

Silylene and Disilene Additions to an Octa-1,3,5,7-tetrayne: Formation of a C–C-Linked Quatersilirene^{1,2}

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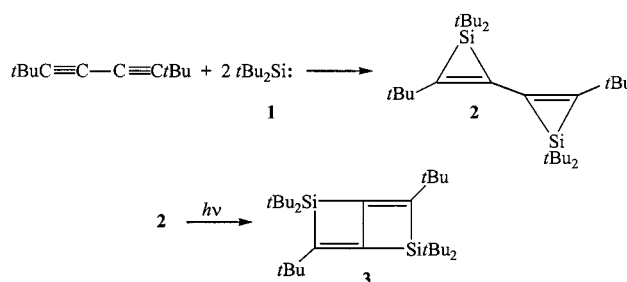
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Summary: Tetra-*tert*-butyldisilene and di-*tert*-butylsilylene (**1**), generated by photolysis of hexa-*tert*-butylcyclotrisilane, react with 1,8-di-*tert*-butylocta-1,3,5,7-tetrayne to furnish a C–C-linked bis(disilacyclobutene) derivative with terminal alkynyl groups **7** and a quatersilirene **8** by addition of **1** to all C–C triple bonds. Upon prolonged irradiation, **8** rearranges partly to the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene with terminal silylene groups **9**. The structures of **7**, **8**, and **9** were determined by X-ray crystallography.

The additions of silylenes with sterically demanding substituents to C–C triple bonds usually proceed smoothly to afford thermally stable or even air-stable silirenes (silacyclopropenes).^{3–11} The formation of disilacyclobutenes from thermally or marginally stable disilenes and unsymmetrically substituted alkynes is also a well-documented mode of reactivity.^{12–15}

We recently investigated the additions of various silylenes to buta-1,3-diynes^{16,17} and observed, for example, that the reaction of di-*tert*-butylsilylene (**1**), generated either photochemically from the cyclotrisilane

Scheme 1



4¹⁸ or from 1,1-di-*tert*-butyl-*trans*-2,3-dimethyl-1-silacyclopropane,¹⁹ with 1,4-di-*tert*-butyl-1,3-diyne furnished the isolable bis(silacyclopropene) **2**, which, upon continued irradiation, underwent rearrangement to yield the bicyclic compound **3**.¹⁷ We have now addressed the question of whether more extended systems with conjugated C–C triple bonds would also participate in analogous cycloadditions and report here on the additions of silylenes and disilenes to a 1,3,5,7-tetrayne.

We chose the cyclotrisilane **4** as the source for di-*tert*-butylsilylene (**1**) and tetra-*tert*-butyldisilene (**5**) because it decomposes into these two species upon irradiation. Among the several tested 1,3,5,7-tetraynes with terminal trimethylsilyl or *tert*-butyl groups only compound **6** proved to be sufficiently stable under these conditions.

Cophotolysis of **4** and **6** furnished a mixture of products from which three homogeneous compounds were separated by fractional crystallization and isolated in yields of between 7 and 10% (Scheme 2). The almost identical analytical data obtained for these products suggested that isomers had probably been formed.

The ¹³C NMR spectrum of one of these compounds contained two signals each for olefinic and acetylenic carbon atoms, thus demonstrating that only a part of the C–C triple bonds in **6** had participated in the addition reactions. The ²⁹Si NMR spectrum provided more information: it contained two signals at 23.16 and 40.74 ppm, in the typical region for silicon atoms in four-

