# Radical Anion of Isolable Dialkylsilylene

S. Ishida, T. Iwamoto, and M. Kira*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Received August 19, 2002 ; E-mail: mkira@si.chem.tohoku.ac.jp

Because silylene and the related singlet group-14 divalent compounds[1] have low-lying vacant pπ orbitals, the corresponding radical anions as a unique class of reactive intermediates are expected to be generated by one-electron reduction. Although radical anions of stable germylene and stannylene have been produced recently by alkali metal reduction in solution and characterized by ESR spectroscopy,[2] no ESR studies of carbene and silylene radical anions in solution have been reported so far.[3] Parent silylene radical anion $SiH_2^{•-}$ produced in a low-pressure discharge source upon admission of SiH_4 has been studied by laser photoelectron spectroscopy.[4] West et al. recently reported that the reduction of a stable diaminosilylene with potassium graphite in THF gives the corresponding 1,2-dilithiodisilane, which would be formed via the fast dimerization of the silylene radical anion (eq 1).[5] We report herein that the one-electron reduction of an isolable cyclic dialkylsilylene[6] using alkali metals generates the corresponding radical anion as a relatively persistent species at low temperatures in solution (eq 2). Unique structural characteristics of the radical anion have been revealed by an ESR study.

(1)

(2)

M = Cs, Rb, K, Na, Li/4,4'-di-*tert*-butylbiphenylide
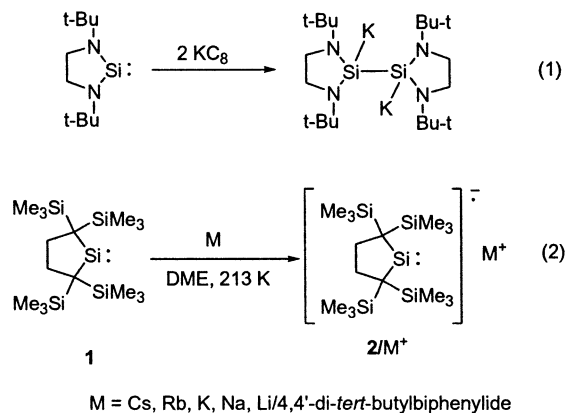
When a dimethoxyethane (DME) solution of silylene **1** was allowed to be in contact with a potassium mirror for 5−10 s at 213 K, the solution turned from yellow to brown-red,[7] and an intense ESR spectrum ($g = 2.0077$) was observed as shown in Figure 1a.[8] The spectral features are assigned unambiguously to the radical anion of **1** ($2/K^+$ in eq 2) on the basis of the following discussion. The central signal splits into more than 20 lines as shown in an expanded spectra (Figure 1b); the hyperfine splitting pattern is well reproduced by a computer simulation[9] using the hyperfine splitting constants (hfs's) of 0.0189 mT due to 36 protons of 4 trimethylsilyl groups and 0.0378 mT due to 4 protons of ethylene moiety in the silacyclopentane ring (half line width = 0.019 mT; Figure 1c). The central pattern was concluded not to involve an hfs due to ^{39}K ($I = {}^3/_2$) because the central splitting pattern was independent of the countercations (vide infra). The most prominent feature of this spectrum is the satellite spectral pattern due to ^{29}Si nuclei in natural abundance, which is composed of three sets of
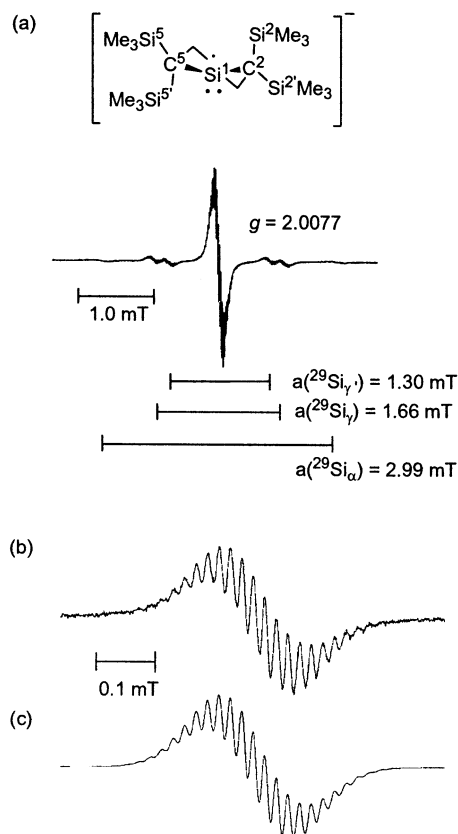
Figure 1. (a) A whole ESR spectrum of $2/K^+$ in DME solution at 213 K. (b) An expanded central part of the above spectrum. (c) Computer simulation of the central part using ^1H hfs's of 0.0189 mT for 36H and 0.0378 mT for 4H (half line width = 0.019 mT).

