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1,2-Bis(ferrocenyl)disilene: A Multistep Redox System with an $\mathrm{Si{=}Si}$ Double Bond

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Summary: A new type of disilene substituted by ferrocenyl groups, 1,2-bis(ferrocenyl)disilene, was synthesized as a good candidate for a novel d−π electron system, and the unique properties of the $\mathrm{Si{=}Si}$ π bond of this new disilene were revealed. On the basis of the results of the electrochemical analyses, 1,2-$\mathrm{Tip_2}$*-1,2-*$\mathrm{Fc_2}$*-disilene (Tip = 2,4,6-triisopropylphenyl, Fc = ferrocenyl) was found to be a stable five-electron redox system with four steps.*

The d−π-conjugated systems, multinuclear transition-metal complexes bridged by organic π-conjugated systems, have attracted considerable attention from the viewpoint of their electrochemical properties.[1] Particularly, stable multistep redox systems should be good model systems for the elucidation of the properties of mixed-valence states.[1] Therefore, there has been much interest in ferrocene oligomers bearing a π-conjugated spacer, e.g., $\mathrm{FcC{\equiv}CFc}$[2] and $\mathrm{FcN{=}NFc}$ (Fc = ferrocenyl),[1b,3] as the models of mixed-valence states, while a ferrocene is known to show unique electrochemical properties as a stable redox system.[4] On the other hand, several kinetically stabilized disilenes have been reported[5] since the first isolation of $\mathrm{Mes_2Si{=}SiMes_2}$ by West and co-workers,[6] showing that disilenes generally have higher HOMO and lower LUMO levels than those of olefins due to smaller overlapping between the 3p orbitals of Si atoms.[5] Such unique properties of disilenes have prompted many chemists to explore the chemistry of novel extended π-conjugated systems containing $\mathrm{Si{=}Si}$ units from the standpoint of material science.[7] In the case of phosphorus, which is the adjacent element of silicon in the periodic table, Protasiewicz and co-workers opened the door for the chemistry of π-conjugated systems containing $\mathrm{P{=}P}$ moieties, and this chemistry has attracted much interest from the viewpoint of their photochemical and electrochemical properties.[8] Recently, we have reported the synthesis of stable ferrocenyl- and anthryl-substituted diphosphenes together with their unique physical properties as novel conjugated systems containing a $\mathrm{P{=}P}$ unit.[9,10] In the case of silicon, however, the redox behavior of disilenes has been less explored and the stable disilenes reported so far showed only irreversible reduction and oxidation waves in the cyclic voltammograms.[5,11] These situations prompted us to design and synthesize a new type of disilene substituted by ferrocenyl groups, i.e., 1,2-bis(ferrocenyl)disilene, as a good candidate for a novel conjugated system, which should be an attractive target compound to reveal the unique properties of the bridging $\mathrm{Si{=}Si}$ π bond. The ferrocenyl moieties should make it possible to construct a stable multistep redox system through electronic conjugation.

We chose a 2,4,6-triisopropylphenyl group (denoted as Tip) as a steric protection group for the reactive $\mathrm{Si{=}Si}$ bond on the basis of the recent report on the synthesis of $\mathrm{Tip_2Si{=}Si(Ph)Tip}$[7a] as a stable crystalline compound. Dichlorosilane **2**, which was prepared by the reaction of FcLi with $\mathrm{TipSiCl_3}$, was reduced by lithium naphthalenide (2.2 equiv) in THF at −78 °C to afford the 1,2-bis(ferrocenyl)disilene **1** as orange-red crystals in 49%

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(1) For recent reviews, see: (a) Kaim, W.; Lahiri, G. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 1778. (b) Kurihara, M.; Nishihara, H. *Coord. Chem. Rev.* **2002**, *226*, 125. (c) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655. (d) Distefano, A. J.; Wishart, J. F.; Isied, S. S. *Coord. Chem. Rev.* **2005**, *249*, 507.

(2) (a) Mcmanis, G. E.; Gochev, A.; Nielson, R. M.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 7733. (b) Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1990**, *94*, 1788. (c) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

(3) (a) Kurosawa, M.; Nankawa, T.; Matsuda, T.; Kubo, K.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **1999**, *38*, 5113. (b) Kurihara, M.; Matsuda, T.; Hirooka, A.; Yutaka, T.; Nishihara, H. *J. Am. Chem. Soc.* **2000**, *122*, 12373. (c) Nishihara, H. *Coord. Chem. Rev.* **2005**, *249*, 1468.

(4) (a) *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995,and references cited therein. (b) Yamaguchi, Y.; Ding, W.; Sanderson, C. T.; Borden, M. L.; Morgan, M. J.; Kutal, C. *Coord. Chem. Rev.* **2007**, *251*, 515.

