

Cyclotetrasilenylyl: The First Isolable Silyl Radical

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The silyl radical is one of the most important reactive intermediates in organosilicon chemistry, and its spectroscopic characterization has been reported.¹ In particular, the stable silyl radical has become of interest in recent years, and persistent silyl radicals stabilized by bulky substituents have been reported.² However, isolation of the silyl radical and its structural characterization have not yet been reported.³

Very recently, we have succeeded in synthesizing a cyclotetrasilenylium ion **1**⁺ by the reaction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene⁵ with [Et₃Si(benzene)]⁺·TPFPB⁻ (TPFPB⁻ = tetrakis(pentafluorophenyl)borate).⁶ The cyclotetrasilenylium ion **1**⁺ is not only a free silyl cation in the condensed phase but also a homoaromatic compound consisting of silicon atoms. It is quite reasonable to assume that the reaction of **1**⁺ with nucleophiles may afford cyclotetrasilene⁷ and tetrasilabicyclo[1.1.0]butane derivative.⁸ Indeed, **1**⁺ smoothly reacts with small nucleophiles such as methyllithium in diethyl ether, to produce yellow crystals of cyclotetrasilene derivative **2** in 97% yield (Scheme 1).⁹ However, the reaction of **1**⁺ with the bulky trialkylsilylsodium compounds ^tBu₃SiNa and ^tBu₂MeSiNa did not produce the corresponding cyclotetrasilene or bicyclo[1.1.0]butane compounds. Instead, cyclotetrasilenylyl radical was formed as a result of one-electron reduction. Herein we report the first isolation and full characterization of the stable silyl radical **1**[•].

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(3) Recently, a stable three-membered cyclotrigermeryl radical and a stable anion radical [ArSnSnAr]^{-•} (Ar = -C₆H₃-2,6(2,4,6-*i*-Pr₃C₆H₂)₂) were reported: (a) Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *Chem. Commun.* **1997**, 1595. (b) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705.

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(9) Spectral data of **2**: air-sensitive yellow crystals; mp 174–177 °C. ¹H NMR (C₆D₆, δ) 0.37 (s, 3 H), 0.45 (s, 3 H), 0.46 (s, 3 H), 0.85 (s, 3 H), 1.18 (s, 9 H), 1.19 (s, 9 H), 1.197 (s, 9 H), 1.200 (s, 9 H), 1.21 (s, 9 H), 1.24 (s, 9 H), 1.39 (s, 9 H), 1.49 (s, 9 H); ¹³C NMR (C₆D₆, δ) -3.3, -3.2, -3.0, 5.2, 21.6, 21.7, 22.0, 22.1, 22.6, 23.1, 23.9, 24.8, 30.1, 30.2, 30.4, 30.5, 30.7, 31.4, 32.9, 33.4; ²⁹Si NMR (C₆D₆, δ) -34.6, 14.4, 17.3, 19.2, 43.9, 158.1, 182.7; HRMS calcd for C₃₆H₈₄Si₇: 712.4958; found 712.4960.

