Hetero π Systems, 25[◇]

Silylenes of the Elemental Composition $C_2H_4Si_2$: Generation and Matrix-Spectroscopic Identification

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Pulsed flash pyrolysis in combination with matrix isolation of three precursor molecules (**10**, **11**, **12**) led to the formation of silylsilacyclopropenylidene (**1**), which was identified by comparison of experimental and calculated (BLYP/6-31G*) IR spectra for both, unlabeled **1** and its perdeuterated isotopomer. Upon irradiation of matrix-isolated silylsilacyclopropenylidene (**1**) a second $C_2H_4Si_2$ isomer, namely (silylethynyl)silylene (**4**) was formed. However, no evidence could be found for the formation of disilatetrahedrane or 1,2- or 1,3-disilacyclobutadiene.

Having discussed C_3X_2 (X = H, Cl, F)[1][2][3][4] and C_2H_2Si[5][6] species in earlier papers, we concentrate in this study on the generation and properties of the silyl-substituted silacyclopropenylidene **1**. Irradiation of this compound was expected to open an entry to other $C_2H_4Si_2$ isomers, including not only open-chain silylenes but also such fascinating species like disilatetrahedrane and disilacyclobutadienes.

Calculations

$C_2H_4Si_2$ species are of considerable interest with respect to the peculiar bonding properties of silicon. In this system silicon can be di- or tetravalent, it can participate in double bonds to silicon or carbon and it can be part of heterocyclobutadienes or heterotetrahedrane.

In 1984 M. S. Gordon et al. calculated structures and energies of thirteen $C_2H_4Si_2$ isomers at the MP3/6-31G*//3-21G level of theory[7]. Unfortunately, the IR spectra of these isomers were not calculated. Since we needed these data for the interpretation of our experimental IR spectra we repeated the calculations on the BLYP/6-31G* level of theory[8]. Scheme 1 shows the structures and energies of eight $C_2H_4Si_2$ isomers, which are minima on the energy hypersurface and whose spectra were of interest to us.

As expected, the global minimum is silylsilacyclopropenylidene **1**. Of nearly the same energy is disilacyclobutenylidene **2**, which could be a suitable photochemical precursor for 1,2-disilacyclobutadiene. Similarly, photolysis of disilylene **3** could result in the formation of 1,3-disilacyclobutadiene **8**. The weak Si−Si bond in silylene **6** makes this compound much less stable than (silylethynyl)silylene **4**.

We were not able to find a minimum for disilatetrahedrane (**9**). This compound represents a second order saddle point lying 64.9 kcal/mol above silacyclopropenylidene **1**. 1,2-Disilacyclobutadiene also deserves a special comment. Whereas nearly planar 1,3-disilacyclobutadiene (**8**) is a real minimum on the $C_2H_4Si_2$ energy hypersurface, there is, in accordance with earlier calculations[7], no minimum for a planar 1,2-disilacyclobutadiene (formula **7**,$\mathbf{C_{2v}}$). Dropping of symmetry restrictions leads to the "real" minimum structure **7**, which corresponds to a 1,2-disilabicyclobutane-2,4-diyl type structure. In addition to diradical **7**, in which the hydrogens at the Si atoms are in a formal *anti* position there exists a second minimum **5**, in which these two hydrogens are *syn* oriented.

Syntheses of Precursors 10, 11, and 12

Our standard method for the generation of silylenes consists in the pyrolytic α-elimination of trimethylsilane from suitable precursors. The primarily formed noncyclic silylenes undergo a thermal rearrangement to the corresponding silacyclopropenylidenes[4][5]. In the present case, three candidates can formally yield open-chain $C_2H_4Si_2$ silylenes upon extrusion of trimethylsilane, namely 5,5-dimethyl-1,4,5-trisilahex-2-yne (**10**), 1,1,1-trimethyl-2-ethynyltrisilane (**11**), and 1,1,1-trimethyl-3-ethynyltrisilane (**12**).

