ORGANOMETALLICS

Volume 27, Number 3, February 11, 2008

Communications

Reduction of a Kinetically Stabilized Silabenzene Leading to the Formation of the Corresponding Anion Radical Species[†]

Takeshi Matsumoto,[‡] Takahiro Sasamori,[‡] Kazunobu Sato,[§] Takeji Takui,[§] and Norihiro Tokitoh*,[‡]

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan, and Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received October 22, 2007

*Summary: An electrochemical study of kinetically stabilized silabenzene, 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silabenzene (**1**), revealed that its reduction potential is –2.96 V (vs Cp_2Fe/Cp_2Fe^+), which is lower than that of naphthalene. The anion radical species of **1** was generated by one-electron reduction using lithium naphthalenide and characterized by ESR spectroscopy.*

Aromatic compounds such as benzene and naphthalene are among the most fundamental classes of organic compounds and play very important roles in organic chemistry. Although aromatic compounds containing a silicon atom have attracted considerable interest from the viewpoint of their unique properties as the heavier element congeners, it has been difficult to synthesize and isolate silaaromatics due to their extremely high reactivity.[1] We have succeeded in synthesizing several kinds of silaaromatic compounds,[2,3] i.e., 1-Tbt-silabenzene (**1**), 1-Tbt-1-silanaphthalene, 2-Tbt-2-silanaphthalenes, 9-Tbt-9-silaanthracene, and 9-Tbt-9-silaphenanthrene, as stable crystalline compounds by taking advantage of the steric protection using a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) group.[4] Although the redox behavior of several kinds of aromatic

---

* To whom correspondence should be addressed. Tel: +81-774-38-3200. Fax: +81-774-38-3209 . E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

[†] Dedicated to Prof. Renji Okazaki on the occasion of his 70th birthday.

[‡] Kyoto University.

[§] Osaka City University.

(1) For recent reviews, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 1102–1108. (c) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 151–166. (d) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (e) Apeloig, Y.; Karni, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2.

(2) (a) Tokitoh, N. *Acc. Chem. Res.* **2004**, *37*, 86. (b) Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 429. (c) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951. (d) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336. (e) Wakita, K.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2157. (f) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 636. (g) Wakita, K.; Tokitoh, N.; Okazaki, R.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648. (h) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 256. (i) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 4024. (j) Shinohara, A.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2003**, *125*, 10805. (k) Shinohara, A.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 977. (l) Tokitoh, N.; Shinohara, A.; Matsumoto, T.; Sasamori, T.; Takeda, N.; Furukawa, Y. *Organometallics* **2007**, *26*, 4048.

(3) We have also succeeded in the synthesis of much heavier analogues: i.e., germa- and stannaaromatic compounds. See: (a) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2001**, *20*, 5507. (b) Nakata, N.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2002**, 818. (c) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2002**, *124*, 6914. (d) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Organomet. Chem.* **2003**, *672*, 66. (e) Nakata, N.; Takeda, N.; Tokitoh, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 115. (f) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2003**, *22*, 481. (g) Sasamori, T.; Inamura, K.; Hoshino, W.; Nakata, N.; Mizuhata, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Organometallics* **2006**, *25*, 3533. (h) Mizuhata, Y.; Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1050.

(4) (a) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293. (b) Okazaki, R.; Tokitoh, N.; Matsumoto, T. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Thieme: New York, 1996; Vol. 2, pp 260–269.

10.1021/om701060a CCC: $40.75

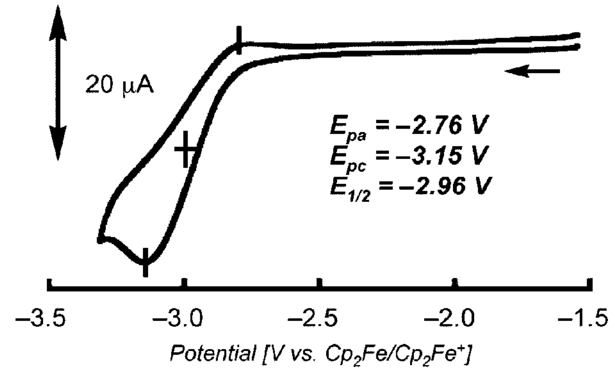


Figure 1. Cyclic voltammogram of silabenzene **1** (2 mM) at a GC working electrode in THF in the presence of 0.1 M $n\text{-Bu}_4\text{NPF}_6$ (sweep rate 100 mV/s).

hydrocarbons has been reported,[5] the molecular structures of the corresponding anion[6] or cation[7] radical species have not been fully disclosed until recently. The comparison of redox properties between silaaromatics and hydrocarbons and the structural features of the corresponding radical species of silaaromatics should be of great interest and importance in terms of the unique properties of "*heavy aromatics*". We report here the electrochemical properties and the chemical reduction reaction of the kinetically stabilized silabenzene **1**.

