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Quest for Silaketene: A Matrix-Spectroscopic and Theoretical Study[1]

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Co-condensation of thermally generated silicon atoms with formaldehyde in an argon matrix and subsequent irradiation is used as an access to compounds of the composition CH_2OSi. Isolation and matrix-spectroscopic identification of siloxiranylidene (**2**) and the $H_2Si{\cdot}CO$ complex **1** are described. The comparison of the experimental and calculated IR spectra shows that **1** has a pyramidal and not a planar ketene-like structure.

Introduction

The impetus for this study has four sources. First, we learned during the last two years[2] that the reaction of matrix-isolated silicon atoms with co-condensed substrate molecules is a versatile method for the generation of highly reactive silicon compounds, which are otherwise not or only hardly accessible. Second, these species very often possess unusual structures, caused by the fact that silicon—in contrast to carbon—does not like to appear in a trigonal planar form. Third, the adduct between carbon monoxide and dimethylsilylene[3,4] raised the question about its structure and prompted an ab initio investigation of the parent compound,[5] but the calculation could not explain the experimental IR spectroscopic results. In other words, the generation and spectroscopic identification of the unsubstituted silaketene may represent another example of the importance of the interplay between experiment and theory in the structural elucidation of silicon π systems. Fourth, in connection with our current interest in minima on the C_2H_2O energy hypersurface[6] it was tempting to search for other members of the elemental composition CH_2OSi. The only experimental description of such a species was reported by Schwarz et al.,[7] who observed diradical **10** during NRMS experiments with tetramethoxysilane as substrate. Apart from the ab initio study mentioned above, Chu et al.[8] investigated the gas-phase reaction of silylene with carbon monoxide. Contrary to methylene, which reacts smoothly with CO under formation of ketene,[9] no reaction at all was observed in the case of silylene.

Generation of CH_2OSi Species

The obvious entry onto the CH_2OSi energy hypersurface is the reaction of silicon atoms with formaldehyde. A gaseous mixture of monomeric formaldehyde, D_2-formaldehyde, and ^{13}C-formaldehyde, prepared by depolymerizing paraformaldehyde at ca. 100 °C, and argon (ratio ca. 1:100) was deposited onto a CsI window at 12 K. At the same time silicon atoms, prepared by vaporization of silicon at ca. 1500 °C[10,11] using a boron nitride crucible, were condensed. Of the thus formed matrix FT-IR and UV/vis spectra were taken. In addition to the absorptions of unreacted formaldehyde and some side-products, which are always found in comparable experiments (SiH_2, SiH_4, Si_2H_6, SiN_2, SiCO, SiO, etc.),[2c] several new bands were recorded which should originate from a reaction of formaldehyde and silicon atoms. After co-condensation the matrix was irradiated with light from a mercury high-pressure lamp in combination with various filters or a monochromator. The initiated photochemical reactions were monitored by IR and UV/vis spectroscopy.

Calculations

For the identification of the compounds formed in the reaction of silicon atoms with formaldehyde it was necessary to obtain the calculated vibrational spectra of the expected isomers. In addition to earlier theoretical studies[5,12] we carried out some calculations on our own

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Scheme 1. Relative Energies [kcal mol^{-1}] (B3LYP/6-31G; Corrected by Zero-Point Vibrational Energies) and Calculated Geometries of Several CH_2OSi Isomers**

