

# The Isolable Cation Radical of Disilene: Synthesis, Characterization, and a Reversible One-Electron Redox System

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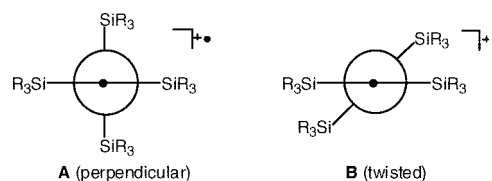
Alkenes with a C=C double bond are the simplest  $\pi$ -system compounds, and the cation radical or anion radical formed by one-electron oxidation or reduction are highly reactive intermediates in various organic reactions.<sup>1</sup> The  $\pi$ -electron redox system provides a significant contribution to various applications, for example, in electrochemistry, material sciences, and polymer chemistry. In general, the alkene cation radical is stabilized by electron-donating substituents,<sup>2</sup> whereas the alkene anion radical is stabilized by electron-withdrawing substituents.<sup>3</sup> Therefore, this hampers the preparation of both cation radical and anion radical from the same parent in alkene systems.

In contrast to alkenes, disilenes with a Si=Si double bond are known to readily undergo oxidation or reduction because of their high-lying HOMOs and low-lying LUMOs compared with those of the corresponding alkene analogues,<sup>4</sup> which makes possible the construction of a one-electron reversible redox system. There are some examples of the one- or two-electron reduction of disilenes.<sup>5,6</sup> However, there is no precedent for the one- or two-electron oxidation of a disilene to form the cation radical or dication, respectively.<sup>7</sup> The disilene cation radical is very interesting, being not only a silyl cation<sup>8</sup> but also a silyl radical.<sup>9</sup> We report here the isolation and structural characterization of the isolable cation radical of a disilene, representing the first isolable example of a heavy alkene analogue. In addition, an interesting reversible one-electron redox system is also reported.

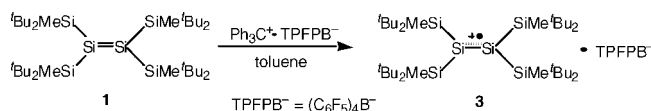
We recently reported the synthesis of a highly twisted tetrakis(*tert*-butylmethylsilyl)disilene (**1**),<sup>5b</sup> (Bu<sub>2</sub>MeSi)<sub>2</sub>Si=Si(SiMe<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>, which showed a characteristic intense blue color as the result of the small HOMO–LUMO energy gap.<sup>10</sup> Indeed, disilene **1** readily undergoes one-electron reduction by <sup>t</sup>BuLi to give an isolable anion radical **2** (for the synthesis of **2**, see Scheme 2),<sup>5b,10</sup> which has a highly twisted central Si–Si bond (twisting angle 88°). We have also used disilene **1** for the synthesis of the cation radical because it has four <sup>t</sup>Bu<sub>2</sub>MeSi groups on the sp<sup>2</sup>-Si atoms, and hence the resulting cation radical could be stabilized by  $\sigma$ – $\pi$  hyperconjugation of the four silyl groups, considering either perpendicular structure **A** or twisted structure **B** (Chart 1). Moreover, the central Si=Si bond in **1**<sup>5b</sup> is highly twisted (54.5°) as a result of steric reasons, which may facilitate such hyperconjugation.

As expected, disilene **1** readily undergoes chemical oxidation with Ph<sub>3</sub>C<sup>+</sup>·BAR<sub>4</sub><sup>–</sup> (BAR<sub>4</sub><sup>–</sup>: TFPFB<sup>–</sup> = tetrakis(pentafluorophenyl)borate). When a mixture of **1** and 1.1 equiv of Ph<sub>3</sub>C<sup>+</sup>·BAR<sub>4</sub><sup>–</sup> in toluene was stirred at room temperature over 30 min, it formed two liquid phases, accompanied with a color change from the dark blue of **1** to dark brown.<sup>11</sup> The lower layer was separated and washed with benzene/hexane to remove neutral materials. The disilene cation radical **3** was isolated as its borate salt in 65% yield as air- and moisture-sensitive red-brown crystals (Scheme 1). The structure of **3** was unequivocally characterized by X-ray crystallographic analysis and EPR spectroscopic data.<sup>11</sup>

