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C_3H_4Si Species: Generation and Matrix-Spectroscopic Identification of Some Silacyclobutadiene Isomers

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Flash pyrolyses of four suitable precursors – namely 1,1,1-trimethyl-2-propargyldisilane (**32**), its allenyl (**34**) and propynyl isomer (**35**), as well as 2-ethynyl-1,1,1,2-tetramethyldisilane (**31**) – lead to the formation of three C_3H_4Si species (**7**, **11**, and **15**). By examination of their photochemistry five additional compounds of the same composition (**12**, **13**, **14**, **17**, and **18**) were identified. Except ethynylsilaethene (**18**), all compounds observed are silylenes. Their identification is based on the comparison of the experimental and calculated (BLYP/6-31G*) IR spectra. Silacyclobutadiene (**4**) or silatetrahedrane (**25**) could not be detected.

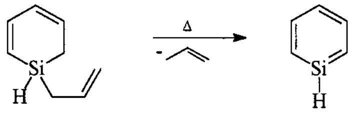
In contrast to the predictions of the classical double bond rule, the generation and identification of several compounds containing Si−C double bonds could be achieved in the last two decades. Among the candidates, which are not kinetically stabilized by substitution with bulky groups, are silaethene (**5a**)[1], the simplest possible member of the class, as well as the mono- (**2**)[2] and a disila analogue[3] of benzene.

However, another challenging task in this field is still unsolved: the matrix-isolation of the unsubstituted silacyclobutadiene (**4**). In this species the presence of a Si−C double bond is accompanied by the appearance of four cyclicly conjugated π electrons. Both characteristics, in combination with a high value of ring strain energy, are strongly destabilizing, what makes silacyclobutadiene (**4**) a very rewarding synthetic target.

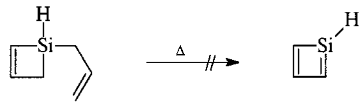
Muetterties et al. already reported its formation in the desorption of silacyclobutane from a palladium surface, but the characterization was based exclusively on mass spectroscopic data[4]. Furthermore a highly substituted analogue could be prepared in hydrocarbon matrices by Fink et al.[5].

Our first attempt to matrix-isolate the parent silacyclobutadiene (**4**) was modelled on the generation of silabenzene (**2**) from precursor **1** in a retro-ene reaction[2]. However, the pyrolysis of **3** did not yield the target compound **4** but only acetylene, ethene, allene, propyne, and benzene[6]. The finding that propene was not among the detected products, rules out that silacyclobutadiene was actually formed but did not pass the pyrolysis tube.

In a new effort we used a different concept for the generation of the target molecule **4**. It is based on the photochemical interconversion of silaethenes and appropriate silylenes. This type of reaction is well known[1c] for methylsilylene **6** and the parent silaethene **5.**

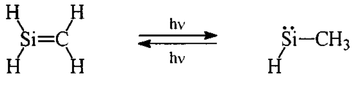


1 **2**

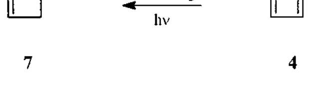


3 **4**

In order to examine whether silacyclobutenylidene **7** undergoes an analogous photochemical rearrangement to silacyclobutadiene (**4**), silylene **7** itself had to be generated and matrix-isolated. A promising way for this purpose can be envisioned from the pyrolysis of ethynyldisilane **8**. This precursor yields silacyclopropenylidene **10** via ethynylsilylene (**9**) upon trimethylsilane extrusion[7]. Silacyclobutenylidene **7** differs from the known silacyclopropenylidene **10** only by the presence of an additional methylene unit. The formal insertion of this fragment in precursor **8** leads to propargyl-



5 **6**

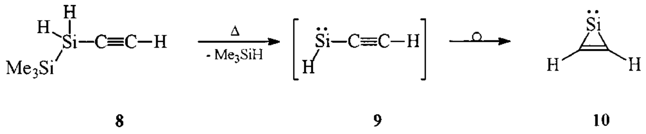


7 **4**

[◇] Part 25: Ref.[13].

1434−193X/98/0707−1297 $ 17.50+.50/0

disilane **32** as a promising candidate for the generation of **7**. Three further suitable sources (**31**, **34**, and **35**) should also lead to C_3H_4Si species. Note that propynyldisilane **35** could yield methylsilacyclopropenylidene **11**, which represents the global minimum on the C_3H_4Si potential energy surface (see below).



Calculations

The theoretical data available in the literature concerning the C_3H_4Si potential energy surface are relatively scarce[8][9][10]. Gordon and Schriver give geometries and relative energies for a number of species, but no vibrational frequency data[8]. These are only available for silacyclobutadiene (**4**)[10].

For the identification of the generated C_3H_4Si species geometry optimizations and calculations of the harmonic vibrational frequencies for seventeen species (**4**, **7**, **11–25**) of this elemental composition have been carried out assuming singlet multiplicities. All calculations have been performed at the BLYP/6-31G* level of theory, using the GAUSSIAN 94 package of programs[11]. The obtained geometries and relative energies are summarized in Scheme 1.

According to these calculations and consistent with the results achieved by Gordon and Schriver[8] the structure of lowest energy and presumably the global minimum of the hypersurface is represented by methylsilacyclopropenylidene **11**, whereas silatetrahedrane (**25**) corresponds to the least stable of the examined species. The particular stability of silacyclopropenylidenes is founded by the fact that structures of this type also represent the global minima of the C_2H_2Si[7],the $C_2H_4Si_2$[12], and the C_4H_2Si[13] hypersurfaces.

In the region up to 20 kcal mol^{-1} nine further minima were found. Among them silacyclobutenylidene **7**, which lies just 5.1 kcal mol^{-1} above methylsilacyclopropenylidene **11**. The target molecule, silacyclobutadiene (**4**), is 45.3 kcal mol^{-1} higher in energy than the global minimum (**11**), and hence potentially accessible from silylene **7** only by photoisomerization. The two bicyclobutanediyl diradicals **21** and **22** deserve special attention because of their unusual structures. The *anti* isomer (relative position of the hydrogens at the silicon and the neighbored carbon atom) is comparable in energy with silacyclobutadiene **4**. *syn*-Diradical **21** with a nearly planar four-membered ring is even 7.1 kcal/mol more stable than **22**.

