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Silacyclopropyne: Matrix Spectroscopic Identification and ab Initio Investigations[†]

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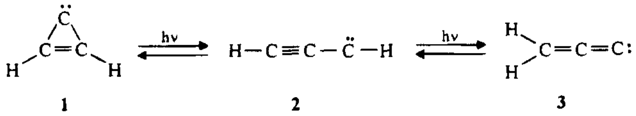
Abstract: Matrix-isolated 1-silacyclopropenylidene (**7**) has been generated by pulsed flash pyrolysis of 2-ethynyl-1,1,1-trimethyldisilane (**4**). By subsequent photolysis **7** can be isomerized into ethynylsilanediyl (**5**), vinylidenesilanediyl (**8**), and silacyclopropyne (**9**). The identification of the C_2H_2Si isomers and their ^{13}C and D isotopomers is based on the comparison of their experimental and calculated (MP2/6-31G**) infrared spectra. In case of **9**, the first example of a "formal" cyclopropyne, the definitive assignment of the structure was only possible by studying ^{13}C isotopomers. Detailed ab initio calculations have been carried out in order to understand the unique bonding situation in **9**. It is found that the Lewis structure **9B**, where the dashed line indicates an electron pair which occupies a CĊ nonbonding orbital, is the best possible compromise to describe the electronic structure of **9** correctly. The value of 6.2 kcal mol^{-1} for the barrier of **9** to the planar transition structure **13** represents the lowest inversion barrier of tetra-coordinated silicon described so far.

I. Introduction

The first detection of cyclopropenylidene (**1**) was achieved by us in 1984.[1a] Shortly afterward we were able to show that upon irradiation **1** is photoisomerized into propynylidene (propargylene, **2**) and in a second photostep into a new C_3H_2 isomer, namely propadienylidene (vinylidenecarbene, **3**).[1b] The matrix spectroscopic identification and photochemical interconversion of the three carbenes (**1**−**3**) are of interest in many ways. Very subtle structural problems have to be solved. This is especially true for propargylene (**2**).[1c,d] The structural assignments for these species are based on the comparison of the experimentally observed and calculated IR spectra and, therefore, emphasize the importance of simultaneously applying quantum chemical calculations and spectroscopic measurements. Additional examples for this interplay between theory and experiment are our studies on chlorinated[2] and fluorinated[3] derivates of **1**−**3**. It should also be mentioned that **1**[4] and **3**[5] play a decisive role in the chemistry of interstellar clouds. Eventually this might also be the case for the corresponding silicon-containing derivatives.[6] Moreover, only a few examples exist for carbene−carbene rearrangements of type $\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{3}$, and practically nothing is known about similar reactions on the C_2H_2Si hypersurface.



Having discussed the C_3X_2 (X = H, Cl, F) species in earlier papers,[1−3] we now concentrate on the series C_2H_2Si.[7] The most attractive member with this composition is silacyclopropyne (**9**), whose identification will be described together with the theoretical elucidation of the peculiar bonding properties of this "exotic" molecule, which is formally the most strained cycloalkyne ever prepared.[8]

According to calculations by Schaefer et al.,[9] 1-silacyclopropenylidene (**7**) should be the C_2H_2Si species of highest stability. In accordance with this prediction, **7** has been described as the adduct of a silicon atom with acetylene.[10] Schwarz et al.[11] have shown that, if one ionizes chlorotrimethylsilane in the gas phase, neutralization−reionization mass spectrometry allows detection of a particle whose connectivities are indicative of structure **7**.[12]

[†] Hetero π Systems, Part 22. For Part 21 see ref 21.

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

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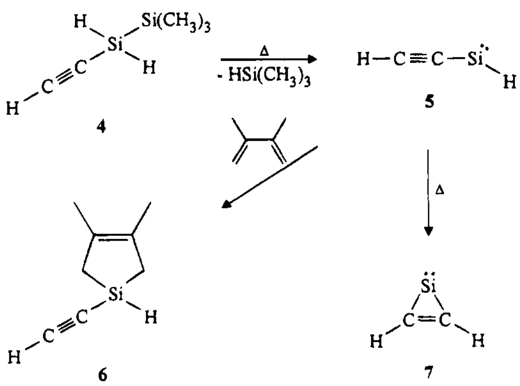


Much better access to the C_2H_2Si potential energy surface is offered by pyrolysis of 2-ethynyl-1,1,1-trimethyldisilane (**4**).[7] Using this procedure 1-silacyclopropenylidene (**7**) can be isolated in an argon matrix at 10 K. Irradiation of matrix-trapped **7** results in a series of photochemical rearrangements leading to ethynylsilanediyl (ethynylsilylene, **5**), vinylidene-silanediyl (vinylidenesilylene, **8**), and a third isomer, to which we tentatively assigned the silacyclopropyne structure **9**.[7] Some unanswered questions remained. First, calculations on the RHF/DZ level[9] indicate that this constitution represents a transition structure. Only if one takes electron correlation energy into account[7] is **9** a minimum. Second, the experimentally measured and calculated spectra for **9** are in less satisfactory agreement than those for **5**, **7**, and **8**. Third, if one compares this with the carbocyclic systems[8] it is hard to believe that, due to the expected extremely high strain energy of a cyclopropyne type molecule, **9** can exist at all.

Therefore we needed a final structural proof for **9**. By studying a ^{13}C isotopomer, as was done with the cyclic C_2Si molecule **10**,[13] it is possible to elucidate the structure of **9** unequivocally. To the best of our knowledge, **9** represents the first example of a "formal" cyclopropyne.

II. Preparation of Precursor Molecules

In our first version,[7] unlabeled 2-ethynyl-1,1,1-trimethyldisilane (**4**) was prepared by reaction of 1,1,1-trimethyl-2-phenyldisilane[14] with trifluoromethanesulfonic acid[15] to give the corresponding triflate, which was then treated with mesityllithium to form 2-mesityl-1,1,1-trimethyldisilane. Reaction again with trifluoromethanesulfonic acid and treatment with sodium acetylide finally yielded precursor molecule **4**.

An improved version for the preparation of **4** consists of the direct reaction of the triflate formed from the trimethylphenyldisilane with ethynylmagnesium chloride.

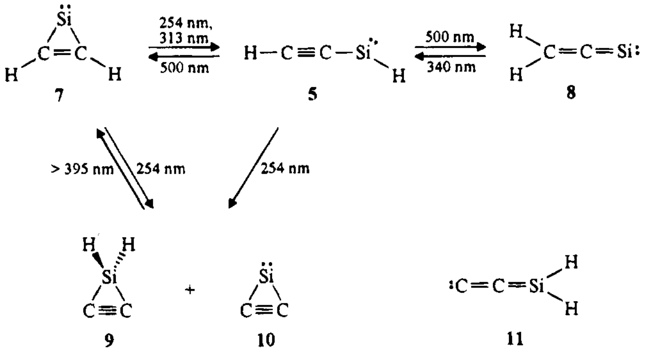
^{13}C-labeled disilane **4** has been prepared in the following manner. Amorphous carbon (70% ^{13}C) is treated with calcium cyanamide.[16] Hydrolysis of the partially ^{13}C-labeled calcium carbide delivers labeled acetylene which is transformed with *n*-butylmagnesium chloride into the acetylenic Grignard reagent. Thus a mixture of ^{13}C isotopomers of **4** can be isolated (e.g. **4**, $[1'\text{-}^{13}C]$-**4**, $[2'\text{-}^{13}C]$-**4**, and $[1',2'\text{-}^{13}C_2]$-**4** in the ratio 2.3:1:1:0.4).

The deuteriated isotopomers of **4**, which can be used as precursors for $[D_1]$-**9** and $[D_2]$-**9**, are easily accessible. 2-(Deuterioethynyl)-1,1,1-trimethyldisilane ($[D_1]$-**4**) has been prepared by reaction of calcium carbide with D_2O, metalation of the dideuteriated acetylene, and treatment of the Grignard reagent with the triflate described above. In an analogous manner, 2,2-dideuterio-2-(deuterioethynyl)-1,1,1-trimethyldisilane ($[D_3]$-**4**) can be synthesized from 2,2-dideuterio-1,1,1-trimethyl-2-phenyldisilane via the triflate and reaction with (deuterioethynyl)magnesium chloride.

