An Isolable Boryl-substituted Disilene from the Reaction of an sp^2-type Silyl Anion with Haloboranes: Synthesis and Characterization

Shigeyoshi Inoue, Masaaki Ichinohe, and Akira Sekiguchi*
Department of Chemistry, Graduate School of Pure and Applied Sciences,
University of Tsukuba, Tsukuba 305-8571

(Received July 17, 2008; CL-080703; E-mail: sekiguch@chem.tsukuba.ac.jp)

The disilenyllithium, $(t\text{-Bu}_2\text{MeSi})_2\text{Si}{=}\text{Si}(\text{SiMe}t\text{-Bu}_2)\text{Li}$ (**2a**), reacted with *B*-chloropinacolborane (pin)BCl, or *B*-chlorocatecholborane (cat)BCl in toluene to produce the corresponding boryl-substituted disilenes **3a** and **3b**, which were isolated as air-sensitive yellow crystals. X-ray crystallographic analysis of **3b** showed a nearly planar geometry around the Si=Si bond lacking π-conjugation between the Si=Si bond and a vacant p orbital of boron.

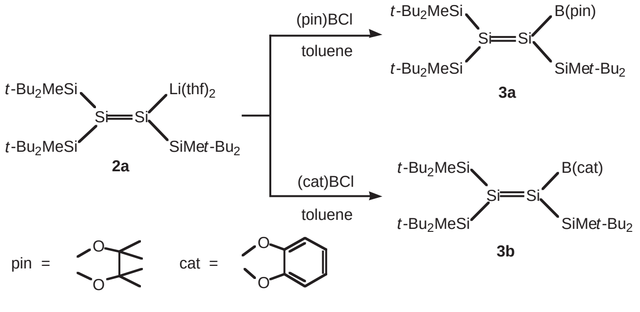
Since the first isolation of a compound with a silicon–silicon double bond by West et al. in 1981,[1] great progress has been made in the chemistry of stable disilenes.[2] In particular, electron-donating substituents, such as the silyl group, are well known to favor a planar Si=Si bond and increase the bond dissociation energy of disilenes.[3] Boron is also an electropositive element with vacant p orbitals, and its electronegativity is close to that of silicon: 2.04 (Pauling scale) for B, 1.90 for Si.[4] However, there have been no reports until now on the chemistry of isolable boryl-substituted disilenes, owing to lack of suitable routes in their preparation. Silylboranes are most commonly prepared by the reaction of silyllithium with haloboranes (R_2BX: X = F, Cl, Br, and I).[5] In this paper, we report the first synthesis of boryl-substituted disilenes by the reaction of an sp^2-type silyl anion with haloboranes.[6]

Recently, we reported the synthesis and isolation of sp^2-type silyl anions $(t\text{-Bu}_2\text{MeSi})_2\text{Si}{=}\text{Si}(\text{Mes})\text{M}$ (Mes = 2,4,6-trimethylphenyl, M = Li, and K),[7] $(t\text{-Bu}_2\text{MeSi})_2\text{Si}{=}\text{Si}(\text{SiMe}t\text{-Bu}_2)\text{M}$ (M = Li (**2a**), Na (**2b**), and K (**2c**)),[8] and $\text{Dsi}_2i\text{-PrSi(H)Si}{=}\text{Si(Li)Si}i\text{-PrDsi}_2$ [Dsi = $\text{CH(SiMe}_3)_2$].[9] Among these sp^2 silyl anions, the disilenyllithium **2a** is readily available on a relatively large scale from the two-electron reduction of tetrakis(di-*tert*-butylmethylsilyl)disilene $(t\text{-Bu}_2\text{MeSi})_2\text{Si}{=}\text{Si}(\text{SiMe}t\text{-Bu}_2)_2$ (**1**)[10] by LiNp in THF, which forms a dianion that can then be converted to **2a** by changing the solvent from THF to aromatic solvents. Scheschkewitz also reported the disilenyllithium $\text{Tip}_2\text{Si}{=}\text{Si(Tip)Li}$ (Tip = 2,4,6-triisopropylphenyl) from the reaction of $\text{Tip}_2\text{SiCl}_2$ with lithium metal.[11] Disilenyllithiums, such as **2a** and $\text{Tip}_2\text{Si}{=}\text{Si(Tip)Li}$, show interesting reactivity and have recently become very powerful synthetic tools in organosilicon chemistry.[12] For instance, we and Scheschkewitz et al. demonstrated that novel silenes with an Si=C bond can be synthesized by the reaction of disilenyllithiums with 2-adamantanone,[12e] 1-adamantanecarbonyl chloride,[12f] and vinyl bromides.[12h] We report here that disilenyllithium **2a** is a promising reagent for the synthesis of unprecedented boryl-substituted disilenes, which will be interesting as a new type of disilenes with a boron atom.