The preparation of precursors **10**, **11**, and **12** turned out to be difficult, but we succeeded in preparing at least sufficient amounts of each for matrix-isolation studies. 5,5-Dimethyl-1,4,5-trisilahex-2-yne (**10**) was synthesized in the following way: A mixture of phenylsilane (**13**) and phenyldisilane **15** was treated with the stoichiometric amount of trifluoromethanesulfonic acid yielding the corresponding triflates **14** and **16**. Reaction of the resulting solution with a freshly prepared suspension of Li_2C_2 led to three products,

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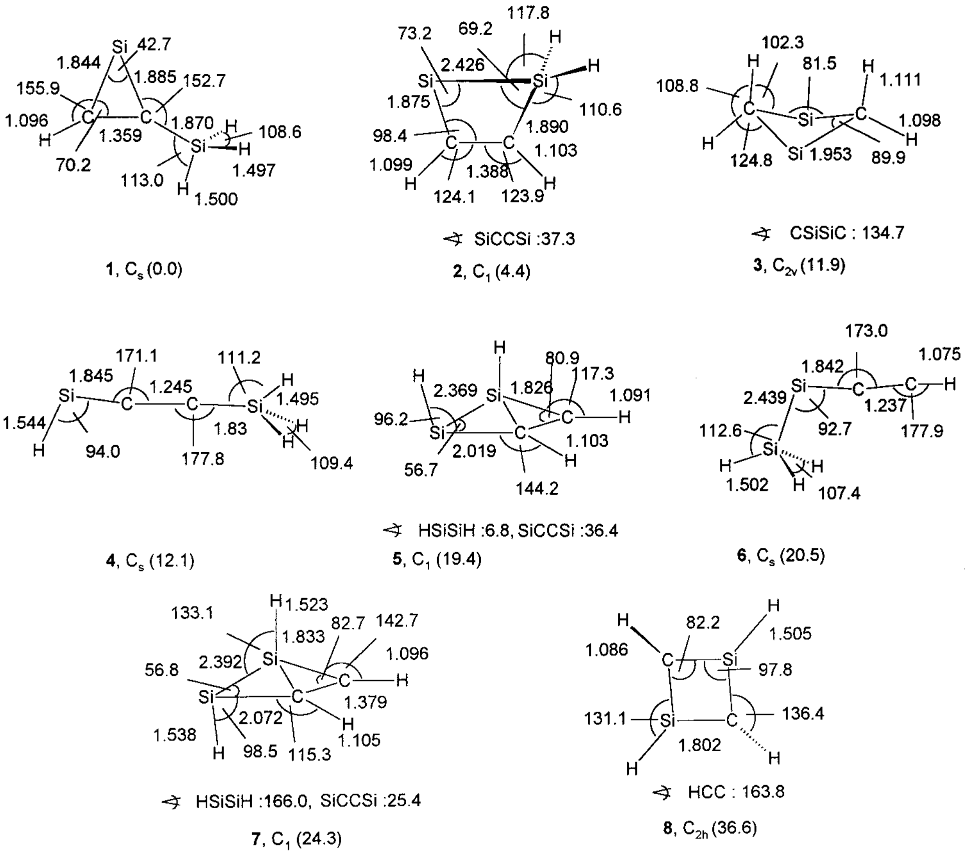
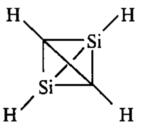
[◇] Part 24: Ref.[6].

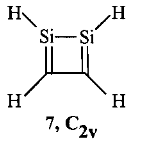
1434−193X/98/0707−1291 $ 17.50+.50/0

Scheme 1. Calculated (BLYP/6-31G*) relative energies (in parentheses; kcal/mol; corrected by zero-point vibrational energies) and geometries of selected $C_2H_4Si_2$ isomers.