Scheme 1. Synthesis of the Silabenzene Anion Radical 2

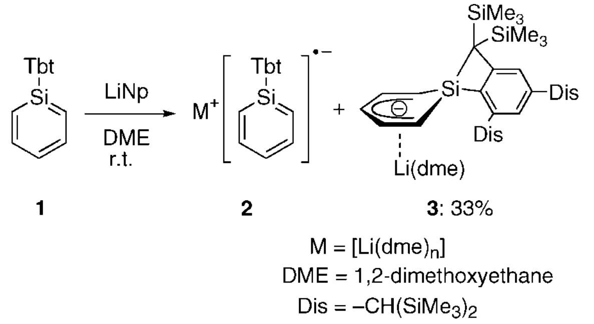


Table 1. Calculated Spin Densities for $\mathbf{1}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$–$\mathbf{6}^{\bullet-}$ and hfcc Values for $\mathbf{1}^{\bullet-}$

	spin density				
	Si	C(1), C(5)	C(2), C(4)	C(3)	C(6), C(7)
$\mathbf{1}^{\bullet-}$[a]	0.81	0.12, 0.09	−0.13, −0.12	0.24	0.05
$\mathbf{4}^{\bullet-}$[b]	0.55	0.13	−0.07	0.27	
$\mathbf{5}^{\bullet-}$[b]	0.23	0.17	−0.04	0.06	0.01
$\mathbf{6}^{\bullet-}$[b]	0.42	0.19	−0.09, −0.08	0.26	0.04, 0.00

	hfcc for $\mathbf{1}^{\bullet-}$ (in units of MHz)[c]				
	Si	H(1), H(5)	H(2), H(4)	H(3)	H(6), H(7)
$\mathbf{1}^{\bullet-}$	−296.39	−8.26, −8.39	4.52, 5.47	−11.84	−8.83, −0.04

[a] Values were calculated by using Gaussian 03 with the UB3LYP/6-31+G(2d) level. [b] Values were calculated by using Gaussian 98 with the UB3LYP/6-31G(d) level. [c] The hfcc values of $\mathbf{1}^{\bullet-}$ were calculated by using the ADF 2006 program package with TZ2Pae basis sets.

The cyclic voltammogram (in THF at room temperature in the presence of $n\text{-Bu}_4\text{NPF}_6$) for silabenzene **1**, which was prepared according to the reported procedures,[2f] shows a quasi-reversible reduction couple at $E_{1/2}^{\mathrm{red}}$ = –2.96 V(vs Cp_2Fe/Cp_2Fe^+) (Figure 1), indicating that the anion radical species of **1** should be considerably stable under these conditions. The observed reduction potential ($E_{1/2}^{\mathrm{red}}$) of **1** was found to lie between those of naphthalene (−3.14 V) and anthracene (−2.54 V), which were measured under the same conditions. Since $E_{1/2}^{\mathrm{red}}$ of benzene was not obtained under these conditions, the theoretical calculations of adiabatic electron affinity (EA)[8] for the related compounds were performed to give us insight into the redox properties. As a result, the calculated EA of the less hindered model compound of **1** bearing a 2,6-dimethylphenyl (Dmp) group instead of the Tbt group was computed as –0.16 eV, which was intermediate between those of naphthalene (−0.57 eV) and anthracene (0.27 eV), being in good agreement with the tendency of the observed $E_{1/2}^{\mathrm{red}}$ values. Hence, it can be considered that the $E_{1/2}^{\mathrm{red}}$ value of **1** should be lower than that of benzene, since the calculated EA of benzene (−1.76 eV) is much more negative than that of naphthalene. In other words, **1** is more easily reduced compared with benzene due to its lower LUMO level, reflecting the Si=C double-bond character in the silabenzene skeleton.[9]

The result of the cyclic voltammetry for **1** naturally prompted us to examine the chemical reduction of **1**, leading to the formation of the corresponding anion radical species. Treatment of a colorless DME solution of **1** with lithium naphthalenide (1 equiv) afforded a dark red suspension (Scheme 1). The ESR spectrum of the crude mixture in THF at room temperature showed characteristic, well-separated multiple lines, indicating the generation of the silabenzene anion radical **2**. To identify the anionic species **2**, theoretical calculations using the model compounds of silabenzene anion radical species ($\mathbf{1}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$–$\mathbf{6}^{\bullet-}$) were performed (Table 1).