III. Matrix Isolation and Spectroscopic Identification

When gaseous mixtures of disilane **4** and argon (1:1000–2000) were subjected to *high-vacuum* flash pyrolysis followed by the direct condensation of the reaction products onto a spectroscopic window at 10 K, only trimethylsilane and small amounts of acetylene were detected. Any C_2H_2Si isomer that might have been formed was too unstable to be observed under these routine pyrolysis conditions.

The breakthrough was found in the *pulsed* flash pyrolysis[17] of the gaseous mixture.[7] Under these conditions, the IR spectrum of the products condensed at 10 K shows, apart from the bands of trimethylsilane, the bands of 1-silacyclopropenylidene (**7**), even though the structure of reactant **4** suggests formation of ethynylsilanediyl (**5**) in the first step. This is in fact the case as can be shown by carrying out a pyrolysis in a flow system with 2,3-dimethylbutadiene as a trapping reagent. Under these conditions, adduct **6** can be isolated in a reasonable yield. Any other trapping product, especially that of **7**, cannot be detected.



1-Silacyclopropenylidene (**7**) can be identified by comparison of the experimental with the calculated (at the MP2/6-31G** level) spectrum. In accordance with the calculation, its IR spectrum shows two bands for the CH stretching vibrations (3048.7 and 3026.5 cm^{-1}) and five additional absorptions between 1100 and 600 cm^{-1}, which, by calculation, can be attributed to the HCSi bending and SiC stretching vibrations. A band for the CC stretching vibration is not observed; theory predicts a corresponding band at 1515.8 cm^{-1} with a relative intensity of 0.1%, which is apparently too weak to be detected.

The pulsed flash pyrolysis of ^{13}C-labeled **4** supports this assignment. Only one singly ^{13}C-labeled isotopomer of **7** can be observed, additional proof for the cyclic structure of this C_2H_2Si isomer (Table 1). In addition all bands show the expected isotopic shifts. This is not only true for the ^{13}C-labeled but also for the D-labeled isotopomers. In $[D_1]$-**7** even a weak CC stretching vibration at 1414.0 cm^{-1} can be detected. In the UV region **7** shows a weak, broad absorption between 320 and 260 nm ($\lambda_{max} = 286$ nm). Due to this band, 1-silacyclopro-

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Table 1. IR Spectral Data of 1-Silacyclopropenylidene (**7**): Experimental (Ar Matrix, 10 K) and Corresponding Calculated and Corrected Wavenumbers (cm^{-1}) of the Observed Vibrations, Intensities (Relative to the Strongest Band) in Parentheses

7		mode		MP2/6-31G**	corr[a]	experiment
ν_1	a_1	CH str		3295.0 (8)	3048.7	3048.7 (10)
			$^{13}C_1$	3289.8	3043.9	3044.1
			$^{13}C_2$	3281.9	3036.6	3035.8
			D_1	3283.7 (13)	3038.0	3035.8 (19)
			D_2	2470.3 (3)	2285.5	2313.6 (3)
ν_7	b_2	CH str		3271.8 (8)	3026.5	3026.5 (9)
			$^{13}C_1$	3265.4	3020.6	3020.6
			$^{13}C_2$	3261.8	3017.2	3016.6
			D_1	2439.8 (3)	2257.3	2285.7 (2)
			D_2	2408.6 (6)	2227.9	2248.7 (5)
ν_2	a_1	CC str		1515.8 (0.1)		
			$^{13}C_1$	1488.4		
			$^{13}C_2$	1460.3		
			D_1	1485.8 (0.3)		1414.0 (3)
			D_2	1456.5 (0.1)		
ν_8	b_2	CH def		1143.9 (76)	1085.8	1085.8 (87)
			$^{13}C_1$	1134.5	1076.9	1077.1
			$^{13}C_2$	1124.8	1067.7	1067.9
			D_1	1092.5 (82)	1037.0	1036.7 (74)
			D_2	981.4 (33)	931.6	938.6 (20)
ν_3	a_1	CH def		932.8 (5)	875.3	875.3 (26)
			$^{13}C_1$	931.3	873.9	873.9
			$^{13}C_2$	930.1	872.8	872.7
			D_1	765.6 (45)[b]	728.9	736.8 (35)
			D_2	651.6 (3)	611.2	
ν_4	a_1	SiC str		788.5 (49)	761.9	761.9 (56)
			$^{13}C_1$	781.7	755.3	755.5
			$^{13}C_2$	774.6	748.5	748.8
			D_1	817.9 (53)[b]	778.6	781.6 (91)
			D_2	798.6 (86)[c]	760.3	769.1 (100)
ν_6	b_1	CH def		681.1 (100)[d]	677.2	677.2 (100)
			$^{13}C_1$	679.1	675.2	675.3
			$^{13}C_2$	677.2	673.2	673.5
			D_1	574.6 (100)[e]	571.5	572.7 (100)
			D_2	518.5 (89)	515.6	518.4 (81)
ν_9	b_2	SiC str		683.4 (68)	672.1	672.1 (90)
			$^{13}C_1$	675.5	664.3	664.5
			$^{13}C_2$	668.2	657.2	657.6
			D_1	611.1 (84)[b]	581.8	595.2 (56)
			D_2	593.7 (100)[f]	583.4	583.9 (87)

[a] $\tilde{\nu}_{corr} = \tilde{\nu}_{exp}(^{12}C_2)/\tilde{\nu}_{calc}(^{12}C_2)\cdot\tilde{\nu}_{calc}$. [b] Better described as DCCH def + SiC str. [c] Better described as SiC str + DCCH def. [d] Abs int 60 km/mol. [e] Abs int 38 km/mol. [f] Abs int 36 km/mol.

Table 2. IR Spectral Data of Ethynylsilanediyl (**5**): Experimental (Ar Matrix, 10 K) and Corresponding Calculated and Corrected Wavenumbers (cm^{-1}) of the Observed Vibrations, Intensities (Relative to the Strongest Band) in Parentheses

5		mode		MP2/6-31G**	corr[a]	experiment
ν_1	a′	CH str		3518.2 (14)	3304.2	3304.2 (31)
			1′-$^{13}C_1$[b]	3517.3	3303.4	3304.2
			2′-$^{13}C_1$	3501.9	3288.9	3288.9
			$^{13}C_2$	3501.1	3288.1	3288.9
			C-D_1	2696.8 (4)	2532.3	2569.6 (4)
			Si-D_1	3518.2 (26)	3304.2	3304.2 (52)
			D_2	2696.8 (8)	2532.3	2570.1 (5)
ν_2	a′	SiH str		2156.5 (100)[c]	1969.9	1969.9 (100)
			1′-$^{13}C_1$	2156.4	1969.8	1969.9
			2′-$^{13}C_1$	2156.4	1969.8	1969.9
			$^{13}C_2$	2156.4	1969.8	1969.9
			C-D_1	2156.4 (100)[d]	1969.8	1970.2 (100)
			Si-D_1	1551.4 (100)[e]	1471.2	1435.2 (100)
			D_2	1551.4 (100)[f]	1416.4	1435.3 (100)
ν_3	a′	CC str		2049.4 (26)	1995.7	1995.7 (27)
			1′-$^{13}C_1$	2004.1	1951.6	1951.9
			2′-$^{13}C_1$	2021.4	1968.4	1965.5
			$^{13}C_2$	1975.1	1923.3	1923.9
			C-D_1	1935.6 (29)	1884.9	1879.6 (38)
			Si-D_1	2049.5 (45)	1995.8	1995.4 (44)
			D_2	1935.7 (54)	1885.4	1879.7 (56)
ν_4	a′	SiH def		864.3 (44)	814.8	814.8 (49)
			1′-$^{13}C_1$	861.9	812.5	812.5
			2′-$^{13}C_1$	864.3	814.8	814.8
			$^{13}C_2$	861.9	812.5	812.5
			C-D_1	862.2 (41)	812.9	813.9 (39)
			Si-D_1	675.7 (89)[g]	679.1	644.6 (86)
			D_2	669.7 (81)	631.5	641.6 (82)
ν_8	a′	CH def		677.6 (10)	722.8	722.8 (14)
			1′-$^{13}C_1$	677.0	722.2	722.8
			2′-$^{13}C_1$	672.6	717.5	717.1
			$^{13}C_2$	672.0	716.8	717.1
			C-D_1	529.6 (4)	564.9	
			Si-D_1	677.5 (18)	722.6	722.6 (23)
			D_2	529.5 (9)	565.0	479.9 (21)
ν_6	a′	CH def		606.6 (12)	613.9	613.9 (32)
			1′-$^{13}C_1$	606.0	613.3	613.9
			2′-$^{13}C_1$	602.3	609.5	608.4
			$^{13}C_2$	601.7	608.9	608.4
			C-D_1	472.1 (6)	477.8	
			Si-D_1	615.2 (35)[h]	626.3	600.1 (46)
			D_2	472.1 (11)	477.8	
ν_5	a′	SiC str		624.1 (27)	605.0	605.0 (41)
			1′-$^{13}C_1$	618.7	599.8	601.0
			2′-$^{13}C_1$	616.6	597.7	599.4
			$^{13}C_2$	611.7	593.0	595.0
			C-D_1	615.2 (25)	596.4	610.0 (24)
			Si-D_1	590.4 (4)[h]	601.0	
			D_2	593.3 (18)	574.9	575.5 (19)

