Silicon Compounds with Strong Intramolecular Steric Interactions, 71[‡]

Silylene Reactions with Buta-1,3-diynes: Cycloadditions, Insertions, and Rearrangements

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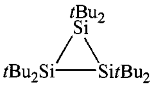
Di-*tert*-butylsilylene, generated by photolysis of hexa-*tert*-butylcyclotrisilane **1** or 1,1-di-*tert*-butyl-*trans*-2,3-dimethylsilirane (**2**), reacts with the 1,3-diyne (tBu–C≡C–)$_2$ **9** to furnish the dialkynylsilane **11** via the isolable alkynylsilirene **10**. Photolysis of excess **1** in the presence of **9** furnishes the C–C linked 2,2′-disilirene **12** which, upon prolonged irradiation, rearranges to the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (**13**). Treatment of **9** with diarylsilylenes, formed by irradiation of hexamethyl-2,2-dimesityltrisilane (**3**) or hexamethyl-2,2-bis(2,4,6-triisopropylphenyl)trisilane (**4**), gives the corresponding alkynylsilirenes **14** and **15**, respectively. Photolysis of **1** or **2** in the presence of (Me_3Si–C≡C–)$_2$ **16** yields the dialkynylsilane **17** which, on further reaction with **2**, yields the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (**18**). Irradiation of **3** in the presence of **16** affords the *cis*- and *trans*-isomeric 1,3-dimethylene-2,4-disilacyclobutane derivatives *cis*-**21** and *trans*-**21**, presumably via a 1-silaallene intermediate. The structures of **12**, **15**, **18**, *cis*-**21**, and *trans*-**21** have been determined by X-ray crystallography.

Dialkyl- and diarylsilylenes (silanediyls), R_2Si:, are highly reactive intermediates capable of undergoing numerous addition and insertion reactions. When the groups R on silicon are small, the initial products are usually unstable and often undergo a series of subsequent transformations before the thermodynamically stable final products are reached.[1] Silylenes bearing bulky substituents behave differently and, for example, undergo smooth addition reactions with multiple bond systems to furnish three-membered ring compounds that can often be isolated in spite of their high degrees of ring strain.[2]

Examples of silylenes of this type are di-*tert*-butylsilylene, generated photolytically from the cyclotrisilane **1**[3] or the silirane **2**,[4] and the 2,4,6-trialkylphenyl-substituted silylenes, also accessible from the acyclic trisilanes **3**[5] and **4**[6] under the action of light. We recently studied the photolysis of **1**, which decomposes under these conditions to give di-*tert*-butylsilylene **5** and tetra-*tert*-butyldisilene **6**, in the presence of hexa-1,3-diyne. From these experiments, the bicyclic compounds **7** and **8** were isolated as the final products and their structures were confirmed by X-ray crystallography.[7] In order to obtain further information relating to the formation of these compounds, especially the bicyclic system **7**, we have now examined the reactions of the 1,3-diynes 1,4-bis(trimethylsilyl)buta-1,3-diyne **16** and 2,2,7,7-tetramethylocta-3,5-diyne **9** with the silylene sources **1−4** and report here on the resultant cycloaddition, formal insertion, and rearrangement reactions leading to the formation of novel mono- and bicyclic systems.



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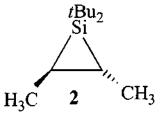
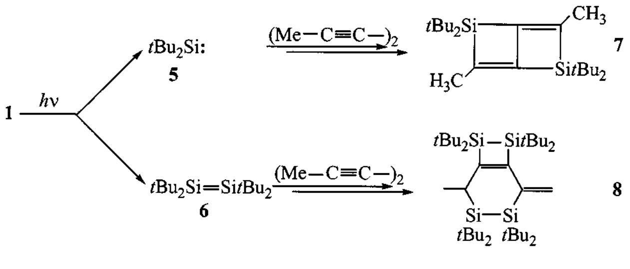


2

$(Me_3Si)_2SiR_2$

3 $R = 2,4,6\text{-}Me_3C_6H_2$
4 $R = 2,4,6\text{-}iPr_3C_6H_2$



Photolysis of the cyclotrisilane **1** in the presence of the diyne **9** in a ratio of approximately 1:1 furnished the alkynylsilirene **10** as a colorless oil in 30% yield; the constitution of this product was confirmed by a complete NMR analysis. The position of the ^{29}Si-NMR signal is of particular diagnostic value: it appears upfield at $\delta = -63.3$, which is typical for silirenes with *tert*-butyl substituents at the silicon atom.[7][8]

When the silirane **2** is used instead of **1** for the generation of di-*tert*-butylsilylene, colorless crystals are obtained in 52% yield, the analytical and mass spectral data of which

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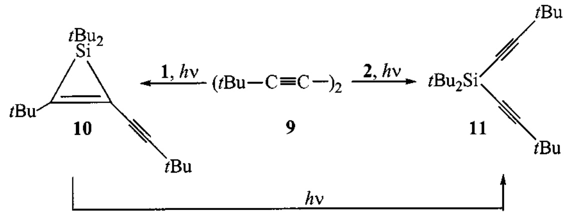
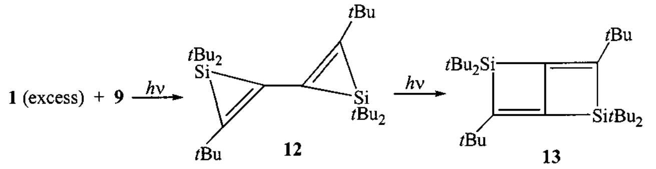
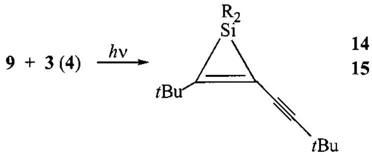