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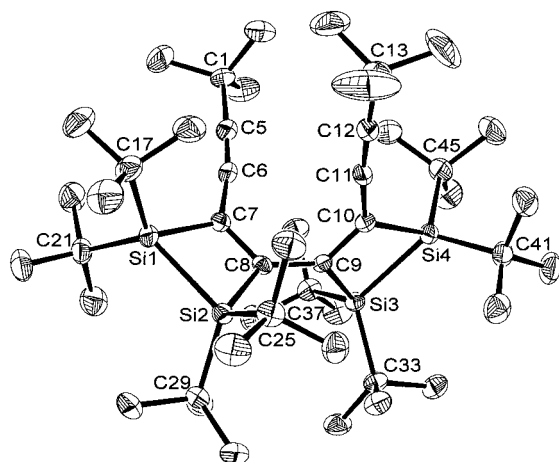
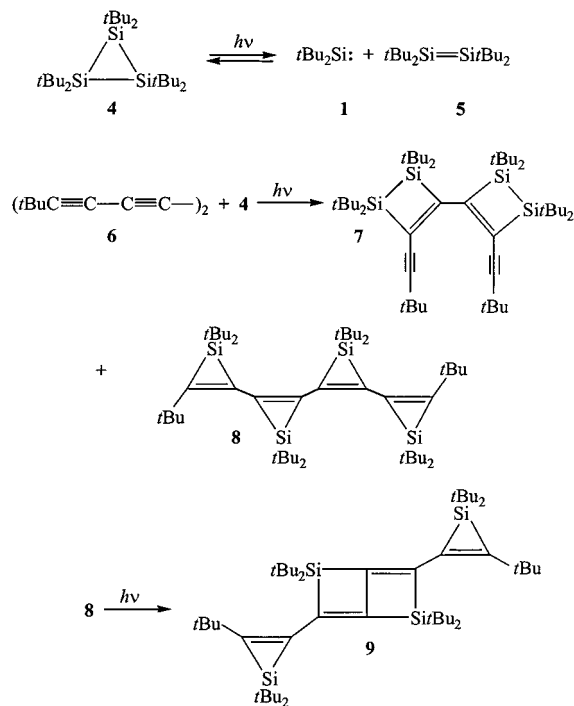


Figure 1. Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C(7)–C(8) 1.372(3), C(8)–C(9) 1.496(3), C(9)–C(10) 1.371(3), Si(1)–Si(2) 2.424(1), Si(3)–Si(4) 2.422(1), C(5)–C(6) 1.199(3), C(11)–C(12) 1.203(3), C(7)–Si(1)–Si(2) 73.30(7), Si(1)–Si(2)–C(8) 74.81(7), Si(2)–C(8)–C(7) 102.58(15), C(8)–C(7)–Si(1) 109.16(16), C(9)–Si(3)–Si(4) 74.79(7), Si(3)–Si(4)–C(10) 73.35(7), Si(4)–C(10)–C(9) 108.66(15), C(10)–C(9)–Si(3) 103.05(15).

Scheme 2



membered rings. The assumptions from the spectral data are supported by the X-ray crystallographic analysis of the colorless crystals, which revealed that a 2-fold [2+2] cycloaddition of **5** to the internal C–C triple bonds had occurred to afford the molecule **7** (Figure 1).

An interesting feature in the structure of **7** is the presence of an *s-cis*-butadiene unit bridged by two disilene moieties. In contrast, the *s-trans*-form dominates in butadiene itself and many of its derivatives, with the *s-cis*-arrangement only occurring in excited states.²⁰ Also conspicuous is the fact that **7** possesses

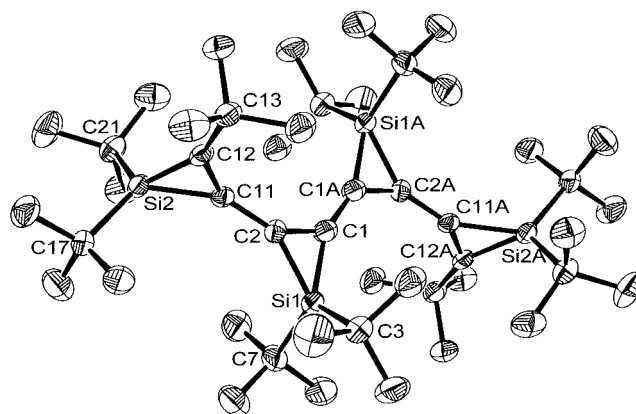


Figure 2. Molecule of **8** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C(12)–C(11) 1.343(3), C(11)–C(2) 1.349(3), C(1)–C(1') 1.438(5), Si(2)–C(11) 1.838(2), Si(2)–C(12) 1.813(3), Si(1)–C(8) 1.803(3), Si(1)–C(2) 1.836(2), C(11)–Si(2)–C(12) 43.18(10), Si(2)–C(12)–C(11) 69.39(15), C(12)–C(11)–Si(2) 67.34(14), C(1)–Si(1)–C(2) 43.50(11), C(1)–C(2)–Si(1) 66.94(14), C(2)–C(1)–Si(1) 69.56(15).

two terminal alkynyl groups that are presumably protected against further cycloaddition reactions by the presence of 10 bulky *tert*-butyl groups.

In contrast with **7**, the ¹³C NMR spectrum of the second isolated compound exhibits four signals in the region typical for C–C double bonds and no signals for acetylenic carbon atoms. Together with the ²⁹Si NMR spectrum showing two signals shifted to high field at –62.69 and –61.56 ppm, i.e., in the region known for silirenes with this substitution pattern,^{11,16,17} these observations suggest the structure of the quatersilirene **8** formed by [2+1] cycloadditions of **1** to all four C–C triple bonds.