[a] $\tilde{\nu}_{corr} = \tilde{\nu}_{exp}(^{12}C_2)/\tilde{\nu}_{calc}(^{12}C_2)\cdot\tilde{\nu}_{calc}$. [b] Numbering HC(2′)≡C(1′)-SiH. [c] Abs int 294 km/mol. [d] Abs int 296 km/mol. [e] Abs int 159 km/mol. [f] Abs int 159 km/mol. [g] Better described as CH def + SiD def. [h] Better described as CH def + SiC str.

penylidene (**7**) upon irradiation with monochromatic light (λ = 313 nm) is transformed into ethynylsilanediyl (**5**).

Particularly characteristic for **5** are the bands of the CH (3304.2 cm^{-1}), the CC (1995.7 cm^{-1}), and the SiH (1969.9 cm^{-1}) stretching vibrations. The spectral pattern of the remaining bands at lower wavenumbers (Table 2) is also in satisfactory agreement with the calculation. As expected for an open chain structure, bands for two nonidentical C-1 or C-2 singly ^{13}C-labeled isotopomers of **5** can be registered (Table 2).

Since **5** shows a broad absorption in the visible region with a maximum at λ_{max} = 500 nm (calculations recently carried out by Y. Apeloig et al.[18] predict a band at λ = 520 nm), it is not surprising that with visible light of wavelength λ = 500 nm reisomerization of **5** to **7** occurs. A small amount of a new species is also formed, and two weak IR bands at 1667.9 and 957.7 cm^{-1} and a UV band with vibrational fine structure (λ = 340, 325, and 310 nm) are recorded. Irradiation into this absorption (λ = 340 nm) leads back to **5**; hence, this species is another isomer of C_2H_2Si. By comparison with the calculated IR spectra, this isomer is identified as vinylidenesilanediyl (**8**), for which the strongest band (CC stretching vibration) is predicted at 1745.2 cm^{-1}. Again this assignment is supported by the study of the ^{13}C isotopomers. As shown in Table 3, the observed wavenumbers fit quite nicely with the corrected calculated values, and in agreement with the open chain structure two singly ^{13}C-labeled isotopomers of **8** can be differentiated.

Irradiation of **7** with light of wavelength λ = 254 nm leads in the first place (as with λ = 313 nm, see above) to the formation of **5**. Upon longer irradiation (λ = 254 nm), three new compounds can be detected, which originate from **5** or still unreacted starting material **7**. One of these can easily be identified by its characteristic IR bands at 1741.0 and 826.4 cm^{-1} (ref 13 and 19a–c, 1741 and 824 cm^{-1}) and by its

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Table 3. IR Spectral Data of Vinylidenesilanediyl (**8**): Experimental (Ar Matrix, 10 K) and Corresponding Calculated and Corrected Wavenumbers (cm^{-1}) of the Observed Vibrations, Intensities (Relative to the Strongest Band) in Parentheses

8		mode		MP2/6-31G**	corr[a]	experiment
ν_2	a_1	CC str		1745.2 (100)[b]	1667.9	1667.9 (100)
			$1'$-$^{13}C_1$[c]	1708.0	1632.3	1631.8
			$2'$-$^{13}C_1$	1721.4	1645.2	1645.2
			$^{13}C_2$	1683.0	1608.5	1607.6
			D_1	1707.0 (100)[d]	1631.4	1643.4
			D_2	1725.4 (100)[e]	1648.9	1648.3
ν_5	b_1	CH def		1012.0 (20)	957.7	957.7 (100)
			$1'$-$^{13}C_1$	1011.2	956.9	956.6
			$2'$-$^{13}C_1$	1002.3	948.5	948.6
			$^{13}C_2$	1001.5	947.8	947.6
			D_1	915.2 (15)	866.1	
			D_2	807.2 (10)	763.9	

[a] $\tilde{\nu}_{corr} = \tilde{\nu}_{exp}(^{12}C_2)/\tilde{\nu}_{calc}(^{12}C_2)\cdot\tilde{\nu}_{calc}$. [b] Abs int 96 km/mol. [c] Numbering $H_2C(2')$=$C(1')$=Si. [d] Abs int 92 km/mol. [e] Abs int 86 km/mol.

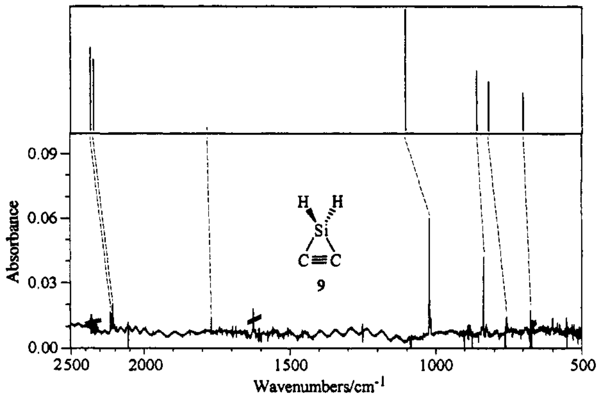

Figure 1. Comparison of experimental (bottom) and theoretical (bars at top) infrared spectrum of silacyclopropyne (**9**). The experimental spectrum (Ar matrix, 10 K) is a difference spectrum of the photoreaction **9** → **7**. IR bands due to carbon dioxide and water have been crossed.

electronic transition band[19c] (λ = 400–500 nm) as the well-known cyclic C_2Si **10**.[19d] The second compound is considered by us as an adduct of **10** with hydrogen, **10**·H_2 ($\tilde{\nu}$ = 1745.3, 826.4 cm^{-1}). We have found such an association of hydrogen also with various other unsaturated silicon compounds.[20] The third and most surprising photoproduct shows IR absorptions at 2228.9 and 2214.4 cm^{-1}, which are typical for SiH_2 groups (symmetric and asymmetric SiH stretching vibrations). Furthermore, a weak band at 1769.8 cm^{-1} and additional bands at 1023.1, 836.5, 757.4, 676.4, and 600.7 cm^{-1} are observed. Upon long-wavelength irradiation (λ > 395 nm), this compound is retransformed into **7**. Therefore, both species have to be isomers. There are two candidates for the unknown substance: silavinylidenecarbene (**11**) and silacyclopropyne (**9**). The experimental spectrum (Figure 1) is in better agreement for **9** than for **11**.[7] In addition the bands at 1769.8 (CC stretching vibration) and 836.5 cm^{-1} (symmetric SiC stretching vibration) have similiar positions in the cyclic C_2Si molecule **10** (1741.0 and 826.4 cm^{-1}, respectively). The band at 836.5 cm^{-1} can be correlated with the calculated band at 858.4 cm^{-1}. Theory predicts two additional, relatively intense bands at 818.6 and 696.6 cm^{-1}. In the experimental spectrum three unidentified bands at 757.4, 676.4, and 600.7 cm^{-1} can be detected.