Synthesis of Precursors

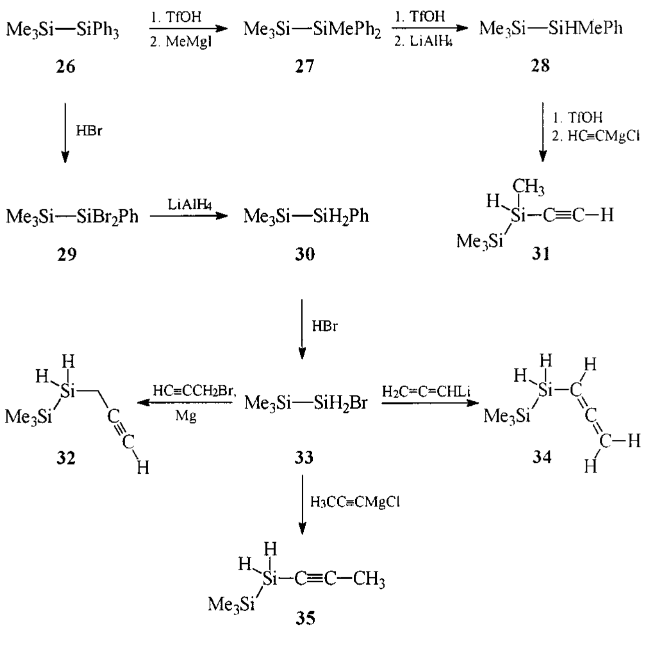
Starting from trimethyltriphenyldisilane **26**, the four precursors **31**, **32**, **34**, and **35** were synthesized as outlined in the following sequences.

The routes to the trimethyldisilanes **32**, **34**, and **35** are identical, apart from the last step. At first, two phenyl groups were removed with liquid HBr at −78°C. The resulting dibromodisilane **29** was then reduced with lithium aluminum hydride and the formed phenyldisilane **30** treated with liquid HBr again. In this way bromodisilane **33**, the key intermediate on the route to the precursors **32**, **34**, and **35**, was accessible. Its reaction with propargyl bromide and magnesium turnings in THF yielded a mixture of propargyldisilane **32** and allenyldisilane **34**. The product ratio varied from about 4:1 to 10:1, depending mainly on the reaction temperature. To get a maximum yield of propargyldisilane, it was necessary to cool the reaction vessel with ice. Precursor **32** was purified by means of preparative GC, what allows an almost entire separation from its isomer **34**.

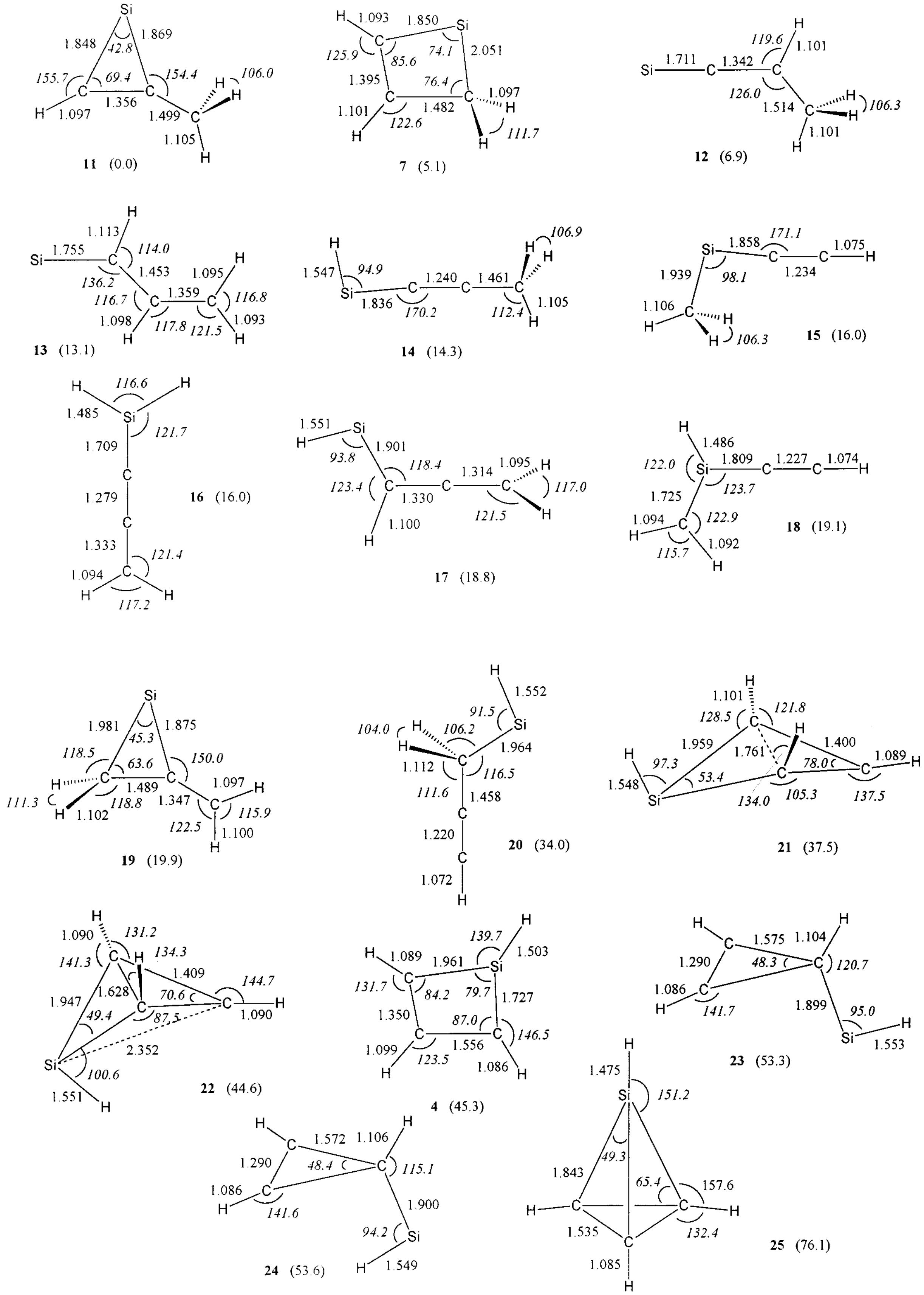
Since the amount of allenyl compound **34** accessible by this route was too low for a convenient isolation, **34** was synthesized from bromodisilane **33** by reaction with allenyllithium, which was prepared by transmetallation of bromoallene with *n*-butyllithium. Under carefully controlled conditions no isomeric by-products were formed, simplifying the purification by preparative GC considerably.

For the preparation of propynyldisilane **35**, the third precursor in this series, bromodisilane **33** was treated with propynylmagnesium chloride. The formation of isomeric by-products was not expected in this reaction and indeed none were found.

To synthesize the remaining precursor **31**, the three phenyl groups in disilane **26** have to be replaced by three different substituents. This can be done by alternating treatment with trifluoromethanesulfonic acid and the respective nucleophile (methylanion or hydride ion). Trifluoromethanesulfonic acid is liquid at room temperature and therefore relatively easy to scale, whereas with the gaseous HBr it is much more difficult to work with the required equimolar amounts.