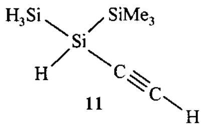


9, C_{2v}



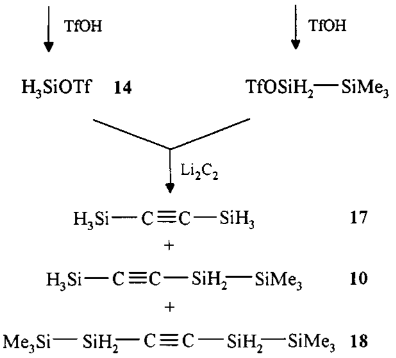
7, C_{2v}

$H_3Si—C≡C—SiH_2—SiMe_3$ **10**



11

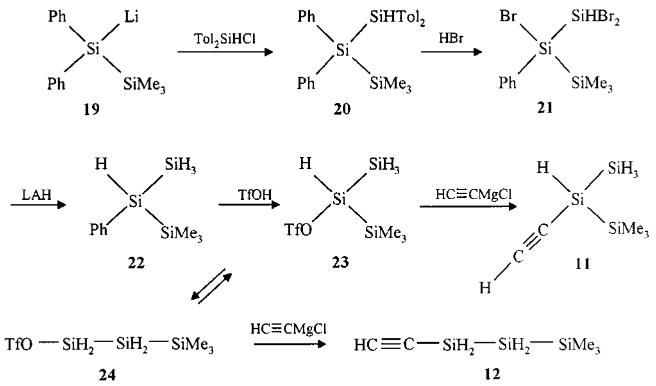
$HC≡C—SiH_2—SiH_2—SiMe_3$ **12**



namely the disilylacetylenes **10**, **17**, and **18**. The desired precursor **10** could be isolated by preparative GC.

1,1,1-Trimethyl-2-ethynyltrisilane (**11**) and 1,1,1-trimethyl-3-ethynyltrisilane (**12**) could be synthesized as follows: Lithiodisilane **19** was generated by reaction of hexamethyl-2,2-diphenyltrisilane and one equivalent of methyllithium in THF and treated with chlorodi(*p*-tolyl)silane. The resulting trisilane **20** is the key intermediate. In the reaction with liquid HBr donor substituted aryl functions at silicon are exchanged much faster by bromine than phenyl substituents[9], whereas electronegative groups bonded directly to silicon retard or even prevent protodesilylation. Therefore, after primary substitution of the *p*-tolyl substituents, only one of the phenyl groups of **20** was split off, resulting in tribromotrisilane **21**. By reduction with $LiAlH_4$ phenyltrisilane **22** was formed and could be isolated by distillation. Its reaction with one equivalent of trifluoromethanesulfonic acid (formation of triflate **23**) followed by addition of ethynylmagnesium chloride was expected to result in the selective formation of precursor **11**.

To our surprise, not only 1,1,1-trimethyl-2-ethynyltrisilane (**11**) was found, but also 1,1,1-trimethyl-3-ethynyltrisilane (**12**). This can be explained only by a positional exchange of hydrogen and the triflate substituent in trisilanyltriflate **23** (perhaps via a dyotropic reaction). The resulting triflate **24** reacted with the Grignard reagent under forma-



tion of precursor **12**. Longer standing of triflate **23** before addition of ethynylmagnesium chloride resulted in a higher **11**/**12** ratio. Nevertheless, the maximum ratio we could observe was 3:2, which probably reflects the relative stabilities of triflates **23** and **24**. Fortunately, both compounds **11** and **12** could – despite of their very similar retention times – be separated by preparative GC.

Pulsed Flash Pyrolyses of Precursors 10, 11, and 12

When gaseous mixtures of one of the precursors **10**, **11**, or **12** and argon (1:1000) were subjected to *pulsed* flash pyrolysis followed by the direct condensation of the reaction products onto a spectroscopic window at 10 K, large amounts of trimethylsilane were formed. In all cases the parent silacyclopropenylidene (**1**, SiH_3 replaced by H[6]) was found in moderate yields. Apart from this compound, another species was present in the argon matrix in all three pyrolyses. This compound showed broad bands around 2190 and a very intense absorption at 919 cm^{-1}, which are typical for a SiH_3 group. Together with one ν_{CH} at 3017 and one ν_{CC} at 1499 cm^{-1}, the spectral data fit quite well for silylsilacyclopropenylidene **1**, the global minimum of the $C_2H_4Si_2$ energy hypersurface. A detailed comparison of the observed and calculated IR spectrum for compound **1** confirms this assignment (Table 1).