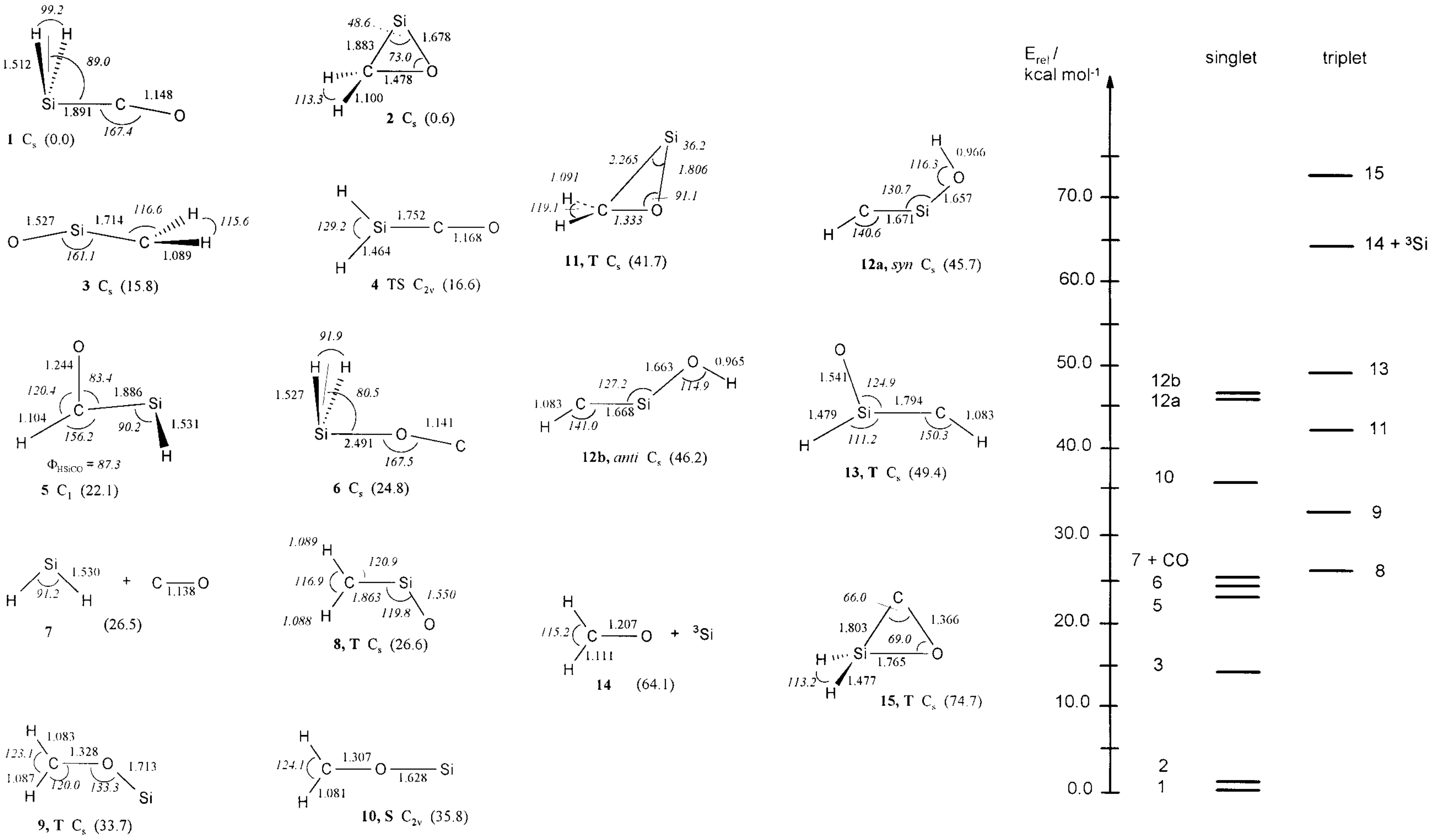

Table 1. Results of Calculations for Complex 1

method	$\Delta E_r{}^a$	$d_{CO}{}^b$	$d_{SiC}{}^b$	$d_{SiH}{}^b$	$\angle_{SiCO}{}^c$	$\angle_{CSiH}{}^c$	$\angle_{HSiH}{}^c$	$\tilde{\nu}_{CO}(1)^d$	$\tilde{\nu}_{CO}(CO)^d$	$\Delta\tilde{\nu}_{CO}{}^d$
RHF/6-31G**	−7.7	1.110	2.036	1.505	172.7	86.3	97.1	2446.4	2439.0	+7.4
CISD/V95**	−6.5	1.137	1.959	1.504	170.4	86.8	97.8	2247.3	2244.9	+2.4
CISD/6-31G**	−7.7	1.134	1.947	1.499	169.8	87.0	98.2	2255.4	2264.1	−8.7
QCISD/6-31G**	−14.4	1.149	1.933	1.504	167.3	87.5	99.1	2109.7	2162.2	−52.5
MP2/6-31G**	−21.5	1.159	1.893	1.497	166.7	89.2	100.4	2043.6	2119.2	−75.6
B3LYP/6-31G**	−26.5	1.147	1.891	1.512	167.3	89.4	99.2	2129.4	2209.5	−80.1
B3LYP/6-311+G**	−23.4	1.139	1.885	1.511	167.6	88.9	99.5	2116.3	2212.5	−96.2

[a] Calculated energy difference for the reaction CO + SiH_2 → **1**. [b] Bond lengths in Å. [c] Angles in deg. [d] Wavenumbers in cm^{-1}.

Table 2. Experimental (Ar Matrix; 12 K; Wavenumbers in cm^{-1}; Intensities Relative to the Strongest Band in Parentheses) and Calculated (B3LYP/6-31G; C_s Symmetry; Absolute Intensities [km·mol^{-1}] in Parentheses) IR Spectrum of 1-Silaketene (3)**