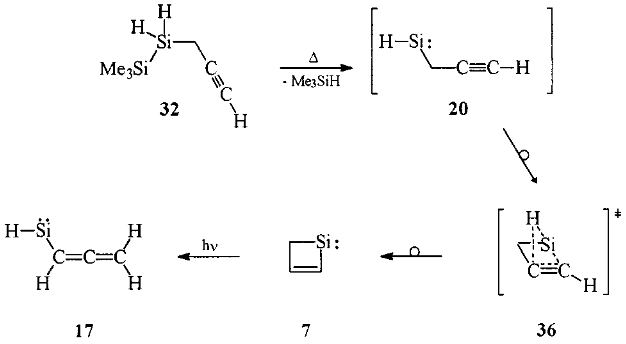
Scheme 1. Relative energies [kcal mol^{-1}] (corrected by zero point vibrational energies) of selected C_3H_4Si isomers



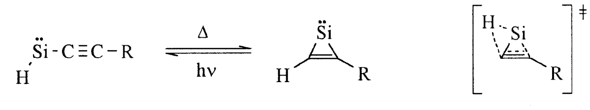
Flash Pyrolysis of 1,1,1-Trimethyl-2-propargyldisilane (32) and Photoisomerization of the Resulting C_3H_4Si Species

Gaseous mixtures of propargyldisilane **32** and argon (1:1000) were subjected to *high-vacuum* flash pyrolyses and *pulsed* flash pyrolyses in ovens which were directly flanged to a cryostat for matrix isolation studies. The pyrolysis products formed were condensed immediately after leaving the hot zone of the pyrolysis tube on the surface of a CsI window cooled to about 10 K. The thus formed argon matrices were examined by IR- and UV/Vis spectroscopy. Both pyrolysis techniques (*high-vacuum* or *pulsed*) gave the same results.

Beside the absorptions of the expected extrusion product trimethylsilane additional bands appeared in the vibrational spectrum, the most prominent lying at 765.0 cm^{-1}. Upon subsequent irradiation with light of the wavelength λ = 313 nm this set of bands vanished and new absorptions with the most intense bands at 1915.5 and 1988.3 cm^{-1} became visible. Particularly telling for the elucidation of this photoreaction is the corresponding difference IR spectrum (Figure 1), which helps to clear up the identity of both species involved in the transformation. From the comparison of the observed bands with the calculated IR spectra of the C_3H_4Si isomers it is evident, that the pyrolysis yields the expected silacyclobutenylidene **7** (Figure 1, Table 1). Apart from discrepancies in the relative intensities, the agreement between theory and experiment is good and leaves little doubt about the identity of the pyrolysis product.



From the mechanistic point of view the formation of silacyclobutenylidene **7** is the result of a rearrangement of the supposed primary pyrolysis product propargylsilylene (**20**) via the transition state **36**. This type of reaction is very similar to the transformation **9** → **10**, for which a transition state **41** can be found by MP2/6-31G** calculation, which lies 29.9 kcal mol^{-1} above **9**[14].



9: R = H; **14**: R = CH_3 **10**: R = H; **11**: R = CH_3
37: R = SiH_3; **39**: R = C_2H **38**: R = SiH_3; **40**: R = C_2H

However, irradiation of silylene **7** with light of the wavelength λ = 313 nm did not yield the expected silacyclobutadiene (**4**). According to the calculations, the latter species should have its by far most intense absorption at 2143 cm^{-1} (SiH stretching vibration), what is incompatible with the spectrum of the compound formed in the photoreaction. Its spectrum is dominated by two broad and strong bands at 1915.5 and 1988.3 cm^{-1} (Figure 1, Tables 1 and 2). They fit to an asymmetric CCC stretching vibration of an allene and a SiH stretching vibration of a silylene. Although the congruence of theory and experiment is not as good as in the case of silacyclobutenylidene **7**, the spectrum of the photoproduct of **7** can be assigned to allenylsilylene (**17**).

Figure 1. Comparison of experimental (Ar, 10 K) and theoretical (BLYP/6-31G*) infrared spectra of silacyclobutenylidene **7** and allenylsilylene (**17**). Bars at top: Calculated IR spectrum of **7**. Centre: Difference spectrum belonging to the photoisomerization **7** → **17** with light of the wavelength λ = 313 nm. Bars at bottom: Calculated IR spectrum of **17**. IR bands due to trimethylsilane have been crossed.

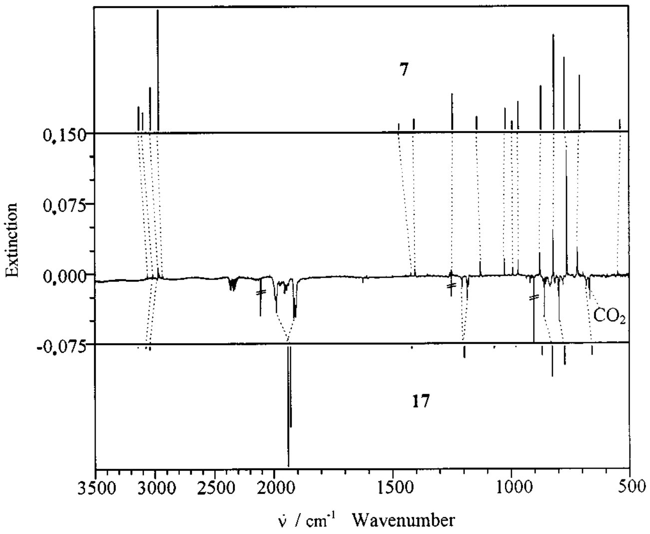


Table 1. Calculated and experimental IR spectrum of silacyclobutenylidene **7** (wavenumbers in cm^{-1}; intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G*	Experiment
C(2-H) str.	3131.2 (19)	3062.6 (3)
CH_2 str.	3097.7 (14)	3017.3 (4)
CH_2 str.	3033.3 (35)	2972.0 (32)
C(3-H) str.	2965.6 (100)[a]	2931.5 (2)
CH_2 scis.	1470.5 (4)	1422.1 (3)
C(3-H) bend.	1407.0 (8)	1405.0 (7)
HC=CH def.	1244.9 (29)	1247.7 (1)[b]
CH_2 twist.	1142.0 (10)	1129.2 (15)
HC=CH def.	1022.9 (17)	1028.6 (15)
C^3C^4 str.	994.1 (6)	993.0 (7)
CH_2 wag.	968.5 (23)	970.2 (17)
HC=CH def.	872.8 (36)	879.2 (27)
HC=CH def.	818.4 (79)	823.2 (58)
SiC^2 str.	773.4 (60)	765.0 (100)
SiC^2C^3 def.	708.4 (45)	719.8 (19)
CCC def.	537.3 (7)	549.3 (5)
SiCCC def.	417.3 (10)	–
CCC def.	334.3 (9)	–

[a] Abs. int. 59.1 km mol^{-1}. – [b] Absorption almost coincides with an intense band of trimethylsilane at 1251.6 cm^{-1}; the integration is therefore inaccurate.