14 R = 2,4,6-$Me_3C_6H_2$
15 R = 2,4,6-$iPr_3C_6H_2$

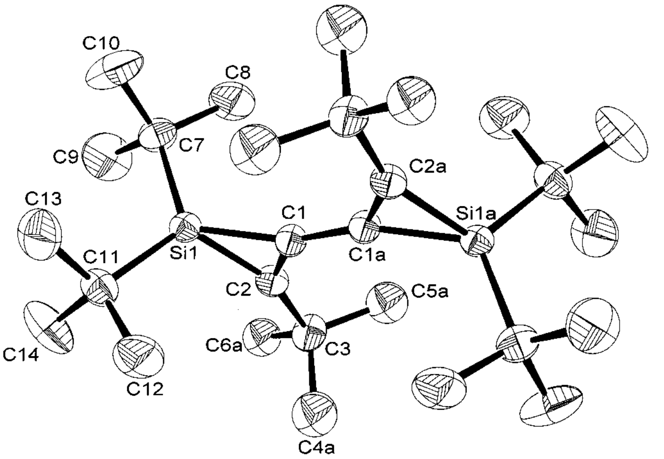


Figure 1. Molecular structure of **12** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at a 50% probability level; selected bond lengths [pm] and angles [°]: C(1)−C(2) 133.8(3), C(1)−C(1a) 145.1(4), Si(1)−C(1) 182.2, Si(1)−C(2) 181.9(2); C(2)−C(1)−Si(1) 68.3(1), C(2)−Si(1)−C(1) 43.1, C(2)−C(1)−C(1a) 137.4(3), C(1a)−C(1)−Si(1) 154.3(2)

again point to the formation of **10**. However, the NMR data are not compatible with structure **10**. Thus, no signals attributable to olefinic carbon atoms can be seen in the ^{13}C-NMR spectrum and the ^{29}Si-NMR spectrum features a singlet at $\delta = -20.04$. These data, as well as an X-ray crystallographic analysis,[9] showed that, instead of the silirene **10**, the dialkynylsilane **11** had been formed as the product of a formal silylene insertion into the central C−C single bond. The X-ray crystal structure did not exhibit any unusual features compared to those of other alkynylsilanes.[10]

The formation of different products from the photolysis of **1** or **2** in the presence of **9** is presumably due to the impeded liberation of **5** from the silirane **2**, as is reflected in the appreciably longer photolysis time. In order to obtain information on the mode of formation of the formal insertion product **11**, the silirene **10** was subjected to a further photolysis, which afforded the silane **11** in almost quantitative yield. The isomerization **10** → **11** can most simply be rationalized by a 1,2-migration of the alkynyl group in combination with a cleavage of the three-membered ring. Ishikawa et al.[11] have previously observed a similar rearrangement on heating a dimesitylsilacyclopropene to 250°C, which also furnished the corresponding dialkynylsilane.

The reaction to afford **10** from the cyclotrisilane **1** and the diyne **9** also furnished a second crystalline product in 15% yield, the spectral data of which showed it to be the C−C linked bis(silirene) **12**. The yield of this compound could be increased to 37% by increasing the proportion of **1** in the photolysis mixture to a ratio of 1:1.5. An X-ray crystallographic analysis (Figure 1) confirmed not only the constitution of **12**, but also revealed some interesting features.

Compound **12** not only represents the first C−C linked bis(silirene),[12] but is also a *trans*-butadiene with both double bonds bridged by silylene units. A comparison of the structure with that of the parent butadiene[13] reveals a somewhat shortened C−C single bond length of 145.1(4) pm instead of 148.3 pm in the butadiene. The difference in the C=C−C angles is more pronounced; 137.4(3)° in **12** is markedly larger than the 122.4° in the parent compound. Furthermore, the endocyclic Si−C bond lengths, with an average of 182 pm, are short and the C1−Si1−C2 angle of 43.1(1)° is very small.

The bis(silirene) **12** is thermally stable and, for example, is recovered unchanged after 30 d at 120°C. Its behavior under photochemical conditions is completely different: after only 6 h at room temperature the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene **13** is isolated from the reaction mixture in 52% yield. The formation of **13** is thought to proceed through cleavage of two Si−C bonds in **12**, followed by reformation of two σ-bonds to afford the rearranged bicyclic compound. The constitution of **13** was confirmed by comparison of its NMR data with those of compounds **7** and **18**, the structures of which have been verified by X-ray crystallography. Thus, we have unambiguously demonstrated all intermediate steps involved in the formation of **13** and have also found a feasible explanation for the formation of the bicyclic compound **7**, which remained as an open question from a previous publication.[7]

The photochemical lability of the Si−C bonds in **12** is also manifested in the concomitant formation of the molecules **10** and **11**, clearly showing that cycloreversion with cleavage of a silylene molecule **5** is possible besides the rearrangement **12** → **13**.

Although the dialkylsilylene **5** can participate in a variety of cycloaddition and rearrangement reactions, analogous photolyses of the 1,3-diyne with the trisilanes **3** and **4**, which also readily liberate the corresponding diarylsilylene under these conditions, merely furnish the [2+1] cycloadducts **14** and **15**, as indicated by the typical highfield signals in the ^{29}Si-NMR spectra at $\delta = -106$ (**14**) and $\delta = -109.5$ (**15**). Since the reaction of **3** with the 1,4-bis(trimethylsilyl)-1,3-diyne **16** gives rise to a completely different palette of products (see below), we have determined the structure of

15 by X-ray crystallography (Figure 2). The structure revealed a very small endocyclic C−Si−C angle of 43.2(2)°, very short Si−C1 and Si−C2 bond lengths in spite of the steric crowding, as well as a short exocyclic C2−C3 bond. All other features were unremarkable.

