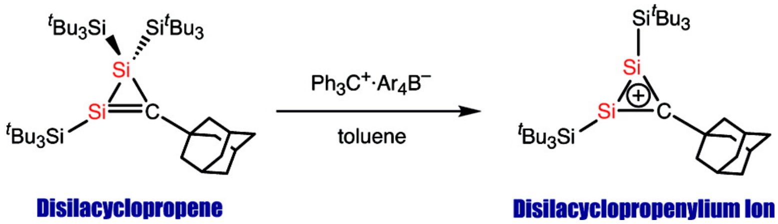
Communication

Air-Stable Disilacyclopropene with a SiC Bond and Its Conversion to Disilacyclopropenylium Ion: Silicon–Carbon Hybrid 2π-Electron Systems

Masayasu Igarashi, Masaaki Ichinohe, and Akira Sekiguchi

J. Am. Chem. Soc., **2007**, 129 (42), 12660-12661• DOI: 10.1021/ja075740n • Publication Date (Web): 29 September 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Air-Stable Disilacyclopropene with a Si═C Bond and Its Conversion to Disilacyclopropenylium Ion: Silicon−Carbon Hybrid 2π-Electron Systems

Masayasu Igarashi, Masaaki Ichinohe, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

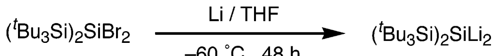
Received August 1, 2007; E-mail: sekiguch@chem.tsukuba.ac.jp

The cyclopropenylium ion is the smallest member of the Hückel aromatic systems, and numerous investigations have been carried out on this class of cation.[1] Despite a great interest in the heavy congeners of the cyclopropenylium ion, the chemistry of heavy analogues in which the skeletal carbon atoms are fully or partially replaced with heavier group 14 elements was missing until recently because of the synthetic difficulty associated with the lack of an appropriate precursor. We reported the synthesis of the cyclotrigermenylium ion, $(^t\mathrm{Bu_3Si})_3\mathrm{Ge_3}^+$, obtained by the reaction of the cyclotrigermenes with $\mathrm{Ph_3C^+{\cdot}BPh_4^-}$ in 1997,[2] and then in 2005, the cyclotrisilenylium ion $\{(^t\mathrm{Bu_2MeSi})(\mathrm{Si}^t\mathrm{Bu_3})_2\}\mathrm{Si_3}^+$ by the reaction of a highly crowded cyclotrisilene, $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiSi_2}(\mathrm{Si}^t\mathrm{Bu_3})_2$ with $\mathrm{Ph_3C^+{\cdot}BAr_4^-}$ ($\mathrm{BAr_4^-}$: TPFPB = tetrakis(pentafluorophenyl)borate, TSFPB$^-$ = tetrakis[4-(*tert*-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate, TTFPB$^-$ = tetrakis(2,3,5,6-tetrafluorophenyl)-borate).[3] We also reported that the reaction of cyclotrisilene $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiSi_2}(\mathrm{SiMe}^t\mathrm{Bu_2})_2$ with $[\mathrm{Et_3Si(benzene)}]^+{\cdot}$TPFPB caused demethylation and subsequent ring expansion to give the cyclotetrasilenylium ion, $[(^t\mathrm{Bu_2MeSiSi})_3\mathrm{Si}^t\mathrm{Bu_2}]^+$, having 2π-electron homoaromatic character.[4] The cyclotrigermenylium ion, the cyclotrisilenylium ion, and cyclotetrasilenylium ion were characterized to be not only "free" germyl and silyl cations but also 2π-electron aromatic compounds,[5] composed solely of germanium and silicon atoms, respectively.[2a,3,4]

We have also developed the chemistry of dilithiosilane,[6] which offered a straightforward method for the synthesis of dimetallenes of the type >Si═E< (E = B,[7d] Al,[7c] Ga,[7c] Si,[7a] Ge,[7a] Sn,[7b] Hf[7e]) by a coupling reaction of $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiLi_2}$ with the appropriate dihalogenated compounds. Bis(tri-*tert*-butylsilyl)dilithiosilane **1** with two extremely bulky $^t\mathrm{Bu_3Si}$ groups would be very interesting for synthetic applications to the new type of unsaturated heavier group 14 elements. Indeed, **1** is a promising reagent for the synthesis of hitherto unknown unsaturated silicon compounds, and we succeeded in synthesizing a heteronuclear cyclopropene with one C and two Si atoms, which was subsequently converted to the disilacyclopropenylium ion with a silicon−carbon hybrid 2π-electron system. In this paper, we wish to report the synthesis and characterization of the new dilithiosilane **1**, disilacyclopropene **2** with a Si═C double bond,[8] and its conversion to disilacyclopropenylium ion **3**$^+$.

