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# 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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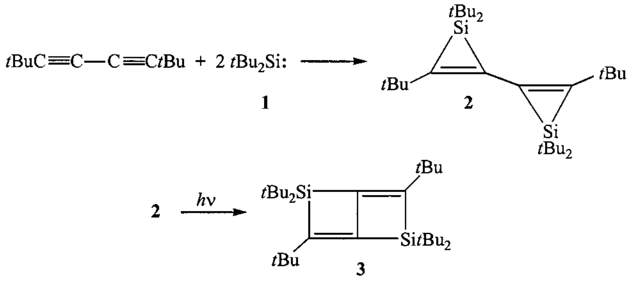
*Summary: Tetra-tert-butyldisilene and di-tert-butylsilylene (**1**), generated by photolysis of hexa-tert-butylcyclotrisilane, react with 1,8-di-tert-butylocta-1,3,5,7-tetrayne to furnish a C−C-linked bis(disilacyclobutene) derivative with terminal alkynyl groups **7** and a quatersilirene **8** by 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 silirene 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 **4**[18] 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.

**Scheme 1**



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 $^{13}C$ 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 $^{29}Si$ 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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(1) Silicon Compounds with Strong Intramolecular Steric Interactions. Part 73. Part 72: Willms, S.; Grybat, A.; Saak, W.; Weidenbruch, M.; Marsmann, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1148.

(2) Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday.

(3) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715.

(4) Seyferth, D.; Annarelli, D. C., Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6832.

(5) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C12.

(6) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Organomet. Chem.* **1980**, *190*, 117.

(7) Ishikawa, M.; Nishinura, K.; Sugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147.

(8) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yanabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872.

(9) Hirotsu, K.; Higushi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726.

(10) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

(11) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824.

(12) Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(13) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem* **1985**, *282*, 305.

(14) DeYoung, D. J.; West, R. *Chem. Lett.* **1986**, 883.

(15) DeYoung, D. J.; Fink, M. J.; West, R.; Michl, J. *Main Group Met. Chem.* **1987**, *10*, 19.

(16) Kirmaier, L.; Weidenbruch, M.; Marsmann, H.; Peters, K.; von Schnering, H. G. *Organometallics* **1998**, *17*, 1237.

(17) Ostendorf, D.; Kirmaier, L.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 2301.

(18) Schäfer, A.; Weidenbruch, M.; Peters, K.; von Schnering, H. G. *Angew. Chem.* **1984**, *96*, 311; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302.

(19) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrisciel, J. *Angew. Chem.* **1988**, *100*, 1406; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

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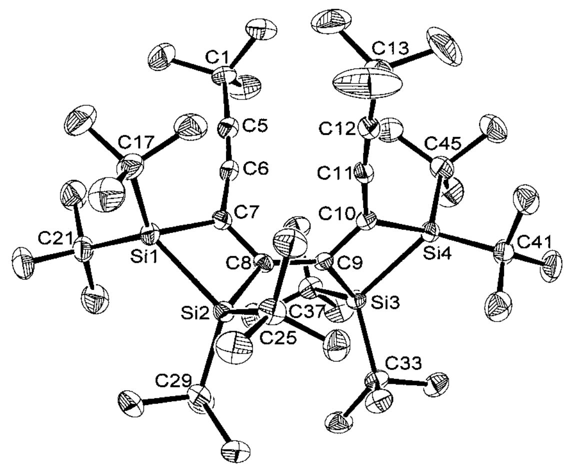
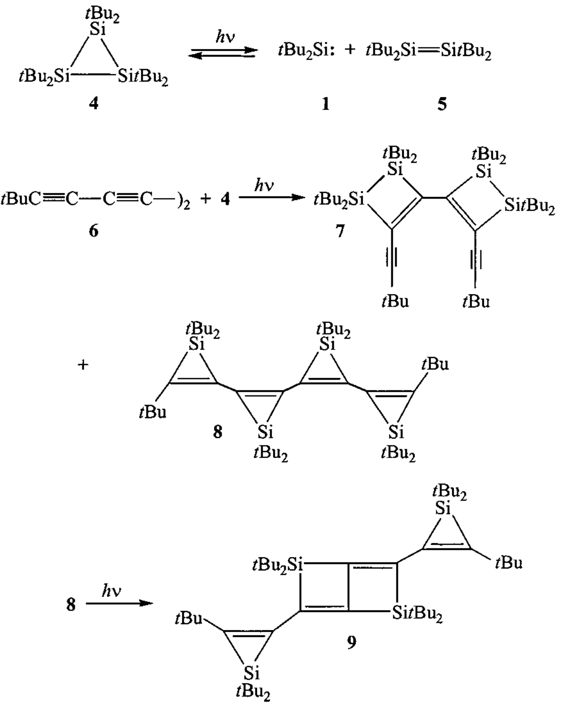


**Figure 1.** Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C(7)–C(8) 1.372(3), C(8)–C(9) 1.496(3), C(9)–C(10) 1.371(3), Si(1)–Si(2) 2.424(1), Si(3)–Si(4) 2.422(1), C(5)–C(6) 1.199(3), C(11)–C(12) 1.203(3), 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 two terminal alkynyl groups that are presumably protected against further cycloaddition reactions by the presence of 10 bulky *tert*-butyl groups.

