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S-Heterocyclic Carbene with a Disilane Backbone**

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Recently, Wiberg and co-workers reported the preparation of tetrathiofulvalene (TTF) analogue **1** with a disilane backbone (see Scheme 1), obtained from the reaction of the isolable disilene **2** with carbon disulfide.[1] Compound **1**, with a Si–Si bond instead of a C=C bond in the TTF ring, may be potentially useful as a new electron donor because of the intriguing electronic properties of the silicon σ-conjugate system (Si–Si), which resembles the carbon π-conjugate system (C=C). Apparently, **1** was formed by the dimerization of the S-heterocyclic carbene (SHC) **3** as the proposed

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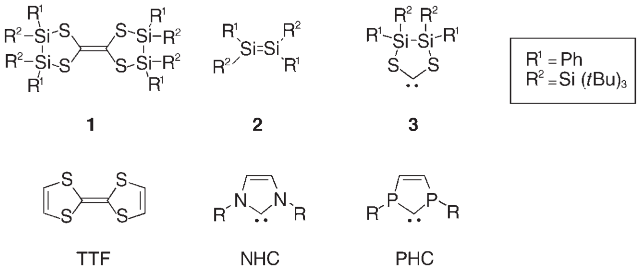


Scheme 1. TTF analogue **1** and S-heterocyclic carbene **3** with a disilane backbone.

intermediate. Meanwhile, since the discovery of the first stable carbenes by Arduengo and co-workers,[2] heterocyclic carbenes have attracted special attention as ligands, catalysts, and spin sources because of their unique coordination properties based on good σ-donor and poor π-acceptor properties.[3] A large variety of stable N-heterocyclic carbenes (NHC) have been reported so far which have various substitution patterns,[4] ring sizes that vary from four to six,[5] and inorganic backbones;[6] furthermore, a P-heterocyclic carbene (PHC) has also been reported.[7] To the best of our knowledge, only theoretical investigations into the formation of SHCs by a [2+3] cycloaddition of an alkyne with CS_2 and subsequent dimerization have been reported.[8] In this context, the generation of a carbene by the reaction of disilene with CS_2 would be a new synthetic approach to SHCs. The reactivity of a SHC with a disilane backbone and the properties of a TTF analogue with a disilane backbone prompted us to investigate the reaction of the disilene with CS_2. We have reported the photochemical generation of cyclotetrasilene **4** (see Scheme 2), which has a higher reactivity than **2**,[9] and the use of C_{60} as a probe, which is a nonspectroscopic method to confirm the formation of a carbene.[10,11] We report herein the generation of SHC **6** with a cyclotetrasilane backbone by a [2+3] cycloaddition of cyclotetrasilene, prepared by the photolysis of *anti*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane[12] (**5**), with CS_2. Carbene **6** then reacts with C_{60} to result in the formation of methanofullerene **7** (Scheme 2).

Irradiation of a solution of *anti*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane **5** in toluene in the presence of C_{60} and CS_2 in a degassed sealed tube at room temperature using a high-pressure mercury arc lamp resulted in the formation of the corresponding adduct $C_{60}(C_{19}H_{42}S_2Si_4)$ (**7**) in 20% yield. Compound **7** was then purified by preparative HPLC. The MALDI-TOF mass spectrum of **7** exhibits a molecular ion peak at *m/z* 1172–1166 and a peak at *m/z* 723–720 (C_{60}) because of the loss of the substituent $C_{19}H_{42}S_2Si_4$ (**8**). The UV/Vis absorption peak of **7** appears at 433 nm, which is indicative of the formation of a 6,6-adduct of C_{60}.[13]

The ^{13}C NMR spectrum of **7** shows 32 signals for the C_{60} cage, of which four peaks are at half intensity and 28 peaks are at full intensity. These results are consistent with the appropriate number and ratio of peak intensities for the C_{60} adduct with C_s symmetry. The signals at $\delta = 83.36$ and 80.63 ppm, assigned to the sp^3 carbon atom on the fullerene cage, indicate a methanofullerene structure.[13] The signal at $\delta = 58.54$ ppm is assigned to the sp^3 carbon atom on the spiro ring system. The carbon atoms in the isopropyl group on cyclotetrasilane may be observed at $\delta = 23$–14 ppm. The ^{29}Si NMR spectrum of **7** shows two signals at $\delta = 20.36$ and 0.31 ppm.