Table 4. IR Spectral Data of Silacyclopropyne (**9**): Experimental (Ar Matrix, 10 K) and Corresponding Calculated and Corrected Wavenumbers (cm^{-1}) of the Observed Vibrations, Intensities (Relative to the Strongest Band) in Parentheses

9		mode		MP2/6-31G**	corr[a]	experiment
ν_6	b_1	SiH str		2370.5 (69)	2228.9	2228.9 (49)
			$^{13}C_1$	2370.5	2228.9	2228.9
			$^{13}C_2$	2370.5	2228.9	2228.9
			D_1	2366.2 (67)	2224.9	2218.6(57)
			D_2	1714.7 (39)	1612.2	1626.3(40)
ν_1	a_1	SiH str		2361.8 (59)	2214.4	2214.4 (49)
			$^{13}C_1$	2361.8	2214.4	2214.4
			$^{13}C_2$	2361.8	2214.4	2214.4
			D_1	1702.9(44)	1596.6	1612.9 (39)
			D_2	1691.4 (41)	1585.9	1601.9 (36)
ν_2	a_1	CC str		1778.7 (0.1)	1769.8	1769.8 (7)
			$^{13}C_1$	1744.1	1735.4	1736.0
			$^{13}C_2$	1708.8	1700.2	1701.4
			D_1	1779.5 (0.5)	1770.6	1770.4 (4)
			D_2	1780.0 (0.2)	1771.1	1771.1 (4)
ν_3	a_1	SiH def		1102.2 (100)[b]	1023.1	1023.1 (100)
			$^{13}C_1$	1102.1	1023.0	1023.1
			$^{13}C_2$	1102.0	1022.9	1023.1
			D_1	991.7 (100)[c]	920.5	922.3 (100)
			D_2	763.8 (4)[d]	726.6	722.2 (13)
ν_4	a_1	SiC str		858.4 (50)	836.5	836.5 (50)
			$^{13}C_1$	849.7	828.0	
			$^{13}C_2$	839.9	818.8	
			D_1	850.8 (38)	829.1	827.0 (25)
			D_2	880.9 (100)[e,f]	838.0	842.3 (100)
ν_8	b_2	SiH def		818.6 (41)	757.4	757.4 (42)
			$^{13}C_1$	816.5	755.5	
			$^{13}C_2$	815.4	754.4	
			D_1	734.9 (30)	680.0	678.2 (34)
			D_2	628.6 (14)	581.6	604.2 (21)
ν_7	b_1	SiH def		696.6 (32)	676.4	676.4 (25)
			$^{13}C_1$	695.9	675.4	
			$^{13}C_2$	695.2	675.0	
			D_1	576.1 (24)	559.4	543.4 (8)
			D_2	530.9 (21)	515.5	500.5 (24)

[a] $\tilde{\nu}_{corr} = \tilde{\nu}_{exp}(^{12}C_2)/\tilde{\nu}_{calc}(^{12}C_2)\cdot\tilde{\nu}_{calc}$. [b] Abs int 214 km/mol. [c] Abs int 206 km/mol. [d] Better described as SiD def + SiC str. [e] Better described as SiC str + SiD def. [f] Abs int 229 km/mol.

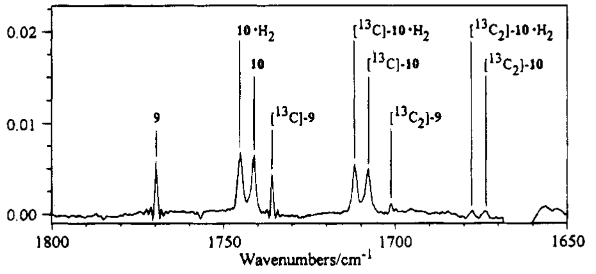

Figure 2. Infrared spectrum (Ar matrix, 10 K) of **9**, [^{13}C]-**9**, [$^{13}C_2$]-**9**, **10**, [^{13}C]-**10**, [$^{13}C_2$]-**10**, **10**·H_2, [^{13}C]-**10**·H_2, and [$^{13}C_2$]-**10**·H_2 in the region of the CC stretching vibration.

We looked for a way which will give us a final answer concerning the structure of **9**. The study of the singly ^{13}C-labeled isotopomer of **9** fills this need. As shown by the calculations (Table 4), the isotopic shift should easily be detectable in the region of the CC stretching vibration. As expected for a cyclopropyne structure only one band (Figure 2) at 1736.0 cm^{-1} is observed in case of the singly ^{13}C-labeled isotopomer (calculated and corrected: 1735.4 cm^{-1}). The doubly ^{13}C-labeled isotopomer gives a band at 1701.4 cm^{-1} (calculated and corrected: 1700.2 cm^{-1}). The appearance of only one singly ^{13}C-labeled isotopomer is definite proof for a cyclic structure of this C_2H_2Si isomer, and it has, as originally suggested,[7] to be described as silacyclopropyne (**9**). In case of constitution **11**, one would have expected two different singly

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(19) (a) Shepherd, R. A.; Graham, W. R. M. *J. Chem. Phys.* **1985**, *82*, 4788–4790. (b) Shepherd, R. A.; Graham, W. R. M. *Ibid.* **1988**, *88*, 3399–3401. (c) Weltner, W., Jr.; McLeod, D., Jr. *Ibid.* **1964**, *41*, 235–245. (d) Kleman, B. *Astrophys. J.* **1956**, *123*, 162–165.

(20) Maier, G.; Glatthaar, J. *Angew. Chem.* **1994**, *106*, 486–488; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 473–475.

Table 5. MP2/6-311G(d,p) Geometries (Å, deg) and Total Energies (AU)

7		**9**($^1A_1$)		**9**($^3B_2$)		**13**(TS)		**10**		**12**		**14**(TS)	
C_{2v}		C_{2v}		C_{2v}		C_{2v}(planar)		C_{2v}		C_{2v}		C_{2v}(planar)	
SiC	1.832	SiC	1.817	SiC	1.906	SiC	1.854	SiC	1.838	SiC	1.817	SiC	1.812
CC	1.350	CC	1.279	CC	1.323	CC	1.301	CC	1.285	CC	1.347	CC	1.395
CH	1.081	SiH	1.469	SiH	1.464	SiH	1.471			SiH	1.471	SiH	1.504
HCSi	155.7	HSiH	108.6	HSiH	115.1	HSiH	105.5			CH	1.085	CH	1.094
										HSiH	111.0	HSiH	96.6
										HCSi	155.8	HCSi	163.3
−366.114405		−366.032677		−365.963825		−366.020732		−364.841440		−367.312008		−367.231027	

^{13}C-labeled isotopomers. Again in accordance with the calculations, the SiH stretching and a_1 SiH deformation vibrations of **9** show no isotopic shifts or only tiny ones (Table 4). The analysis of the SiC stretching vibrations is difficult due to overlapping bands of **10** and **10**·H_2. The bands for the b_1 and b_2 SiH deformation vibrations of the labeled species are too weak to be identified.

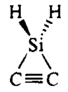
[D_1]-**9** and [D_2]-**9** also show the expected isotopic shifts (Table 4). In the experimental spectrum of the deuteriated silacyclopropynes, the bands originating from the SiH_2 deformation vibrations (b_1, b_2) can be detected and identified by comparison with the calculated positions and intensities. On this basis, the bands observed in the protonated case (757.4, 676.4, and 600.7 cm^{-1}) can also be analyzed. The best correlation is found if one assumes that the bands at 757.4 and 676.4 cm^{-1} (and not 600.7 cm^{-1})[7] belong to silacyclopropyne (**9**).