An X-ray crystallographic analysis of the colorless crystals of **8** (Figure 2) not only confirmed its constitution but also revealed some interesting details. The polyene chain of **8** adopts the *s-cis-trans-cis*-form, apparently to minimize the intramolecular interactions between the bulky *tert*-butyl groups. On the other hand, the bond lengths and angles in this novel molecule with four C–C-linked silirenes are almost the same as those determined for similar molecules such as the bis(silirene) **2**.¹⁷

Like **8**, the ¹³C NMR spectrum of the colorless crystals of the third isolated compound also contains only four signals for olefinic carbon atoms, which, however, cannot be unambiguously assigned. The ²⁹Si NMR spectrum, on the other hand, does reveal a clear difference and contains two signals at –65.46 and 33.65 ppm. While the signal at higher field can again be assigned to a silirene moiety, the position of the signal at lower field is in good agreement with that of the silicon atom in **3** (36.7 ppm).¹⁷ These data suggest the existence of a 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (**9**) with two terminal silirene groups. This assumption was confirmed by an X-ray crystallographic analysis (Figure 3).

The observed rearrangement of **8** to **9** is no longer unusual since, for example, the bis(silirene) **2** is also converted smoothly to the bicyclic species **3** upon renewed irradiation.¹⁷ The isolation of **8** and **9** from the same reaction mixture clearly illustrates that the time

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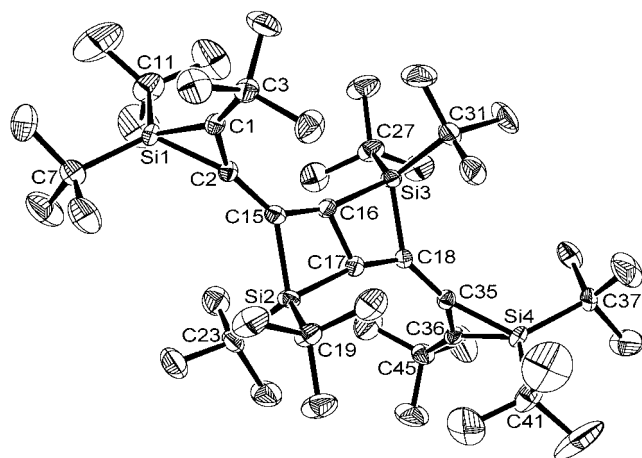


Figure 3. Molecule of **9** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.810(5), Si(1)–C(2) 1.849(4), C(1)–C(2) 1.361(5), C(2)–C(15) 1.444(5), C(15)–C(16) 1.366(5), C(15)–Si(2) 1.900(3), C(16)–C(17) 1.484(4), C(17)–C(18) 1.370(5), C(18)–Si(3) 1.897(3), C(18)–C(35) 1.447(4), C(35)–C(36) 1.343(5), C(35)–Si(4) 1.825(4), C(36)–Si(4) 1.815(5), C(1)–Si(1)–C(2) 43.63(16), C(15)–Si(2)–C(17) 75.61(15), C(16)–Si(3)–C(18) 75.49(14), C(35)–Si(4)–C(36) 43.31(15).

required for the complete cleavage of the cyclotrisilane **4** is also sufficient for a portion of the quatersilirene **8** to undergo isomerization to **9**. A rearrangement with participation of all four silirene rings of **8**, which would lead to a spirocyclic compound of two such bicyclic molecules, has not been observed.

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out at room temperature by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM 300 or ARX 500 spectrometer using C_6D_6 as solvent. The ^{29}Si NMR spectra were recorded on a Bruker AMX 300 spectrometer. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. The mass spectra were recorded on a Finnigan MAT 212 spectrometer. Elemental analyses were performed by Analytische Laboratorien, D-51789 Lindlar, Germany.

2,2,11,11-Tetramethyldodeca-3,5,7,9-tetrayne (**6**)²¹ and the cyclotrisilane¹⁸ were prepared according to the literature procedures.

Photolysis of 4 in the Presence of 2,2,11,11-Tetramethyldodeca-3,5,7,9-tetrayne (6). A solution of **4** (1.4 g, 3.5 mmol) and **6** (0.37 g, 1.8 mmol) in *n*-hexane (80 mL) was irradiated for 7 h at room temperature. After this time, the reaction was shown to be complete by the disappearance of **4** (TLC monitoring). The dark green-brown solution was concentrated in vacuo to a volume of 10 mL and kept at -70°C for several weeks to yield a mixture of compounds, which were separated by fractional crystallization. The products were isolated in the following order.