In all cases of $\mathbf{1}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$–$\mathbf{6}^{\bullet-}$, the central silicon atom has the highest spin density on the silabenzene skeleton. Furthermore, the order of the spin densities in the C_5H_5 units is as C(3) > C(1,5) > C(2,4), being in good agreement with the experimental results obtained by ESR spectroscopy (see below for the experimentally determined hfcc values). Interestingly, the theoretical calculations for $\mathbf{1}^{\bullet-}$ indicate that the C(6) and C(7) atoms of the Tbt group have an appreciable amount of spin density (0.05). Whereas the calculated hfcc values for H(6) and H(7) are different in magnitude, probably due to the asymmetric molecular structure (vide infra), the benzyl protons of H(6) and H(7) can be thought to affect the electronic spin

---

(5) Chen, E. S.; Chen, E. C. M.; Sane, N.; Talley, L.; Kozanecki, N.; Shulze, S *J. Chem. Phys.* **1999**, *110*, 9319 and references therein.

(6) (a) Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V. *J. Am. Chem. Soc.* **2001**, *123*, 189. (b) Bock, H.; Arad, C.; Näther, C.; Halvas, Z. *Chem. Commun.* **1995**, 2393. (c) Bock, H.; Ansari, M.; Nagel, N.; Halvas, Z. *J. Organomet. Chem.* **1995**, *499*, 63. (d) Näther, C.; Bock, H.; Halvas, Z.; Hauk, T. *Organometallics* **1998**, *17*, 4707. (e) Janiak, C.; Hemling, H. *Chem. Ber.* **1994**, *127*, 1251. (f) Noordik, J. H.; Beurskens, P. T.; van den Hark, T. E. M.; Smits, J. M. M. *Acta Crystallogr., Sect. B* **1979**, *35*, 621. (g) Grovenstein, E., Jr.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2800.

(7) For recent reviews, see: (a) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399. (b) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847. (c) Elbl, K.; Krieger, C.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1023. (d) Thomaides, J. S.; Maslak, P.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 3970. (e) Dixon, D. A.; Calabrese, J. C.; Harlow, R. L.; Miller, J. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 92. (f) Matsuura, A.; Nishinaga, T.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 10007.

(8) Theoretical calculations were performed by using Gaussian 98 at the B3LYP/6-31G(d) level. B3LYP was selected as a calculation method, because the adiabatic EA values calculated by the DFT method for several examples of atoms and molecules containing heavier main-group elements are known to be in excellent agreement with the corresponding experimental data; see: (a) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231. (b) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582. (c) Sasamori, T.; Mieda, E.; Nagahora, N.; Takeda, N.; Takagi, N.; Nagase, S.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 166.

(9) Apeloig and Becker et al. reported that $H_2Si{=}CH_2$ had much lower LUMO energies than $H_2C{=}CH_2$ and that the Si=C framework is more easily reduced than the C=C framework; see: Bendikov, M.; Kravchenko, V.; Apeloig, Y.; Becker, J. Y. *Organometallics* **2004**, *23*, 921.

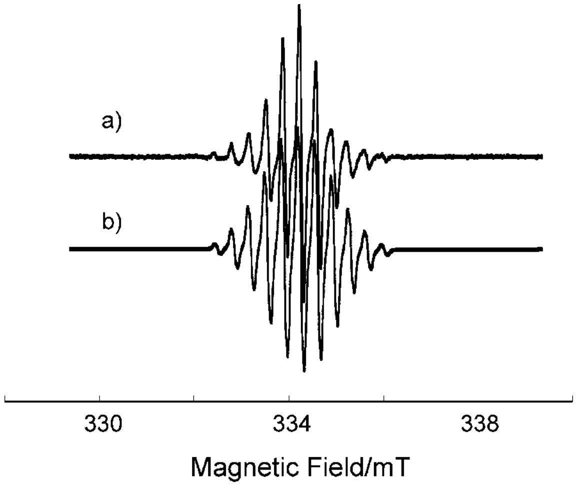


Figure 2. (a) Observed ESR spectrum at 293 K (microwave frequency 9.367 489 GHz) for **2**. (b) Corresponding simulated spectrum.