IV. Ab Initio Calculations

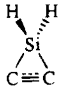
In this section the electronic structure and related properties of the C_2SiH_2 isomer **9** should be characterized. The nuclear arrangement of **9** has C_{2v} symmetry where the HSiH plane is perpendicular to the CSiC plane. Therefore, unique properties can be expected for the three-membered ring and the CC bond therein. For comparison the systems **7**, **10**, and silacyclopropene (**12**)[21] will also be studied. In accordance with literature, the MP2/6-31G** level was used for the calculation of IR spectra as well as for homodesmic reactions. Geometries, relative energies, and the NBO analysis were carried out at the MP2/6-311G(d,p) level of theory. The geometries of minima as well as transition structures are listed in Table 5, together with the corresponding total energies. The stationary points are characterized by means of the complete sets of harmonic vibrational frequencies. The ab initio calculations for the harmonic vibrational frequencies and absolute absorption intensities have been performed at the computer center of the Justus-Liebig-University in Giessen on a Siemens S 100 computer employing the GAUSSIAN 92, Revision B package of programs.[22] The ab initio calculations on the electronic structure and related properties, described in this section, have been carried out at the computer center of the University of Graz on a Titan 3040 computer employing the GAUSSIAN 92, Revision C.4 programs.[22]

A. NBO Lewis Structures. The NBO method seeks to represent the electronic structure of a molecule in terms of the best possible resonance Lewis structure.[23] For the ideal case, it is composed of core, lone pair, and strictly localized two-center bond orbitals which all have occupation numbers of 2. If necessary three-center bond orbitals can also be occupied. The corresponding antibonding two-center orbitals and the single-center Rydberg orbitals have occupation numbers of 0. For the nonideal case, the NBO Lewis structure is allowed to delocalize so that all core, lone pair, and bond orbitals become doubly occupied, forming the natural localized molecular orbitals (NLMO). The NLMO's have occupancies of either exactly two or zero. In the present case, the NBO analysis of the MP2/6-311G(d,p) density has been performed by means of the program G92NBO.[24]

Silacyclopropyne (9). For the cyclic C_{2v} structure of **9** any attempt of fulfilling the usual criteria for the occupation numbers of the orbitals failed. The most successful result for a Lewis structure has been obtained when the NBO method was forced to occupy the natural orbitals according to **9A**. The corresponding results will be described in the following.



9A



9B

Structure 9A. The bonding situation in the three-membered ring is formally described by means of five two-center bonds. The term formally refers to the CC bond orbital σ'. Its overlap of the pair of hybrids is as low as 0.204 which is only 39% of the CC π bond, and the antibonding counterpart (σ'^*) exhibits an occupation number of 0.238 (Table 6). The hybridization in σ' is low (6% s and 93% p character), but the pair of hybrids σ_1' and σ_2' points away from each other (Figure 3). The pair of hybrids σ_1 and σ_2 for the description of the CC σ bond deviates from the CC line by only 25.8° and is composed of 45% s and 55% p character. The angle between the hybrids σ_1 and σ_1' at a common center was found to be 101.7°. The CC π-bond orbital in **9** has the same shape as the one in ethylene. The SiC bond orbitals indicate strongly bent bonds. The directions of the hybrids σ_1'' and σ_2'' at the carbon centers 1 and 2 deviate from the corresponding SiC lines by 62.0°. The SiC bonds are polarized 77% toward C and are composed from hybrids of 77% p character on Si and 50% p character on C. **9A** is not a perfect Lewis structure. The best possible compromise is the description **9B**, where the dashed line indicates an electron pair which occupies a more or less CC nonbonding orbital (σ' in Table 6).

Silacyclopropynylidene (10). The cyclic C_2Si molecule **10** has already been identified spectroscopically.[13,19] The MP2/

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[21] Maier, G.; Pacl, H.; Reisenauer, H. P. *Angew. Chem.* **1995**, *107*, 1627−1629; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1439−1441.

[22] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Gaussian, Inc., Pittsburgh, PA, 1992.

[23] (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218. (b) Reed, A. E.; Weinhold, F.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899−926. (c) Reed, A. E.; Schleyer, P. v. R.; Janoschek, R. *J. Am. Chem. Soc.* **1991**, *113*, 1885−1892.

[24] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

Table 6. NBO Analysis of Structure **9A** Compared to Acetylene[a]

NBO	NBO occupancy	bond order	hybrid overlap
		9A	
SiH-σ	1.954	0.807	0.809
SiC-σ	1.855	0.449	0.654
CC-σ	1.954	0.996	0.834
CC-σ'	1.842	0.962	0.204
CC-π	1.819	0.944	0.515
SiH-σ^*	0.076		
SiC-σ^*	0.060		
CC-σ^*	0.025		
CC-σ'^*	0.238		
CC-π^*	0.055		
		Acetylene	
CC-σ	1.966	0.997	0.862
CC-π	1.932	1.000	0.498
CC-π	1.932	1.000	0.498
CC-σ^*	0.024		
CC-π^*	0.052		

[a] Bond orders and the overlaps between the hybrids are presented for NLMO's in which the given corresponding NBO's dominate by at least 94% throughout.

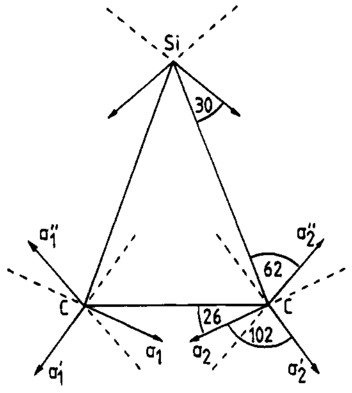
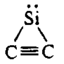
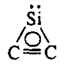


Figure 3. Angular properties of the σ natural hybrid orbitals of **9** (C_{2v}). The vectors are from the negative (small) to the positive (large) lobe; angles are in degrees.

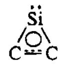
6-311G(d,p) calculated C_{2v} structure is (SiC = 1.838 and CC = 1.285 Å) quite similar to that of **9** (SiC = 1.817 and CC = 1.279 Å). Notwithstanding this geometrical similarity, the two electronic structures **10A** and **10A'** will be analyzed by means of NBO calculations.



10A



10A'

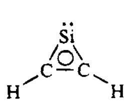


10B

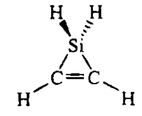
Structure 10A. The bonding situation in **10A** is described by five two-center bonds and a lone pair on the Si. The NBO results for the σ bonds are quite similar to those of **9A**. The CC π-bond orbital, however, has a remarkably low occupation number of 1.663. Consequently, Si has a π-type lone pair orbital with a high occupation number of 0.290. These results are far from a relevant Lewis structure and lead to the analysis of another electronic structure.

Structure 10A'. The NBO program is forced to form a Lewis structure with four two-center σ bonds and a three-center orbital for the π system. The occupation number of the π orbital resulted to be 1.921 with 14% Si contribution. Finally, the structure **10B** is the only useful description.

In addition to the NBO analysis of compounds **9** and **10**, further similar three-membered ring compounds can be characterized by means of their calculated Lewis structures. The application of the NBO method to silacyclopropenylidene (**7**) and silacyclopropene (**12**) yields as the best Lewis structures **7A'** with a three-center π-bond orbital and **12A** with a localized double bond, respectively.



7A'



12A

B. Ring Strain Energies, Delocalization Stabilization, and Si Inversion. The two opposite effects of ring strain and delocalization can both be defined by means of a common homodesmic equation. The study of a series of related three-membered ring compounds such as **7A'**, **9B**, **10B**, and **12A** allows the separation of these two effects. The following homodesmic equations were used

$$\mathbf{7A'} + C_2H_6 + Si_2H_6 \rightarrow Si(CH_3)_2 + (Z)\text{-}H_3SiHC{=}CHSiH_3 + 10.1 \quad (1a)$$

$$\mathbf{9B} + C_2H_6 + Si_2H_6 \rightarrow H_2Si(CH_3)_2 + H_3SiC{\equiv}CSiH_3 + 98.5 \quad (1b)$$

$$\mathbf{10B} + C_2H_6 + Si_2H_6 \rightarrow Si(CH_3)_2 + H_3SiC{\equiv}CSiH_3 + 56.6 \quad (1c)$$

$$\mathbf{12A} + C_2H_6 + Si_2H_6 \rightarrow H_2Si(CH_3)_2 + (Z)\text{-}H_3SiHC{=}CHSiH_3 + 48.2 \quad (1d)$$

The MP2/6-31G(d,p) calculated reaction energies are given in kcal mol^{-1}. All three-membered ring compounds are destabilized with respect to the reference compounds on the right-hand side of the homodesmic equations. The reaction energies show an unexpectedly great range of variation between 10.1 and 98.5 kcal mol^{-1}. Comparison of the reaction energies of **7A'** and **12A** as well as **9B** and **10B** yields a delocalization stabilization of about 40 kcal mol^{-1} (derived from the differences 48.2 − 10.1 = 38.1 kcal mol^{-1} and 98.5 − 56.5 = 42.0 kcal mol^{-1}, respectively). Stabilization of 40 kcal mol^{-1} by delocalization is very high, and the origin of this effect must be due to differences in the silanediyl structure. Strain energies can be taken from eqs 1b and 1d (**9B** and **12A** are not stabilized by delocalization). The silacyclopropene systems **7A'** and **12A** have ring strain energies of about 50 kcal mol^{-1} as is expected for heterocyclic three-membered rings.[25] In contrast, the silacyclopropyne systems **9B** and **10B** have ring strain energies of roughly 100 kcal mol^{-1}. The high values of the strain energies of **9B** and **10B** can be explained by the fact that on the right-hand side of the homodesmic equations (1b and 1c) the highly stable acetylenic C≡C triple bond is used as the reference for the CC fragment in the ring. However, on the left-hand side no true C≡C triple bond could be identified in the framework of the NBO method. The dashed line in the CC fragment indicates a more or less nonbonding interaction (Table 6).