		mode	label	calcd	exptl
ν_6	a′	CSiO def		185.0 (29)	
			^{13}C	183.3 (29)	
			D_2	184.4 (29)	
ν_9	a″	CSiO def/		233.4 (9)	
		CH_2 rock	^{13}C	233.2 (9)	
			D_2	198.3 (12)	
ν_5	a′	CH_2 wag		559.7 (49)	
			^{13}C	555.0 (47)	
			D_2	432.5 (29)	
ν_8	a″	CH_2 rock		739.0 (26)	675.9 (42)
			^{13}C	734.7 (26)	671.1 (22)
			D_2	575.5 (24)	537.5 (30)
ν_4	a′	CSiO str s		833.4 (11)	
			^{13}C	816.4 (11)	
			D_2	761.8 (3)	
ν_3	a′	CSiO str as/		1295.3 (56)	1289.9 (100)
		CH_2 scis	^{13}C	1294.1 (59)	1284.4 (100)
			D_2	1296.8 (72)	1290.8 (100)
ν_2	a′	CH_2 scis		1359.7 (21)	1355.5 (27)
			^{13}C	1352.4 (18)	1355.5 (19)
			D_2	1030.0 (3)	
ν_1	a′	CH str s		3148.4 (7)	3016.7 (20)
			^{13}C	3142.9 (6)	3011.9 (19)
			D_2	2281.8 (6)	
ν_7	a″	CH str as		3246.9 (3)	3108.3 (8)
			^{13}C	3234.0 (3)	3096.8 (8)
			D_2	2412.9 (3)	

using the Gaussian package of programs.[13] To get an overview of the singlet and triplet CH_2OSi potential-energy surface, several stationary points were calculated with the standard 6-31G** basis set and the B3LYP functional. Scheme 1 shows their calculated geometries and relative energies.

The global minimum is the SiH_2·CO complex **1**. This is in contrast to the analogous C_2H_2O series,[6] in which the planar ketene is the most stable isomer. Siloxiranylidene (**2**) is 0.6 kcal mol^{-1} higher in energy than **1**. Astonishingly stable is the slightly bent 1-silaketene (**3**), despite the two formal double bonds. In agreement with former calculations,[3,5,12,14] the planar 2-silaketene (**4**) with C_{2v} symmetry represents the transition structure for the automerization reaction (inversion) of **1**. If no symmetry restriction is enforced, only complex **1** can be found. The next higher member in the energy scale is formylsilylene (**5**), followed by the SiH_2·OC complex **6**, which differs from **1** only by the orientation of the CO molecule. Both **1** and **6** are stabilized relative to the building blocks SiH_2 and CO. But the gain in energy is much greater for **1** (26.5 kcal mol^{-1}) than for **6** (1.7 kcal mol^{-1}). The triplet species are important with respect to the reaction mechanism. Since the ground state of atomic silicon possesses triplet multiplicity, the primary reaction product should also be a triplet molecule. The lowest triplet species has the planar structure **8** and may be regarded as the excited triplet state of 1-silaketene (**3**). The planar structure of triplet **9** results from an attack of a silicon atom on the lone pair of the oxygen atom of formaldehyde (HOMO of formaldehyde). The corresponding singlet species **10**, which stands for the excited singlet state of diradical **9**, shows C_{2v} symmetry and is only 2.1 kcal mol^{-1} higher in energy. Species **11** looks like the product of an attack of a silicon atom to the π electrons of the CO double bond perpendicular to the molecular plane of formaldehyde and may be regarded as the excited triplet state of siloxiranylidene (**2**), although the CSi distance is rather long (2.265 Å).

Our B3LYP/6-31G** calculations for complex **1** yield a shift of the carbonyl frequency of −80.1 cm^{-1} (in Table 5 a rounded value of 2129−2210 = −81 cm^{-1} is given) relative to free carbon monoxide. This is in conflict with the predicted[5] shift of +7 cm^{-1} (CISD/DZP). To solve this discrepancy, additional calculations have been carried out (Table 1). It turned out that the calculated shift is very sensitive to the method applied, ranging from +7.4 (RHF/6-31G**) to −96.2 cm^{-1} (B3LYP/6-311+G**), whereas the geometry remains virtually the same. Very small positive or negative shifts are found at the RHF and CISD level, whereas MP2, QCISD, and the hybrid density functional method B3LYP yield large negative values.

Results and Discussion

IR Spectroscopic Observations. After the co-condensation of silicon atoms and formaldehyde the matrix was irradiated with light of various selected wavelengths in order to initiate selective photoreactions. With a wavelength of $\lambda = 435$ nm one set of IR bands with the most prominent absorptions at 1289.9 and 675.9 cm^{-1} totally vanished during about 30 min. For reasons discussed below we would like to assign these bands to 1-silaketene (**3**) (Table 2).

Another group of bands, already present before irradiation, grew in intensity by about 30% during irradiation with 435 nm light (Table 3). These absorptions can easily be assigned to the six most intense bands of