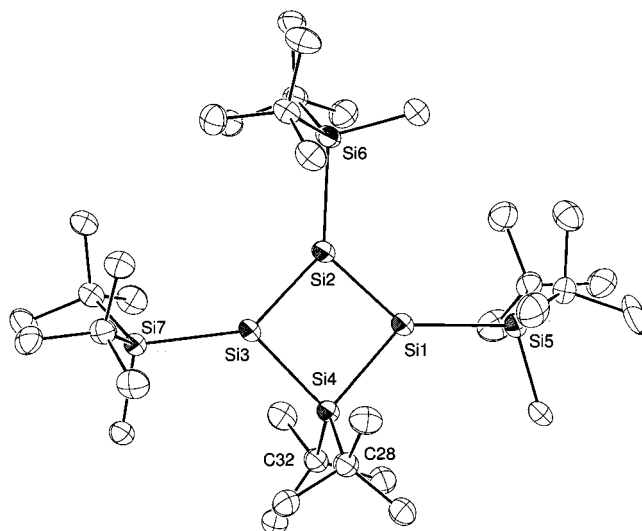


Figure 1. ORTEP Drawing of cyclotetrasilenylyl **1**[•]. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2, 2.226(1); Si1–Si4, 2.358(1); Si1–Si5, 2.372(1); Si2–Si3, 2.263(1); Si2–Si6, 2.377(1); Si3–Si4, 2.364(1); Si3–Si7, 2.372(1). Selected bond angles (deg): Si2–Si1–Si4, 91.41(6); Si2–Si1–Si5, 138.30(7); Si4–Si1–Si5, 130.29(7); Si1–Si2–Si3, 91.89(6); Si1–Si2–Si(6), 130.82(7); Si3–Si2–Si6, 136.35(7); Si2–Si3–Si4, 90.33(6); Si2–Si3–Si7, 139.20(7); Si4–Si3–Si7, 126.67(7); Si1–Si4–Si3, 86.18(6).

A mixture of **1**⁺·TPFPB⁻ and ^tBu₃SiNa in diethyl ether, which was initially a yellow suspension, became a red-purple solution within 5 min with stirring at room temperature. The resulting Na⁺·TPFPB⁻ salt was removed by filtration after exchange of solvent to heptane, and subsequent evaporation of heptane gave a red-purple solid containing **1**[•]. Pure **1**[•] was obtained as red-purple crystals by recrystallization from hexane in 67% yield. One-electron reduction of **1**⁺ could also be achieved by potassium graphite (KC₈) in diethyl ether, and **1**[•] was easily isolated in 83% yield (Scheme 1).¹⁰ Radical **1**[•] is quite stable at room temperature in the absence of air and moisture, and an intense ESR signal was observed for both solid **1**[•] and heptane solution of **1**[•].

The structure of **1**[•] was determined by X-ray analysis,¹¹ and an ORTEP drawing of the molecular structure of **1**[•] and its important structural parameters are given in Figure 1. The closest intermolecular distances between silicon atoms of the radical part (Si1, Si2, and Si3) range from 8.401(2) to 9.914(2) Å, indicating that cyclotetrasilenylyl **1**[•] is a free silyl radical in the solid state. The four-membered ring is almost planar with the dihedral angle between the radical part Si1–Si2–Si3 and Si1–Si4–Si3 being 4.7°. This is in marked contrast to the precursor silyl cation **1**⁺, which has a largely folded four-membered ring (the corresponding folding angle: 46.6°), caused by 1,3-orbital interaction due to the homoaromatic character.⁴ The sum of the bond angles around the three coordinated silicon atoms of the radical part (Si1, Si2, and Si3) are 360.0, 359.1, and 356.2°, respectively. The Si1 and

(10) The crystals of **1**⁺·TPFPB⁻ (70 mg, 0.051 mmol) and KC₈ (7 mg, 0.050 mmol) were placed in a reaction tube with a magnetic stirrer and degassed. Dry oxygen-free diethyl ether (1 mL) was introduced by vacuum transfer, and the mixture was stirred at room temperature to give a purplish-red solution within 5 min. After the solvent was removed in vacuo, degassed heptane was introduced. After the resulting K⁺·TPFPB⁻ salt and graphite had been removed, the solution was cooled to produce red-purple crystals of **1**[•] (29 mg, 83%); UV-vis (hexane) λ_{max/nm} (ε) 241 (sh, 23500), 302 (9600), 331 (sh, 6300), 365 (sh, 4700), 483 (2100), 541 (9400).

(11) The single crystals for X-ray analysis were obtained by the recrystallization from hexane. Crystal data of **1**[•] at 120 K: MF = C₃₅H₈₁Si₇, MW = 698.63, triclinic, space group P1, a = 8.906(1) Å, b = 15.076(3) Å, c = 16.939(4) Å, α = 90.97(1)°, β = 90.82(1)°, γ = 91.92(1)°, V = 2272.5(8) Å³, Z = 2, D_{calcd} = 1.021 g·cm⁻³. The final R factor was 0.0767 with I_o > 2σ(I_o) (R_w = 0.2148 for all data, 7836 reflections). GOF = 1.044.