(5) For recent reviews, see: (a) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73. (b) Sasamori, T.; Tokitoh, N. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; Wiley: Chichester, U.K., 2005; p 1698. (c) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, p 391.

(6) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(7) (a) Bejan, I.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 5783. (b) Fukazawa, A.; Li, Y. M.; Yamaguchi, S.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2007**, *129*, 14164. (E_{ind} = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl). (c) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. (d) Nguyen, T.-l.; Scheschkewitz, D. *J. Am. Chem. Soc.* **2005**, *127*, 10174.

(8) For examples, see: (a) Smith, R. C.; Chen, X. F.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468. (b) Smith, R. C.; Chen, X. F.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468. (c) Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, 998. For a review, see: (d) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681.

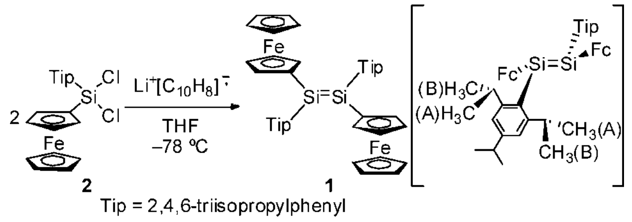
(9) Although Niecke et al. have succeeded in the synthesis of a marginally stable ferrocenyldiphosphene, $\mathrm{Mes^*P{=}PFc}$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) as a novel conjugated system, they reported that this diphosphene undergoes ready dimerization under ambient conditions. See: Pietschnig, R.; Niecke, E. *Organometallics* **1996**, *15*, 891.

(10) (a) Nagahora, N.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Eur. J.* **2004**, *10*, 6146. (b) Nagahora, N.; Sasamori, T.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 220. (c) Nagahora, N.; Sasamori, T.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1884. (d) Sasamori, T.; Tsurusaki, A.; Nagahora, N.; Matsuda, K.; Kanemitsu, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 1382. Pietschnig et al. have independently reported the synthesis of 1,1′-bis(diphosphenyl)ferrocenes; see: (e) Moser, C.; Nieger, M.; Pietschnig, R. *Organometallics* **2006**, *25*, 2667.

(11) Shepherd, B. D.; West, R. *Chem. Lett.* **1988**, *17*, 183.

10.1021/om8003543 CCC: $40.75

Scheme 1



yield[12] (Scheme 1). After heating of the toluene-d_8 solution of **1** in a sealed tube at 90 °C for 10 days, no change was observed in the ^{1}H NMR spectra, showing the high thermal stability of **1** in solution.

X-ray crystallographic analysis revealed that **1** has a center of symmetry in the middle of its Si═Si bond with an Si═Si bond length of 2.1733(15) Å (Figure 1, which is slightly longer than that of $Tip_2Si{=}SiTip_2$ (2.144 Å)[13] and close to those of the recently reported, π(phenyl)-conjugated disilenes (2.1593(16) Å for $E_{ind}(Ph)Si{=}Si(Ph)E_{ind}$,[7b] 2.1754 (11) Å for $Tip_2Si{=}Si(Ph)Tip$[7a]). The Si−C(Tip) bond length (1.880(3) Å) is slightly longer than the Si−C(Fc) bond length (1.848(3) Å), indicating the weak conjugation between the ferrocenyl and Si═Si moieties of **1**. In addition, **1** exhibits a characteristic trans-bent structure with a trans-bent angle (θ) of 27.9°, in contrast to the almost planar structure of $Tip_2Si{=}SiTip_2$[13] (ca. 1°) and $E_{ind}(Ph)Si{=}Si(Ph)E_{ind}$[7b] (2.7°). The character of the Si═Si bond of **1** was further examined by vibrational spectra. In the solid-state Raman spectra, **1** exhibited an intense Raman line at 595 cm^{-1}, which should predominantly correspond to the Si═Si vibration.[14] Although only a few examples have been reported for the measurement of vibrational spectra of stable disilenes, the Si═Si vibrational frequencies generally depend on the substituents and are observed around 500−550 cm^{-1}.[5] This suggests a relatively strong Si═Si bond in **1**.

In the ^{29}Si NMR (C_6D_6) spectrum, **1** showed a signal at 72.6 ppm in the low-field region characteristic of low-coordinated silicon atoms, supporting the symmetric structure and the disilene character of **1** in solution. Although the ^{1}H NMR spectrum (C_6D_6) of **1** suggested that the ferrocenyl and Tip groups should freely rotate without any steric restriction at room temperature, two doublet signals are observed for the methyl groups (CH_3(A) and CH_3(B) in Scheme 1) of *o*-isopropyl groups, suggesting the trans-bent structure of **1** in solution due to the diastereotopically independent methyl groups.