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Table 3. Experimental (Ar Matrix; 12 K; Wavenumbers in cm^{-1}; Intensities Relative to the Strongest Band in Parentheses) and Calculated (B3LYP/6-31G; C_s Symmetry; Absolute Intensities [km·mol^{-1}] in Parentheses) IR Spectrum of Siloxiranylidene (2)**

		mode	label	calcd	exptl
ν_6	a′	ring def		628.7 (44)	626.8 (100)
			^{13}C	619.6 (43)	618.3 (100)
			D_2	584.7 (45)	589.5 (100)
ν_5	a′	CH_2 def/		718.3 (30)	695.2 (39)
		ring def	^{13}C	709.5 (28)	684.7 (52)
			D_2	696.4 (23)	
ν_9	a″	CH_2 def		741.0 (3)	
			^{13}C	739.1 (3)	
			D_2	548.0 (2)	
ν_4	a′	CH_2 def/		1004.2 (26)	965.2 (78)
		ring str	^{13}C	992.8 (29)	957.0 (96)
			D_2	963.5 (28)	933.7 (43)
ν_3	a′	CH_2 def		1105.1 (18)	1069.7 (48)
			^{13}C	1095.0 (18)	1060.0 (39)
			D_2	903.0 (2)	
ν_8	a"	CH_2 def		1137.6 (1)	
			^{13}C	1133.1 (1)	
			D_2	859.6 (1)	
ν_2	a′	CH_2 def		1498.2 (3)	
			^{13}C	1494.2 (3)	
			D_2	1126.7 (7)	1086.4 (8)
ν_1	a′	CH str s		3088.7 (25)	2968.8 (25)
			^{13}C	3083.6 (25)	2963.0 (59)
			D_2	2235.0 (12)	2143.6 (35)
ν_7	a"	CH str as		3171.0 (23)	3027.9 (12)
			^{13}C	3158.1 (23)	3019.0 (13)
			D_2	2360.6 (14)	2250.7 (34)

Table 4. Experimental (Ar Matrix; 12 K; Wavenumbers in cm^{-1}; Intensities Relative to the Strongest Band in Parentheses) and Calculated (B3LYP/6-31G; C_s Symmetry; Absolute Intensities [km·mol^{-1}] in Parentheses) IR Spectrum of $H_2Si·CO$ Complex (1)**

		mode	label	calcd	exptl
ν_9	a′	SiCO def		271.6 (9)	
		oop	^{13}C	266.0 (9)	
			D_2	240.1 (8)	
ν_6	a′	SiCO def		299.3 (10)	
		ip	^{13}C	294.4 (9)	
			D_2	262.1 (7)	
ν_5	a′	SiC str		476.7 (5)	
			^{13}C	472.4 (5)	
			D_2	467.2 (8)	
ν_4	a′	SiH_2 def		658.9 (8)	
			^{13}C	653.4 (8)	
			D_2	547.2 (5)	
ν_8	a"	SiH_2 def		753.7 (14)	
			^{13}C	747.6 (15)	
			D_2	604.5 (4)	
ν_3	a′	SiH_2 def		952.8 (59)	925.1 (5)
			^{13}C	952.0(59)	918.5 (9)
			D_2	699.3 (28)	689.0 (1)
ν_2	a′	SiH str		2099.7 (157)	2038−2047^a (100)^a
		s	^{13}C	2102.8 (68)	2044.9^b (26)
			D_2	1504.8 (45)	1479.1 (5)
ν_7	a″	SiH str		2109.8 (159)	2038−2047^a (100)^a
		as	^{13}C	2108.8 (159)	2044.9^b (26)
			D_2	1521.1 (82)	1490.9 (7)
ν_1	a′	CO str		2129.2 (526)	2038−2047^a (100)
			^{13}C	2077.3 (584)	1996.0 (100)
			D_2	2127.1 (603)	2043.9 (100)

[a] Three overlapping bands at 2037.9, 2046.8, and 2049.5 cm^{-1}, definite assignment not possible. [b] Doublet.

siloxiranylidene (**2**) by comparison with the calculated IR spectrum of **2** (Figure 1, Table 3). The shifts of these bands, which are observed when using ^{13}C- or D_2-formaldehyde, are in very good agreement with the theoretical prediction as well. Therefore, there is hardly any doubt about the identity of **2.**

Table 5. Comparison of Experimental (Ar Matrix) and Calculated (B3LYP/6-31G) IR Bands (cm^{-1}) of CO, Silylene (7), and the $H_2Si·CO$ Complex 1**

		experiment		calculation	
species	vibration	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
CO	CO str	2138		2210	
1	CO str	2043^a	−95	2129	−81
18	CO str	1962^b	−176	2073	−137
7	SiH_2 str	1969^{c,d}		2040^d	
1	SiH_2 str	2043^a	+74	2105^d	+65
7	SiH_2 bend	995^c		1035	
1	SiH_2 bend	925	−70	953	−82

[a] Mean value of observed bands. [b] Ref 3. [c] Ref 11c. [d] Mean value of sym and asym SiH_2-stretching vibration.