Table 2. Calculated and experimental IRspectrum of allenylsilylene (**17**) (wavenumbers in cm^{-1}; intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G	Experiment
CH_2 str.	3139.0 (0.1)	–
CH_2 str.	3073.7 (0.4)	3023.9 (1)
C–H str.	3038.8 (2)	2980.2 (1)
CCC str.	1940.2 (100)[a]	1915.5, 1908.0 (100)[b]
SiH str.	1928.6 (67)	1993.8, 1988.3 (83)[b]
CH_2 scis.	1419.0 (1)	–
SiCC str.	1195.5 (9)	1184.4, 1179.4 (23)[b]
CH bend.	1069.3 (1)	–
CH_2 rock.	978.8 (0.1)	–
CH bend.	867.9 (7)	–
Si–H bend.	826.0 (25)	860.4 (16)
CH_2 wag.	771.6 (15)	798.4 (28)
HSiCH def.	656.8 (7)	682.3 (9)
SiCCC def.	455.9 (7)	–
SiCCC def.	419.2 (0.001)	–
SiCCC def.	400.9 (1)	–
CH_2tors.	150.5 (0.2)	–
SiCCC def.	149.2 (0.1)	–

[a] Abs. int. 418.4 km mol^{-1}. – [b] Split by matrix effects; integration includes all respective bands.

Since the described irradiation did not yield silacyclobutadiene (**4**), we repeated the experiment with light of the wavelength λ = 405 nm. As before, the absorptions of silacyclobutenylidene **7** vanished within minutes, while new ones appeared. These were not identical with the described absorptions of allenylsilylene (**17**). Since again no vibration was detected in the region near 2143 cm^{-1}, they also could not belong to silacyclobutadiene (**4**). The spectrum of the photoproduct is rather characterized by an intense absorption at 877.3 cm^{-1}. This band in combination with two others at 979.7 and 1760.3 cm^{-1} indicates the presence of a vinyl fragment in the species (the first absorption is interpreted as a $CH_{2\ \mathrm{wagging}}$ vibration, the second as an *out of plane* vibration of the two non adjacent hydrogen atoms and the last as the first's overtone). Supposed this is true, then the most likely structure for the new species is that of silabutadienylidene **13**. And indeed, a fairly good agreement between the theoretical and experimental spectrum is found (see Figure 2 and Table 3). If silabutadienylidene **13** is irradiated with light of the wavelength λ = 313 nm, the known bands of allenylsilylene (**17**) reappear.

Obviously, the hoped 1,2 H shift from silacyclobutenylidene **7** to silacyclobutadiene (**4**) cannot be induced by irradiation, ring opening takes place instead. The mechanistic interpretation of these results is not difficult. Silabutadienylidene **13** is the product of a photochemically allowed [$\pi 2_s + \sigma 2_s$] process with subsequent rotation around the single bond. If the isomerization is carried out with light of the wavelength λ = 313 nm, silabutadienylidene **13** is not detectable, because it rapidly undergoes in a second step an 1,3 H shift to allenylsilylene (**17**).

To generate additional species of the composition C_3H_4Si, allenylsilylene **17** was subjected to further irradiations with light of the wavelength λ = 313 or 254 nm. After relatively long reaction periods (about one day for both wavelengths) its absorptions decreased significantly and new ones became visible. Two of these bands at 3308.6 (CH stretching vibration) and at 2001.2 cm^{-1} (CC stretching vibration) are typical for a substituted acetylene. Among all conceivable C_3H_4Si species with a $-C{\equiv}C-H$ fragment in the molecular framework the accordance of the theoretical and experimental IR spectrum is best for ethynylmethylsilylene (**15**) (see further discussion below in context with the photoisomerization of **14**).

The formation of ethynylmethylsilylene **15** from allenylsilylene **17** can be interpreted as a series of 1,3 shifts (of H or a CH_3 group) with species like **12** and **14** as intermediates. Indeed, a small band at 1681.4 cm^{-1} appears in the IR spectrum during the described photoreaction **17** → **15.** This position fits well with the calculated spectrum of methylvinylidenesilylene (**12**) (BLYP/6-31G*: 1680.7 cm^{-1}; this vibration is due to the SiCC stretching mode and by far more intense then all other vibrations of that species).

Figure 2. Comparison of the experimental (Ar matrix, 10 K) and theoretical (BLYP/6-31G*) spectrum of silabutadienylidene **13**. Bars at top: Calculated IR spectrum of **13**. Bottom: Difference spectrum belonging to the photoisomerization **7** → **13** with light of the wavelength λ = 405 nm.

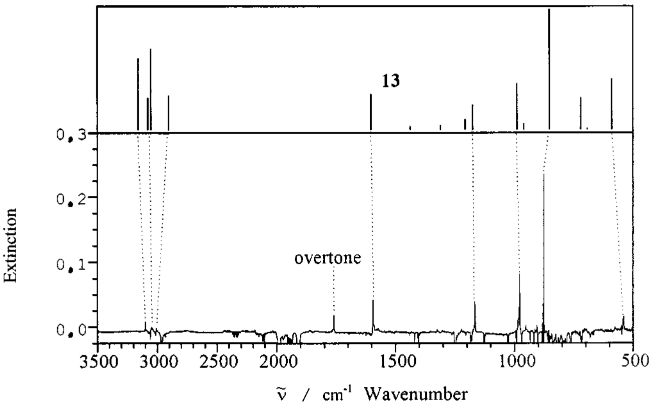
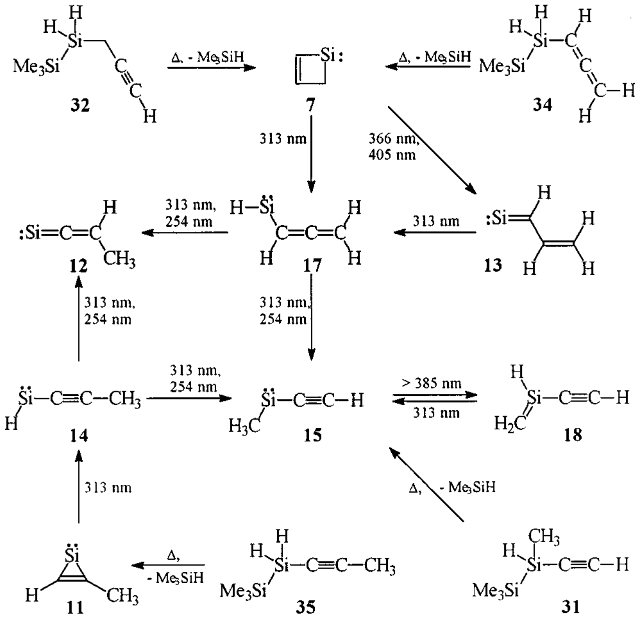


Table 3. Calculated and experimental IR spectrum of silabutadiene **13** (wavenumbers in cm^{-1}; intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G*	Experiment
CH_2 str.	3159.8 (59)	3103.4 (21)
CH_2 str.	3078.5 (26)	3052.5 (3)
C(3-H) str.	3054.9 (67)	3040.3 (1)
C(2-H) str.	2907.5 (28)	3010.6 (4)
overtone		1760.3 (14)
C=C str.	1603.2 (29)	1594.6 (26)
CH_2 scis.	1437.3 (2)	–
CH bend.	1310.0 (3)	–
CH bend.	1207.6 (8)	–
C^2C^3 str.	1176.2 (20)	1167.5 (26)
CH bend.	989.5 (38)	979.7 (33)
CH_2 rock.	960.3 (4)	–
CH_2 wag.	852.0 (100)[a]	881.0, 877.3 (100)[b]
SiCCC def.	720.8 (26)	–
SiC str.	693.2 (0.3)	–
CH_2 twist.	588.4 (42)	541.2 (8)
CCC bend.	396.4 (11)	–
SiCC bend.	153.6 (1)	–
SiCC bend.	137.6	–

[a] Abs. int.: 36.5 km mol^{-1} – [b] Split by matrix effects; integration includes all respective bands.