Table 2. Observed and Calculated Bond Lengths (Å) for 1 and 1$^{\bullet-}$

	Si–C(1,5)	C(1,5)–C(2,4)	C(2,4)–C(3)
1$^{\bullet-a}$	1.848	1.388	1.413
1^{b}	1.780	1.401	1.402
1 (X-ray)^{b}	1.765(4)	1.391(6)	1.399(6)
	1.770(4)	1.397(6)	1.381(6)

[a] Calculated by using Gaussian 03 at the B3LYP/6-31+G(2d) level. [b] Reference 2f.

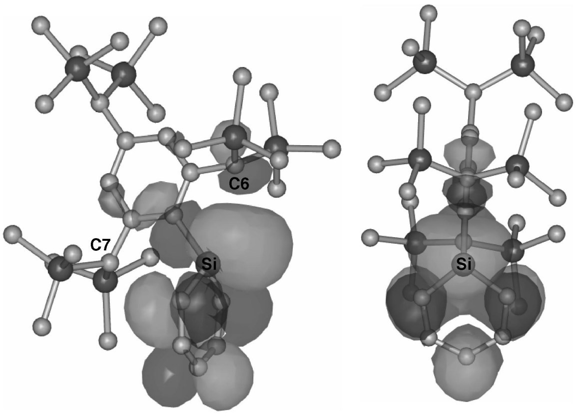
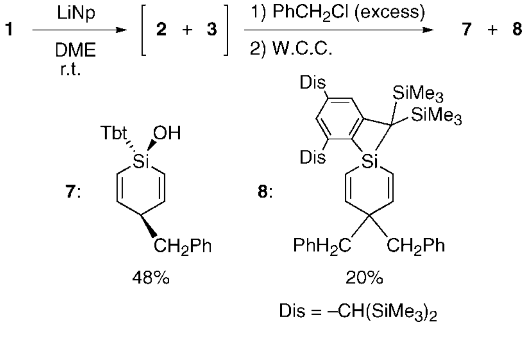


Figure 3. Optimized structure of **1**$^{\bullet-}$ and its SOMO calculated at the UB3LYP/6-31+G(2d) level. Hydrogen atoms are omitted for clarity.

Scheme 2. Trapping Reaction of the Silabenzene Anion Radical 2



Scheme 3. Plausible Mechanism for the Formation of 7

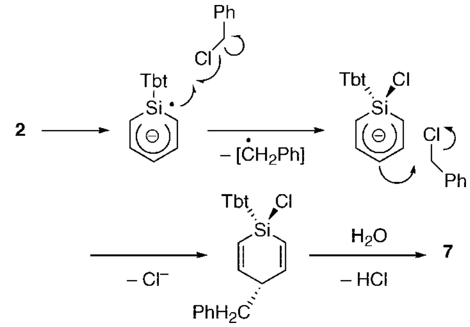
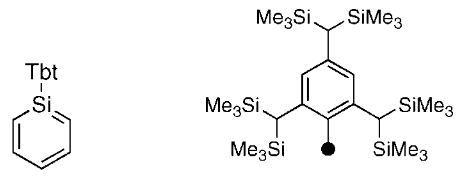
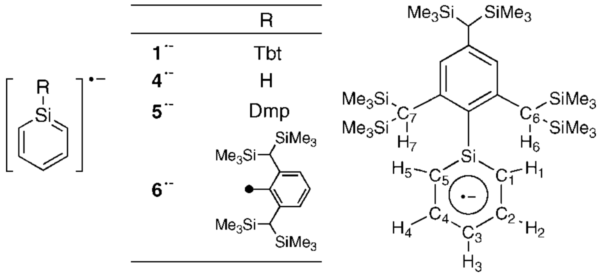


Chart 1



1 **Tbt group**

Chart 2



structure to a large extent. It should be noted that the optimized structure of **1**$^{\bullet-}$ shows a pyramidalized geometry for the central silicon atom, in sharp contrast to the planar structure of the six-membered ring of 1-Tbt-silabenzene (**1**), indicating that the hybridization of the central silicon atom should be changed from sp^2 (in **1**) to sp^3 (in **1**$^{\bullet-}$) upon the one-electron reduction (Figure 3). Although the spin density seems to be dominantly localized at the central silicon atom, the SOMO of **1**$^{\bullet-}$ suggests the somewhat delocalized unpaired electron on the SiC_5 ring, which was also supported by the longer Si–C(1,5), C(2,4)–C(3) and shorter C(1,5)–C(2,4) bond lengths of **1**$^{\bullet-}$ as compared to those of **1** (Table 2). In addition, the central silicon atom has a large coefficient of the SOMO, which is close to that of H(6). Taking the calculated hfcc values into consideration,[10] the observed ESR spectrum is most reasonably simulated as one arising from **2** with the parameters of $g = 2.0022$ and $a(^1H) = 0.708$ mT (19.84 MHz) for H(3), $a(^1H) = 0.701$ mT (19.64 MHz) for H(1) and