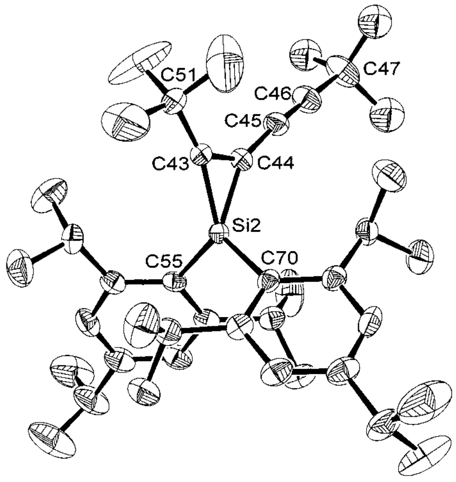
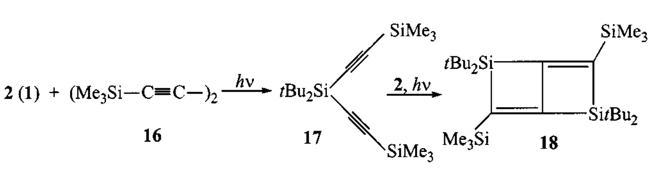


Figure 2. Molecular structure of **15** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at a 50% probability level; selected bond lengths [pm] and angles [°]: C(1)−C(2) 134.5(5), Si−C(1) 181.9(3), Si−C(2) 181.7(3); C(2)−Si−C(1) 43.4(1), C(2)−C(1)−Si 68.2(2), C(1)−C(2)−Si 68.4(2)

An unusual result, however, was that dark-yellow crystals of tetrakis(2,4,6-triisopropylphenyl)disilene were isolated together with the colorless crystals of **15**. This compound had previously been obtained by dehalogenation of dichlorobis(2,4,6-triisopropylphenyl)silane[14] and by photolysis of the trisilane **4**.[15] The fact that the dimerization process of the silylene accessible from **4** to give the disilene proceeds in competition with the [2+1] cycloaddition is possibly due to steric repulsion between the *tert*-butyl and triisopropylphenyl groups in the cycloaddition process. This hypothesis was supported by the photolysis of **4** in the presence of hexa-2,4-diyne, which gave an appreciably higher yield of the corresponding alkynylsilirene (**15**; Me instead of *t*Bu).



Analogously performed reactions of the cyclotrisilane **1** or − preferentially − the silirane **2** with the trimethylsilyl-substituted 1,3-diyne **16** seem to proceed according to the same pattern as observed for the 1,3-diyne **9**, except that in no case was a [2+1] cycloadduct of the type **10** isolated. Presumably as a consequence of the greater mobility of the trimethylsilylethynyl group,[11] the formal insertion product **17** is obtained in 46% yield; its structure, like that of **11**, was confirmed by X-ray crystallography.[16] Further treatment of the dialkynylsilane **17** with the silirane **2** led to an unexpected result: light-yellow crystals of the bicyclic product **18** were obtained in 32% yield. Similar reactions have previously been observed when zirconocene was treated with a dialkynylsilane[17] or a dialkynylzirconocene derivative;[18] these reactions also furnished bicyclic products in which one or two zirconium atoms had been incorporated into the ring skeletons. However, these results cannot be directly compared with the silylene situation because of the different bonding possibilities available to the 14-electron zirconocene complex.

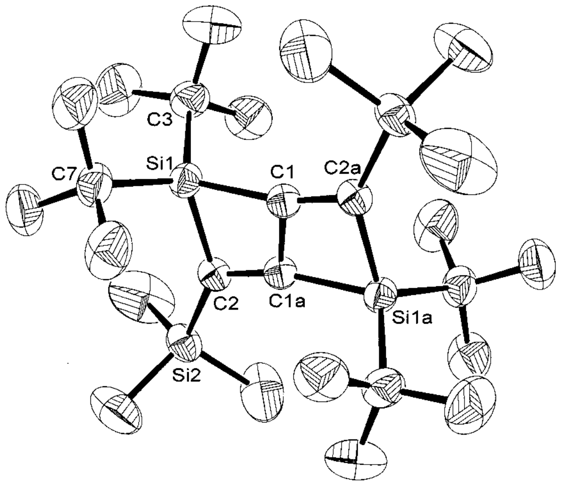
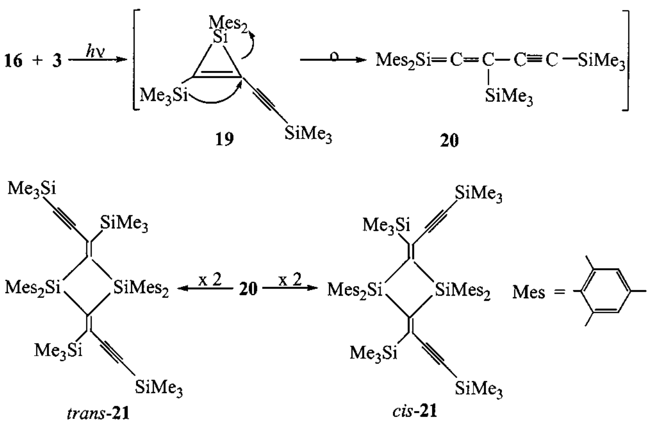