Scheme 2. Thermal preparation of silylenes **7**, **11**, and **15** and their photoinduced isomerizations into the isomers **12**, **13**, **14**, **17**, and **18**



Pulsed Flash Pyrolysis of 1-Ethynyl-1,2,2,2-tetramethyldisilane (31) and Photoisomerzation of the Resulting C_3H_4Si Species

In order to prove the structural assignment of ethynylmethylsilylene (**15**) we carried out a pulsed flash pyrolysis of its "direct" precursor ethynyltetramethyldisilane **31**. As expected, the absorptions assigned to **15** appeared (see Figure 5 and Table 7 for a spectrum of **15**). Notably, no rearrangement **15** → **11** as in the case **9** → **10** took place here. Obviously, the migration tendency of the methyl group is too low and ethynylmethylsilylene (**15**) is stable enough to pass the pyrolysis tube.

Since **15** is a methylsilylene, it should undergo a reaction of type **5** → **6** to the corresponding silaethene upon photolysis. So we studied irradiations with light of wavelengths $\lambda > 385$ nm. Within 18 h a significant conversion of **15** had taken place and new bands appeared. The comparison with the calculated spectrum of ethynylsilaethene (**18**) led to a fairly good coincidence; especially the characteristic absorptions of the acetylenic CH (3314.5 cm^{-1}) and CC (2047.5 cm^{-1}) as well as the SiH stretching vibration were registered (Figure 3, Table 4). Upon irradiation with light of the wavelength $\lambda = 313$ nm the conversion was reversed within one hour.

Flash Pyrolysis of 1-Allenyl-2,2,2-trimethyldisilane (34)

At this point, pyrolysis experiments with the two additional precursors **34** and **35** were carried out, in order to get new accesses to the C_3H_4Si hypersurface.

Assuming that the thermolysis of allenyldisilane **34** takes a similar course as that of propargyldisilane **32**, the formation of two different products can be expected. The interaction between the silylenic centre of allenylsilylene – which is very likely formed initially – and the closer π system should lead to methylenesilacyclopropylidene **19**. In contrast, the already known silacyclobutenylidene **7** should be formed by interaction between the subvalent silicon atom and the terminal π system.

Figure 3. Comparison of the experimental (Ar matrix, 10 K) and theoretical (BLYP/6-31G*) spectrum of ethynylsilaethene (**18**). Bars at top: Calculated IR spectrum of **18**. Bottom: Difference spectrum belonging to the photoisomerization **15** → **18** with light of wavelengths $\lambda > 385$ nm. IR bands due to trimethylsilane have been crossed

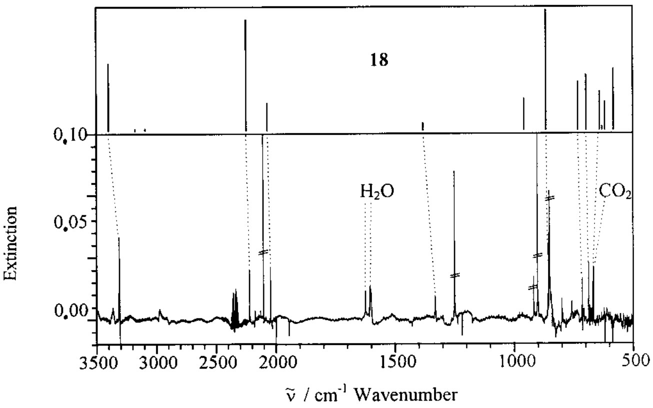


Table 4. Calculated and experimental IR spectrum of ethynylsilaethene **18** (wavenumbers in cm^{-1}; intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G*	Experiment
≡C–H str.	3397.4 (56)	3314.5 (100)
CH_2 str.	3176.6 (1)	–
CH_2 str.	3091.1 (1)	–
SiH str.	2245.9 (92)	2224.0 (71)
C≡C str.	2068.9 (22)	2047.5 (69)
CH_2 scis.	1380.4 (6)	1331.6 (24)
Si=C str.	957.4 (26)	–
SiH bend.	864.2 (100)[a]	858.2 (96)
CH_2 wag.	730.4 (40)	716.2 (49)
CH_2 rock.	696.8 (46)	689.5 (75)
≡C–H bend.	639.9 (32)	669.2 (56)
CH_2 twist	630.4 (3)	–
Si–C str.	617.6 (23)	–
≡C–H bend.	581.5 (51)	–
CCSiC def.	325.4 (14)	–
CCSiC def.	324.6 (16)	–
CCSi bend.	234.3 (2)	–
CCSi bend.	151.4 (1)	–

[a] Abs. int.: 86.7 km mol^{-1}.

High vacuum flash pyrolysis as well as pulsed flash pyrolysis of an gaseous mixture of allenyldisilane **34** and argon resulted in the generation of **7** as the first species detectable in the matrix; the absorptions of **19** or another so far unknown C_3H_4Si species were not registered.

Flash Pyrolysis of 1,1,1-Trimethyl-2-propynyldisilane (35) and Photoisomerization of the Resulting C_3H_4Si Species

The expected product in the pyrolysis of the fourth precursor, propynyldisilane **35**, is methylsilacyclopropenylidene **11**. Although the photochemical generation of silacyclobutadiene (**4**) from **11** was not anticipated, it was an interesting synthetic target. Since it would be an additional silacyclopropenylidene (the parent compound[7], a silyl[12], and an ethynyl analogue[13] are already known), it could enhance our knowledge about this class of compounds. In addition, due to its low energy it should be found easily and by these means **11** should be a good candidate for subsequent photochemical studies.

In contrast to the experiments with propargyldisilane **32** and allenyldisilane **34**, *high-vacuum* flash pyrolysis and *pulsed* flash pyrolysis of **35** gave different results. The former yielded only acetylene and propyne beside the extrusion product trimethylsilane, whereas the latter led to the generation of the expected methylsilacyclopropenylidene **11**. This is in accordance with the experiences we made with the parent silacyclopropenylidene **10**, which also could be isolated only under the conditions of *pulsed* flash pyrolysis[7]. Characteristic IR bands for **11** are found at 3014.9 (CH str., olefinic H), 1562,8 (CC str., cyclopropene double bond) and at 1440.5, 1433.9, and 1360.9 cm^{-1} (deformation vibrations of the methyl group). Again theory and experiment coincide well (Figure 4 and Table 5) concerning the overall spectral pattern.