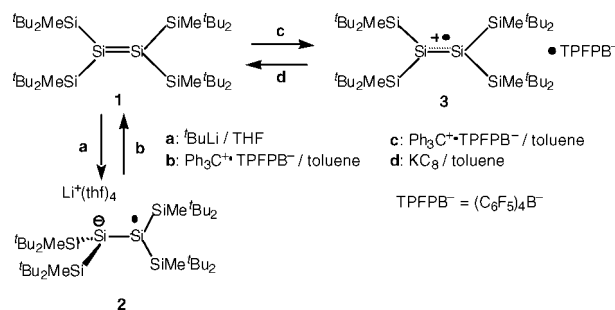
Chart 1



Scheme 1

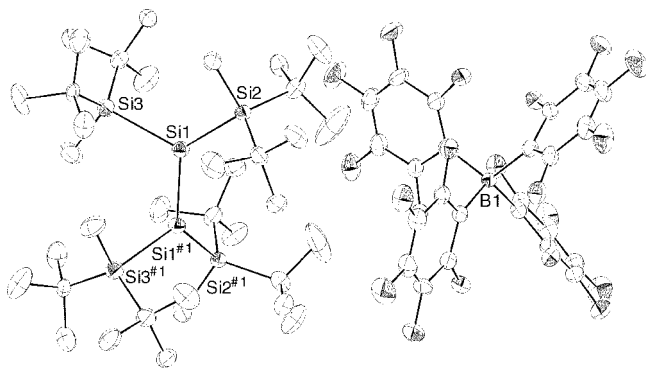


Scheme 2



Single crystals of **3** were grown from concentrated benzene solution. The crystal structure of **3** was determined by X-ray crystallography (Figure 1).<sup>11</sup> The shortest distance between the borate ion and the central silicon atoms of **3** is greater than 5.9 Å, indicating no interactions between them. The most peculiar structural features are the central Si–Si bond and its twisting angle. Thus, upon oxidation, this bond became highly twisted (64.9°) and 2.1% stretched (2.307(2) Å), compared with that of the starting disilene **1**<sup>5b</sup> (54.5°, 2.2598(18) Å). This phenomenon should certainly be ascribed to a decrease in the bond order after the one-electron oxidation. The geometry around the Si1 and Si1<sup>#1</sup> atoms is nearly planar. This is in marked contrast to the disilene anion radical **2** (twisting angle 88°, the central Si–Si bond 2.341(5) Å);<sup>5b</sup> the unpaired electron and negative charge in **2** are in the diagnostically planar geometry of one of the central Si atoms (radical center) and distinct pyramidity of the other central Si atom (anionic center).

The structure of the ethylene cation radical is predicted to be twisted by 30° because of the contributions from both the planar structure ( $\pi$ -bonding) and the perpendicular structure ( $\sigma$ – $\pi$  hyperconjugation of C–H bonds).<sup>12</sup> Experimentally, Kochi et al. reported the twisted structures of cation radicals of sesquihomoada-



**Figure 1.** ORTEP drawing of  $3 \cdot 2(\text{C}_6\text{H}_6)$  (30% probability level). #1 indicates the following symmetry transformations: #1 =  $-x, -y + 1/2, z$ . Hydrogen atoms and benzene molecules as crystal solvent are omitted for clarity.  $\text{Bu}_2\text{MeSi}$  groups on the Si1 atom were disordered with 50:50 probability and one of them is shown. Selected bond lengths ( $\text{\AA}$ ):  $\text{Si1}-\text{Si1}^{\#1} = 2.307(2)$ ,  $\text{Si1}-\text{Si2} = 2.463(2)$ ,  $\text{Si1}-\text{Si3} = 2.466(2)$ . Selected bond angles (deg):  $\text{Si1}^{\#1}-\text{Si1}-\text{Si2} = 128.25(5)$ ,  $\text{Si1}^{\#1}-\text{Si1}-\text{Si3} = 111.09(6)$ ,  $\text{Si2}-\text{Si1}-\text{Si3} = 120.10(10)$ .