Figure 3. Molecular structure of **18** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at a 50% probability level; selected bond lengths [pm] and angles [°]: Si(1)−C(1) 189.9(2), Si(1)−C(2) 189.9(2), C(1)−C(2a) 136.2(3); C(1)−Si(1)−C(2) 76.2(1), C(1)−C(1a)−C(2) 110.0(2), Si(1)−C(2)−C(1a) 88.8(1), Si(1)−C(1)−C(1a) 85.1(2), C(1a)−C(2)−Si(2) 128.5(2), Si(1)−C(2)−Si(2) 142.7(1)

A plausible mechanistic sequence leading to formation of the bicyclic compound **18** consists of the [2+1] cycloaddition of a silylene molecule **5** to one of the C/C triple bonds, followed by a 1,2-shift of a trimethylsilyl group with intermediate formation of a 1-silaallene derivative. A subsequent intramolecular [2+2] cycloaddition can then furnish the bicyclic system of **18**. The constitution of **18** was confirmed by X-ray crystallography (Figure 3). This revealed that **18** possess a crystallographic center of inversion in the middle of the C1−C1a bond. In spite of the sterically voluminous *tert*-butyl groups, both the endo- and the exocyclic Si−C bonds are only slightly extended. However, the steric influence of these groups is apparent in the Si1−C2−Si2 angle of 142.7°, which reflects the repulsion of the trimethylsilyl groups.

In order to obtain further support for the postulated sequence proceeding via a 1-silaallene, we subjected trisilane **3** to photolytic conditions in the presence of the 1,3-diyne **16**. Fractional crystallization of the reaction mixture first gave colorless, high-melting crystals composed, according to NMR and mass spectral data, of two molecules each of the diyne and the diarylsilylene. The ^{13}C-NMR spectrum revealed the presence of both olefinic and acetylenic carbon atoms. The ^{29}Si-NMR spectrum featured three signals of equal intensity at $\delta = -2$, -19, and -22.

An X-ray crystallographic analysis of the isolated crystals (Figure 4) showed that the compound *trans*-**21** had been



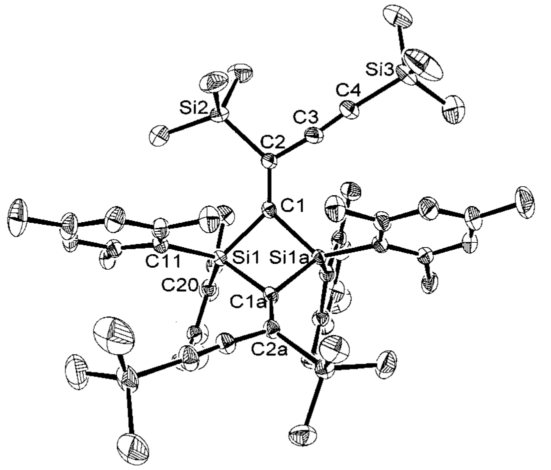


Figure 4. Molecular structure of *trans*-**21** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at a 50% probability level; selected bond lengths [pm] and angles [°]: Si(1)−C(1) 192.1(2), Si(1a)−C(1) 191.9(2), C(1)−C(2) 135.7(3), C(3)−C(4) 120.4(3); C(1)−Si(1)−C(1a) 83.1(1), Si(1)−C(1)−Si(1a) 91.70(9), C(1)−C(2)−C(3) 120.0(2)

formed. This structure has a C_2 symmetry axis perpendicular to the middle of the four-membered ring, which accounts for the fact that only three signals are observed in the ^{29}Si-NMR spectrum. The four-membered ring is folded, with an angle of 33° between the planes formed by the atoms Si1−C1−Si1a and Si1a−C1a−Si1. Within the ring, the smaller angles are found at the silicon atoms and the larger ones at the carbon atoms. This situation, together with the slightly extended Si−C bond lengths of all substituents on the four-membered ring, results in a strain-free structure. The 1,3-dimethylene-2,3-disilacyclobutane structure described here is novel. Barton, Gordon et al.[19] recently reported on a similar ring obtained by dehalogenation of α-(bromovinyl)chlorodimethylsilane, although without an unambiguous structural characterization.

After several weeks standing at −30 °C, a second fraction was obtained from the above mentioned reaction mixture, also as colorless crystals with a high melting point. The mass, ^{1}H-, and ^{13}C-NMR spectral data of this fraction did not show any major changes in comparison with those of *trans*-**21**. However, in the ^{29}Si-NMR spectrum, two signals at δ = −2.6 and −18.87 with higher intensity and another

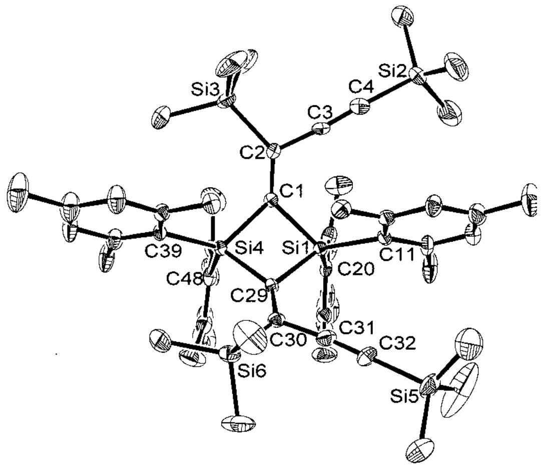


Figure 5. Molecular structure of *cis*-**21** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at a 50% probability level; selected bond lengths [pm] and angles [°]: Si(1)−C(1) 192.1(6), C(1)−Si(4) 191.9(4), Si(4)−C(29) 191.6(4), C(29)−Si(1) 192.3(4), C(1)−C(2) 135.8(6), C(2)−C(3) 144.0(7), C(3)−C(4) 122.1(7), Si(1)−C(1)−Si(4) 91.4(2), C(1)−Si(1)−C(2) 82.7(2), C(29)−Si(4)−C(1) 82.9(2), Si(4)−C(29)−Si(1) 91.5(2)