---

(10) Indeed, our attempt to reproduce the observed hfcc' values of **1**$^{\bullet-}$ with the help of quantum-chemical calculations has been only semiquantitatively successful, but to our knowledge spin Hamiltonian parameters for exotic open-shell entities such as silabenzene anion radicals have rarely been calculated in order to assign well-resolved ESR spectra. In this context, the silabenzene anion radical **1**$^{\bullet-}$ gives a testing ground for the establishment of the DFT approaches.

(11) Our close study of the well-resolved isotropic ESR spectrum, which was observed under the conditions of sideband free field modulation as shown in Figure 2a, has revealed that hyperfine splittings from a minor unidentified silabenzene-based species contribute to the observed spectrum, resulting in a departure from the perfect agreement between experiment and theoretical simulation. Particularly, the discrepancy is appreciable in the intensity of the hyperfine lines in the central part. The minor species should be characterized by a set of hfcc values different from those of **1**$^{\bullet-}$. Chemical identification of the minor byproduct is underway using solution ENDOR/TRIPLE spectroscopy, experimentally determining small hfcc values of protons.

H(5), $a(^1H) = 0.352$ mT (9.86 MHz) for H(2) and H(4), and $a(^1H) = 0.348$ mT (9.75 MHz) for H(6) and H(7) (Figure 2b), indicating the observed lines should be assigned to those of $\mathbf{1}^{\bullet-}$.[11] The hfcc value of the ^{29}Si atom could not be experimentally derived due to its low natural abundance (4.7%).[12]

Although the generation of **2** was revealed by ESR spectroscopy, the reprecipitation of the reaction mixture from hexane afforded an NMR-active byproduct, **3**, in 33% yield as pale yellow crystals (Scheme 1).[13] At present, the isolation of **2** has not been achieved yet due to the inseparable byproduct, **3**. To estimate the formation ratio for **2**, the trapping reaction of **2** with the alkyl halide was examined. The reduction of **1** with lithium naphthalenide under the same conditions followed by the addition of an excess amount of $PhCH_2Cl$ resulted in the formation of **7** (48%) and **8** (20%) (Scheme 2). The formation of **7** can most likely be interpreted in terms of the reaction of **2** with two molecules of $PhCH_2Cl$ (Scheme 3). In addition, **8** may be generated from **3**, though the reaction mechanism is unclear at present. Therefore, it was presumed that **2** should be generated in the reduction reaction in ca. 50% yield, as estimated on the basis of the isolated yield of **7**.

In summary, we have examined the electrochemical properties of a kinetically stabilized silabenzene, **1**, and succeeded in generating the corresponding anion radical species **2**. The results of ESR spectroscopic analysis and DFT-based theoretical calculations revealed spin distributions characteristic of **2**. Further investigations on the redox behavior of kinetically stabilized metallaaromatic compounds are in progress.

Acknowledgment. This work was partially supported by Grants-in-Aid for Creative Scientific Research (No. 17GS0207), Science Research on Priority Areas (No. 19027024, "Synergy of Elements"), Young Scientist (B) (No. 18750030), and the 21st Century COE and the Global COE Programs, Kyoto University Alliance for Chemistry from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Text, tables, and figures giving experimental procedures and spectral data for new compounds and the calculated hfcc values for $\mathbf{1}^{\bullet-}$ and CIF files giving crystallographic data for **3** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701060A

---

(12) Some examples of hfcc values assignable to the ^{29}Si atom were reported; see: (a) Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155. (b) Lee, V. Ya.; Sekiguchi, A. In *Reviews of Reactive Intermediate Chemistry*; Platz, M. S., Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 2007; pp 47–120. (c) Power, P. P. *Chem. Rev.* **2003**, *103*, 789. (d) Lee, V. Ya.; Sekiguchi, A. *Eur. J. Inorg. Chem.* **2005**, 1209. (e) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 12436. (f) Sekiguchi, A.; Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 9865. (g) Sekiguchi, A.; Inoue, S.; Ichinohe, M.; Arai, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9626–9629. (h) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 26–27. (i) Lee, V. Y.; Sekiguchi, A. *Acc. Chem. Res.* **2007**, *40*, 410.

(13) Chemical data and the results of the crystallographic analysis supported the structure of **3**. See the Supporting Information.