doublets with hfs's of 2.99, 1.66, and 1.30 mT. On the basis of the intensities relative to the central lines, the outermost doublet and the inner two doublets are assigned to the central silicon (Si_α) and two types of trimethylsilyl silicons [Si_γ (Si^2 and $Si^{5'}$) and $Si_{\gamma'}$ ($Si^{2'}$ and Si^5)], respectively. The inequivalence of the trimethylsilyl groups is consistent with the twisted silacyclopentane ring as found in the X-ray structure of silylene **1**, where the torsion angles of Si^2-C^2 ($Si^{5'}-C^5$) and $Si^{2'}-C^2$ (Si^5-C^5) bonds from the $C^2-Si^1-C^5$ plane are 91.5° and 72.8°, respectively. In agreement with this assignment, the satellite pattern is significantly temperature-dependent, probably because of the facile ring flipping in the ESR time scale. Whereas the outermost signals are almost intact, the inner two doublets coalesce to a doublet with an hfs of 1.48 mT at higher temperatures than 275 K; the activation free energy at the coalescence temperature (275 K) is estimated to be 6.9 kcal/mol. The radical anion is sufficiently persistent at temperatures lower than 213 K, while at 298 K, the signal intensity gradually decreases with a half-life of ca. 20 min.

Table 1. ESR Parameters of Radical Anion **2** with Various Countercations and Related Silyl Radicals

radical	g-factor	$a(^{29}Si_\alpha)$/mT	$a(^{29}Si_\gamma)$/mT	ref
2/Cs$^+$	2.0077	3.03	1.40, 1.55	a
2/Rb$^+$	2.0077	3.01	1.34, 1.61	a
2/K$^+$	2.0077	2.99	1.30, 1.66	a
2/Na$^+$	2.0081	2.99	1.28, 1.70	a
2/Li$^+$	2.0082	3.02	1.28, 1.67	a
Me$_3$Si·	2.0031	18.3		b
[(Me$_3$Si)$_2$CH]$_3$Si·	2.0027	19.3		c
(Me$_3$Si)$_3$Si·	2.0053	6.4		d
(t-BuMe$_2$Si)$_3$Si·	2.0055	5.7		e
[(i-Pr)$_3$Si]$_3$Si·	2.0061	5.6		f
Li[(i-Pr)$_3$Si]$_2$Si· (**3**)	2.0073	3.20		g

a This work. *b* Reference 11. *c* Reference 12. *d* Reference 13. *e* Reference 14. *f* Reference 15. *g* Reference 10.

Reduction of **1** with other reducing agents such as cesium, rubidium, sodium, and lithium [4,4′-di(*tert*-butyl)-biphenylide] (LiDTBB) in DME gave intense ESR spectra similar to those obtained by K reduction assignable to the corresponding radical anion **2**/M$^+$ (M = Cs, Rb, K, Na, and Li). Radical anion **2**/Cs$^+$ in DME was rather unstable, and the ESR signals disappeared much faster than other **2**/M$^+$. The central patterns of the ESR spectra of **2**/Rb$^+$ and **2**/Na$^+$ at 213 K were simulated using the same set of ^{1}H hfs's with that determined for **2**/K$^+$ with a little broader half line width (0.020 mT). Because the splitting pattern of the central part was independent of the countercations, it is concluded that both **2**/K$^+$ and **2**/Rb$^+$ exist as a solvent-separated ion pair (or a free ion) in DME. The ESR spectrum of **2**/Na$^+$ in DME showed shoulders due to a contact ion pair with an hfs due to ^{23}Na ($I = \frac{3}{2}$) of 0.13 mT at both ends of the central signal. As expected, the shoulder was not observed in the ESR spectrum of **2**/Na$^+$ in the presence of 15-crown-5 ether in DME. Silylene **1** was reduced using lithium in the presence of a catalytic amount of 4,4′-di(*tert*-butyl)-biphenyl (DTBB) in DME. No contamination of the ESR signals due to LiDTBB was observed, but the central line was broad and not resolved by the ^{1}H hfs probably because of the facile spin exchange between **2** and DTBB. The reduction of **1** with lithium metal in the absence of DTBB was unsuccessful. The ESR parameters of these silylene radical anions and related silyl radicals are shown in Table 1.