mantene and 1,1,2,2-tetrakis(4-methoxyphenyl)ethylene by X-ray crystallography, the twisting angles being 29 and  $30.5^\circ$ , respectively.<sup>2</sup> In the present case, the disilene cation radical **3** prefers a more twisted structure than those of alkenes, due to the strong electronic effect of silyl substitution. There are four silyl substituents in **3**, which effectively stabilize the disilene cation radical by significant twisting of the central Si-Si bond (**B** in Chart 1). However, the perpendicular structure (**A** in Chart 1) completely breaks  $\text{Si}=\text{Si}$   $\pi$ -bonding. Thus, the magnitude of the twisting of the central bond of **3** is controlled by these two opposite factors. Evidence for  $\sigma$ - $\pi$  hyperconjugation comes from the elongation of the Si-Si bond lengths attached to the two central Si atoms; the bond lengths of 2.463(2)  $\text{\AA}$  for Si1-Si2 and 2.466(2)  $\text{\AA}$  for Si1-Si3 are stretched by 1.9% compared with that of **1** (av. 2.418  $\text{\AA}$ ). On the other hand, these Si-Si bond lengths are shortened in the anion radical **2** (av. 2.399  $\text{\AA}$ ), due to negative hyperconjugation ( $\alpha$ -effect). Most interestingly, the twisting angle in **3** is increased by  $10.4^\circ$  relative to **1**, even though the central Si-Si bond in **3** is stretched upon the one-electron oxidation. Thus, the most important factor leading to the increase of the twisting angle in **3** is this hyperconjugation of the silyl groups, rather than any steric reason.

The above discussion is well supported by the theoretical calculations. DFT calculations of the model compounds of  $(\text{Me}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiMe}_3)_2$  (**4**) and  $[(\text{Me}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiMe}_3)_2]^{\cdot+}$  (**5**) were performed at the (U)B3LYP/6-31G(d) level.<sup>13</sup> The structure of **5** is more twisted ( $34.2^\circ$ ) than that of disilene **4** ( $8.8^\circ$ ), and the central Si-Si bond length of **5** (2.277  $\text{\AA}$ ) is stretched by 5.5% compared with that of **4** (2.159  $\text{\AA}$ ). The  $\text{Si}_{(\text{sp}^2)}-\text{SiMe}_3$  bond lengths of **5** are also stretched by 1.1% relative to **4** due to the hyperconjugation.

The EPR spectrum of **3** measured at 298 to 200 K in fluorobenzene showed a strong signal with a  $g$  value of 2.0049, accompanied by a pair of satellite signals (2.30 mT) due to coupling of the unpaired electron with the central  $^{29}\text{Si}$  nuclei. The magnitude of  $h\nu_{\text{cc}}(\alpha\text{-}^{29}\text{Si})$  of 2.30 mT is less than half that of the similar  $\text{per}(\text{silyl})\text{silyl}$  radical  $(\text{Bu}_2\text{MeSi})_3\text{Si}^\bullet$  (5.80 mT),<sup>14</sup> implying delocalization of the unpaired electron over both Si1 and Si1<sup>#1</sup> atoms in **3**. The behavior of the cation radical **3** in solution contrasts with that of anion radical **2**; the latter showed a rapid spin exchange between the two central Si atoms on the EPR time scale.<sup>5b</sup> These differences assumed that cation radical **3** possesses a delocalized system, whereas anion radical **2** features an  $\text{sp}^3$ -silyl anion and an  $\text{sp}^2$ -silyl radical.

Finally, it is particularly interesting that cation radical **3** and anion radical **2** could be quantitatively converted back to the starting

material **1** by reduction and oxidation processes, respectively, making a fully reversible redox system. Thus, the one-electron reduction of **3** with  $\text{KC}_8$  in toluene proceeds rapidly to form **1** (Scheme 2). On the other hand, the one-electron oxidation of **2** with  $\text{Ph}_3\text{C}^+\cdot\text{BAR}_4^-$  in toluene also cleanly formed **1**.