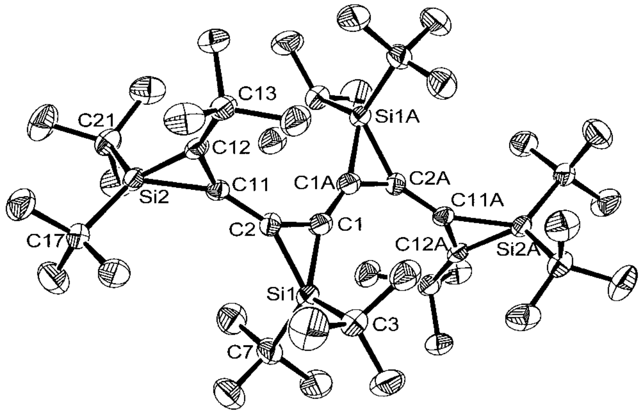


**Figure 2.** Molecule of **8** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C(12)–C(11) 1.343(3), C(11)–C(2) 1.349(3), C(1)–C(1′) 1.438(5), Si(2)–C(11) 1.838(2), Si(2)–C(12) 1.813(3), Si(1)–C(8) 1.803(3), Si(1)–C(2) 1.836(2),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

In contrast with **7**, the $^{13}$C 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 $^{29}$Si 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 $^{13}$C 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 $^{29}$Si 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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(20) Squillacote, M. E.; Sheridan, R. S.; Chapman, D. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657.

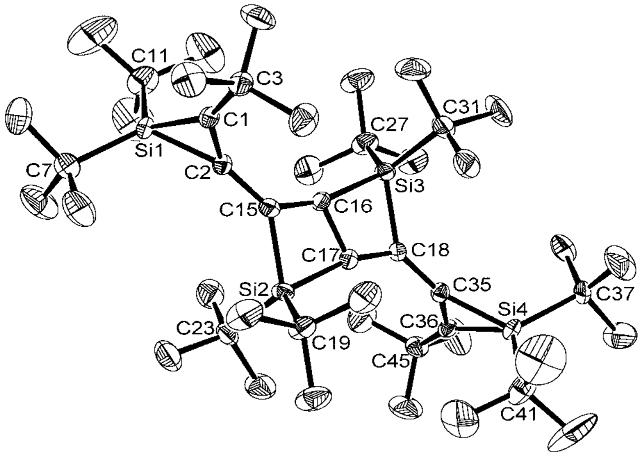

**Figure 3.** Molecule of **9** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si(1)−C(1) 1.810(5), Si(1)−C(2) 1.849(4), C(1)−C(2) 1.361(5), C(2)−C(15) 1.444(5), C(15)−C(16) 1.366(5), C(15)−Si(2) 1.900(3), C(16)−C(17) 1.484(4), 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 $^{1}H$ 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 cyclotrisilane[18] 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 246−251 °C; $^{1}H$ NMR (500 MHz) $\delta$ 1.20 (s, 36 H), 1.32 (s, 36 H), 1.37 (s, 18 H); $^{13}C$ NMR (125.7 MHz) $\delta$ 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) $\delta$ −65.46, 37.65; MS (CI, isobutane) *m*/*z* (%) 778 [M$^+$] (100); IR (KBr) n 1632 (C=C) cm$^{-1}$. Anal. Calcd for $C_{48}H_{90}Si_4$: 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; $^{1}H$ NMR (300 MHz) $\delta$ 1.25 (s, 18 H), 1.42 (s, 36 H), 1.46 (s, 36 H); $^{13}C$ NMR (125.7 MHz) $\delta$ 28.88 ($C_q$, *t*Bu), 31.13 ($C_p$, *t*Bu), 31.90−32.69 (broad, unresolved), 82.81 ($C_q$, C≡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) $\delta$ 23.16, 40.74; MS (CI, isobutane) *m*/*z* (%) 778 [M$^+$] (100), 721 [M-*t*Bu]$^+$ (85); IR (KBr) $\nu$ 1632 (C=C) cm$^{-1}$, 2175 cm$^{-1}$ (C≡C). Anal. Calcd for $C_{48}H_{90}Si_4$: C, 73.95; H, 11.64. Found: C, 73.63; H, 11.81.

**1,1,3,1′,l′,1″,1″,1‴,1‴,3‴-Deca-*tert*-butyl-1*H*,1′*H*,1″*H*,1‴*H*-[2′2′;3′,2″;3″,2‴]-quater(silacyclopropene) (8).** Recrystallization from *n*-hexane at −25 °C afforded 0.12 g (8%) of colorless crystals: mp 143−150 °C; $^{1}H$ NMR (300 MHz) $\delta$ 1.22 (s, 36 H), 1.28 (s, 36 H), 1.33 (s, 18 H); $^{13}C$ NMR (75.5 MHz) $\delta$ 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) $\delta$ −62.69, −61.56; MS (CI, isobutane) *m*/*z* (%) 778 [M$^+$] (100), 721 [M − *t*Bu]$^+$ (9); IR (KBr) $\nu$ 1636 (C=C) cm$^{-1}$. Anal. Calcd for $C_{48}H_{90}Si_4$: 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 Ka 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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[21] Bohlmann, F. *Chem. Ber.* **1953**, *86*, 657.

[22] Sheldrick, G. M. *SHELXL-97. Program for crystal structure refinement*; Universität Göttingen: Göttingen, Germany 1997.