Table 1. IR spectral data (BLYP/6-31G*) of silylsilacyclopropenylidene (**1**) and its perdeuterated isotopomer: Experimental (Ar matrix, 10 K) and corresponding calculated and corrected wavenumbers (cm^{-1}). Intensities (relative to the strongest band) in parentheses

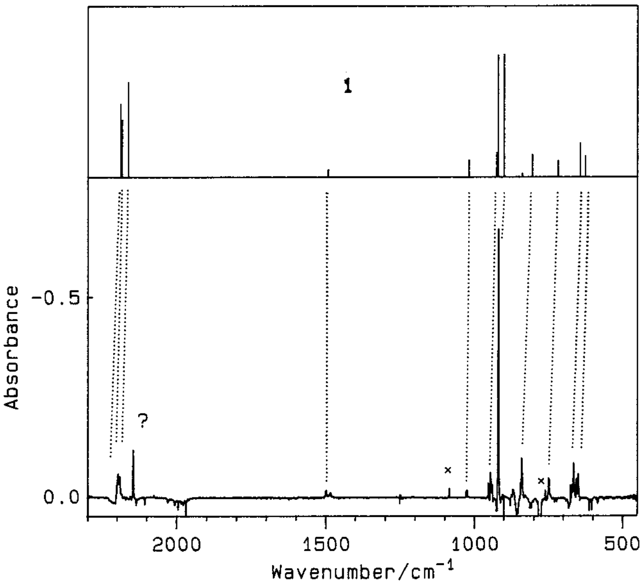
mode		$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{corr.}$[a]	$\tilde{\nu}_{obs.}$[d]
CH str		3074.6 (9)	3017.2	3017.2 (4)
SiH str		2189.8 (60)	2190	ca. 2190[e,f]
	D_4	1582.4 (51)	1582	ca. 1600[e,f]
SiH str		2185.2 (46)	2190	ca. 2190[e,f]
	D_4	1575.2 (50)	1570	ca. 1600[e,f]
SiH str		2164.3 (77)	2190.8	ca. 2190
	D_4	1544.5 (58)	1531.5	ca. 1600
CC str		1495.0 (6)	1498.9	1498.9 (11)/1484.0
	D_4	1469.7 (7)	1473.5	1472.5 (3)
CH def		1020.5 (14)	1029.3	1029.3/1026.6
	D_4	877.9(8)	885.5	911.2(6)
SiH def		927.4 (19)	953.1	953.1 (18)
	D_4	664.1 (17)	682.5	677.9 (3)
SiH def		922.4 (99)	921.8	921.8[f]
	D_4	655.7 (28)	655.3	695.4
SiH def		903.0 (100) [b]	919.3	919.3 (100)
	D_4	681.9 (100) [c]	694.2	694.4 (100)
SiC str.		807.2 (18)	840.8	840.8 (23)
	D_4	778.8	811.2	803.2 (55)
SiC str.		720.0 (13)	749.7	749.7 (15)
	D_4	636.0 (20)	662.0	652.0 (12)
SiC def		645.3 (28)	665.7	665.7 (11)
	D_4	509.2 (23)	525.3	522.0 (11)
SiH + CH def		627.9 (17)	650.6	650.6 (16)/655.5
	D_4	491.5	509.3	508.3/505.8

[a] $\tilde{\nu}_{corr.} = \tilde{\nu}_{obs.} (C_2H_4Si_2) / \tilde{\nu}_{calc.} (C_2H_4Si_2) \times \tilde{\nu}_{calc.}(C_2D_4Si_2)$. – [b] Abs. int. 214.6 km/mol. – [c] Abs. int. 149.4 km/mol. – [d] Split by matrix effects. – [e] Broad band. – [f] Overlap with bands of **4**.

Photochemistry of the $C_4H_2Si_2$ Silylenes

Upon irradiation of the matrix-isolated pyrolysis products with light of wavelength 313 or 366 nm the IR absorptions of **1** vanished within a few minutes and two sets of new bands belonging to the isomeric silylenes **4** and **6** appeard. A difference spectrum of this reaction is shown in Figure 1. Since the bands which are typical for the SiH_3 groups in each of the compounds **1**, **4**, and **6** are strongly overlapping they are cancelling each other in the difference-spectrum, leading to incorrect relative intensities around 2190 and 920 cm^{-1}. Nevertheless the pattern of the remaining bands is sufficient for a satisfactory assignment to **4** and **6** by comparing the observed absorptions with the calculated values (Figure 1, Tables 2, 3).