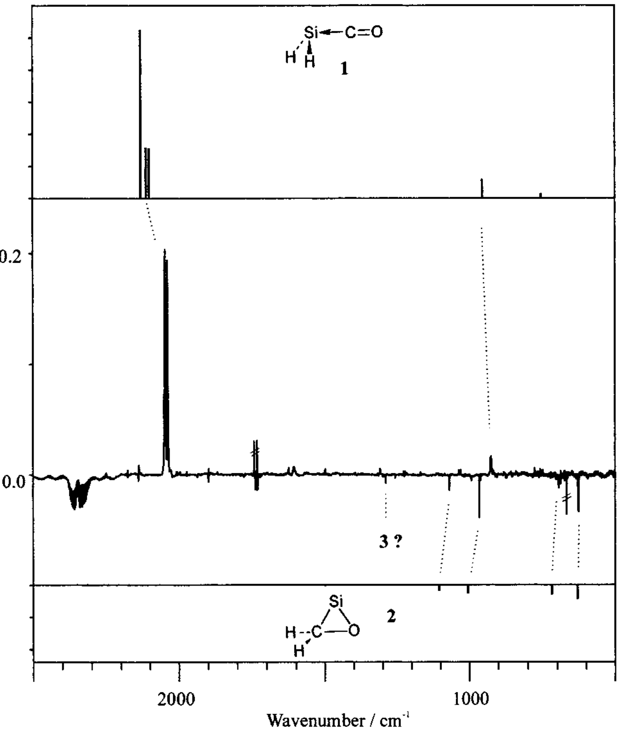
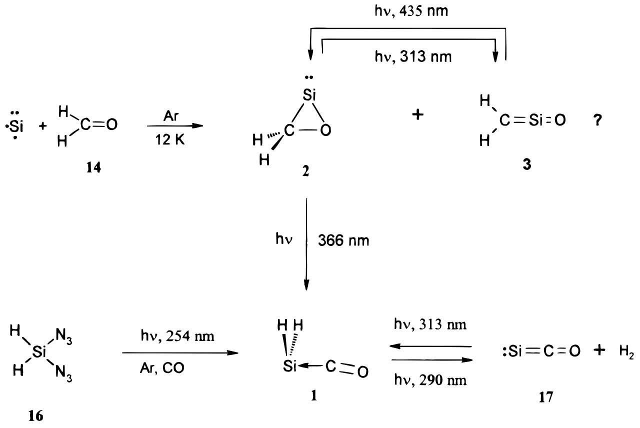


Figure 1. Comparison of experimental (Ar, 12 K) and theoretical (B3LYP/6-31G**) infrared spectra of siloxiranylidene (**2**) and $H_2Si·CO$ complex **1.** Center: Difference IR spectrum of the photoreaction (λ > 385 nm) **2** → **1**. The bands with negative values diminish, while those with positive values are enhanced upon irradiation. Bars at top: Calculated IR spectrum of **1**. Bars at bottom: Calculated IR spectrum of **2**.

If the irradiation was continued using 313 nm light, the IR bands of **2** diminished again and those of the first set of bands were partially reformed. These obervations indicate that the first set (Table 2) also stems from a compound of the elemental composition CH_2OSi. But the elucidation of its structure on the basis of the measured IR absorptions is less certain than for **2.** In addition to the absorptions at 1289.9 and 675.9 cm^{-1}, attributed to **3**, two small, but distinctive IR bands at 3108.3 and 3016.7 cm^{-1} showed the appropriate shift upon ^{13}C labeling and are consistent with the assumption that the molecule contains a CH_2 group. As can be seen from Scheme 1, there are—besides siloxiranylidene (**2**)—five alternative CH_2OSi structures with a CH_2 group, i.e., compounds **3**, **8**, **9**, **10**, and **11.** Inspection of their calculated IR spectra together with the expected and

Chart 1



observed isotopic band shifts indicate that 1-silaketene (**3**) is the best candidate.

The most important observation was made when the primary irradiation (435 nm) leading to **2** was followed by a second irradiation with the wavelength $\lambda = 366$ nm or, alternatively, with filtered light ($\lambda > 385$ nm). The bands of **2** diminished once more, and two new strong absorptions in the range 2038−2047 cm^{-1} and a weak band at 925.1 cm^{-1} appeared. This spectrum is in good accordance with the calculated spectrum of $H_2Si{\cdot}CO$ complex **1** (Figure 1). Theory predicts a very strong CO- and two weaker SiH-stretching vibrations, lying rather closely together in a region around 2100 cm^{-1}, and an additional, much weaker, band for the SiH_2-bending vibration. The remaining five fundamental vibrations should not lead to IR absorptions strong enough for an experimental observation. In the observed spectrum of the unlabeled compound **1** it is not possible to assign the overlapping bands around 2040 cm^{-1} either to SiH- or to CO-stretching vibrations. But in the case of the deuterated and the ^{13}C-labeled complex **1** the spectroscopic information is much clearer because of the specific isotopic band shifts. **[D₂]1** shows a CO-stretching band at 2043.9 cm^{-1} and two well-separated SiD-stretching bands at 1490.9 and 1479.1 cm^{-1}. In the spectrum of the ^{13}C-isotopomer the two weak SiH-stretching bands still overlapped (2044.9 cm^{-1}), but the very strong CO-absorption was shifted to 1996.0 cm^{-1}. All observed isotopic band shifts correspond well with the values predicted by the calculations and confirm the structural assignment (Figures 1 and 2, Table 4).