UV/vis spectra of **1** (hexane) showed two characteristic absorption maxima at 332 nm (ϵ 5900) and 427 nm (ϵ 24 000). TD-DFT calculations for **1**[14] indicated the former weak absorption should predominantly correspond to the d(Fe)−π*(Si═Si) electron transition and the latter should be assignable to the π−π* (Si═Si) electron transition, though it was difficult to make a detailed assignment for the observed absorbance, since several d−π* electron transitions were estimated to be around 400−500 nm.[5] The latter λ_{max} value for the π−π* electron transition (Si═Si) is similar to those of previously reported stable disilenes (400−440 nm), indicating the π conjugation between the Cp and Si═Si moieties of **1** should not be effective in the electronic spectra. As shown in Figure 2), the KS-HOMO and KS-LUMO of **1** predominantly consist of Si═Si π and π* orbitals, respectively, while π and d orbitals of ferrocenyl units contribute to the frontier orbitals to some extent.[14] It should be noted that the absorption for d(Fe)−π*(Si═Si) electron transitions was clearly observed in the visible light region.

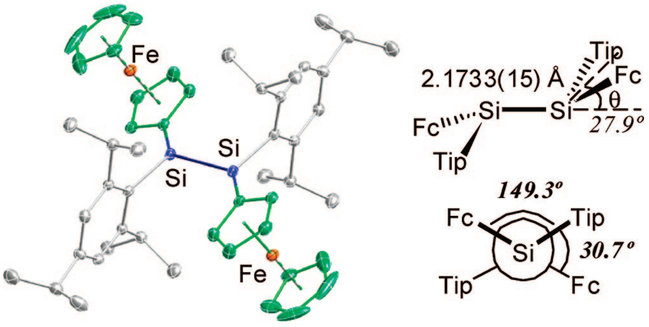


Figure 1. Structure of 1,2-bis(ferrocenyl)disilene **1**. Displacement ellipsoids were drawn at the 30% probability level.

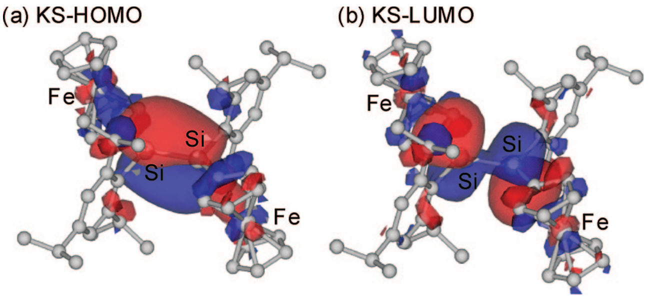


Figure 2. Kohn−Sham (KS) frontier orbitals of **1** (B3PW91/Si:6-31+G(2d) for C, H; 6-31G(d) for Fe; DZVP).

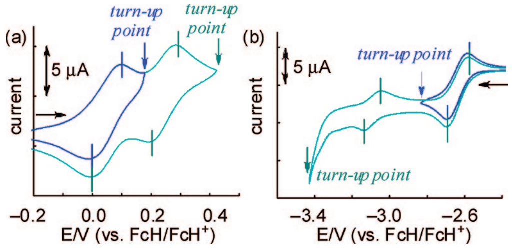


Figure 3. Cyclic voltammograms of disilene **1** (V vs FcH/FcH$^+$): (a) oxidation region measured in 0.1 M $Bu_4NB(C_6F_5)_4$ in *o*-dichlorobenzene ($E_{1/2}$ (FcH/FcH$^+$) = +0.34 V vs Ag/Ag$^+$); (b) reduction region measured in 0.1 M Bu_4NBF_4 in THF ($E_{1/2}$ (FcH/FcH$^+$) = +0.57 V vs Ag/Ag$^+$). The scan rate was 0.01 V/s.

The redox behavior of **1** was revealed by the cyclic and differential pulse voltammetric analyses (Figure 3). In the oxidation region, **1** exhibits two-step one-electron redox waves as reversible couples at $E_{1/2}$ = +0.05 and +0.24 V (vs FcH/FcH$^+$). The difference between the two redox potentials is $\Delta E_{1/2}$ = 0.19 V, which is comparable to that of the corresponding carbon analogue, (*E*)-Ph(Fc)C═C(Fc)Ph ($\Delta E_{1/2}$ = 0.18 V),[15a] indicating significant coupling between the two ferrocenyl groups of **1** through the Si═Si π bond, as in the case of the carbon analogue.[16] On the other hand, two-step reversible redox

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(12) Experimental procedures and chemical data for the newly obtained compounds are given in the Supporting Information.

(13) Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, *16*, 1341.