3,6-Bis[1,1,3-tri-*tert*-butyl-1*H*-silacyclopropene]-2,2,5,5-tetra-*tert*-butyl-2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (9). Recrystallization from *n*-hexane at -25°C provided 0.10 g (7.1%) of colorless crystals: mp $246\text{--}251^\circ\text{C}$; ^1H NMR (500 MHz) δ 1.20 (s, 36 H), 1.32 (s, 36 H), 1.37 (s, 18 H); ^{13}C NMR (125.7 MHz) δ 21.49 (C_q , *t*Bu), 21.95 (C_q , *t*Bu), 28.90 (C_p , *t*Bu), 30.98 (C_p , *t*Bu), 31.85 (C_p , *t*Bu), 35.33 (C_q , *t*Bu), 148.19 (C_q , *t*Bu–C=C), 150.25 (C_q , C=C), 155.40 (C_q , C=C), 171.29 (C_q , *t*Bu–C=C) (C_p and C_q refer to primary and quaternary carbon atoms); ^{29}Si NMR (59.6 MHz) δ –65.46, 37.65; MS (CI, isobutane) m/z (%) 778 [M^+] (100), 1632 ($\text{C}=\text{C}$) cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{90}\text{Si}_4$: C, 73.95; H, 11.64. Found: C, 73.69; H, 11.78.

4,4'-Bis(3,3-dimethylbut-1-ynyl)-1,1,1',1',2,2,2',2'-octa-*tert*-butyl-1*H*,1'*H*,2*H*,2'*H*-3,3'-bis(disilacyclobutene) (7). Recrystallization from *n*-hexane/DME (3:1) at -25°C yielded 0.14 g (10%) of colorless crystals: mp 237°C ; ^1H NMR (300 MHz) δ 1.25 (s, 18 H), 1.42 (s, 36 H), 1.46 (s, 36 H); ^{13}C NMR (125.7 MHz) δ 28.88 (C_q , *t*Bu), 31.13 (C_p , *t*Bu), 31.90–32.69 (broad, unresolved), 82.81 (C_q , C \equiv C), 112.69 (C_q , C=C), 148.32 (C_q , C=C), 178.09 (C_q , C=C); ^{29}Si NMR (59.6 MHz) δ 23.16, 40.74; MS (CI, isobutane) m/z (%) 778 [M^+] (100), 721 [$\text{M}-\text{tBu}$] $^+$ (85); IR (KBr) ν 1632 (C=C) cm^{-1} , 2175 cm^{-1} (C \equiv C). Anal. Calcd for $\text{C}_{48}\text{H}_{90}\text{Si}_4$: C, 73.95; H, 11.64. Found: C, 73.63; H, 11.81.

1,1,3,1',1'',1''',1''',3'''-Deca-*tert*-butyl-1*H*,1'*H*,1''*H*,1'''*H*-[2',2':3',2'':3'',2''']-quater(silacyclopentene) (8). Recrystallization from *n*-hexane at -25°C afforded 0.12 g (8%) of colorless crystals: mp $143\text{--}150^\circ\text{C}$; ^1H NMR (300 MHz) δ 1.22 (s, 36 H), 1.28 (s, 36 H), 1.33 (s, 18 H); ^{13}C NMR (75.5 MHz) δ 21.94 (C_q , *t*Bu), 22.47 (C_q , *t*Bu), 30.48 (C_p , *t*Bu), 30.79 (C_p , *t*Bu), 31.21 (C_p , *t*Bu), 35.29 (C_q , *t*Bu), 136.46 (C_q , C=C), 144.70 (C_q , C=C), 146.94 (C_q , C=C), 153.39 (C_q , C=C); ^{29}Si NMR (59.6 MHz) δ –62.69, –61.56; MS (CI, isobutane) m/z (%) 778 [M^+] (100), 721 [$\text{M}-\text{tBu}$] $^+$ (9); IR (KBr) ν 1636 (C=C) cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{90}\text{Si}_4$: C, 73.95; H, 11.64. Found: C, 73.83; H, 11.64.

Crystallographic Analyses. Compound **7** was recrystallized from methylcyclopentane. In each case, the crystal was mounted in an inert oil. Data collection was performed at 193(2) K with a Stoe IPDS area-detector using graphite-monochromated Mo K α radiation (0.71073 Å). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.²² Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-148 056 (**7**), CCDC-148 057 (**8**), CCDC-149 138 (**9**).

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Supporting Information Available: Listing of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **7**, **8**, and **9**. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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