Low inversion barriers for the tetra-coordinated silicon atom in **9B** and **12A** can be expected if planar transition structures exist which are stabilized by delocalization. The MP2/6-311G(d,p) calculated transition structures **13** and **14** for the inversion at silicon in **9B** and **12A**, respectively, are planar (C_{2v})

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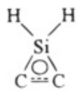
[25] Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408–3414.

Table 7. NBO Analysis of Structures **9B** and **12A** with Corresponding Transition Structures **13** and **14** for Silicon Inversion[a]

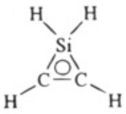
	9B	**13**	**12A**	**14**
Interatomic Distances				
r(Si−H)	1.469	1.471	1.471	1.502
r(Si−C)	1.817	1.854	1.818	1.813
r(C−C)	1.279	1.301	1.345	1.393
Energy Barriers				
ΔE	0.0	7.5	0.0	50.8
$\Delta(E + \mathrm{ZPE})$	0.0	6.2	0.0	49.6
Bond Order (Hybrid Overlap)				
Si−H	0.807 (0.809)	0.802 (0.808)	0.819 (0.811)	0.712 (0.802)
Si−C σ	0.449 (0.654)	0.368 (0.616)	0.621 (0.679)	0.447 (0.732)
Si−C π		0.355 (0.373)		0.294 (0.374)
C−C σ	0.996 (0.834)	0.996 (0.828)	0.993 (0.765)	0.994 (0.755)
C−C σ'	0.962 (0.204)	0.956 (0.196)		
C−C π	0.944 (0.515)	0.822 (0.525)	0.957 (0.471)	0.853 (0.457)
Total Bond Order				
Si−H	0.742	0.739	0.752	0.693
Si−C	0.785	0.794	0.742	0.786
C−C	1.625	1.609	1.333	1.179

[a] Interatomic distances, *r*, are given in Å. Energy barriers, ΔE, are reported in kcal mol^{-1} for the inversion at Si and for zero point energy (ZPE) corrected energy barriers. Bond orders are given with the hybrid overlaps in parentheses for the NLMO's. Total bond orders are atom−atom overlap-weighted NAO bond orders.

and exhibit aromatic stabilization according to the NBO analysis (Table 7).



13



14

For comparison, the inversion barrier of SiH_4 toward the square planar transition structure (D_{4h}) has also been calculated. The MP2/6-311G(d,p) + ZPE value was found to be 92.3 kcal mol^{-1}. At the same level of theory, the inversion barriers for **9B** → **13** and **12A** → **14** are 6.2 and 49.6 kcal mol^{-1}, respectively, and are considerably lower compared to that of SiH_4. Aromatic stability of transition structures can be identified by means of the SiC π-bond order in Table 7. However, this cannot be the only reason for low inversion barriers. In particular, the difference between the inversion barriers of **9B** → **13** and **12A** → **14** cannot be understood. A remarkable difference between the two processes can be seen in the weakening of SiH and CC bonds in **12** which is missing in **9** (compare interatomic distances in Table 7). To our knowledge, the value of 6.2 kcal mol^{-1} for **9B** → **13** is the lowest inversion barrier of tetra-coordinated silicon described so far. The all-silicon analogue (Si_3H_2) exhibits a calculated planar structure which is more stable than the corresponding perpendicular arrangement (**9**).[26] The objection that **9B** should be regarded as a $C_2 \cdots SiH_2$ complex rather than a three-membered ring seems to be supported by the low CSiC angle of 41.2° and the low inversion barrier at silicon. However, the results of the NBO analysis as well as the calculated "complexation energy" for $C_2 + SiH_2$ with an amount of 124.4 kcal mol^{-1} are not consistent with a complex.

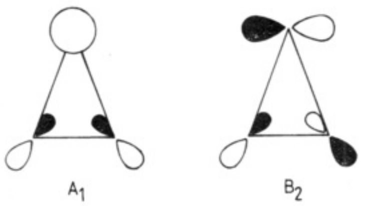


Figure 4. Schematic representation of HOMO and LUMO of **9** (C_{2v}) discussed in the text. Symmetries and orbital energies (AU): A_1 (CC-σ', HOMO) −0.389, B_2 (CC-σ'^*, LUMO) 0.005.

C. Canonical Orbitals and Diradical Character. It is of interest to note the relationship of occupied valence NBO's to canonical MO's. The energies (AU) and symmetries of the HOMO and LUMO describing the unique bonding situation in **9** are shown in Figure 4. The most striking feature of the canonical orbitals is the fact that the CC-σ' analogue (A_1) is the HOMO which lies higher in energy by 0.01 AU than the CC-π orbital (B_1). Nonbonding or formally antibonding σ orbitals for the CC interaction in closed-shell carbon compounds have already been described on the linear C_3 molecule.[27] The symmetric combination of the two SiC-σ NBO's mixes with the CC-σ' NBO in the formation of the HOMO (A_1), whereas the antisymmetric combination of the two SiC-σ NBO's mixes with the low-occupancy CC-σ'^* NBO in the formation of the LUMO (B_2).

The calculation of a perfect NBO Lewis structure for **9** failed in the CC-σ' bond orbital (see Table 6) which has an occupancy of 1.842. The antibonding counterpart σ'^* is a low-occupancy NBO with a remarkably high occupation number of 0.238. This situation indicates diradical character that will be analyzed by a rigorous application of the energy variation principle. The corresponding CASSCF(8,8)/6-31G(d,p) calculation is based on the active space which is composed of four bonding and four antibonding orbitals. The occupation numbers of HOMO and LUMO were found to be $(A_1)^{1.913}(B_2)^{0.095}$. The diradical character of **9**, measured by the deviations of the occupation numbers for HOMO and LUMO from the values 2 and 0, respectively, is similar to that of the planar closed-shell ethylene, $(\pi)^{1.914}(\pi^*)^{0.086}$. However, the comparison of the two compounds should be made with caution because the HOMO in ethylene is the bonding π orbital, but in **9** the HOMO is the almost nonbonding σ' orbital.

The highly strained silacyclopropyne (**9**) is unusual in the following sense. In a traditional diradical, there are similar occupation numbers for the two nonbonding orbitals. For silacyclopropyne (**9**), there is a minimal overlap of the two hybrids σ_1' and σ_2' (Table 6) that would normally form the in-plane π bond. The $\pi-\pi^*$ mixing is really secondary to the description of the in-plane π bond, and the occupation number of the higher energy orbital remains surprisingly low, similar to the closed-shell ethylene, even though the bond is virtually "broken". Thus, silacyclopropyne (**9**) is like a singlet diradical, but with only one "nonbonding" orbital. The lowest triplet state ($^3B_2$) exhibits a nonvertical relative energy with respect to the singlet ground state of 1.87 eV, calculated at the MP2/6-311G-(d,p) level of theory. The triplet structure (SiC = 1.906 and CC = 1.323 Å) is similar to the singlet ground state structure.

V. Conclusions

The study of the ^{13}C isotopomer of silacyclopropyne (**9**) can be taken as good proof for the proposed structure. Correspond-

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[26] Ernst, M. C.; Sax, A. F.; Kalcher, J.; Katzer, G. *THEOCHEM* **1995**, *334*, 121−126.