two at δ = −21.74 and −24.04 with lower intensity were observed, indicating a different structure. Again, X-ray crystallography (Figure 5) allowed an unequivocal structural assignment and revealed that *cis*-**21** had been obtained. As in the case of the *trans* isomer, the central ring is not planar, but has a folding angle of 34.7°. The molecule possesses a mirror plane dissecting the folding angle, which explains the number (four) and relative intensities of the ^{29}Si-NMR signals. The remaining structural parameters are more or less the same as those of the *trans* form.

The isolation of both *cis*- and *trans*-isomers of **21** supports the assumption that their mechanisms of formation do indeed proceed via a 1-silaallene derivative. The reaction sequence may be initiated by the [2+1] cycloaddition of the diarylsilylene to one of the triple bonds in **16** to form the silirene **19**, which is then transformed to the 1-silaallene **20** through 1,2-silyl group migration and concomitant cleavage of a ring Si−C bond. In contrast to alkyl groups, the silyl groups in this and related systems are able to undergo such 1,2-migrations.[19] Although 1-silaallenes with sterically demanding groups can be isolated as thermally stable molecules,[20][21] the steric shielding in **20** is not sufficient so that intermolecular [2+2] cycloaddition occurs to furnish the *cis*- and *trans*-isomers of compound **21**.

The results presented here serve not only to clarify the individual steps in the formation of the bicyclic systems **7**, **13**, and **18**, but also to illustrate the sensitivity with which the reaction system 1,3-diyne/silylene can depend on the terminal groups of the diacetylene, the substituents of the silylene, and the duration of photolysis

Experimental Section

General: All manipulations were performed using standard Schlenk techniques under dry argon. − ^{1}H and ^{13}C NMR: Bruker AM 300 or Bruker ARX 500. The assignments of the ^{1}H- and ^{13}C-NMR signals were confirmed with the aid of COSY and COLOC spectra. − ^{29}Si NMR: Bruker AMX 300. − MS: Finnigan MAT 212. − Elemental analyses: Analytische Laboratorien, D-51789 Lindlar, Germany. − IR spectra: Bio-Rad FTS-7. − Photolyses: High-pressure mercury immersion lamp (Heraeus TQ 150).

1,1,3-Tri-*tert*-butyl-2-(3,3-dimethylbut-1-ynyl)-1*H*-silacyclopropene (10): A solution of **1** (1.5 g, 3.5 mmol) and **9** (0.65 g, 4.0 mmol) in *n*-hexane (80 mL) was irradiated for 5 h at room temperature. After this time, TLC monitoring showed the reaction to be complete as **1** had been fully consumed. The solvent was removed and the oily residue was transferred to a molecular still. Distillation at 60°C/1.5 mbar yielded 0.32 g (30%) of **10**. − ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 1.04 (s, 18 H), 1.22 (s, 9 H, *t*BuC≡C), 1.34 (s, 9 H, *t*BuC=C). − ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 21.59 (C_q), 28.89 (C_q), 30.00 (C_p), 30.25 (C_p), 31.24 (C_p), 36.67 (C_q), 74.16 (C_q, C≡*Ct*Bu), 111.01 (C_q, *C*≡C*t*Bu), 131.33 (C_q, *C*=C*t*Bu), 172.07 (C_q, C=*Ct*Bu); C_p and C_q refer to primary and quaternary carbon atoms; the assignment of the ^{13}C-NMR signals was confirmed by a COLOR spectrum. − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −63.3. − MS (CI, isobutane): *m*/*z* (%) = 305 (100) [MH$^+$]. − $C_{18}H_{36}Si$ (304.4): calcd. C 78.88, H 11.92; found C 78.62, H 12.00.

The residue was dissolved in the minimum volume of *n*-pentane and this solution was kept at −65°C for 12 h to afford 0.075 g (10% yield) of colorless crystals of **12**. For spectroscopic data, see below.

Di-*tert*-butylbis(3,3-dimethylbut-1-ynyl)silane (11): A solution of **2** (1.20 g, 6.05 mmol) and **9** (0.76 g, 4.68 mmol) in *n*-hexane (80 mL) was irradiated for 11 h at room temperature. The solvent was then removed by vacuum distillation and the brown oily residue was transferred to a molecular still. Distillation at 60°C/0.4 mbar yielded 0.89 g of a colorless oil, which was redissolved in the minimum volume of *n*-hexane. Cooling of this solution to −17°C furnished 0.74 g (52%) of colorless, transparent crystals of **11**; m.p. 45−46°C. − ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ = 1.09 (s, 18 H, *t*Bu$_2$Si), 1.30 (s, 18 H, *t*BuC≡C). − ^{13}C NMR (C_6D_6, 125.75 MHz, 298 K): δ = 19.59 (C_q), 28.13 (C_p), 28.33 (C_q, C≡C−*C*CH$_3$), 30.78 [C_p, (*C*H$_3$)$_3$CC≡C], 77.36 (C_q, *C*≡C*t*Bu), 117.50 (C_q, C≡*Ct*Bu). − ^{29}Si NMR: (C_6D_6, 59.6 MHz, 298 K): δ = −20.04. − MS (CI, isobutane): *m*/*z* (%) = 305 (100) [MH$^+$]. − $C_{18}H_{36}Si$ (304.4): calcd. C 78.88, H 11.92; found C 78.69, H 12.07.