It is interesting to note that the g-factor and the ^{29}Si hfs due to the central silicon nucleus [$a(^{29}Si_\alpha)$] of **2** are similar to those for lithio[bis(triisopropylsilyl)]silyl radical [Li(i-Pr$_3$Si)$_2$Si·, **3**], which has been generated recently by the photolysis of a Hg−Si bond in hexane[10](Table 1). The present results indicate not only that a silylene radical anion can be formed by a standard one-electron reduction of the corresponding silylene with alkali metals but also that lithiosilyl radical **3** is considered as a limiting species of the corresponding silylene radical anion with lithium ion as a countercation ($a(^7$Li) = 0.125 mT).[10]

The $a(^{29}Si_\alpha)$'s and the g-factors of **2** and **3** are the smallest and the largest, respectively, among those of the related trialkylsilyl[11−13] and tris(trialkylsilyl)silyl radicals[14,15] (Table 1). According to the local symmetry of silylenes (R$_2$Si:; C_{2v}), the singly occupied MO of **2** should be 1b$_1$, which is comprised of a pure 3p orbital perpendicular to the R$_2$Si plane. Because the $a(^{29}Si_\alpha)$ value involves no direct contribution of the s character of the SOMO, the hfs would originate mostly from the spin polarization of the C^2−Si^1 and C^5−Si^1 σ bonds. The largest g-factor is ascribed to the smallest excitation energy of n → SOMO(3pπ) in **2** in comparison to the σ(CSi) → SOMO, σ(SiSi) → SOMO, and even to the σ(SiLi) → SOMO excitation energies in the trialkylsilyl, tris(trialkylsilyl)silyl, and lithiosilyl radicals, respectively.[16]

Supporting Information Available: Temperature-dependent ESR and UV−vis spectra of **2**/K$^+$ and ESR spectra of **2**/Cs$^+$, **2**/Rb$^+$, **2**/Na$^+$, and **2**/Li$^+$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For a recent review of silylenes, see: Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds Volume 2*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1999; Part 3, Chapter 43, pp 2463−2568.

(2) Egorov, M. P.; Nefedov, O. M.; Lin, T.-S.; Gaspar, P. P. *Organometallics* **1995**, *14*, 1539.

(3) Carbene anion radicals have been suggested as reactive intermediates in several reactions: Bethell, D.; Parker, V. D. *Acc. Chem. Res.* **1988**, *21*, 400.

(4) Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* **1972**, *62*, 541.

(5) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; West, R. *Can. J. Chem.* **2000**, *78*, 1526.

(6) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.

(7) The UV−vis spectrum of the solution did not show any apparent absorption band but tailed off into a visible region (∼700 nm). See the Supporting Information for the UV/vis spectrum of **2**/K$^+$.

(8) ESR spectra were recorded on a Bruker ESP300E EPR spectrometer (X-band). All reactions were carried out in carefully dried solvents in sealed glass tubes.

(9) The computer simulation was performed using SimFonia software.

(10) Bravo-Zhivotovskii, D.; Yuzefovich, M.; Sigal, N.; Korogodsky, G.; Klinkhammer, K.; Tumanskii, B.; Shames, A.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 649.

(11) Bennett, S. W.; Eaborn, C.; Hudson, A.; Jackson, R. A.; Root, K. D. J. *J. Chem. Soc. A* **1970**, 348.

(12) Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369.

(13) Krusic, P. J.; Kochi, K. *J. Am. Chem. Soc.* **1969**, *91*, 3938.

(14) Kira, M.; Obata, T.; Kon, I.; Hashimoto, H.; Ichinohe, M.; Sakurai, H.; Kyushin, S.; Matsumoto, H. *Chem. Lett.* **1998**, 1097.

(15) Kyushin, S.; Sakurai, H.; Matsumoto, H. *Chem. Lett.* **1998**, 107.

(16) Atherton, N. M. *Electron Spin Resonance*; Wiley: Chichester, 1973; Chapter 6.

JA028192G