(14) Theoretical calculations for **1** were performed at the (U)B3PW91/Si:6-31+G(2d) (C, H) and 6-31G(d) levels (Fe), with DZVP (See: Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.). The molecular orbital coefficients of HOMO of **1** dominantly consist of 3PZ (0.339 95), 4PZ (0.245 95), and 5S (0.276 87) orbitals of Si atoms along with 9D-2 orbitals (0.176 02) of Fe atoms. The Si═Si bond length for the optimized structure of **1** was 2.194 Å. The characteristic vibrational mode for ν_{SiSi} was estimated as 606 cm^{-1}.

couples were observed in the reduction region at $E_{1/2} = -2.64$ (two electrons) and -3.09 V (one electron) (vs FcH/FcH$^+$), in contrast to the case of (*E*)-Ph(Fc)C═C(Fc)Ph, which was reported to show no evident reduction wave.[15a] The differential pulse voltammograms suggested that the first redox wave should be related with two electrons and the second one should be a one-electron-transfer process, on the basis of a comparison with those of the FcH/FcH$^+$ redox system. Therefore, it was demonstrated that the ferrocenyl groups of **1** should stabilize the corresponding anion and cation species of **1**, probably due to electronic conjugation, in contrast to the case of tetraaryldisilenes such as $Mes_2Si═SiMes_2$ and $Tip_2Si═SiTip_2$,[11] which showed only irreversible reduction wave in the cyclic voltammogram. In the first step of the oxidation and reduction process of **1**, the corresponding cation radical and dianion species should be generated, respectively. Structural optimization[14] of cation and dianion species of **1** showed the structural change of **1** through the oxidation and reduction process. The optimized structure of $[\mathbf{1}]^+$ shows a slightly planar geometry (trans-bent angle 13.3°) as compared with **1** and slightly elongated Si−Si bond (2.259 Å), indicating the effective interaction between the two ferrocenyl groups through the Si−Si unit in $[\mathbf{1}]^+$. The second oxidation step of **1** should correspond to the elimination of an electron from the SOMO of $[\mathbf{1}]^+$. On the other hand, the highly bent structure (trans-bent angle 68.3°) and much longer Si−Si bond length (2.487 Å) of $[\mathbf{1}]^{2-}$ as compared with those of **1** suggest that the structure of $[\mathbf{1}]^{2-}$ should be interpreted in terms of a bis silyl anion species, $Tip(Fc)Si^-{-}Si^-(Fc)Tip$, the HOMO of which reflects the LUMO of **1**. Since the LUMO of $[\mathbf{1}]^{2-}$ should dominantly consist of π^* orbitals of the Tip groups, the second step of the reduction of **1** should occur on the π orbitals of the Tip groups, which seem to be conjugated through the Si−Si σ bond.[17] Thus, disilene **1** was found to exhibit unique electrochemical properties quite different from those of the ferrocenyl-substituted olefins,[15] which were reported to show multistep redox behavior only in the oxidation region. The novel character of disilene **1** as a stable four-step redox system with five electrons should be interpreted in terms of the unique electronic conjugation between the ferrocenyl and Si═Si π-bond moieties.

In summary, the 1,2-bis(ferrocenyl)disilene **1** was synthesized and characterized as a novel d−π electron system containing an Si═Si bond. It was demonstrated that **1** exhibits unique multistep redox behavior, indicating the possible application of π-electron systems between heavier main-group elements toward electrochemical materials. Further investigations on the properties of **1** are currently in progress.

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Supporting Information Available: Text, tables, and figures giving experimental procedures and spectral data for new compounds and CIF files giving X-ray data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Skibar, W.; Kopacka, H.; Wurst, K.; Salzmann, C.; Ongania, K. H.; de Biani, F. F.; Zanello, P.; Bildstein, B. *Organometallics* **2004**, *23*, 1024. (b) Bildstein, B.; Hradsky, A.; Kopacka, H.; Malleier, R.; Ongania, K. H. *J. Organomet. Chem.* **1997**, *540*, 127. (c) Hradsky, A.; Bildstein, B.; Schuler, N.; Schottenberger, H.; Jaitner, P.; Ongania, K. H.; Wurst, K.; Launay, J. P. *Organometallics* **1997**, *16*, 392.

(16) The carbon analogue, (*E*)-Ph(Fc)C═C(Fc)Ph, was reported to show two reversible redox waves in the oxidation region at +0.35 and +0.53 V (vs SCE, 0.5×10^{-3} M $Bu_4NB(C_6F_5)_4$, CH_2Cl_2),[15a] which should be convertible to−0.11 and +0.07 V (vs FcH/FcH$^+$), respectively, indicating oxidation potentials lower than those of **1**. However, it should be difficult to draw a conclusion on the basis of these results, since the solvent effects should not be negligible.

(17) The second step of the oxidation and reduction process should reflect the HOMO and LUMO of the cation and dianion species of **1**, respectively, though the definitive conclusion of the theoretical calculations on the dication and trianion species of **1** has not been obtained at present. Optimized structures of the neutral, cation, and dianion species of **1** are given in the Supporting Information.