[27] Kalcher, J.; Janoschek, R. *THEOCHEM* **1991**, *234*, 509−514.

ing to the intrinsic electronic situations in systems **7**, **9**, **10**, and **12**, different Lewis structures have to be used in order to describe the molecules adequately: 1-silacyclopropenylidene (**7**) by **7A′** (delocalized three-center π-bond orbital), silacyclopropyne (**9**) by **9B** (localized π-bond orbital and an almost nonbonding CC-σ' orbital), silacyclopropynylidene (**10**) by **10B** (delocalized three-center π-bond orbital and an almost nonbonding CC-σ' orbital), and silacyclopropene (**12**) by **12A** (localized π-bond orbital). The value of 6.2 kcal mol^{-1} for **9** → **13** represents the lowest inversion barrier of tetra-coordinated silicon described so far.

Finally, we attempted to answer a crucial question. Why is silacyclopropyne (**9**) a stable structure but the all-carbon analogue cyclopropyne is not? A simple answer can be given by the inspection of the corresponding propadienylidene isomers $:C{=}C{=}XH_2$ (X = C (**3**), Si (**11**)), which have to be formed upon ring opening. For X = C, **3** is more stable than the transition structure cyclopropyne by 43.8 kcal mol^{-1}. In contrast, **11** (X = Si) is less stable than silacyclopropyne (**9**) by 8.7 kcal mol^{-1} (MP2/6-31G(d,p)). These numbers fulfill a "basic statement" for understanding the contrasting behavior of carbon and silicon structures: Silicon is unlikely to appear in a trigonal planar form.[28]

VI. Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen or argon. Solvents were dried using standard techniques. All glassware was thoroughly dried in an oven at 130 °C prior to use. NMR spectra were recorded on Bruker AM-400 or AC-200 spectrometers. IR spectra were recorded on a Bruker IFS 25 spectrometer. Mass spectra were obtained on a Varian Mat 111 or Varian Mat 311 A spectrometer. A Carlo-Erba Fractovap 2900 gas chromatograph with a flame ionization detector and a 10 m × 0.3 mm column coated with silicone phase OV 101 was used for analytical gas chromatography. Preparative gas chromatography was performed on a Carlo-Erba Fractovap 2450 using a thermal conductivity detector and helium as the carrier gas (4 m × 6 mm, OV 101).

2-Mesityl-1,1,1-trimethyldisilane. A solution of 3.78 g (21.0 mmol) of 1,1,1-trimethyl-2-phenyldisilane[14] in 100 mL of toluene was treated at 0 °C with 3.15 g (21.0 mmol) of trifluoromethanesulfonic acid.[15] After 4 h, 21.0 mmol of mesityllithium in 50 mL of Et$_2$O was added at −40 °C during 15 min.[15] The reaction mixture was partitioned between pentane and aqueous NH$_4$Cl solution. The organic layer was dried (MgSO$_4$), the solvent was removed, and the residue was distilled at 68 °C/0.1 mbar to afford 2.04 g (44%) of 2-mesityl-1,1,1-trimethyldisilane as a colorless liquid: ^{1}H NMR ([D$_6$]benzene) δ 6.77 (s, 2 H), 4.38 (s, 2 H), 2.37 (s, 6 H), 2.12 (s, 3 H), 0.13 (s, 9 H); ^{13}C NMR ([D$_6$]benzene) δ 144.3, 138.6, 134.7, 126.3, 24.4, 21.1, −0.6; ^{29}Si NMR ([D$_6$]benzene) δ −17.1, −75.3; IR (neat) 2952, 2920, 2122, 1604, 1552, 1449, 1245, 946, 837, 781, 702, 624 cm^{-1}; mass spectrum *m/e* 222 (14), 207 (7), 148 (40), 105 (14), 73 (100); HRMS calcd for $C_{12}H_{22}Si_2$ 222.1260, obsd 222.1250.

2-Ethynyl-1,1,1-trimethyldisilane, (4). (a) First Version. A solution of 930 mg (4.18 mmol) of 2-mesityl-1,1,1-trimethyldisilane in 10 mL of pentane was treated with 627 mg (4.18 mmol) of trifluoromethanesulfonic acid at 0 °C. After 4 h, 201 mg (4.18 mmol) of sodium acetylide in 15 mL of Et$_2$O was added. The reaction mixture was stirred for 18 h. The solvents were removed, and the product was isolated by preparative gas chromatography: ^{1}H NMR (CDCl$_3$, capillary) δ 4.34 (d, 2 H, *J* = 1.5 Hz), 3.00 (t, 1 H, *J* = 1.5 Hz), 0.89 (s, 9 H); ^{13}C NMR (CDCl$_3$, capillary) δ 98.3, 80.4, −1.0; ^{29}Si NMR (CDCl$_3$, capillary) δ −16.3, −85.7; IR (gas) 3311, 2965, 2143, 2042, 1255, 940, 844, 787, 744, 668, 616 cm^{-1}; mass spectrum *m/e* 128 (5), 113 (22), 73 (100), 59 (15), 53 (5); HRMS calcd for $C_5H_{12}Si_2$ 128.0478, obsd 128.0472.

(b) Second, Improved Version. To a solution of 9 g (0.05 mol) of 1,1,1-trimethyl-2-phenyldisilane in 100 mL of pentane was added 7.5 g (0.05 mol) of trifluoromethanesulfonic acid at 0 °C. After stirring for 10 min, 0.05 mol of ethynylmagnesium chloride in THF was added dropwise. The salts were removed by filtration, and after the removal of the solvents the residue was distilled on a spinning band column at 101 °C to afford 2.29 g (36%) of **4** as a colorless liquid.

^{13}C-Labeled 2-Ethynyl-1,1,1-trimethyldisilane, (4). ^{13}C-labeled calcium carbide was prepared from amorphous carbon (70 atom % ^{13}C) and calcium cyanamide at 1130 °C.[16] A 4.32 g sample of partially labeled carbide was hydrolyzed with hydrochloric acid. After being dried with concentrated sulfuric acid and sodium hydroxide, the developing acetylene was bubbled through a solution of 3.60 mmol of *n*-butylmagnesium chloride in 8 mL of THF to form partially labeled ethynylmagnesium chloride. From 650 mg (3.60 mmol) of 1,1,1-trimethyl-2-phenyldisilane, the corresponding triflate was prepared using the improved version described above. After the ^{13}C-labeled ethynylmagnesium chloride was added, the salts and the solvents were removed, and the product was isolated by preparative gas chromatography. ^{1}H NMR studies showed that the isotopomers **4**, [1′-^{13}C]-**4**, [2′-^{13}C]-**4**, and [1′, 2′-^{13}C$_2$]-**4** were formed in a ratio of 2.3:1:1:0.4. In the infrared spectrum of the mixture only the CC stretching vibration could be assigned to the respective isotopomer. [1′-^{13}C]-**4**: ^{1}H NMR ([D$_6$]benzene) δ 3.92 (d, 2 H, *J* = 1.6 Hz), 2.03 (dt, 1 H, *J* = 43.3, 1.6 Hz), 0.10 (s, 9 H); ^{13}C NMR ([D$_6$]benzene) δ 98.4 (d, *J* = 136.8 Hz), 80.0, −1.8; ^{29}Si NMR ([D$_6$]benzene) δ −17.3, −86.6; IR (neat) 1991 cm^{-1}. [2′-^{13}C]-**4**: ^{1}H NMR ([D$_6$]benzene) δ 3.92 (d, 2 H, *J* = 1.6 Hz), 2.03 (dt, 1 H, *J* = 239.0, 1.6 Hz), 0.10 (s, 9 H); ^{13}C NMR ([D$_6$]benzene) δ 98.4, 80.0 (d, *J* = 136.8 Hz), −1.8; ^{29}Si NMR ([D$_6$]benzene) δ −17.3, −86.6; IR (neat) 2008 cm^{-1}. [1′, 2′-^{13}C$_2$]-**4**: ^{1}H NMR ([D$_6$]benzene) δ 3.92 (d, 2 H, *J* = 1.6 Hz), 2.03 (ddt, 1 H, *J* = 239.0, 43.3, 1.6 Hz), 0.10 (s, 9 H); ^{13}C NMR ([D$_6$]benzene) δ 98.4 (d, *J* = 136.8 Hz), 80.0 (d, *J* = 136.8 Hz), −1.8; ^{29}Si NMR ([D$_6$]benzene) δ −17.3, −86.6; IR (neat) 1962 cm^{-1}.