Figure 1. Comparison of the experimental (Ar matrix, 10 K) and theoretical (BLYP/6-31G*) infrared spectrum of silylsilacyclopropenylidene (**1**). Centre: Difference spectrum of the photoreaction **1** → **4** (×: silacyclopropenylidene). Bars at top: Calculated IR spectrum of **1**. For problems in the determination of bands intensities in the regions around 2190 and 920 cm^{-1} see text.



On prolonging the 313 nm irradiation for several hours the bands of **4** and **6** vanished completely. The higher rate of disappearance of **4** allows it to distinguish between the bands of the two silylenes. A growth of new discrete absorptions originating from any reaction product could not be registered during the long-time irradiation. On the other hand stopping the 313 nm excitation after some minutes

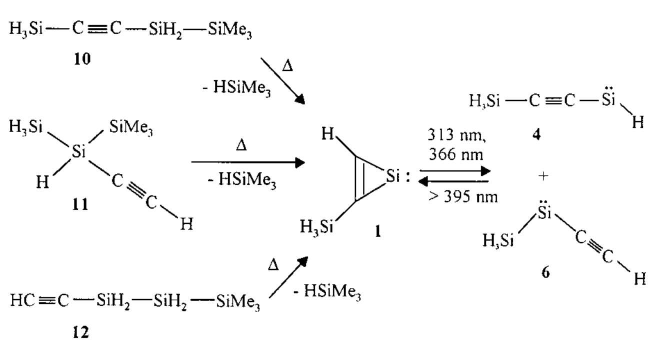


Table 2. IR spectral data (BLYP/6-31G*) of (silylethynyl)silylene (**4**) and its perdeuterated isotopomer: Experimental (Ar matrix, 10 K) and corresponding calculated and corrected wavenumbers (cm^{-1}). Intensities (relative to the strongest band; vs = very strong, s = strong, m = middle, w = weak, vw = very weak) in parentheses

mode		$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{corr.}$[a]	$\tilde{\nu}_{obs.}$
SiH str		2201.6 (32)	2212.0	ca. 2200 (w)[d,e]
	D_4	1591.1 (21)	1594.4	ca. 1600 (w)[d,e]
SiH str		2200.0 (35)	2208.6	ca. 2200 (w)[d,e]
	D_4	1590.3 (23)	1594.5	ca. 1600 (w)[d,e]
SiH str		2194.1 (32)	2206.0	ca. 2200 (w)[d,e]
	D_4	1560.6 (23)	1569.1	ca. 1600 (w)[d,e]
SiH str		1951.7 (81)	2006.6	2030.2/2006.6 (vw)
	D_4	1404.3 (47)	1443.8	1477.0/1458.7 (vw)
SiH def		926.8 (12)	938.3	938.3 (vw)[e]
SiH def		927.0 (100)[b]	922.5.	922.5 (vs)[e]
	D_4	681.2 (42)	677.8	686.1 (s)
SiH def		799.2 (19)	808.0	808.0 (vw)
	D_4	614.8 (25)	621.6	622.0 (vw)
SiC str		774.2 (81)	780.0	784.0/780.0 (s)
	D_4	775.4 (100) [c]	781.2	782.8 (vs)
SiH + SiC def		666.4 (13)	680.2	680.2 (vw)
	D_4	534.1 (8)	545.2	531.0 (vw)

[a] $\tilde{\nu}_{corr.} = \tilde{\nu}_{obs.} (C_2H_4Si_2) / \tilde{\nu}_{calc.} (C_2H_4Si_2) \times \tilde{\nu}_{calc.} (C_2D_4Si_2)$. – [b] Abs. int. 355.7 km/mol. – [c] Abs. int. 323.4 km/mol. – [d] Very broad band. – [e] Overlap with bands of **1**.