X-ray crystallographic analysis[14] unambiguously confirms the structure of **7** (Figure 1) as having a *cis*-fused bicyclic structure and a spiro ring system, which has C_1 symmetry in the crystalline state. The dithiadisilolane ring possesses a half-chair structure, and the cyclotetrasilane ring has a moderately holded structure with hold angles of 18.9 and 19.2°. (The Si–Si bond lengths range from 2.358(3) to 2.407(3) Å with an average of 2.378 Å.) As the Si(3)–Si(4) bond is within the bicycle ring, its length (2.358(3) Å) is the shortest among the others (2.362(3)–2.407(3) Å). The

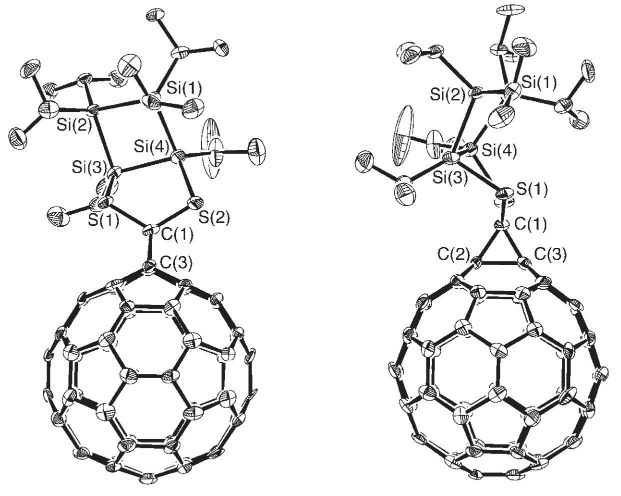
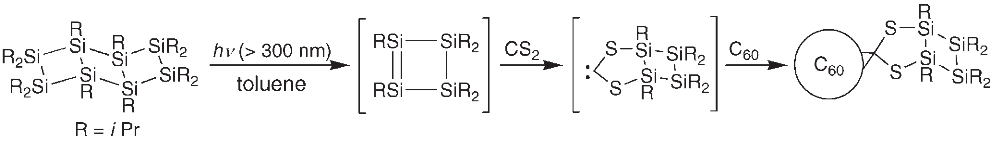


Figure 1. ORTEP drawing of $C_{60}(C_{19}H_{42}S_2Si_4)$ **7** showing thermal ellipsoids at the 30% probability level. The CS_2 molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–Si(2) 2.385(3), Si(2)–Si(3) 2.362(3), Si(3)–Si(4) 2.358(3), Si(1)–Si(4) 2.407(3), Si(3)–S(5) 2.182(3), Si(4)–S(6) 2.188(3), C(1)–S(5) 1.822(7), C(1)–S(6) 1.774(7), C(1)–C(2) 1.553(10), C(1)–C(3) 1.518(10), C(2)–C(3) 1.634(10), Si(1)-Si(2)-Si(3) 88.66(11), Si(2)-Si(1)-Si(4) 89.10(11), Si(2)-Si(3)-Si(4)/S(1) 90.83(11)/99.32(12), Si(1)-Si(4)-Si(3)/S(2) 88.23(11)/113.42(12), S(1)-Si(3)-Si(4) 91.52(12), Si(3)-Si(4)-S(2) 102.65(12), Si(4)-S(2)-C(1) 99.1(2), S(1)-C(1)-S(2) 117.5(4), C(1)-S(1)-Si(3) 98.2(2), C(1)-C(2)-C(3) 56.8(4), C(2)-C(3)-C(1) 58.9(4), C(2)-C(1)-C(3) 64.3(4).



5 **4** **6** **7**

Scheme 2. Synthesis and trapping of S-heterocyclic carbene **6**.

Si-Si-Si bond angles of the $\{Si_4\}$ rings range from 88.2(11) to 90.8(11)°, with an average of 89.2°.