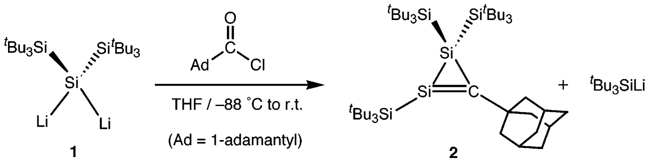
The dilithiosilane $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiLi_2}$ was prepared by the Si−C bond cleavage reaction of 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)silacycloprop-2-ene with lithium.[7a] However, the synthesis of the corresponding silacyclopropene with two $^t\mathrm{Bu_3Si}$ groups failed because of the severe steric bulkiness. After several attempts, the dilithiosilane **1** was successfully prepared as a yellow solid by the direct reaction of $(^t\mathrm{Bu_3Si})_2\mathrm{SiBr_2}$ with lithium in THF at −60 °C for 48 h (Scheme 1).[9,10] The prolonged reaction time at low temperature is crucial for the successful synthesis of **1**, otherwise intramolecular insertion of the silenoid $(^t\mathrm{Bu_3Si})_2\mathrm{SiLiBr}$ occurred to produce the 1,2-disilacyclobutane derivative.[11]

Scheme 1



$$(^t\mathrm{Bu_3Si})_2\mathrm{SiBr_2} \xrightarrow[-60\ ^\circ\mathrm{C},\ 48\ \mathrm{h}]{\mathrm{Li\ /\ THF}} \underset{\mathbf{1}}{(^t\mathrm{Bu_3Si})_2\mathrm{SiLi_2}}$$

Scheme 2



1 **2**

The adamantyl-substituted disilacyclopropene **2** was synthesized by the reaction of **1** with 1-adamantanecarbonyl chloride (Scheme 2).[12,13] The reaction using the dilithiosilane is a novel synthetic protocol for making Si═C double bonds, and disilacyclopropene **2** represents the first $\mathrm{CSi_2}$ hybrid heavy analogue of cyclopropene[14] featuring a skeletal Si═C double bond. Although **2** has a reactive Si═C double bond, **2** is amazingly stable in air because of the extreme steric protection of the double bond. Thus, it was possible to handle **2** in air and to employ HPLC chromatography (*tert*-butyl methyl ether/methanol = 1:1 mixed solvent) to isolate **2** as air-stable yellow crystals.

In the ^{29}Si and ^{13}C NMR spectra of **2**, the signals assigned to sp^2-silicon and sp^2-carbon atoms were observed at 79.2 and 188.4 ppm, respectively, which were in the typical range of resonance of Si═C sp^2-silicon and sp^2-carbon atoms.[15] The sp^3-skeletal Si atom resonates at high field ($\delta = -88.9$), as expected for tetrahedral Si atoms incorporated in a three-membered ring system. The longest wavelength absorption maximum of **2**, assigned to a $\pi-\pi^*$ transition, was observed at 394 nm ($\epsilon = 1800$) in hexane, being the most red-shifted among other known silenes.[15] The HOMO of disilacyclopropene has a contribution from both the Si═C π-orbital and the exocyclic Si−Si σ-orbitals. As a result of such a σ(Si−Si)−π(Si═C) interaction, the HOMO level of **2** is raised compared with acyclic silenes, leading to the significant red shift of the UV−vis absorption.

The X-ray crystal structure analysis proved that **2** was an unsaturated three-membered ring with a Si═C double bond having a length of 1.745(2) Å (Figure 1), being in the range of the normal Si═C double bond length.[15] The remaining two sides of the $\mathrm{CSi_2}$ triangle are made up of a C−Si single bond (1.936(2) Å) and a Si−Si single bond (2.3070(8) Å). The most striking feature is the bond lengths of the exocyclic Si−Si bonds (2.5991(9) Å for Si2−Si4 and 2.5797(8) Å for Si2−Si5), which are remarkably elongated compared with the normal Si−Si single bond length (2.34 Å) because of the great steric interaction of the bulky $^t\mathrm{Bu_3Si}$ groups on the skeletal sp^3-silicon and $^t\mathrm{Bu_3Si}$ and 1-adamantyl groups on the Si═C bond.[16] The sp^2-Si and C atoms are essentially planar despite the introduction of bulky $^t\mathrm{Bu_3Si}$ and adamantyl groups, as determined by the sum of the bond angles: 359.98(7)° for the Si1