Table 3. IR spectral data (BLYP/6-31G*) of ethynylsilylsilylene (**6**): Experimental (Ar matrix, 10 K) and corresponding calculated wavenumbers (cm^{-1}). Intensities (relative to the strongest band) in parentheses

mode	$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{obs.}$
CH str	3386.4 (18)	3294.1/3291.1 (17)
SiH_3 str	2164.7 (68)/2152.6 (53)/2135.9 (32)	2168[b,c]
SiH_3 def	839.6 (100)[a]	856.0/854.5 (100)
HCC def	708.9 (9)	690.1 (19)
SiC str	606.0(15)	586.0 (32)

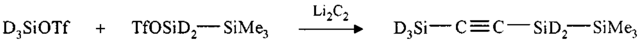
[a] Abs. int. 234.3 km/mol. – [b] Very broad band. – [c] Overlap with bands of **1** and **4**.

and continuing the irradiation with visible light (λ > 395 nm) led to a partial reformation of the silacyclopropenylidene **1**.

One rather prominent band in the IR spectrum of the pyrolysis product of the precursor molecules **10** and **11** at 2146 cm^{-1} (band with a question mark in Figure 1) had to be left unassigned. At a first glance this absorption (most likely a Si–H stretching vibration) seemed to belong to **1**, since it showed the same changes in intensity on irradiation as the other bands of **1**. But since the band was not observable when **1** was formed by pyrolysis of precursor **12**, it must originate from a different species.

Generation of $C_2D_4Si_2$ Isomers

Further support for the assignments discussed above should be possible by complete substitution of the hydrogen by deuterium atoms and observing the resulting isotopic shifts in silylenes **1**, **4**, and **6**. As the easiest accessible precursor for $C_2D_4Si_2$ isomers compound **27** was selected. Its synthesis was achieved as in case of the unlabeled 5,5-dimethyl-1,4,5-trisilahex-2-yne (**10**). Reaction of the deuterosilyltriflates **25** and **26**, which are easily accessible, with Li_2C_2 resulted in the formation of compound **27**.



$$\underset{\textbf{25}}{D_3SiOTf} + \underset{\textbf{26}}{TfOSiD_2—SiMe_3} \xrightarrow{Li_2C_2} \underset{\textbf{27}}{D_3Si—C≡C—SiD_2—SiMe_3}$$

Pulsed flash pyrolysis of precursor **27** yielded [D_4]silylsilacyclopropenylidene ([D_4]**1**), which was interconvertible with [D_4]**4** and [D_4]**6** photochemically. All observed isotopic shifts confirm our assignments (Tables 1, 2, and 3). The above-mentioned absorption at 2146 cm^{-1} is shifted to 1573 cm^{-1}, in accordance with the expectation for a Si–H stretching vibration.

Conclusion

We were able to generate and matrix-isolate three isomeric silylenes of composition $C_2H_4Si_2$, namely silylsilacyclopropenylidene (**1**), (silylethynyl)silylene (**4**), and ethynylsilylsilylene (**6**) by pulsed flash pyrolysis of three different precursors and subsequent matrix photolysis of the thermolysis products. The IR spectra of the parent compounds as well as those of the respective $C_2D_4Si_2$ isotopomers correspond satisfactorily well with the calculated vibrational spectra.

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Experimental Section

Equipment Used for Matrix Isolation, Photolyses, and Pyrolyses: See Ref.[6], preceding paper.

Pulsed Flash Pyrolyses: For a description see Ref.[4][5][6]. The thermolysis products were deposited together with a large excess of Ar on a CsI window cooled to 12 K.

General: See Ref.[6], preceding paper. – Trichlorosilane, dichlorodiphenylsilane, and phenyltrichlorosilane were purchased from Fluka. 1,1,1-Trimethyl-2-phenyldisilane (**15**) and [D_2]1,1,1-trimethyl-2-phenyldisilane were prepared according to literature procedures[5][10]. Li_2C_2 was generated by reaction of trichloroethylene and *n*-butyllithium as described by W. Uhlig[11]. Phenylsilane (**13**) and trideuterophenylsilane were prepared by reduction of phenyltrichlorosilane using $LiAlH_4$ resp. $LiAlD_4$ in diethylether. The synthesis of 1-lithio-2,2,2-trimethyl-1,1-diphenyldisilane (**19**) has been described[6] in the preceding paper. Chlorodi(*p*-tolyl)silane was synthesized by the reaction of two equivalents of *p*-tolylmagnesium bromide and trichlorosilane. Trifluoromethanesulfonic acid was freshly distilled prior to use.