Figure 4. Comparison of experimental (Ar, 10 K) and theoretical (BLYP/6-31G*) infrared spectra of methylsilacyclopropenylidene **11** and propynylsilylene (**14**). Bars at top: Calculated IR spectrum of **11**. Centre: Difference spectrum belonging to the photoisomerization **11** → **14** with light of the wavelength λ = 313 nm. Bars at bottom: Calculated IR spectrum of **14**

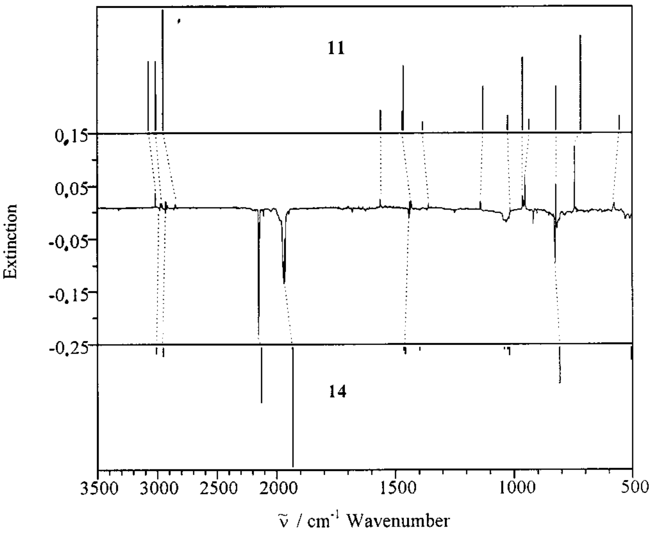


Table 5. Calculated and experimental IR spectrum of methylsilacyclopropenylidene **11** (wavenumbers in cm^{-1}, intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G*	Experiment
CH str.	3074.5 (57)	3014.9 (25)
CH_3 str.	3013.4 (57)	2973.4, 2963.6 (52)[a]
CH_3 str.	3012.7 (30)	2929.5, 2915.3 (35)[a]
CH_3 str.	2950.6 (100)[b]	2850.0 (21)
C=C str.	1560.4 (16)	1562.8 (16)
CH_3 def.	1469.2 (15)	1440.5 (16)
CH_3 def.	1464.4 (53)	1433.9 (15)
CH_3 def.	1383.3 (6)	1360.9 (4)
CH_3 rock.	1128.4 (36)	1140.4 (20)
CH_3 rock.	1025.0 (11)	1016.9 (7)
CH bend.	964.1 (60)	964.1 (27)
C−C str.	936.2 (8)	953.3 (69)
C−H bend.	822.0 (36)	823.4 (39)
Si−(CH) str.	718.3 (78)	744.0 (100)
Si−(CCH_3) str.	553.7 (11)	576.5 (39)
C−CH_3 bend.	325.4 (15)	−
C−CH_3 bend.	269.7 (4)	−
CH_3 tors.	69.9 (4)	−

[a] Split by matrix effects; integration includes all respective bands. − [b] Abs. int.: 40.8 km mol^{-1}.

Table 6. Calculated and experimental IR spectrum of propynylsilylene (**14**) (wavenumbers in cm^{-1}; intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G*	Experiment
CH_3 str.	3007.6 (5)	2982.0 (1)
CH_3 str.	3005.9 (2)	2933.0 (1)
CH_3str.	2951.3 (7)	2860 (1)
C≡C str.	2127.5 (46)	2151.1, 2142.7 (58)[a]
SiH str.	1931.2 (100)[b]	1970.8, 1964.1 (100)[a]
CH_3 def.	1464.2 (2)	1442.5 (2)
CH_3 def.	1456.9 (5)	1437.6 (0.3)
CH_3 def.	1396.5 (2)	−
CH_3 rock.	1040.7 (1)	−
CH_3 rock.	1027.5 (1)	−
SiCCC str.	1018.8 (6)	−
SiH bend.	806.7 (30)	826.7 (25)
SiCC str.	506.3 (10)	−
SiCCC def.	391.2 (0.1)	−
SiCCC def.	326.0 (0.2)	−
SiCC bend.	146.7 (1)	−
SiCC bend.	124.7 (1)	−
CH_3 tors.	40.8 (0.01)	−

[a] Split by matrix effects; integration includes all respective bands. − [b] Abs. int.: 323.7 km mol^{-1}.

Irradiation of **11** with light of the wavelength λ = 313 nm resulted in ring opening to propynylsilylene **14**. This reaction seems to be common for all silacyclopropenylidenes[7][12][13]. As in the cases before, the experimental and calculated spectra of **14** are in good accordance (see Figure 4 and Table 6). Especially the absorptions at 1970.8 and 2151.1 cm^{-1}, that are related to the SiH and the C≡C stretching vibrations, are expressive.

It has been mentioned above, that propynylsilylene (**14**) is assumed to be an intermediate in the photoisomerization of allenylsilylene (**17**) resulting in the formation of ethynylmethylsilylene (**15**). Supposed this is true, irradiation of **14** should also lead to **15**. And in fact, when propynylsilylene (**14**) was subjected to light of the wavelengths λ = 313 or 254 nm for several hours, the already known bands of ethynylmethylsilylene (**15**) appeared (see Figure 5 and Table 7). In addition, the characteristic absorption of methylvinylidenesilylene **12** at 1681.4 cm^{-1} became visible. This species is accessible from **14** by an 1,3 H or from **15** by an 1,3 methyl shift. Furthermore, a band at 765.0 cm^{-1} was detected which could be due to silacyclobutenylidene **7**. This complicated photobehavior of **14** indicates that all the photoisomerizations shown in the Scheme 2 are in principle reversible.