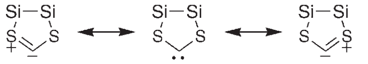
Table 1 shows the redox potentials of **7** and C_{60},[15] together with the 6,6-adduct of C_{60}-adamantylidene (6,6-C_{60}-Ad)[10] as a reference compound. Compound **7** exhibits three one-electron reversible reduction waves and one irreversible oxidation wave, as observed for C_{60} and 6,6-C_{60}-Ad. The salient feature is that the redox potentials of **7** are cathodically shifted, thus indicating that the introduction of substituent **8** results in a decrease in the electron-acceptor property.

Table 1: Redox potentials[a] (V) of $C_{60}(C_{42}H_{18}Si_4)$, 6,6-C_{60}-Ad,[10] and C_{60}[15].

Compound	oxE_1	redE_1	redE_2	redE_3
$C_{60}(C_{42}H_{18}Si_4)$	+1.04[d,e]	−1.16	−1.52	−2.01
6,6-C_{60}-Ad	+1.07[d,e]	−1.21	−1.58	−2.06
C_{60}	+1.21[d,e]	−1.12	−1.50	−1.95

[a] Versus Fc/Fc$^+$ in 1,2-dichlorobenzene with 0.1 M $(n\mathrm{Bu})_4NPF_6$ at a Pt working electrode; scan rate = 20 mV s^{-1}. [b] Irreversible. [c] Values were obtained by differential pulse voltammetry: pulse amplitude = 50 mV; scan rate 20 mV s^{-1}.

To characterize carbene **6**, generated by a [2+3] cycloaddition of cyclotetrasilene with CS_2, theoretical calculations were carried out.[16] The singlet state of **6** was calculated to be 23.4 kcal mol^{-1} more stable than the triplet state. The dithiadisilolane ring of **6** in the singlet state has an envelope structure with a dihedral angle of 1.6°, and the cyclotetrasilane ring has a moderately holded structure with hold angles of 8.8 and 8.9°. The carbon–sulfur bond lengths are 1.678 and 1.679 Å, which are considerably shorter than typical C−S single bond lengths (1.758–1.854 Å).[17] These bond lengths are ascribed to the conjugative donation of the lone-pair electrons on the sulfur atoms into the vacant p_π orbital at the carbene center (Scheme 3). Because of its dipolar character, **6** has a high nucleophilicity; therefore, it is not surprising that **6** reacts readily with the electrophilic C_{60}, as in the reaction of the dimethoxy carbene[18] and C_{60}.[19]



Scheme 3. Resonance structure of S-heterocyclic carbene **6**.

We have demonstrated that carbene **6** can be generated by the [2+3] cycloaddition of cyclotetrasilene **4** with CS_2 by trapping **6** with C_{60} as a chemical probe. NMR spectroscopic measurements and X-ray crystallographic analysis verify that **7** is a methanofullerene (a 6,6-adduct of C_{60}). Theoretical calculations show that **6** has a high nucleophilicity in the singlet ground state. This method to generate SHC **6** may be applied to prepare novel compounds, such as TTF analogue **1**.

Experimental Section

Irradiation of a solution of *anti*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (**5**; 5.1 mg, 6.9×10^{-3} mmol) in toluene in the presence of C_{60} (5.0 mg, 6.9×10^{-3} mmol) and CS_2 (0.4 mL, 6.9×10^{-3} mol) in a degassed sealed tube at room temperature using a high-pressure mercury arc lamp (cut off < 300 nm) resulted in the formation of the adduct $C_{60}(C_{20}H_{42}Si_4S_2)$ (**7**) as a dark-brown solid in 20 % yield, which was purified by preparative HPLC with a Buckyprep column ($\phi 20\times250$ mm; Cosmosil, Nacalai Tesque Inc.). A MALDI-TOF mass spectrum was measured on a BIFLEX III (Bruker, Germany) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. UV/Vis–NIR spectra were measured on a UV 3150 instrument (Shimadzu, Japan) in toluene. ^{1}H, ^{13}C, and ^{29}Si NMR and 2D NMR (HMQC and HMBC) spectra were recorded on Bruker AVANCE 500 spectrometer with a CryoProbe system and Bruker AVANCE 300 spectrometer in CS_2 and $CDCl_3$ (3:1). Cyclic voltammograms were measured on a potentiostat/galvanostat (BAS CW-50) in *o*-dichlorobenzene with 0.1M $(n\mathrm{Bu})_4NPF_6$ at a Pt working electrode.