1-Ethynyl-3,4-dimethyl-1-silacyclopent-3-ene (6). A mixture of 680 mg (5.30 mmol) of **4** and 4.36 g (53.0 mmol) of 2,3-dimethylbutadiene was pyrolyzed at 450 °C. The flow pyrolysis was performed in an apparatus with a quartz tube (length 33 cm, length of heated zone 25 cm, diameter 15 mm) which was filled with quartz Raschig rings. Nitrogen was used as the carrier gas. The yellow pyrolysis product was trapped at 77 K, and after the excess of 2,3-dimethylbutadiene was removed, **6** could be isolated by preparative gas chromatography as a colorless liquid. The yield was approximately 50%: ^{1}H NMR (CDCl$_3$, capillary) δ 4.70 (dq, 1 H, *J* = 3.2, 0.9 Hz), 2.80 (d, 1 H, *J* = 0.9 Hz), 2.12 (m, 6 H), 2.00 (m, 4 H); ^{13}C NMR (CDCl$_3$, capillary) δ 130.4, 96.2, 85.5, 22.5, 19.1; ^{29}Si NMR (CDCl$_3$, capillary) δ −32.8; IR (neat) 3287, 2911, 2158, 2037, 1175, 843, 743, 677 cm^{-1}; mass spectrum *m/e* 136 (100), 135 (36), 121 (74), 110 (41), 95 (42), 93 (34), 69 (22), 53 (51); HRMS calcd for $C_8H_{12}Si$ 136.0708, obsd 136.0690.

2-(Deuterioethynyl)-1,1,1-trimethyldisilane ([D$_1$]-4). Dideuterioacetylene was prepared by dropwise addition of D$_2$O (99.8 atom % D) to lumps of technical CaC$_2$ and metalated with *n*-butylmagnesium chloride according to a literature procedure.[29] (Deuterioethynyl)magnesium chloride (0.01 mol) was added to 0.01 mol of 2,2,2-trimethyldisilanyl trifluoromethanesulfonate (see above) at 0 °C. The volatile materials containing the product were removed in vacuo. After the removal of the solvents by distillation at 1013 mbar, the remaining 2-(deuterioethynyl)-1,1,1-trimethyldisilane was purified by preparative GC: ^{1}H NMR (C$_6$D$_6$, capillary) δ 3.97 (s, 2 H), 0.12 (s, 9 H); ^{13}C NMR (C$_6$D$_6$, capillary) δ 98.3 (*J* = 36.6 Hz), 80.2 (*J* = 6.5 Hz), −0.8 (*J* = 23.7 Hz); IR (gas phase) 2964, 2905, 2587, 2143, 1918, 1254, 1054, 938, 865, 844, 785, 743, 698, 616, 529, 468 cm^{-1}; mass spectrum *m/e* 129 (13), 114 (97), 102 (10), 84 (15), 73 (100), 59 (87); HRMS calcd for $C_5H_{11}DSi_2$ 129.0540, obsd 129.0508.

2,2-Dideuterio-1,1,1-trimethyl-2-phenyldisilane. 1,1-Dibromo-2,2,2-trimethyl-1-phenyldisilane was prepared according to a literature procedure[14] by reaction of 1,1,1-trimethyl-2,2,2-triphenyldisilane with liquid HBr (−72 °C, 24 h). A 34.1 g sample of the dibromide (0.101 mol) in 25 mL of Et$_2$O was added dropwise to 2.10 g of lithium aluminum deuteride (50.5 mmol, 98 atom % D) in 75 mL of Et$_2$O at

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(28) Janoschek, R. In *Organosilicon Chemistry*; Auner, N., Weis, J., Eds. VCH: Verlagsgesellschaft, Weinheim, 1994; p 84.

(29) Houben-Weyl *Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1973; Vol. 13/2a, p 135.

0 °C. The mixture was stirred overnight. After removal of volatiles in vacuo, the residue was extracted three times with 50 mL of pentane. The combined extracts yielded after distillation 12.1 g of 2,2-dideuterio-1,1,1-trimethyl-2-phenyldisilane (66.5 mmol, 67%, bp 60 °C/5 mbar): ^{1}H NMR (C_6D_6) δ 7.32 (m, 5 H), 0.11 (s, 9 H); ^{13}C NMR (C_6D_6) δ 136.1, 134.4, 130.7, 129.2, −1.2; IR (neat) 3068, 3052, 3017, 2953, 2895, 1543, 1528, 1428, 1400, 1246, 1111, 1065, 1027, 998, 857, 837, 743, 699, 662, 629, 584, 527, 445 cm^{-1}; mass spectrum *m/e* 182 (55), 167 (48), 135 (65), 105 (57), 73 (100); HRMS calcd for $C_9H_{14}D_2Si_2$ 182.0916, obsd 182.0937.

2,2-Dideuterio-2-(deuterioethynyl)-1,1,1-trimethyldisilane ([D$_3$]-4). To 1.62 g (8.90 mmol) of 2,2-dideuterio-1,1,1-trimethyl-2-phenyldisilane in 10 mL of pentane were added 1.33 g (8.88 mmol) of trifluoromethanesulfonic acid at 0 °C and, after stirring for 5 min at the same temperature, 8.9 mmol of (deuterioethynyl)magnesium chloride. [D$_3$]-**4**, was isolated in the same manner as [D$_1$]-**4** (see above): ^{1}H NMR (C_6D_6, capillary) δ 1.05 (s); ^{13}C NMR (C_6D_6, capillary) δ 98.2 (J = 36.3 Hz), 80.1 (J = 6.5 Hz), −0.8 (J = 23.8 Hz); IR (gas phase) 2963, 2906, 2586, 1918, 1554, 1254, 860, 844, 748, 677, 653, 614, 570, 526 cm^{-1}; mass spectrum *m/e* 131 (5), 116 (35), 103 (3), 86 (4), 73 (100); HRMS calcd for $C_4H_6D_3Si_2$ ($M^+ - CH_3$) 116.0431, obsd 116.0370.

Argon Matrix Experiments. Cryostat: Displex Closed Cycle System CSA 202 (Air Products). Irradiation: Hg low-pressure spiral lamp (Gräntzel), Hg high-pressure lamp HBO 200 (Osram) with monochromator High Intensity 5 (Bausch & Lomb). Spectrometer: IFS 85 (Bruker), 4000−300 cm^{-1}, resolution 1.0 cm^{-1}, diode array spectrometer HP 8452 A (Hewlett-Packard), 190−820 nm, resolution 2 nm.

Combination flash pyrolysis/matrix isolation: Gaseous mixtures of **4** and argon (1:1000−2000) were subjected to flash pyrolysis at various temperatures and pressures. After leaving the hot zone (quartz tube: diameter 8 mm, length of heated zone 5 cm; ca. 10^{-3} mbar, 600 °C) the reaction products were directly condensed onto a CsI or BaF_2 window at 10 K. The matrix-isolated products were studied by IR and UV/vis spectroscopy.

Combination pulsed flash pyrolysis/matrix isolation: Regulated by a pulsed magnetic valve, a gaseous mixture of **4** and argon (1:1000−2000) was expanded through a corundum tube (inner diameter 1 mm, length of heated zone 10 mm, heated to ca. 1100 °C by a tungsten resistance wire) directly into the high vacuum of the cryostat. Experimental parameters: duration of pulse 0.2 s, equivalent to ca. 1 mL of gas mixture at 1000 mbar/pulse; pulse frequency 10 pulses/min. The matrix-isolated products were studied by IR and UV/vis spectroscopy.

Note. After the manuscript was written, a paper was published in which the authors reached a similar conclusion about the near absence of an in-plane π bond in parent cyclopropyne C_3H_2, and they presented a similar method for the calculation of strain and π-bond energies (Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362−367).

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Supporting Information Available: Figures with the calculated and experimental spectra of ethynylsilanediyl (**5**), 1-silacyclopropenylidene (**7**), silacyclopropyne [D$_1$]-**9**, and silacyclopropyne [D$_2$]-**9** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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