Conclusion

Although the actual goal − namely the generation of silacyclobutadiene or silatetrahedrane − was not achieved,

Figure 5. Comparison of the experimental (Ar matrix, 10 K) and theoretical (BLYP/6-31G*) spectrum of ethynylmethylsilylene **15**. Bars at top: Calculated IR spectrum of **15**. Bottom: Difference spectrum belonging to the photoisomerization **14** → **15** with light of the wavelengths λ = 254 or 313 nm

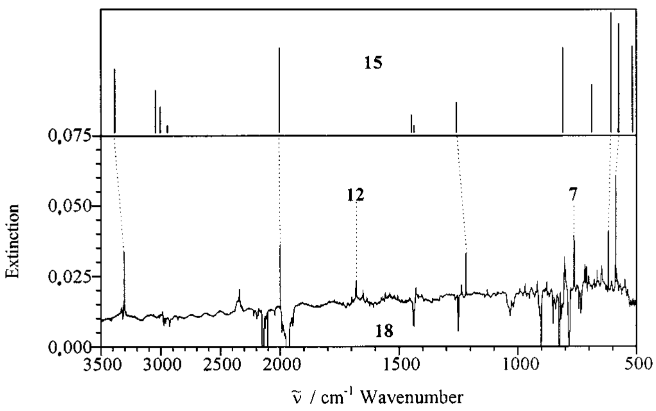


Table 7. Calculated and experimental IR spectrum of ethynylmethylsilylene **15** (wavenumbers in cm^{-1}; intensities in parentheses relative to the strongest band)

Type	BLYP/6-31G*	Experiment
CH str.	3386.2 (53)	3308.6 (85)
CH$_3$ str.	3045.4 (35)	–
CH$_3$ str.	3005.4 (21)	–
CH$_3$ str.	2945.5 (5)	–
C≡C str.	2006.1 (71)	2001.2 (49)
CH$_3$ def..	1448.1 (14)	1430.0 (7)
CH$_3$ def..	1435.7 (5)	–
CH$_3$ def.	1257.0 (25)	1218.8 (32)
CH$_3$ rock.	810.4 (71)	–
≡CH bend.	689.0 (40)	–
Si–(CH$_3$) str.	607.9 (100)[a]	620.2 (60)
CH$_3$ rock	578.8 (2)	–
Si–(CCH) str.	574.3 (91)	588.4 (100)
≡C–H bend.	516.9 (72)	–
CSiCC def.	357.1 (15)	–
SiCC bend.	186.9 (4)	–
CSiCC def.	134.4 (1)	–
CH$_3$ tors.	68.0 (0.02)	–

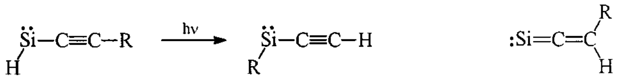
[a] Abs. int.: 59.7 km mol^{-1}.

we were able to get new insights into the diversity of silylene chemistry. In combination with other reports[7][12][13], some common principles become clear:

Silylenes with a hydrogen atom at the subvalent silicon centre and a π system in the neighbourhood of the latter rearrange easily to isomeric cyclic species under the conditions of pyrolysis. Instead of the silylenes containing a SiH group, only the rearranged products are usually detected in solid argon. Examples are the ethynyl silylenes **9**, **14**, and **37**[12] which give upon pyrolysis the corresponding silacyclopropenylidenes **10**, **11**, and **38**. The thermal formation of silacyclopropenylidenes is reversible on irradiation. In case of the ethynyl derivative **39**[13] the ring closure to **40** can be initiated photochemically.

Propargyl- (**20**) and allenylsilylene (**16**), undergo a thermal ring closure to silacyclobutenylidene **7**. Vinylsilylene follows a different reaction path on thermal induction: Instead of silacyclopropylidene one finds silacyclopropene, a cyclic product with a non-silylenic structure[15].

The presence of a hydrogen atom (or a SiH$_3$ group[12]) at the subvalent silicon centre is necessary for the ethynylsilylene/silacyclopropenylidene isomerization. Alkyl-substituted ethynylsilylenes do not react in this manner and can be isolated directly [compare the isolation of **15**, starting from **31**, and of diethynylsilylene (**42**)[13]]. Obviously a hydrogen atom migrates much easier – most likely in a one-step reaction via a transition state of type **41** – than an alkyl group.



14: R = CH$_3$ **15**: R = CH$_3$ **12**: R = CH$_3$

39: R = C$_2$H **42**: R = C$_2$H **43**: R = C$_2$H

Two examples are known for a "double exchange" reaction namely **14** → **15** (R = CH$_3$) and **39** → **42** (R=C$_2$H)[13], which might be common for carbon substituted silylenes (such a reaction was not found for R = SiH$_3$[12]). This transformation can be rationalized either as a twofold 1,3 shift with **12** or **43** as an intermediate or by a sequence of ring closure and opening reactions via **11** or **40**. An indication for the first mechanism is the appearance of methylvinylidenesilylene **12** in the irradiation of propynylsilylene (**14**).

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Experimental Section

Equipment Used for Matrix Isolation, Photolyses, and Pyrolyses: See Ref.[13].

Pulsed Flash Pyrolyses and High Vacuum Flash Pyrolyses: For a description see Ref.[13].

General: See Ref.[13]. 1,1,1-Trimethyl-2,2,2-triphenyldisilane[13][16] (**26**) and bromoallene[17] were prepared as reported in the literature.

1,1,1,2-Tetramethyl-2,2-diphenyldisilane (**27**): 15.00 g of trimethyltriphenyldisilane **26** were dissolved in 90 ml of pentane and treated with 6.77 g of trifluormethanesulfonic acid at 0°C. After stirring one hour, 15 ml of a 3 N solution of methylmagnesium iodide in diethylether were added dropwise. Distillation yielded, after aqueous workup, 8.56 g (70%) of disilane **27** as a colourless liquid of boiling point 103°C/0.05 Torr.

1,1,1,2-Tetramethyl-2-phenyldisilane (**28**): 7.09 g of disilane **27** were dissolved in 50 ml of pentane, 3.93 g of trifluormethanesulfonic acid added at 0°C and the resulting solution was stirred for one hour. Then 0.50 g of LiAlH$_4$ dissolved in 10 ml ether were added. After aqueous workup 2.23 g (44%) of disilane **28** were obtained by distillation as a colourless liquid of boiling point 102°C/34 Torr.

1-Ethynyl-1,2,2,2-tetramethyldisilane (**31**): 1.40 g of disilane **28** were dissolved in 15 ml of pentane, 1.08 g of trifluormethanesulfonic acid added at 0°C and the resulting solution was stirred for one hour. Then 7.2 ml of an 1 N solution of ethynylmagnesium chloride were added. After distillative concentration, disilane **31** was purified by preparative GC. − IR (neat): ν = 3294 cm^{-1} (≡C−H), 2117 (SiH), 2031 (CC), 1248 [Si(CH$_3$)$_3$]. − ^{1}H NMR (CDCl$_3$, capillary): δ = 0.71 [s, 9 H, Si(CH$_3$)$_3$], 0.78 [d, ^3J(H,H) = 4.7 Hz, 3 H, Si-CH$_3$], 2.90 [d, ^4J(H,H) = 1.4 Hz, 1 H, C≡C-H], 4.44 [d×q, ^3J(H,H) = 4.7 Hz, ^4J(H,H) = 1.4 Hz, 1 H, Si-H]. − ^{13}C NMR (CDCl$_3$, capillary): −7.3 (Si-CH$_3$), −1.9 [Si(CH$_3$)$_3$], 85.1 (Si-C≡), 97.0 (≡C-H). − ^{29}Si NMR (CDCl$_3$, capillary): −58.4 (Si-H), −17.4 [Si(CH$_3$)$_3$]. − MS (70 eV); *m/z* (%): 142 (5) [M$^+$], 127 (67) [M$^+$ − CH$_3$], 73 (100) [Si(CH$_3$)$_3$]. − HRMS calcd. for C$_5$H$_{11}$Si$_2$ (M$^+$ − CH$_3$): 127.0399, found 127.0392.

