distance between the bridge head atoms. As shown in Chart 1, the short-bond (SB) isomers are characterized by not only the short-bridge bond distance (r), but also the small interflap angle (ϕ) and the large R−M−M angle (θ), while the long-bond (LB) isomers have long r, large ϕ, and small θ. The bridge bond in an SB isomer is a normal bent σ bond, while the bond in an LB isomer should be ascribed to an inverted σ bond with significant singlet biradical character.

Although theoretical calculations have predicted that the LB isomers are more stable than the SB isomers in 1,3-disilabicyclo-[1.1.0]butane as well as tetrasilabicyclo[1.1.0]butane,[3] no experimental evidence for the LB isomers with the bridge Si−Si bond has been reported so far. We wish herein to report the first synthesis of a 1,3-disilabicyclo[1.1.0]butane derivative, which has characteristics of the LB isomer.

Chart 1



Disilabicyclo[1.1.0]butane **1** was obtained by using a formal double sila-Peterson reaction[5] of tetrakis(*tert*-butyldimethylsilyl)-dilithiodisilane **2**[6] (eq 1). Adamantanone (64 mg, 0.43 mmol) and **2**·6THF (200 mg, 0.20 mmol), which was prepared by the reaction of the corresponding tetrasilyldisilene[7] with lithium metal, was placed in a Schlenk tube under vacuum, and dry benzene (10 mL) was introduced by distillation to the mixture. The mixture was stirred overnight at room temperature to give a bright-yellow solution; the complete conversion was confirmed by ^{1}H NMR. After quenching the mixture by excess Me_3SiCl, the solvent and the resulting t-$BuMe_2SiOSiMe_3$ and lithium chloride were removed. Pure **1** was obtained by crystallization from hexane in 70.1% yield.[8] The structure of **1** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR, MS, and X-ray crystallography.[10,11] Compound **1** is oxygen- and moisture-sensitive, but thermally very stable; **1** melts at 175.2−177.3 °C without decomposition.



(1)

X-ray single-crystal analysis of **1** has shown that **1** has the crystallographical mirror plane which includes eight carbon atoms of adamantane moieties and bisects the bridge Si−Si bond (Figure 1). Two three-membered Si_2C rings are isosceles. The following four important characteristics were found in the structure of **1**: (i) The distance of the bridge Si1−Si1* bond (r) is 2.412(1) Å,

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[8] The mechanism for the formation of **1** remains open. One possible mechanism would be a double addition-1,2-siloxy elimination (sila-Peterson reaction)[5] giving the corresponding 2,3-disila-1,3-butadiene followed by the skeletal rearrangement. Alternatively, **1** would form through the stepwise formation of two disilacyclopropane rings in **1**; each disilacyclopropane ring would form via the addition of a silyllithium moiety of **2** to an adamantanone followed by the 1,3-elimination of a siloxylithium (a double addition-1,3-siloxy elimination). The 1,3-siloxy elimination of a γ-silylpropoxylithium has been known to take place and give the corresponding cyclopropane ring.[9]

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[10] **1**: bright-yellow crystals; mp 175.2−177.3 °C; ^{1}H NMR (C_6D_6, δ) 0.40 (s, 12 H, $SiCH_3$), 1.32 (s, 18 H, t-Bu), 1.74−2.34 (m, 28 H, adamantane); ^{13}C NMR (C_6D_6, δ) −0.4 (CH_3), 20.1 ($\underline{C}(CH_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 29, 4, 38.4, 39.6, 42.2, 43.08, 43.13, 98.3; ^{29}Si NMR (C_6D_6, δ) −104.2 (ring Si), 6.9 (t-$BuMe_2Si$); UV−vis (n-hexane) λ_{max}/nm ($\epsilon/10^3$) 300 (2.1) 420 (6.5); MS (EI, 70 eV) m/z (%) 554 (81.3, M^+), 497 (60.9), 439 (23.4), 381 (10.2), 73 (100); HRMS calcd for $C_{32}H_{58}Si_4$, 554.3616; found, 554.3614.

[11] Crystals data for **1**: formula, $C_{32}H_{58}Si_4$; formula weight, 555.15; yellow prism; crystal dimensions 0.20 × 0.30 × 0.30 mm; orthorhombic; Space group *Pnma* (No. 62); lattice parameters, $a = 21.484(1)$ Å; $b = 11.0229(9)$ Å; $c = 14.019(2)$ Å; $V = 3319.9(5)$ Å^3; $Z = 4$; $D_{calc} = 1.111$ g/cm^3; temperature −123.0 °C; No. observations ($I > 2.0\sigma(I)$) = 2839; No. variables = 184; $R(wR2) = 0.043$ (0.136 for all data); Goodness of Fit = 0.93.

10.1021/ja011658v CCC: $20.00

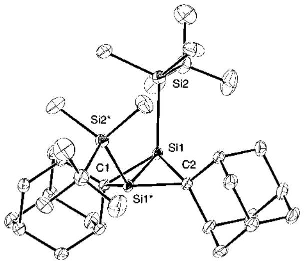
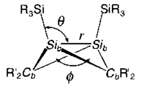


Figure 1. Molecular structure of 1,3-disilabicyclo[1.1.0]butane **1** with selected bond lengths (Å) and angles (deg): Si1−Si1*, 2.412(1); Si1−C1, 1.919(2); Si1−C2, 1.921(1); Si2−Si1−Si1*, 118.76(2); Si1−C1−Si1*, 77.90(9); C1−Si1−Si1*, 51.05(4); Si1−C2−Si1*, 77.78(9); C2−Si1−Si1*, 51.11(5); plane(Si1−C1−Si1*)-plane (Si1−C2−Si1*), 141.1(1).