Rearrangement 10 → 11: A solution of **10** (0.11 g, 0.36 mmol) in C_6D_6 (0.5 mL) was irradiated for 8 h in a sealed quartz NMR tube. After this time, the ^{1}H- and ^{13}C-NMR spectra showed that **10** had been almost quantitatively converted into **11**.

1,1,1′,1′,3,3′-Hexa-*tert*-butyl-1*H*,1′*H*-2,2′-bis(silacyclopropene) (12): A solution of **1** (2.51 g, 5.88 mmol) and **9** (0.69 g, 4.25 mmol) in *n*-hexane (80 mL) was irradiated for 4.5 h at room temperature. The solvent was removed and then 0.47 g (36%) of a mixture of the volatile compounds **10** and **11** was distilled off at 50−60°C/0.03 mbar. The distillation residue was redissolved in the minimum volume of *n*-hexane and this solution was kept at −65°C for 12 h. Recrystallization of the precipitate from *n*-hexane at −20°C yielded 0.70 g (37%) of colorless crystals of **12**; m.p. 124°C. − ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 1.19 (s, 36 H), 1.30 (s, 18 H). − ^{13}C NMR (C_6D_6, 125.7 MHz, 298 K): δ = 22.08 (C_q, Si*t*Bu$_2$), 30.50 (C_p, Si*t*Bu$_2$), 31.13 (C_p, C*C*H$_3$), 35.06 (C_q, *C*CH$_3$), 143.46 (C_q, *C*=C*t*Bu), 153.05 (C_q, C=*Ct*Bu). − ^{29}Si NMR: δ = −64.0. − MS (CI, isobutane): *m*/*z* (%) = 446 (100) [M$^+$].

2,2,3,5,5,6-Hexa-*tert*-butyl-2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (13): A solution of **12** (0.60 g, 1.3 mmol) in *n*-hexane (80 mL) was irradiated for 6 h at room temperature. The solution was then concentrated to a volume of 10 mL and cooled for 6 d at −25°C. The precipitate was subsequently filtered off and recrystallized from the minimum volume of *n*-hexane to provide 0.31 g (52% yield) of colorless crystals of **13**; m.p. 328−330°C (sealed tube). − ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ = 1.18 (s, 36 H), 1.19 (s, 18 H). − ^{13}C NMR (C_6D_6, 125.7 MHz, 298 K): δ = 20.90 (C_q), 28.95 (C_p), 31.62 (C_p), 34.09 (C_q), 166.50 (C_q, *C*=C*t*Bu), 170.78 (C_q, C=*Ct*Bu). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = 36.7. − MS (CI, isobutane): *m*/*z* (%) = 446 (64) [M$^+$], 389 (100) [M$^+$ − *t*Bu]. − $C_{28}H_{54}Si_2$ (446.6): calcd. C 75.25, H 12.18, found C 74.97, H 12.01.

3-*tert*-Butyl-2-(3,3-dimethylbut-1-ynyl)-1,1-bis(2,4,6-trimethylphenyl)-1*H*-silacyclopropene (14): A solution of **3** (0.87 g, 2.1 mmol) and **9** (0.77 g, 4.2 mmol) in *n*-hexane (80 mL) was irradiated for 5 h at room temperature. After this time, TLC monitoring showed the reaction to be complete as **3** had been fully consumed. The dark-yellow solution was concentrated to a volume of 10 mL and kept at −30°C for 12 h. The resulting precipitate was filtered off and recrystallized from toluene to afford 55 mg (8% yield) of colorless **14**; m.p. 100°C. − ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 1.26 (s, 9 H), 1.32 (s, 9 H), 2.06 (s, 6 H, *p*-CH$_3$), 2.60 (s, 12 H, *o*-CH$_3$), 6.67 (s, 4 H). − ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 21.09 (C_p), 24.02 (C_p), 28.99 (C_q), 30.00 (C_p), 31.17 (C_p), 37.29 (C_q), 73.70 (C_q, *t*Bu−*C*≡C-), 113.68 (C_q, *t*Bu−C≡*C*-), 128.72 (C_t), 132.49 (C_q, *ipso*-C), 136.14 (C_q, *t*Bu−C=*C*), 139.19 (C_q), 143.97 (C_q), 173.26 (C_q, *t*Bu−*C*=C). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −106. − MS (CI, isobutane): *m*/*z* (%) = 429 (100) [MH$^+$].

3-*tert*-Butyl-2-(3,3-dimethylbut-1-ynyl)-1,1-bis(2,4,6-triisopropylphenyl)-1*H*-silacyclopropene (15): A solution of **4** (1.50 g, 2.58 mmol) and **9** (0.42 g, 2.59 mmol) in *n*-hexane (80 mL) was irradiated for 9 h at room temperature. After this time, TLC control showed the reaction to be complete as **4** had been fully consumed. The solution was concentrated to a volume of 20 mL and kept at −60°C for 4 d. Repeated crystallization of the resulting solid from *n*-hexane furnished 0.47 g (32% yield) of colorless crystals of **15**; m.p. 117°C. − ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 1.18 (d, 12 H, ^{3}J = 6.9 Hz), 1.22 (d, 24 H, ^{3}J = 6.8 Hz), 1.26 (s, 9H, *t*BuC≡C), 1.38 (s, 9 H, *t*BuC=C), 2.75 (sept, 2 H), 3.89 (sept, 4 H), 7.07 (s, 4 H). − ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 24.06 (C_p), 24.63 (C_p), 25.05 (C_p), 28.98 (C_q), 29.87 (C_p), 31.23 (C_p), 34.69 (C_t), 35.51 (C_t), 37.28 (C_q), 73.73 (C_q, *t*Bu−*C*≡C), 114.58 (C_q, *C*≡C*t*Bu), 121.35 (C_t), 132.96 (C_q, *ipso*-C), 138.02 (C_q, *C*=C*t*Bu), 150.78 (C_q), 154.91 (C_q), 174.04 (C_q, C=*Ct*Bu). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −109.6. − MS (CI, isobutane): *m*/*z* (%) = 597 (42) [MH$^+$], 393 (100) [MH$^+$ − TipH].