1,1,1-Trimethyl-2-phenyldisilane (**30**): 142 g of trimethyltriphenyldisilane **26** were placed in a 1-l flask and HBr gas was condensed at −196°C until the flask was half filled. The mixture was warmed to −72°C and then stirred for two days at this temperature. After the HBr had been evaporated at room temperature and slightly above (45°C), the resulting crude dibromodisilane (**29**) was dissolved in an equal volume of ether and added to a solution of 8.9 g of LiAlH$_4$ in 200 ml of the same solvent. After aqueous workup and distillative purification 55.6 g (72%) of disilane **30** were obtained as a colourless liquid of boiling point 80°C/17−30 Torr.

1-Bromo-2,2,2-trimethyldisilane (**33**): Disilane **33** was always prepared prior to use in the following reactions. Typically, the double volume of HBr gas was condensed to phenyldisilane **30** at −196°C. After warming up to −72°C, the mixture was stirred for one hour and then excess HBr vaporated slightly above room temperature in an argon stream.

1,1,1-Trimethyl-2-propargyldisilane (**32**): Crude bromodisilane **33** from 5.0 g of phenyldisilane **30** was mixed with 3.9 ml of an solution of propargyl bromide in toluene (80%) and the mixture was added dropwise to 4.0 g of magnesium turnings in 50 ml of THF under temporary ice cooling. After the reaction had ceased, the solution was concentrated by distillation. Pure propargyldisilane **30** was obtained by means of preparative GC as a colourless liquid. − IR (gas): ν = 3332 (≡C−H), 2961 (CH), 2906 (CH), 2122 (Si−H), 1253 [Si(CH$_3$)$_3$], 829 [Si(CH$_3$)$_3$]. − ^{1}H NMR (CDCl$_3$, capillary): δ = 0.77 [s, 9 H, Si(CH$_3$)$_3$], 2.20 (m, 2 H, CH$_2$), 2.32 [t, ^4J(H,H) = 2.9 Hz, 1 H, ≡C-H],4.12 [t, ^3J(H,H) = 3.9 Hz, 2 H, SiH$_2$]. − ^{13}C NMR (CDCl$_3$, capillary): δ = −3.13 (*C*H$_2$-C≡C-H), −0.38 [Si(CH$_3$)$_3$], 68.23 (CH$_2$-C≡*C*-H), 82.77 (CH$_2$-*C*≡C-H). − ^{29}Si NMR (CDCl$_3$): δ = −57.51 (SiH$_2$), −16.58 [Si(CH$_3$)$_3$]. − MS (70 eV); *m/z* (%): 141 (3) [M$^+$ − H], 127 (38) [M$^+$ − CH$_3$], 73 (100) [Si(CH$_3$)$_3$$^+$]. HRMS calcd. for C$_5H_{11}Si_2$ (M$^+$ − CH$_3$) 127.0399, found 127.0418.

1-Allenyl-2,2,2-trimethyldisilane (**34**): 2.00 g of bromoallene were mixed with 30 ml of ether, cooled to −72°C, and 10.5 ml of 1.6 N *n*-butyllithium were added in four portions within a few minutes. After stirring for ten minutes, an equimolar amount of bromodisilane **33** (prepared from 3.00 g phenyldisilane **30**) was added at once (important). The mixture was thawn up and concentrated by distillation. The final purification was carried out with preparative GC and afforded allenyldisilane **34** as a colourless liquid. − IR (neat): ν = 2954 cm^{-1} (CH), 2895 (CH), 2113 (SiH) 1932 (C=C=C), 1247 [Si(CH$_3$)$_3$], 926 (Si-H), 839 [Si(CH$_3$)$_3$]. − ^{1}H NMR (C$_6$D$_6$, capillary): δ = 0.87 [s, 9 H, Si(CH$_3$)$_3$], 4.44 (m, 2 H, SiH$_2$), 4.95 [d×t, ^4J(H,H) = 7.2 Hz, ^5J(H,H) = 1.9 Hz, 2 H, CH$_2$], 5.47 (m, 1 H, CH). − ^{13}C NMR (C$_6$D$_6$, capillary): δ = −0.23 [Si(CH$_3$)$_3$], 67.75 (-CH=C=*C*H$_2$), 71.34 (-*C*H=C=CH$_2$), 216.00 (-CH=*C*=CH$_2$). − ^{29}Si NMR (C$_6$D$_6$, capillary): δ = −65.49 (SiH$_2$), −15.72 [Si(CH$_3$)$_3$]. − MS (70 eV); *m/z* (%): = 142 (12) [M$^+$], 127 (83) [M$^+$ − CH$_3$], 97 (28), 73 (100) [Si(CH$_3$)$_3$$^+$]. − HRMS calcd. for C$_5H_{11}Si_2$ (M$^+$ − CH$_3$) 127.0399, found 127.0370.

1,1,1-Trimethyl-2-propynyldisilane (**35**): In order to prepare the propynyl Grignard reagent, a 1.08 N solution of butylmagnesium chloride in THF was saturated with propyne and stirred overnight. 11 ml of the resulting suspension were then added to a mixture of 12 mmol bromodisilane **33** (prepared from 2.0 g of phenyldisilane **30**) and 10 ml of pentane under ice cooling. Again, the solution was concentrated by distillation and disilane **35** isolated by preparative GC as a colourless liquid. − IR (neat): ν = 2954 cm^{-1} (CH), 2184 (C≡C), 2123 (SiH), 1247 [Si(CH$_3$)$_3$], 840 [Si(CH$_3$)$_3$]. − ^{1}H NMR (CDCl$_3$, capillary): δ = 0.15 [s, 9 H, Si(CH$_3$)$_3$], 1.46 [t, ^5J(H,H) = 1.8 Hz, 3 H, CH$_3$], 4.03 [q, ^5J(H,H) = 1.8 Hz, 2 H, SiH$_2$]. − ^{13}C NMR (CDCl$_3$, capillary): δ = −1.58 [Si(CH$_3$)$_3$], 4.68 (-C≡C-*C*H$_3$), 73.11 (-*C*≡C-CH$_3$), 107.73 (-C≡*C*-CH$_3$). − ^{29}Si NMR (CDCl$_3$, capillary): δ = −86.98 (SiH$_2$), −17.21 [Si(CH$_3$)$_3$]. − MS (70 eV); *m/z* (%): 142 (3) [M$^+$], 127 (21) [M$^+$ − CH$_3$], 97 (18), 73 (100) [Si(CH$_3$)$_3$$^+$]. − HRMS calcd. for C$_6H_{14}Si_2$ (M$^+$) 142.0634, found 142.0624.

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