Scheme 1

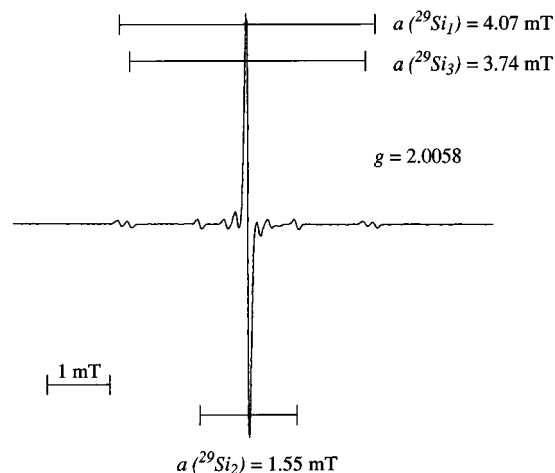
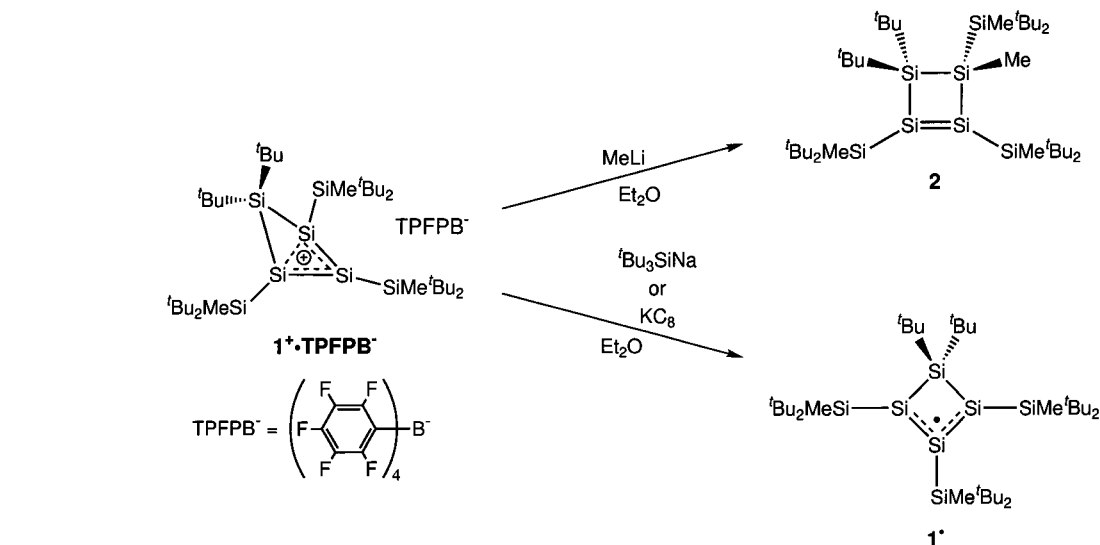


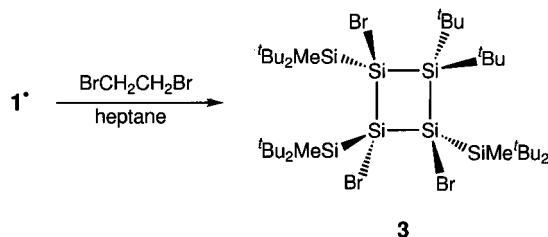
Figure 2. ESR Spectrum of **1*** in heptane at 298 K.

Si2 atoms have planar geometry, but the Si3 atom is slightly pyramidalized. A small unsymmetrical feature for the radical part was also found in the bond lengths: Si1–Si2 [2.226(1) Å] is slightly shorter than Si2–Si3 [2.263(1) Å]. However, these Si–Si bond lengths are comparable with the corresponding Si–Si bond lengths of **1⁺** [2.240(2) and 2.244(2) Å],⁴ being intermediate between the Si=Si double bond [2.174(4) Å] and the Si–Si single bond [2.349(4)–2.450(4) Å] in the four-membered ring of hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene.^{7a,12} The bond lengths of Si1–Si4 [2.358(1) Å] and Si3–Si4 [2.364(1) Å] are slightly longer than the corresponding bond lengths of **1⁺** [2.336(2) and 2.325(2) Å].⁴ The interatomic distance between Si1 and Si3 of **1*** [3.225(2) Å] indicates that the 1,3-orbital interaction observed in **1⁺** is lost by the one-electron reduction.