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**Supporting Information Available:** Experimental procedures and EPR spectrum of **3**, table of crystallographic data including atomic positional and thermal parameters for **3** (PDF/CIF), computational results of **4** and **5**, and molecular orbitals (SOMO) of **3** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269.
- (2) (a) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6931. (b) Kochi, J. K.; Rathore, R.; Zhu, C.; Lindeman, S. V. *Angew. Chem., Int. Ed.* **2000**, *39*, 3671.
- (3) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.
- (4) (a) Escudé, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113. (b) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, Chapter 5. (c) Klinkhammer, K. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 2002; Vol. 2, Part 1, Chapter 4. (d) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. (e) Lee, V. Ya.; Sekiguchi, A. *Organometallics* **2004**, *23*, 2822.
- (5) Disilene anion radicals: (a) Weidenbruch, M.; Kramer, K.; Schäfer, A.; Blum, J. K. *Chem. Ber.* **1985**, *118*, 107. (b) Sekiguchi, A.; Inoue, S.; Ichinohe, M.; Arai, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9626. Distannene anion radical: (c) Fukawa, T.; Lee, V. Ya.; Nakamoto, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 11758. Anion radicals of the alkyne analogues of Si, Ge, and Sn: (d) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705. (e) Pu, L.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626. (f) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 26.
- (6) Disilene dianions: (a) Kira, M.; Iwamoto, T.; Yin, D.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **2001**, 910. (b) Inoue, S.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2005**, *34*, 1564.
- (7) Cyclic voltammetry (CV) of disilenes: (a) Shepherd, B. D.; West, R. *Chem. Lett.* **2000**, 183. (b) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236.
- (8) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (b) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402. (c) Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400. (d) Müller, T.; Zhao, Y.; Lambert, J. B. *Organometallics* **1998**, *17*, 278. (e) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhimann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001. (f) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250. (g) Kim, K. C.; Reed, C. A.; Elliott, D. W.; Mueller, L. J.; Tham, F.; Lin, L.; Lambert, J. B. *Science* **2002**, *297*, 825. (h) Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155. (i) Lee, V. Ya.; Sekiguchi, A. *Acc. Chem. Res.* **2007**, *40*, 410.
- (9) For reviews, see: (a) Chatgililoglu, C. *Chem. Rev.* **1995**, *95*, 1229. (b) Iley, J. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1995; Chapter 5. (c) Chatgililoglu, C.; Schiesser, C. H. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, Chapter 4. (d) Power, P. P. *Chem. Rev.* **2003**, *103*, 789. (e) Lee, V. Ya.; Sekiguchi, A. *Eur. J. Inorg. Chem.* **2005**, 1209. (f) Lee, V. Ya.; Sekiguchi, A. In *Reviews of Reactive Intermediate Chemistry*; Platz, M. S.; Moss, R. A.; Jones, M. J., Jr., Eds.; Wiley: Chichester, U.K., 2007; Chapter 2. (g) Lee, V. Ya.; Nakamoto, M.; Sekiguchi, A. *Chem. Lett.* **2008**, *37*, 128.
- (10) The cyclic voltammogram of disilene **1** in THF shows an irreversible oxidation wave at +0.41 V and a reversible reduction wave at -1.47 V, corresponding to the formation of disilene cation radical and disilene anion radical, respectively.
- (11) For the experimental procedures, EPR spectrum, and crystal data, see the Supporting Information.
- (12) (a) Mulliken, R. S.; Roothaan, C. C. J. *Chem. Rev.* **1947**, *41*, 219. (b) Mulliken, R. S. *Tetrahedron* **1959**, *5*, 253.
- (13) Optimization of model compounds **4** and **5** was performed at the (U)B3LYP/6-31G(d) level; see the Supporting Information.
- (14) Sekiguchi, A.; Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 9865.

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