10.1021/ja075740n CCC: $37.00 © 2007 American Chemical Society

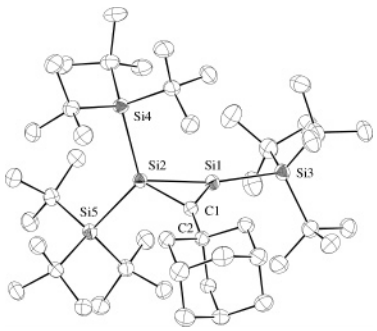
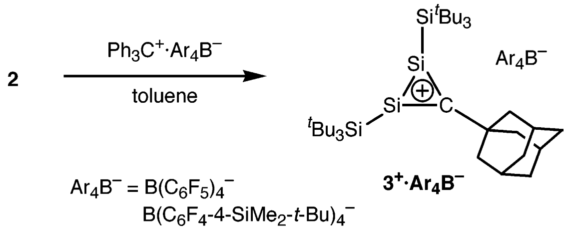


Figure 1. ORTEP drawing of **2** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1−Si1 = 1.745(2), C1−Si2 = 1.936(2), Si1−Si2 = 2.3070(8), Si1−Si3 = 2.4408(8), Si2−Si4 = 2.5991(9), Si2−Si5 = 2.5797(8), C1−C2 = 1.522(3). Selected bond angles (deg): Si1−C1−Si2 = 77.42(9), C1−Si1−Si2 = 54.99(7), C1−Si2−Si1 = 47.59(6). Selected torsional angle (deg): C2−C1−Si1−Si3 = 4.5(2).

Scheme 3



atom and 359.92(15)° for the C1 atom. The Si═C bond is nearly planar, the dihedral angle of C2−C1−Si1−Si3 being 4.5(2)°. Disilacyclopropene **2** was reacted with Ph_3C^+•$TPFPB^-$ in dried and degassed toluene at room temperature for 1 min to form two liquid phases, accompanied by a color change from red-orange to dark-brown. The lower layer was separated and washed with hexane to remove neutral materials to produce the $TPFPB^-$ salt of $\mathbf{3}^+$, isolated as an extremely air- and moisture-sensitive yellow solid in quantitative yield (Scheme 3).[9] The $TSFPB^-$ salt of $\mathbf{3}^+$ could also be synthesized by the reaction of **2** with Ph_3C^+•$TSFPB^-$ in toluene.

The structure of $\mathbf{3}^+$•$TPFPB^-$ was determined by NMR spectroscopy. Thus, the ^1H NMR spectrum shows a singlet at 0.91 ppm corresponding to the two ${}^tBu_3Si$ groups, clearly suggesting the formation of $\mathbf{3}^+$ by the elimination of one ${}^tBu_3Si$ substituent from **2**. In the ^{29}Si NMR spectrum, the only two signals were observed at 53.9 and 208.2 ppm; the former signal was assigned to the ${}^tBu_3Si$ substituents, and the latter signal was assigned to the cationic Si atoms of the three-membered ring. In the ^{13}C NMR spectrum, the signal of the cationic C atom of the three-membered ring was observed at 253.7 ppm. The ^1H, ^{13}C, and ^{29}Si NMR chemical shifts of the disilacyclopropenylium moiety are practically the same, independently not only of the counteranions ($TPFPB^-$, $TSFPB^-$) but also of the solvents (benzene, toluene). The NMR chemical shift of the skeletal carbon and silicon atoms of $\mathbf{3}^+$, compared with those of the cyclopropenylium ion $Ph_3C_3^+$ (^{13}C NMR chemical shift of the skeleton: 154.0 ppm)[1a] and cyclotrisilenylium ion $\{({}^tBu_2MeSi)(Si{}^tBu_3)_2\}Si_3^+$ (^{29}Si NMR chemical shift of the skeleton: 284.6 and 288.1 ppm),[3] are shifted downfield and upfield, respectively. The downfield and upfield shifts of the ^{13}C and ^{29}Si NMR resonances of $\mathbf{3}^+$ have been well reproduced by the GIAO calculation (GIAO/B3LYP/6-311G(d,p)(6-311G(3d,p) for Si)//B3LYP/6-31G(d)) for the model compound $\{({}^tBu)(Me_3Si)_2\}CSi_2^+$ (calculated value: 278.3 ppm (C) and 215.1 ppm (Si)). The NICS value,[17] recognized as an aromaticity probe, was calculated to be negative at 1 Å above the center of the ring: NICS(1) = −13.5 for $\{({}^tBu)(Me_3Si)_2\}CSi_2^+$ (cf. NICS(1) for ${}^tBu_3C_3^+$ = −14.3 and −13.7 for $(Me_3Si)_3Si_3^+$). The skeletal bond orders of the model compound are 1.23 (two C−Si bonds) and 1.19 (one Si−Si bond), which are close to the ideal value of 1.33. Thus, we have established the first synthesis and characterization of a disilacyclopropene by using the reactivity of dilithiosilane and its conversion to disilacyclopropenylium ion containing a silicon−carbon hybrid 2π-electron system.