The reaction of disilenyllithium **2a** with 1 equiv of *B*-chloropinacolborane (pin)BCl, or *B*-chlorocatecholborane (cat)BCl in dry toluene at room temperature for 3 h efficiently produced the corresponding coupling products, the first boryl-substituted disilenes **3a** and **3b**, which were isolated by recrystallization from hexane as air-sensitive yellow crystals in 76% and 78% yields, respectively (Scheme 1).[13] However, the reaction of **2a** with 1.1 equiv of bis(2,4,6-trimethylphenyl)fluoroborane or diphenylchloroborane did not proceed as a coupling reaction, leading to a complex mixture. Molecular structures of boryl-substituted disilenes **3** were determined by spectroscopic data and X-ray crystallographic analysis (for **3b**).

The molecular structure of **3b** as determined by X-ray crystallographic analysis is shown in Figure 1.[14] The Si=Si bond length of **3b** is 2.192(2) Å, which is shorter than that of **1**[10] [2.2598(18) Å] and **2a**[8] [2.1983(18) Å], because of the decrease in steric hindrance. As expected, compound **3b** has a nearly planar geometry: the sums of the bond angles around the skeletal silicon atoms are 359.98° for Si1 and 359.99° for Si2. However, the Si=Si bond is slightly twisted: the twisting angle is 7.1°. The orientation of the catechol boryl substituent to the Si=Si double bond is almost perpendicular because of steric hindrance from the bulky substituents, the torsion angle for Si1–Si2–B1–O1 being 85.4°. Thus, there is essentially no π-conjugation between the Si=Si bond and the boryl group. The Si2–B1 bond length of **3b** [2.022(8) Å] is a typical length for an Si–B single bond (1.984–2.1249 Å) of silylboranes, lithium silyl borates, or the silylborane–isocyanide complex.[15]

The ^{29}Si NMR spectrum of **3a** in C_6D_6 showed resonance signals at 127.0 (B–Si=) and 111.5 ppm (Si–*Si*=), which were assigned to unsaturated skeletal silicon atoms, and at 16.7, 17.9, and 20.8 ppm, which were assigned to the three $t\text{-Bu}_2\text{MeSi}$ groups, respectively. These chemical shifts of the skeletal silicons are comparable to those of tetrasilyl-substituted disilenes.[3c] The ^{11}B NMR spectrum of **3a** showed a broad signal at 21.5 ppm, which is shifted downfield relative to boryl-substituted ethylenes.[16] The ^{29}Si and ^{11}B NMR spectra of **3b** showed signals at 127.3 and 111.7 ppm (^{29}Si NMR), and 22.6 ppm (^{11}B NMR), which are similar to those of **3a**.



Scheme 1.

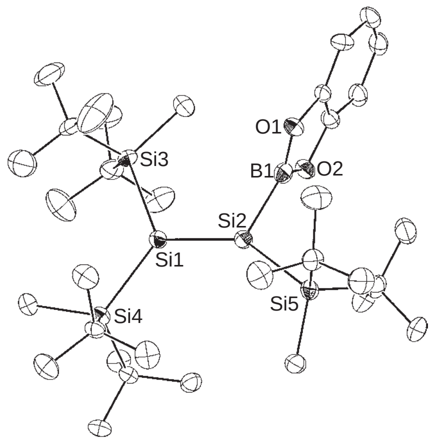


Figure 1. ORTEP drawing of **3b** (30% thermal ellipsoids, benzene molecule as crystal solvent and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Si1–Si2 = 2.192(2), Si1–Si3 = 2.397(3), Si1–Si4 = 2.393(2), Si2–Si5 = 2.386(2), Si2–B1 = 2.022(8), Si2–Si1–Si3 = 115.47(10), Si2–Si1–Si4 = 120.57(10), Si3–Si1–Si4 = 123.94(9), Si1–Si2–Si5 = 143.29(11), Si1–Si2–B1 = 111.3(2), Si5–Si2–B1 = 105.4(2).