5,5-Dimethyl-1,4,5-trisilahex-2-yne (**10**) *and Bis(2,2,2-trimethyldisilanyl)acetylene* (**18**): To a solution of 1.6 g of phenylsilane (**13**) (15 mmol) and 1.8 g of 1,1,1-trimethyl-2-phenyldisilane (**15**) (10 mmol) in 30 ml of pentane 3.8 g of trifluoromethanesulfonic acid (25 mmol) were added dropwise at 0°C. Five minutes after the completion of the addition the resulting solution was added to a suspension of 10 mmol of Li_2C_2 in ether/THF at −72°C under vigorous stirring. The cooling bath was removed. After stirring for one hour at room temperature all volatile materials including the products were removed in vacuo. The solvents were distilled off using a 10-cm Vigreux column. The residue was separated by preparative GC yielding some 10 µl of 5,5-dimethyl-1,4,5-trisilahex-2-yne (**10**) and bis(2,2,2-trimethyldisilanyl)acetylene (**18**).

5,5-Dimethyl-1,4,5-trisilahex-2-yne (**10**): IR (neat): $\tilde{\nu}$ = 2964 cm^{-1} (CH), 2188 (SiH), 2143 (SiH), 1255 ($SiMe_3$). − ^{1}H NMR (C_6D_6, capillary): δ = 1.03 (s, 9 H, $SiMe_3$), 4.49 (s, 2 H, SiH_2), 4.63 (s, 3 H, SiH_3). − ^{13}C NMR (C_6D_6, capillary): δ = −0.56 ($SiMe_3$), 110.68, 106.32 (C≡C). − ^{29}Si NMR (C_6D_6, capillary): δ = −87.64, −85.67 (SiH), −15.74 ($SiMe_3$). − MS (70 eV); *m/z* (%): 157 (17) [M^+ − H], 143 (87), 127 (24), 113 (58), 102 (19), 81 (40), 73 (100). − HRMS calcd. for $C_5H_{14}Si_3$ (M^+-CH_3) 143.0182, found 143.0169.

Bis(2,2,2-trimethyldisilanyl)acetylene (**18**): IR (neat): $\tilde{\nu}$ = 2958 cm^{-1} (CH), 2129 (SiH), 2098 (SiH), 1248 ($SiMe_3$). − UV (cyclohexane): λ_{max} (lg ε) = 224 nm (3.61), 233 nm (3.48). − ^{1}H NMR (C_6D_6, capillary): δ = 0.83 (s, 18 H, $SiMe_3$), 4.33 (s, 4 H, SiH_2). − ^{13}C NMR (C_6D_6, capillary): δ = −0.63 ($SiMe_3$), 109.31 (C≡C). − ^{29}Si NMR (C_6D_6, capillary): δ = −86.48 (SiH_2), −16.15 ($SiMe_3$). − MS (70 eV); *m/z* (%): 230 (2) [M^+], 215 (45), 185 (18), 171 (22), 156 (33), 141 (21), 73 (100). − HRMS calcd. for $C_8H_{21}Si_4$ (M^+ − H) 229.0720, found 229.0668.

1,1,1-Trimethyl-2,2-diphenyl-3,3-di(p-tolyl)trisilane (**20**): This compound was synthesized by dropwise addition of a solution of 1-lithio-2,2,2-trimethyl-1,1-diphenyldisilane (**19**) in THF to a solution of the stoichiometric amount of chlorodi(*p*-tolyl)silane in THF at 0°C. After aqueous workup, drying and removing of volatiles in vacuo, the resulting crude **20** was not further purified in order to avoid loss of the valuable product.

2,3,3-Tribromo-1,1,1-trimethyl-2-phenyltrisilane (**21**): To 100 g of crude trisilane **20**, 50 ml of HBr were condensed at −196°C. After stirring for five hours at −72°C, the excess of HBr and the reaction product benzene were removed. Exceeding the reaction time results in total dephenylation of **20**. The crude tribromotrisilane **21** was also used without further purification for the next step.

1,1,1-Trimethyl-2-phenyltrisilane (**22**): 90 g of crude tribromotrisilane **21** were dissolved in an equal volume of diethyl ether and added dropwise to a suspension of 5.76 g of $LiAlH_4$ (152 mmol) in 200 ml of diethyl ether at 0°C. After completion of the addition the reaction mixture was stirred for 10 minutes and then worked up aqueously. The yield of 1,1,1-trimethyl-2-phenyltrisilane (**22**) was 22 g.