An additonal—chemical—proof of structure **1** was obtained when the irradiation of the matrix was continued with light of wavelength $\lambda = 290$ nm. Under these conditions the bands of **1** slowly diminished, while the absorption of the SiCO molecule **17**, which contains two hydrogens less than **1**, at 1898.2 cm^{-1},[10] grew in intensity. Eight wavenumbers higher (1906.3 cm^{-1}) a second band appeared, which faded again when the excitation wavelength was changed afterward to $\lambda = 313$ nm. At the same time the $SiH_2{\cdot}CO$ complex **1** was partly reformed. Obviously, hydrogen is eliminated from **1** upon irradiation with $\lambda = 290$ nm, leading either to a "free" SiCO molecule (1898 cm^{-1})—indicating that the H_2 molecules have enough excess energy to escape to a certain extent from the matrix cage—or to a weak complex H_2/SiCO (1908 cm^{-1}). Only the latter allows the photochemical back-reaction to **1.** Similar examples for the reversal of a photochemical elimination of hydrogen have been found by us in the systems aminosilylene/silaisonitrile[15] and silacyclopropyne/C_2Si.[16]

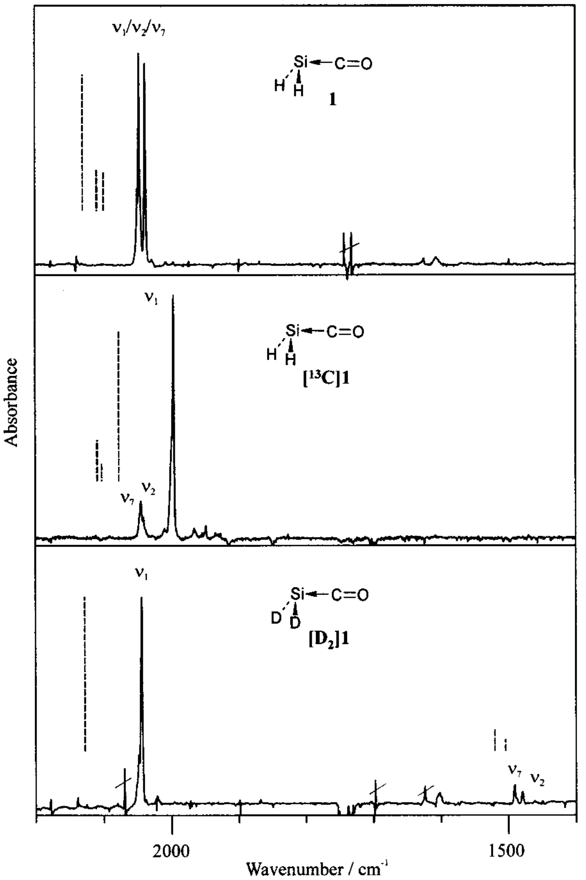


Figure 2. Experimental CO- and SiH_2-stretching vibrations (Ar, 12 K) of $H_2Si{\cdot}CO$ complex **1** (top), **[¹³C]1** (middle), and **[D₂]1** (bottom). Dashed lines: Calculated (B3LYP/6-31G**) vibrations.

Another hint for the correctness of the structural elucidation of **1** is the independent generation of the same species upon irradiation of diazidosilane (**16**).[17] When this compound was photolyzed ($\lambda = 254$ nm) in an argon matrix doped with carbon monoxide (ratio Ar:CO = 1000:1), the bands of the azido groups disappeared completely (probably formation of a $H_2Si{\cdot}N_2$ complex). Upon warmup of the matrix to 35 K, an intense double band at 2054/2051 cm^{-1} and a weak absorption at 912.5 cm^{-1} were observed.[18] These bands are very close to complex **1** obtained photochemically from siloxiranylidene (**2**). The small deviations in the band positions given in Table 4 probably arise from matrix effects.

UV Spectroscopic Observations. The difference UV spectrum of the photoreaction **1** → **17** allows the registration of the absorption maximum of complex **1** at $\lambda_{max} = 296$ nm. Although an electronic spectrum of

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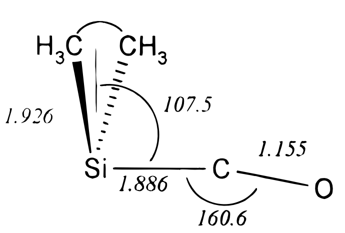
(18) Maier, G.; Glatthaar, J. Unpublished results. It has to be assumed that a band at 2054 cm^{-1}, observed already in 1970 by Milligan and Jacox during the photolysis of silane in a CO-doped argon matrix and assigned to a SiH_xCO species, belongs to **1**: Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1970**, *52*, 2594−2608.

uncomplexed SiH$_2$ in a rare gas matrix is not known, this position is surely much lower than the wavelength region where electronic absorptions of free gaseous SiH$_2$ are found (500−600 nm).[19] A similar large hypsochromic shift was observed in the dimethyl series.[3,4] Dimethylsilylene absorbs at 450 nm, the (H$_3$C)$_2$Si•CO complex at 342 nm[3]. It should be remembered that the UV spectra of silylenes are very sensitive to complexation. Thus we found already in 1984[20] that the UV maximum of methylsilylene strongly depends on the matrix material. In argon it absorbs at $\lambda_{\max}$ = 480 nm, whereas $\lambda_{\max}$ = 330 nm is found if nitrogen is used instead. This large hypsochromic shift of 150 nm is caused by the complexation of the silylene with nitrogen.