On prolonged cooling at −20°C, yellow crystals (90 mg, 12%) of tetrakis(2,4,6-triisopropylphenyl)disilene were isolated, which were identified by comparison of their ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

Di-*tert*-butylbis(3-trimethylsilylethynyl)silane (17): A solution of **2** (1.05 g, 5.3 mmol) and **16** (1.03 g, 5.3 mmol) in *n*-hexane (80 mL) was irradiated for 11 h at room temperature. After this time, NMR monitoring showed the reaction to be complete as **2** had been fully consumed. The solvent was distilled off and the oily residue was transferred to a molecular still. Distillation at 53°C/0.04 mbar afforded a pale-yellow oil, which was recrystallized twice from the minimum volume of *n*-hexane to yield 0.82 g (46%) of colorless **17**; m.p. 35°C. − ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.08 (s, 18 H), 1.28 (s, 18 H). − ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = −0.29 (C_p), 19.36 (C_q), 27.94 (C_p), 108.26 (C_q, *C*≡CSiMe$_3$), 116.79 (C_q, C≡*C*SiMe$_3$). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −20.94, −18.36. − MS (CI, isobutane): *m*/*z* (%) = 337 (30) [MH$^+$].

Table 1. Crystallographic data for **12**, **15**, **18**, *trans*-**21**, and *cis*-**21**

	12	**15**	**18**	*trans*-**21**	*cis*-**21**
Empirical formula	$C_{28}H_{54}Si_2$	$C_{42}H_{64}Si$	$C_{26}H_{54}Si_4$	$C_{56}H_{80}Si_6$	$C_{56}H_{80}Si_6$
Molecular mass	446.90	597.02	479.05	921.74	921.74
Crystal dimensions [mm]	0.70 × 0.43 × 0.17	0.58 × 0.41 × 0.11	1.16 × 0.64 × 0.27	0.65 × 0.33 × 0.16	0.31 × 0.25 × 0.21
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P-1	$P2_1/n$	$C2$	Cc
a [pm]	835.13(6)	1450.46(9)	1165.7(1)	1911.4(1)	2124.7(1)
b [pm]	987.96(9)	1508.6(1)	987.83(8)	1307.3(1)	2121.9(1)
c [pm]	1089.0(1)	2057.9(2)	1429.6(1)	1288.16(7)	2592.0(2)
α [°]	74.61(1)	75.17(1)	90	90	90
β [°]	70.217(9)	72.273(9)	102.581(9)	113.071(7)	97.963(7)
γ [°]	65.06(1)	77.610(9)	90	90	90
V [× 10^6 pm^3]	785.7	4100.6(6)	1606.6(2)	2961.5(4)	11573(1)
Z	1	4	2	2	8
d_{calcd} [g cm^{-3}]	1.0978	0.967	0.990	1.034	1.058
T [K]	213(2)	193(2)	296(2)	193(2)	183(2)
μ [mm^{-1}]	0.129	0.081	0.196	0.172	0.177
$2\Theta_{max}$ [°]	52	52	50	52	52
No. of reflections	9207	50152	2928	11645	42261
No. of unique reflections	2719	14965	2822	5442	20931
No. of observed reflections	2317	7035	2451	4867	12651
No. of parameters	145	769	136	280	1021
R_1 [$I > 2\sigma(I)$]	0.0621	0.0685	0.0460	0.0361	0.0570
wR_2 (all data)	0.1633	0.1812	0.1316	0.0936	0.1303
GOF on F^2	1.045	0.882	1.140	0.994	0.895

− $C_{18}H_{36}Si_3$ (336.4): calcd. C 64.20, H 10.78; found C 64.05, H 10.91.

2,2,5,5-Tetra-*tert*-butyl-3,6-bis(trimethylsilyl)-2,5-disilabicyclo-[2.2.0]hexa-1(6),3-diene (18): A solution of **17** (0.48 g, 1.43 mmol) and **2** (0.34 g, 1.71 mmol) in *n*-hexane (80 mL) was irradiated for 5 h at room temperature. After this time, the solution was concentrated to a volume of 5 mL and kept at −30°C for 3 d. The resulting precipitate was filtered off and recrystallized from *n*-hexane to afford 0.14 g (32% yield) of pale-yellow crystals of **18**; m.p. 269−272°C. − ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.23 (s, 18 H), 1.15 (s, 18 H). − ^{13}C NMR (C_6D_6, 75.5 MHz, 198 K): δ = 0.16 (C_p), 20.89 (C_q), 28.50 (C_p), 162.66 (C_q, *C*=CSiMe$_3$), 196.19 (C_q, C=*C*SiMe$_3$). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −12.66, 46.00. − MS (CI, isobutane): *m*/*z* (%) = 478 (100) [M$^+$]. − $C_{26}H_{54}Si_4$ (479.05): calcd. C 65.19, H 11.36; found C 64.99, H 11.48.