Crystalline **1*** reveals an intense ESR signal with $g = 2.0058$, which is close to the typical values for tris(trialkylsilyl)silyl radicals (2.0053–2.0063).^{1,2} The heptane solution of **1*** also gives a strong ESR signal at room temperature as an unresolved broad singlet ($g = 2.0058$) with the definite five doublet satellite signals, as shown in Figure 2. Three doublet satellite signals with relatively large hyperfine coupling constants (hfcc) (4.07, 3.74, and 1.55 mT) are evidently due to coupling with the ²⁹Si nuclei, judging from their intensities relative to the central peak. The two doublet satellite signals with hfcc of 4.07 and 3.74 mT are broadened by raising the temperature and coalesce at 370 K due to the rotation

(12) 3,4-Diiodo-1,2,3,4-tetrakis(tri-*tert*-butylsilyl)cyclotetrasilene has also been reported.^{7c} Its Si=Si double bond length is reported to be 2.257(2) Å, which is significantly elongated due to the steric reasons.

Scheme 2



of ^tBu₂MeSi groups. Since cyclo-tetrakis(tert-butyl dimethylsilyl)cyclotetrasilene radical **1*** is an allyl-type radical, the largest spin density (α spin) should be located on the terminal Si1 and Si3 atoms, and the second largest spin density (β spin), on the central Si2 atom.¹³ Therefore, the two hfcc of 4.07 and 3.74 mT can be assigned to coupling with the ²⁹Si1 and ²⁹Si3 nuclei, and the hfcc of 1.55 mT is assigned to coupling with the ²⁹Si2 nucleus. The relatively low hfcc due to Si1 and Si3 atoms are consistent with the delocalization of the unpaired electron in the allylic system.^{14,15}

The high reactivity of silyl radicals toward organic halides is well established.¹ The stable silyl radical **1*** also readily reacted with 1,2-dibromoethane to give *trans,trans*-1,2,3-tribromo-4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclo-tetrasilene (**3**) in 79% yield (Scheme 2).¹⁶ The one-electron oxidation of **1*** leading to the starting **1⁺** also occurred. Thus, the reaction of **1*** with Ph₃C⁺·TPFPB⁻ in benzene produced **1⁺**·TPFPB⁻ in 80% yield.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **1*** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>. JA011617Z

(13) The geometry and structural parameters are well reproduced by a DFT calculation of the model compound (H₃Si)₃Si₄Me₂⁺, with C₃ symmetry at the B3LYP/6-31G* level. The calculated spin densities of the model compound are +0.724 for Si1 and Si3, and -0.364 for Si2.

(14) For the similar delocalization of the unpaired electron in the cyclo-tetramer radical, see ref 3a.

(15) For the carbon allyl-type analogous radical with a silacyclobutenyl skeleton, see: Maier, G.; Kratt, A.; Schick, A.; Reisenauer, H. P.; Barbosa, F.; Gescheidt, G. *Eur. J. Org. Chem.* **2000**, 1107.

(16) Spectral data of **3**: colorless crystals; mp 82 °C dec. ¹H NMR (C₆D₆, δ) 0.55 (s, 6 H), 0.63 (s, 3 H), 1.25 (s, 18 H), 1.28 (s, 18 H), 1.34 (s, 18 H), 1.45 (s, 9 H), 1.58 (s, 9 H); ¹³C NMR (C₆D₆, δ) -2.9, -2.3, 23.0 (2C), 23.2, 23.3, 24.4, 31.0, 31.1, 31.2, 33.4, 34.0; ²⁹Si NMR (C₆D₆, δ) -8.2, 9.4, 18.6, 26.4, 37.3; MS m/z (%) 935 (M⁺, 5.0), 700 (M⁺ - ^tBu₂MeSiBr), 643 (33), 555 (36), 73 (100); Anal. Calcd for C₃₅H₈₁Br₃Si₇: C, 44.80; H, 8.70. Found: C, 45.12; H, 8.99.