Spectra data of **7**: ^{1}H NMR (500 MHz Cyroprobe, $CS_2/CDCl_3$ (3:1), 20 °C) δ = (sep, J = 7.4 Hz, 2H; CH), 1.75 (sep, J = 7.5 Hz, 2H; CH), 1.69 (sep, 2H, J = 7.4 Hz, 2H; CH), 1.38 (d, J = 7.3 Hz, 6H; CH_3), 1.36 (d, J = 7.4 Hz, 12H; CH_3), 1.35 (d, J = 7.4 Hz, 12H; CH_3), 1.31 ppm (d, J = 7.5 Hz, 6H; CH_3); ^{13}C NMR (125 MHz Cyroprobe, $CS_2/CDCl_3$ (3:1), 20 °C) δ = 148.2 (s, 2C; C_{60}), 147.6 (s, 2C; C_{60}), 145.3 (s, 2C; C_{60}), 144.9 (s, 2C; C_{60}), 144.9 (s, 2C; C_{60}), 144.8 (s, 2C; C_{60}), 144.8 (s, 2C; C_{60}), 144.7 (s, 2C; C_{60}), 144.5 (s, 2C; C_{60}), 144.4 (s, 4C; C_{60}), 144.3 (s, 1C; C_{60}), 144.3 (s, 1C; C_{60}), 144.2 (s, 2C; C_{60}), 143.8 (s, 2C; C_{60}), 143.6 (s, 4C; C_{60}), 142.9 (s, 2C; C_{60}), 142.8 (s, 2C; C_{60}), 142.7 (s, 2C; C_{60}), 142.7 (s, 2C; C_{60}), 142.6 (s, 2C; C_{60}), 141.9 (s, 4C; C_{60}), 141.9 (s, 4C; C_{60}), 140.6 (s, 4C; C_{60}), 138.5 (s, 2C; C_{60}), 138.3 (s, 2C; C_{60}), 83.3 (s, 1C; CC_{spiro}), 80.6 (s, 1C; CC_{spiro}), 58.5 (s, 1C; C_{spiro}), 22.4 (q, 3C; CH_3), 22.2(q, 3C; CH_3), 22.2(q, 3C; CH_3), 21.2 (q, 3C; CH_3), 21.1 (q, 3C; CH_3), 20.7 (q, 3C; CH_3), 17.0 (d, 3C; CH), 15.4 (d, 3C; CH), 14.5 ppm (d, 3C; CH); ^{29}Si NMR (59.6 MHz, $CS_2/CDCl_3$ (3:1), 20 °C) δ = 20.4, 0.3 ppm; MALDI-TOF mass (negative mode, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): m/z 1166(M), 720(C_{60}); MALDI-TOF mass (positive mode, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): m/z 1166[M], 1123; UV/Vis–NIR (toluene) $\lambda_{max}(\varepsilon)$ 694 (190), 478 (1400), 433 (2100), 330 (35 000) cm^{-1}.

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[14] Crystal data of **7**: $C_{81}H_{42}Si_4S_6$, $M_r = 1166.18$, black crystals, $0.25 \times 0.25 \times 0.25$ mm^3, monoclinic, space group *Cc* (no. 9), $a = 15.660(2)$, $b = 12.887(2)$, $c = 29.559(6)$ Å, $\beta = 96.606(8)°$, $V = 5925(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.479$ g cm^{-3}, $2\theta_{max} = 55.0°$, $\mu(Mo_{K\alpha}) = 3.636$ cm^{-1}; an empirical absorption correction ($0.689 \leq T \leq 0.913$); $\lambda = 0.71069$ Å, ω scans, $T = 293$ K, 22393 reflections that were collected, 21327 were unique ($R_{int} = 0.124$) and 6994 refractions ($I > 3.6\ \sigma(I)$); 863 refined parameters, $R = 0.062$, $R_w = 0.104$, GOF = 1.186. The maximum and minimum residual electron density is equal to 0.65 and −0.75 eÅ^{-3}, respectively. Hydrogen atoms were refined using the riding model. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated $Mo_{K\alpha}$ radiation. All calculations were performed using the Crystal Structure crystallographic software package. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF99). The structure was refined by CRYSTALS. CCDC 281589 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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