Photolysis of 3 in the Presence of 16 − Formation of *cis*- and *trans*-21: A solution of **3** (1.78 g, 4.3 mmol) and **16** (0.84 g, 4.3 mmol) in *n*-hexane (80 mL) was irradiated for 15 h at room temperature. After this time, TLC monitoring showed the reaction to be complete as **3** had been fully consumed. The solution was concentrated in vacuo to a volume of 10 mL and kept at −25°C. After 3 weeks at this temperature, 0.40 g of a solid had precipitated, which was recrystallized from *n*-hexane to provide 0.33 g (17% yield) of colorless crystals of *trans*-**21**; m.p. 265°C. − ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ = −0.01 (s, 18 H), 0.18 (s, 18 H), 1.92 (s, 6 H), 2.09 (s, 6 H), 2.11 (s, 6 H), 2.37 (s, 6 H), 2.74 (s, 6 H), 3.01 (s, 6 H), 6.18 (s, 2 H), 6.60 (s, 2 H), 6.61 (s, 2 H), 6.83 (s, 2 H). − ^{13}C NMR (C_6D_6, 125.7 MHz, 298 K): δ = −0.41 (C_p), −0.18 (C_p), 20.92 (C_p), 21.23 (C_p), 25.55 (C_p), 25.70 (C_p), 26.07 (C_p), 26.95 (C_p), 106.68 (C_q, *C*≡CSiMe$_3$), 109.62 (C_q, C≡*C*SiMe$_3$), 129.23 (C_t), 129.35 (C_t), 130.48 (C_q, *ipso*-C), 131.13 (C_t), 137.04 (C_q), 137.90 (C_q), 139.52 (C_q), 144.53 (C_q), 144.60 (C_q), 146.87 (C_q), 147.92 (C_q), 152.44 (C_q, *C*=CSiMe$_3$), 175.89 (C_q, C=*C*SiMe$_3$). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −22.17, −18.90, −2.24. − MS (CI, isobutane): *m*/*z* (%) = 923 (25) [MH$^+$]. − $C_{56}H_{80}Si_6$ (921.74): calcd. C 72.97, H 8.75; found C 71.82, H 8.93.

The *n*-hexane was then replaced by an *n*-hexane/DME mixture and the resulting solution was cooled for 2 weeks at −30°C. After this time, 0.22 g (11% yield) of colorless crystals of *cis*-**21** were obtained; m.p. 268−270°C. − ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ = −0.02 (s, 18 H), 0.21 (s, 18 H), 1.92 (s, 3 H), 1.94 (s, 3 H), 2.02 (s, 3 H), 2.09 (s, 3 H), 2.11 (s, 3 H), 2.17 (s, 3 H), 2.51 (s, 6 H), 2.61 (s, 6 H), 2.95 (s, 3 H), 2.97 (s, 3 H), 6.38 (s, 2 H), 6.41 (s, 2 H), 6.59 (s, 1 H), 6.61 (s, 1 H), 6.79 (s, 1 H), 6.81 (s, 1 H). − ^{13}C NMR (C_6D_6, 125.7 MHz, 298 K): δ = −0.42 (C_p), −0.17 (C_p), 20.91 (C_p), 21.24 (C_p), 25.33 (C_p), 25.62 (C_p), 25.70 (C_p), 25.78 (C_p), 27.02 (C_p), 106.22 (C_q, *C*≡CSiMe$_3$), 109.87 (C_q, C≡*C*SiMe$_3$), 127.72 (C_t), 128.47 (C_t), 128.69 (C_t), 128.78 (C_t), 130.87 (C_t), 131.55 (C_t), 131.66 (C_q, *ipso*-C), 136.60 (C_q), 137.54 (C_q), 138.34 (C_q), 138.53 (C_q), 140.34 (C_q), 143.81 (C_q), 144.89 (C_q), 146.53 (C_q), 146.98 (C_q), 147.17 (C_q), 148.25 (C_q), 152.80 (C_q, C=*C*SiMe$_3$), 176.84 (C_q, *C*=CSiMe$_3$). − ^{29}Si NMR (C_6D_6, 59.6 MHz, 298 K): δ = −2.60 (2 Si, C=C−SiMe$_3$), −18.87 (2 Si, C≡C−SiMe$_3$), −21.74 (1 Si), −24.04 (1 Si). − MS (CI, isobutane): *m*/*z* (%) = 922 (16) [MH$^+$], 461 (100) [M$^+$/2]. − $C_{50}H_{80}Si_6$ (921.74): calcd. C 72.97, H 8.75; found C 72.72, H 8.92.

X-ray Structure Analyses of 12, 15, 18, *trans*-21, and *cis*-21: Crystal data and numerical data of the structure determinations are given in Table 1. In each case, the crystal was mounted in an inert oil. Data collection was performed with a Siemens Stoe AED 2 diffractometer (**18**) or a Stoe IPDS area detector (**12**, **15**, *trans*-**21**, *cis*-**21**) using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The structures were solved by direct phase determination and refined by full-matrix least-squares against F^2 using the SHELXL-93/97 program systems.[22] Hydrogen atoms were placed in calculated positions, while all other atoms were refined anisotropically.[23]

Acknowledgments

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[23] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-122 319 (**12**), CCDC-122 322 (**15**), CCDC-122 323 (**18**), CCDC-122 321 (*trans*-**21**), and CCDC-122 320 (*cis*-**21**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44(0)1223/336093; E-mail: deposit@ccdc.cam.ac.uk].

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