Structure of Silaketene. Substitution of one of the carbon atoms in ketene by silicon formally leads to two isomeric silaketenes, namely, 1-silaketene (**3**) and 2-silaketene (**4**). According to the calculations of Hamilton and Schaefer III[5] and to the calculations presented here, the latter does not represent an energy minimum, but the saddle point of the automerization reaction (inversion) of the nonplanar, adduct-like structure **1**.

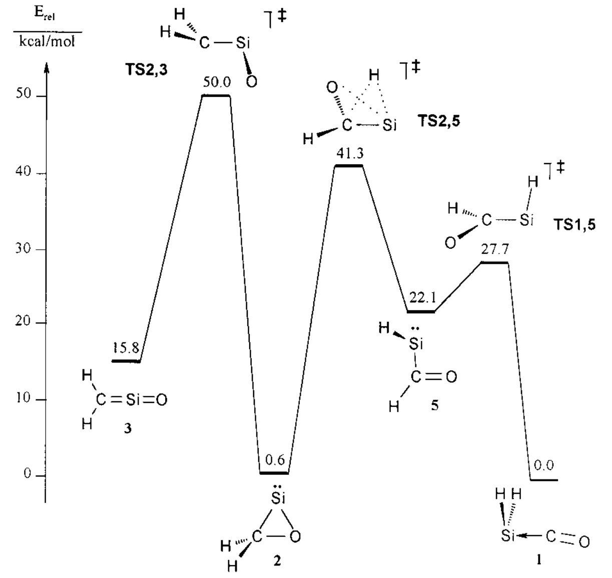
The bonding situation of this compound—which has no analogue in carbon chemistry—becomes clear if the IR bands of **1** are compared with the respective vibrations of the fragments SiH$_2$ (**7**) and carbon monoxide (Table 5). In complex **1** the SiH$_2$-stretching vibrations are observed at 74 cm^{-1} higher and the SiH$_2$-bending vibration at 70 cm^{-1} lower wavenumbers than found for free silylene (**7**) in an argon matrix. Both values are in good agreement with the B3LYP/6-31G** calculation (Table 5). These rather small band shifts reflect the small changes in geometry between free SiH$_2$ and complex **1** (Scheme 1, Table 1). The same is true for the CO fragment. The CO bond is lengthened by only 0.01 Å compared to free CO (Scheme 1). Accordingly, the calculated wavenumber shift of the CO-stretching vibration in **1** is −81 cm^{-1} on the B3LYP/6-31G** level of theory and in good aggreement with the value found experimentally (−95 cm^{-1}). The best accordance with experiment is found at the B3LYP/6-311+G** level (1 − 96.2 cm^{-1}; Table 1).

In this context it is also of interest that Arrington et al.[3] found for the dimethyl derivative (H$_3$C)$_2$Si•CO (**18**) a shift of −176 cm^{-1} to lower frequency. Our B3LYP/6-31G** geometry optimization and frequency calculation of **18** yields a shift $\Delta\tilde{\nu}$(CO) of −137 cm^{-1}, which compares favorably with experiment. Thus far it can be taken for granted that the isolated parent compound has the adduct-like structure **1**.



18

Scheme 2. Relevant Cutouts of the Calculated CH$_2$OSi Energy Hypersurface (B3LYP/6-31G)**



It remains surprising that the dimethyl complex **18** shows a greater experimental shift to lower frequency (−176 cm^{-1}) than **1**. The reason may be found in the slightly different bond angles in SiH$_2$ (91.3°) and (CH$_3$)$_2$Si (98.0°). The widened angle in dimethylsilylene indicates that there is more s-character in the Si−CH$_3$ bonds. As a consequence, the lone pair has more p-character than in the unsubstituted silylene and may contribute a stronger back-donation to the coordinative Si−CO bond. This effect weakens the CO bond and leads to a lower CO-stretching frequency. Indeed the calculation shows that the dimethyl complex **18** is less pyramidalized than **1** and forms a stronger SiC bond.

Mechanistic Considerations. A silicon atom in its triplet ground state should react preferentially with the free electron pair of formaldehyde with formation of triplet diradical **9,T**. The singlet (**10,S**)/triplet (**9,T**) gap is small (Scheme 1: 2.1 kcal•mol^{-1}). That means the ground-state multiplicity of the diradical remains open.[7] But there is no question that the primary addition step of a silicon atom is strongly exothermic. For the reaction ^{3}Si + CH$_2$O → **9,T** a ΔE_r value of 30.4 kcal•mol^{-1} is calculated (Scheme 1).