Table 1. Comparison of Structural Parameters and Chemical Shifts Observed for **1** with Those Calculated for **3**[a]



compound	r/Å	θ/deg	ϕ/deg	δ^{b} Si_b	δ^{b} C_b	ΔE/ (kcal mol^{-1})[c]
1	2.412(1)	118.76(2)	141.1(1)	−104.2	+98.3	−
LB-**3** (C_2)	2.448	106.93	141.48	−107.2	+105.6	0.0
SB-**3** (C_2)	2.201	152.14	126.74	−43.2	+50.8	+11.8

[a] Geometries are optimized at the B3LYP/6-311+G(d,p) level. [b] The δ values for **1** are determined in benzene-d_6. The δ values for **3** are calculated at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-311+G(d,p) level. [c] Relative energy with ZPE correction.

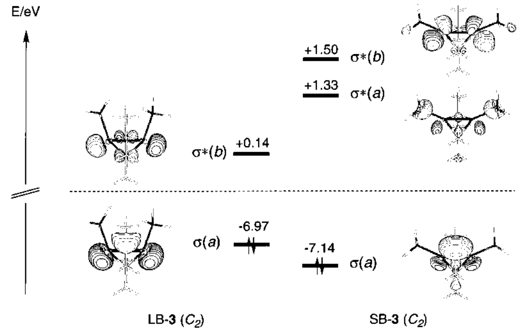
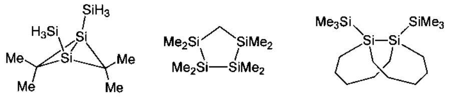


Figure 2. Schematic MO diagram for LB-**3** and SB-**3** (HF/6-311+G-(d,p)//B3LYP/6-311+G(d,p)).

Chart 2



3 **4** **5**

which is considerably longer than the Si−Si bonds of known disiliranes (2.27−2.33 Å).[12] (ii) The four-membered ring of **1** is folded with an interflap angle (ϕ) between two Si_2C ring planes of 141.1(1)°. (iii) The Si2−Si1−Si1* angle (θ) is 118.76(2)°, and bridgehead silicon atoms have inverted-tetrahedral configuration.[4] (iv) **1** has an ideal *cisoid*-tetrasilane unit with the dihedral angle Si2−Si1−Si1*−Si2* of 0.0°.

To characterize the molecular structure of **1**, we have performed the ab initio MO calculations[13] at the B3LYP/6-311+G(d,p) level for 2,2,4,4-tetramethyl-1,3-bis(trihydridosilyl)-1,3-disilabicyclo-[1.1.0]butane (**3**) as a model for **1**. The selected structural parameters are shown in Table 1 with those of **1**. Similarly to the parent 1,3-disilabicyclobutane,[3e] **3** was found to show two local minima with the characteristics of SB (SB-**3**) and LB isomers (LB-**3**); LB-**3** is lower in energy by +11.8 kcal/mol and has a longer central Si−Si distance r (2.448 Å), a narrower Si−Si−Si angle θ (106.9°), and a wider interflap angle ϕ (141.5°) than SB-**3**. All three structural parameters (r, θ, and ϕ) of **1** in the solid state are in good accord with those of LB-**3** but not with those of SB-**3**. While the resonances due to the ^{29}Si and ^{13}C nuclei in the disilabicyclobutane ring calculated at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-311+G(d,p) level are very different between LB-**3** and SB-**3** (Table 1), the corresponding resonances for **1** in benzene-d_6 are well reproduced in LB-**3**. Without doubt, compound **1** is assigned to the LB isomer both in the solid state and in solution.Whereas the SB isomer of a tetrasilabicyclo[1.1.0]-butane reported by Masamune et al. was found to show facile ring-flipping at room temperature, **1** showed no such flipping as evidenced by ^{13}C NMR spectroscopy; seven ^{13}C signals due to the adamantane carbons were observed even at 90 °C.

As shown in a schematic MO diagram in Figure 2, the frontier orbitals of LB-**3** are characterized by the relatively high-lying HOMO and the remarkably low-lying LUMO; at the HF/6-311+G(d,p)//B3LYP/6-311+G(d,p) level, the σ (SiSi) HOMO and σ^* (SiSi) LUMO levels of LB-**3** are −6.97 and +0.14 eV, respectively, while those of SB-**3** are −7.14 and +1.33 eV, respectively. On the basis of this MO diagram, one may expect the absorption maximum of **1** due to the $\sigma \rightarrow \sigma^*$ transition should appear in the visible region. Actually, disilabicyclobutane **1** showed a distinct absorption band at 420 nm (ϵ 6500) assignable to the $\sigma \rightarrow \sigma^*$ transition.[14] The maximum is unusually red-shifted in comparison with the absorption maxima of known *cisoid*-tetrasilanes;[15] λ_{max}/nm (ϵ) 258 (300), 235 (3700) for **4**[15b] and λ_{sh}/nm (ϵ) ~210 (13000) for **5**.[15e] The red-shifted $\sigma \rightarrow \sigma^*$ transition bands of **1** are taken as another indication of the long-bond nature of **1**. Further work is in progress on the reactivity of **1** having the unique weak Si−Si σ bond.

Acknowledgment. We thank a reviewer for pointing out the importance of the NMR chemical shifts in the discussion on the structure of **1** in solution. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [Grants-in-Aid for Scientific Research (B) No.11440185 (M.K. and T. I.) and Encouragement of Young Scientists No. 12740336 (T.I.)].

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**, geometrical parameters of the optimized structures for LB-**3** and SB-**3**, and UV−vis spectrum of **1** (PDF). A crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA011658V

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