In the UV–vis spectra of **3a** and **3b**, the longest wavelength absorption bands are observed at 393 ($\varepsilon = 1450\,\mathrm{M^{-1}\,cm^{-1}}$) and 395 nm ($\varepsilon = 1600\,\mathrm{M^{-1}\,cm^{-1}}$), respectively, and these were assigned to the π–π^* transition of the Si=Si bond. These values are close to those of tetrasilyl-substituted disilene (cf. 412 nm for (i-$\mathrm{Pr_2MeSi)_2Si{=}Si(SiMe}i\text{-}\mathrm{Pr_2)_2}$) with planar geometry of the Si=Si bond, which suggests a small effect of boryl-substitution on the Si=Si bond in disilene **3**.[3c] This is due to the absence of conjugation between a vacant p orbital of boron and the Si=Si π bond, as found in the X-ray structure of **3b**. Indeed, calculation on the model compound, catechol boryl-substituted disilene $\mathrm{(Me_3Si)_2Si{=}Si(SiMe_3)B(cat)}$ (**4b**),[17] with a perpendicular arrangement of the Si=Si double bond plane and catecohol boryl plane at the B3LYP/6-31G(d) level revealed that the HOMO–LUMO energy gap is similar to that of model compound $\mathrm{(Me_3Si)_2Si{=}Si(SiMe_3)_2}$ (**5**) (**4b**: −4.90 eV for HOMO and −1.58 eV for LUMO; **5**: −4.87 eV for HOMO, −1.64 eV for LUMO). The energy levels of **4b** are essentially not influenced by the introduction of the B(cat) group. On the other hand, the HOMO–LUMO energy gap of **4b**′ with a coplanar arrangement of the Si=Si double bond plane and catechol boryl plane (−4.98 eV for HOMO, −1.90 eV for LUMO) is significantly decreased compared with **4b**, because of the interaction between the Si=Si bond and a p-orbital of the boron atom. We are currently preparing such a conjugated system.

References and Notes

1 R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.

2 Reviews on disilenes: a) R. Okazaki, R. West, *Adv. Organomet. Chem.* **1996**, *39*, 231. b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463. c) M. Weidenbruch, in *The Chemistry of Organic Silicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, Wiley, Chichester, U.K., **2001**, Vol. 3, Chap. 5. d) R. West, *Polyhedron* **2002**, *21*, 467. e) M. Weidenbruch, *Organometallics* **2003**, *22*, 4348.

3 a) M. Karni, Y. Apeloig, *J. Am. Chem. Soc.* **1990**, *112*, 8589. b) C. Liang, L. C. Allen, *J. Am. Chem. Soc.* **1990**, *112*, 1039. c) M. Kira, T. Maruyama, C. Kabuto, K. Ebata, H. Sakurai, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.

4 J. Emsley, *The Elements*, 3rd ed., Oxford University Press, **1998**.

5 For example, see: a) H, Nöth, G. Höllerer, *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 551. b) J. D. Buynak, B. Geng, *Organometallics* **1995**, *14*, 3112. c) M. Suginome, T. Matsuda, Y. Ito, *Organometallics* **2000**, *19*, 4647.

6 For the substituent effects of $\mathrm{BH_2}$ on the geometry and energies of the Si=Si bond by theoretical calculations, see ref. 3a.

7 a) M. Ichinohe, K. Sanuki, S. Inoue, A. Sekiguchi, *Organometallics* **2004**, *23*, 3088. b) M. Ichinohe, K. Sanuki, S. Inoue, A. Sekiguchi, *Silicon Chem.* **2007**, *3*, 111.

8 S. Inoue, M. Ichinohe, A. Sekiguchi, *Chem. Lett.* **2005**, *34*, 1564.

9 R. Kinjo, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2007**, *129*, 26.

10 A. Sekiguchi, S. Inoue, M. Ichinohe, Y. Arai, *J. Am. Chem. Soc.* **2004**, *126*, 9626.

11 D. Scheschkewitz, *Angew. Chem., Int. Ed.* **2004**, *43*, 2965.

12 a) D. Scheschkewitz, *Angew. Chem., Int. Ed.* **2005**, *44*, 2954. b) T.-I. Nguyen, D. Scheschkewitz, *J. Am. Chem. Soc.* **2005**, *127*, 10174. c) K. Abersfelder, D. Güclü, D. Scheschkewitz, *Angew. Chem., Int. Ed.* **2006**, *45*, 1643. d) S. Inoue, M. Ichinohe, A. Sekiguchi, *Angew. Chem., Int. Ed.* **2007**, *46*, 3346. e) I. Bejan, D. Güclü, S. Inoue, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Angew. Chem., Int. Ed.* **2007**, *46*, 3349. f) K. Abersfelder, D. Scheschkewitz, *J. Am. Chem. Soc.* **2008**, *130*, 4114. g) I. Bejan, S. Inoue, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Chem.—Eur. J.* **2008**, *14*, 7119.