Supporting Information Available: Experimental procedures and spectral data for **1**, **2**, $\mathbf{3}^+$•$\mathbf{BAr_4}^-$, tables of crystallographic data including atomic positional and thermal parameters for **2** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318. (b) Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991. (c) Breslow, R. *Pure Appl. Chem.* **1971**, *28*, 111. (d) Komatsu, K.; Kitagawa, T. *Chem. Rev.* **2003**, *103*, 1371.

(2) (a) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60. (b) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045. (c) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Ishida, Y. *Eur. J. Inorg. Chem.* **2000**, 1155.

(3) Ichinohe, M.; Igarashi, M.; Sanuki, K.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 9978.

(4) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250.

(5) For the related aromatic silyl cations, see: (a) Nishinaga, T.; Izukawa, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 9312. (b) Ishida, S.; Nishinaga, T.; West, R.; Komatsu, K. *Chem. Commun.* **2005**, 778. (c) Driess, M.; Yao, S.; Brym, M.; Wüllen, V.-C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6730.

(6) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231.

(7) (a) Ichinohe, M.; Arai, Y.; Sekiguchi, A.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 4141. (b) Sekiguchi, A.; Izumi, R.; Lee, V. Ya.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 14822. (c) Nakata, N.; Izumi, R.; Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 5058. (d) Nakata, N.; Sekiguchi, A. *J. Am. Chem. Soc.* **2006**, *128*, 422. (e) Nakata, N.; Fujita, T.; Sekiguchi, A. *J. Am. Chem. Soc.* **2006**, *128*, 16024.

(8) Very recently, a disilaoxetene derivative with a Si═C bond was reported by the reaction of disilenides with a carboxylic acid chloride. Bejan, I.; Güclü, D.; Inoue, S.; Ichinohe, M.; Sekiguchi, A.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3349.

(9) For the experimental procedure and spectral data, see Supporting Information.

(10) Diaryldilithiosilane was reported by the reaction of $ArAr'SiBr_2$ (Ar = 2,6-diisopropylphenyl, Ar′ = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) with LiNp. Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, 931.

(11) (a) Wiberg, N.; Niedermayer, W. *J. Organomet. Chem.* **2001**, *628*, 57. (b) Sekiguchi, A.; Tanaka, T.; Ichinohe, M.; Akiyama, K.; Tero-Kubota, S. *J. Am. Chem. Soc.* **2003**, *125*, 4962.

(12) Spectral data for **2**: yellow crystals, mp 170−171 °C (dec); ^1H NMR (C_6D_6, δ) 1.34 (s, 27 H), 1.48 (s, 54 H), 1.77 (d, 3 H, *J* = 11.4 Hz), 1.89 (d, 3 H, *J* = 11.4 Hz), 2.16 (s, 3 H), 2.37 (s, 6 H); ^{13}C NMR (C_6D_6, δ) 25.2, 27.4, 30.2, 32.1, 34.4, 37.4, 43.2, 45.3, 188.4; ^{29}Si NMR (C_6D_6, δ) −88.9, 28.7, 40.2, 79.2; UV−vis (hexane) λ_{max} (ε) 218 (53000), 304 (21000), 394 (1800). Anal. Calcd for $C_{47}H_{96}Si_5$: C, 70.41; H, 12.07. Found: C, 69.94; H, 11.94. A similar reaction using $({}^tBu_2MeSi)_2SiLi_2$ gave a complicated reaction mixture. The reaction mechanism to form **2** is not clear at this moment, but the formation of ${}^tBu_3SiLi$ was confirmed in the reaction mixture together with **2** in a 1:1 ratio. For the spectral data of ${}^tBu_3SiLi$, see: Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Schuster, H.; Nöth, H.; Krossing, I.; Schmidt-Amelunxen, M.; Seifert, T. *J. Organomet. Chem.* **1977**, *542*, 1.

(13) The choice of carbonyl compound is crucial; the reaction was unsuccessful in the case of less hindered acid halides, such as acetyl and benzoyl chlorides.

(14) Mixed heavy cyclopropenes: (a) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc*. **2000**, *122*, 9034. (b) Lee, V. Ya.; Yasuda, H.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6378. (c) For review: Sekiguchi, A.; Lee, V. Ya. *Chem. Rev.* **2003**, *103*, 1429.

(15) For reviews on silenes: (a) Chaubon, M. A.; Ranaivonjatovo, H.; Escudié, J.; Satgé, J. *Main Group Met. Chem.* **1996**, *19*, 145. (b) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (c) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 2, Chapter 16. (d) Ottosson, H.; Steel, P. G. *Chem.−Eur. J.* **2006**, *12*, 1576.

(16) The Si−Si bond length in ${}^tBu_3Si-Si{}^tBu_3$ is the longest one reported so far (2.697 Å): Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 79.

(17) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

JA075740N