1,1,1-Trimethyl-2-ethynyltrisilane (**11**) *and 1,1,1-Trimethyl-3-ethynyltrisilane* (**12**): 1,1,1-Trimethyl-2-(trifluoromethanesulfonyl)-trisilane (**23**) was generated by reaction of 1,1,1-trimethyl-2-phenyltrisilane (**22**) with one equivalent of trifluoromethanesulfonic acid in pentane according to the general procedure described by Uhlig[12]. To a solution of 10.7 mmol of 1,1,1-trimethyl-2-(trifluoromethanesulfonyl)trisilane (**23**) were added dropwise 10.7 mmol of ethynylmagnesium chloride in THF at 0°C. After completion of the addition, all volatiles including the products were removed in vacuo. The solvents were distilled off leaving behind a solution of precursors **11** and **12** which could be separated by preparative GC.

1,1,1-Trimethyl-2-ethynyltrisilane (**11**): IR (neat): $\tilde{\nu}$ = 3293 cm^{-1} (CH), 2955 (CH), 2143 (SiH), 2029 (C≡C). − ^{1}H NMR (C_6D_6, capillary): δ = 0.70 (s, 9 H, $SiMe_3$), 2.83 (d, 1 H, ≡CH, J = 1.61 Hz), 3.74 (d, 3 H, SiH_3, J = 3.38 Hz), 4.16 (m, 1 H, SiH). − ^{13}C NMR (C_6D_6, capillary): δ = 0.10 ($SiMe_3$), 81.15 (≡CSi), 99.49 (≡CH). − ^{29}Si NMR (C_6D_6, capillary): δ = −97.33 (SiH_3), −94.33 (SiH), −13.08 ($SiMe_3$). − MS (70 eV); *m/z* (%): 158 (7) [M^+], 143 (51), 127 (5), 113 (9), 111 (11), 81 (23), 73 (100). − HRMS calcd. for $C_5H_{14}Si_3$ (M^+) 158.0403, found 158.0348.

1,1,1-Trimethyl-3-ethynyltrisilane (**12**): IR (neat): $\tilde{\nu}$ = 3293 cm^{-1} (CH), 2956 (CH), 2145 (SiH), 1248 ($SiMe_3$). − ^{1}H NMR (C_6D_6, capillary): δ = 0.73 (s, 9 H, $SiMe_3$), 3.44 (t, 2 H, $^{2}SiH_2$, J = 1.59 Hz), 2.83 (t, 1 H, ≡CH, J = 1.59 Hz), 4.41 (m, 2 H, $^{1}SiH_2$). − ^{13}C NMR (C_6D_6, capillary): δ = 1.19 ($SiMe_3$), 81.02 (≡CSi), 99.32 (≡CH). − ^{29}Si NMR (C_6D_6, capillary): δ = −106.23 ($^{1}SiH_2$), −88.08 ($^{2}SiH_2$), −12.51 ($SiMe_3$). − MS (70 eV); *m/z* (%): 158 (4) [M^+], 143 (23), 127 (5), 113 (6), 102 (7), 73 (100). − HRMS calcd. for $C_5H_{14}Si_3$ (M^+) 158.0403, found 158.0348.

[D_5]5,5-Dimethyl-1,4,5-trisilahex-2-yne (**27**): This compound was synthesized and isolated in the same manner as the corresponding unlabeled compound **10** starting from trideuterophenylsilane and 1,1-dideutero-2,2,2-trimethyl-1-phenyldisilane (see above): IR (neat): ν = 2969 cm^{-1} (CD), 1587 (SiD), 1532 (SiD), 1252 ($SiMe_3$). − ^{1}H NMR (C_6D_6, capillary): δ = 0.92 (s, $SiMe_3$). − ^{13}C NMR (C_6D_6, capillary): δ = −0.60 ($SiMe_3$), 106.27, 110.59 (C≡C). − HRMS calcd. for $C_5H_9D_5Si_3$ (M^+ − CH_3) 163.0717, found 163.0694.

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