13 Procedure for the synthesis of **3a**: A mixture of disilenyllithium **2a** (101 mg, 0.148 mmol) and 1.0 equiv of β-chloropinacolborane (pin)BCl (24.3 mg, 0.150 mmol) in toluene was stirred at room temperature for 3 h. After removal of the solvent in vacuo, hexane was added and the boryl-substituted disilene **3a** was isolated as yellow air- and moisture-sensitive crystals (74.5 mg, 76%). Mp 155–156 °C. ^{1}H NMR ($\mathrm{C_6D_6}$, δ) 0.38 (s, 3H, Me), 0.39 (s, 3H, Me), 0.41 (s, 3H, Me), 1.12 (s, 18H, t-Bu), 1.16 (s, 18H, t-Bu), 1.18 (s, 6H, pin-Me), 1.19 (s, 6H, pin-Me), 1.23 (s, 18H, t-Bu); ^{13}C NMR ($\mathrm{C_6D_6}$, δ) −2.6, −1.8, −1.1, 22.0, 22.1, 22.2, 25.0, 29.6, 29.9, 30.4, 87.0; ^{29}Si NMR ($\mathrm{C_6D_6}$, δ) 16.7, 17.9, 20.8, 111.5 (Si–*Si*=), 127.0 (B–Si=); ^{11}B NMR ($\mathrm{C_6D_6}$, δ) 21.5; UV–vis (hexane): 393 nm ($\varepsilon = 1450\,\mathrm{M^{-1}\,cm^{-1}}$); HRMS m/z Calcd for $\mathrm{C_{33}H_{75}BO_2Si_5}$: 654.4706. Found: 654.4721. In a similar manner, **3b** was prepared in 78% yield. Mp 159–160 °C. ^{1}H NMR ($\mathrm{C_6D_6}$, δ) 0.38 (s, 3H, Me), 0.45 (s, 3H, Me), 0.50 (s, 3H, Me), 1.13 (s, 18H, t-Bu), 1.18 (s, 18H, t-Bu), 1.22 (s, 18H, t-Bu), 6.76 (dd, $J = 7.5$ Hz, 8.0 Hz, 2H, cat), 6.82 (dd, $J = 7.5$ Hz, 8.0 Hz, 2H, cat); ^{13}C NMR ($\mathrm{C_6D_6}$, δ) −2.6, −1.8, −1.1, 22.0, 22.1, 22.2, 29.6, 29.9, 30.4, 112.8, 123.2, 123.3; ^{29}Si NMR ($\mathrm{C_6D_6}$, δ) 16.8, 18.0, 20.7, 111.7 (Si–*Si*=), 127.3 (B–Si=); ^{11}B NMR ($\mathrm{C_6D_6}$, δ) 22.6; UV–vis (hexane) 395 nm ($\varepsilon = 1600\,\mathrm{M^{-1}\,cm^{-1}}$); HRMS m/z Calcd for $\mathrm{C_{33}H_{67}BO_2Si_5}$, 646.4080. Found: 646.4072.

14 Crystal data for **3b** at 150 K: $\mathrm{C_{33}H_{67}BO_2Si_5{\cdot}(C_6H_6)_{0.5}}$ $M_\mathrm{r} = 686.18$, Monoclinic, $C2/c$, $a = 22.875(5)$, $b = 24.267(2)$, $c = 17.242(4)$ Å, $\beta = 113.492(9)°$, $V = 8778(2)$ Å^3, $Z = 8$, $D_\mathrm{calc} = 1.038\,\mathrm{g\,cm^{-3}}$, $R = 0.0711$ ($I > 2\sigma(I)$), $R_w = 0.2040$ (all data), GOF = 0.836.

15 a) W. Lippert, H. Nöth, W. Ponikwar, T. Seifert, *Eur. J. Inorg. Chem.* **1999**, 817. b) T. Kajiwara, N. Takeda, T. Sasamori, N. Tokitoh, *Organometallics* **2004**, *23*, 4723. c) T. Kajiwara, N. Takeda, T. Sasamori, N. Tokitoh, *Chem. Commun.* **2004**, 2218. d) N. Nakata, R. Izumi, V. Ya. Lee, M. Ichinohe, A. Sekiguchi, *Chem. Lett.* **2005**, *34*, 582.

16 a) T. Onak, *Organoborane Chemistry*, Academic Press, New York, **1975**, pp. 38–40. b) T. D. Coyle, J. J. Ritter, *Advances in Organometallic Chemistry*, Academic Press, New York, **1972**, Vol. 10, pp. 237–272.

17 The model compound **4b** was optimized under the condition that the dihedral angle of Si=Si–B–O is restricted to 90 degrees. Compared to the conjugated **4b**′, obtained by full optimization without restriction, **4b** is less stable by 12.1 kJ/mol.