On the basis of this large negative reaction enthalpy and knowing that in the addition of a silicon atom to hydrogen cyanide the lone pair of the nitrogen is primarily attacked,[2c] one would expect diradical **9**/**10** as the initial reaction product between formaldehyde (**14**) and silicon. But only siloxiranylidende (**2**) and probably 1-silaketene (**3**) can be detected as the only definite thermal products in the matrix. If the structure of **3** is correct, then an exchange of the O,Si segment in **9** or **10** has occurred, presumably via the ring isomer **2**. It is questionable whether the silicon atoms carry enough energy in order to initiate a final ring cleavage **2** → **3**. Another possible pathway leading from formaldehyde (**14**) and silicon atoms to 1-silaketene (**3**) could involve a π-attack instead of an addition to the lone pair at the oxygen atom, with the triplet species **11,T** and **8,T** as intermediates.

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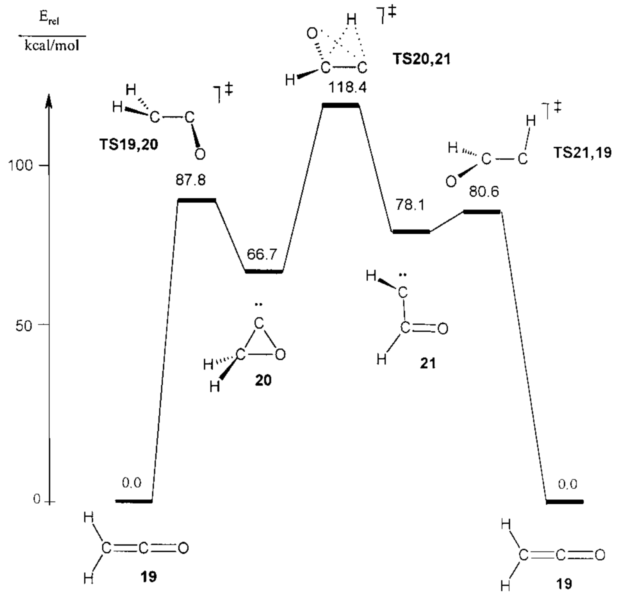
(19) Herzberg G. *Molecular Spectra and Molecular Structure, Vol. III*; Krieger Publishing Company: Malabar, 1991.

(20) Maier, G.; Mihm, G.; Reisenauer, D.; Littmann. *Chem. Ber.* **1984**, *117*, 2369−2381.

Scheme 3. Relevant Cutouts of the Calculated C_2H_2O Energy Hypersurface (B3LYP/6-311++G)**



There are analogies[2c] for ring closure **3** → **2**, in which the sequence of atoms remains unchanged. Just the opposite applies for the second photoreaction **2** →**1**. Together with the cleavage of the Si,O bond both hydrogen atoms must migrate from carbon to silicon.

The calculated reaction coordinate for the thermal reactions have no direct relevance to the photochemical processes **3** → **2** and **2** → **1**. But, nevertheless, the calculated (B3LYP/6-31G**) minima and transition states (Scheme 2) may be used as a guideline for the discussion of the observed interconversions between the different CH_2OSi isomers, at least as far as the relative energies are concerned. As expected, **3** can be transformed to **2** in a one-step process involving a barrier of 34.2 kcal mol^{-1}. The isomerization **2** → **1** follows a two-step process with formylsilylene **5** as the intermediate. The rate-determing step **2** → **5** has a barrier of 40.7 kcal mol^{-1}. This process involving ring cleavage and a synchronously occurring H-shift can be compared with isomerizations of the same type which we recently detected in siliranylidene,[2d] silirenylidene,[2d,21] and even oxiranylidene.[6] The subsequent second hydrogen shift requires only 5.6 kcal mol^{-1} activation energy and ends with $H_2Si{\cdot}CO$ complex **1**, the global minimum.

If one compares the results of this study with those obtained[6] for the C_2H_2O hypersurface (Scheme 3), the effect of the exchange of one carbon by a silicon atom is obvious. Three isomers of the composition C_2H_2O are known: ketene (**19**), oxiranylidene (**20**),[6] and hydroxyacetylene.[22] It is expected that due to the reluctance of silicon to form π bonds, hydroxysilaacetylene (**12**) cannot be detected. As far as the connectivities between ketenic and cyclic isomers are concerned, the reaction coordinates are in principle similar (compare Schemes 2 and 3). But there are two main differences: First, siloxiranylidene (**2**) is lower in energy than the planar silaketenes **3** or **4** (which is only a transition state); the opposite is true for the system **19**/**20**. Second, the global minima are different; formylcarbene (**21**) leads to planar ketene (**19**), and formylsilylene (**5**) gives the pyramidal $H_2Si{\cdot}CO$ complex **1**.

Experimental Section

Equipment used for matrix isolation, photolyses, and pyrolyses has been described before.[23] Silicon was vaporized from a boron nitride crucible, which was surrounded by an aluminum oxide tube. The oven was resistively heated to temperatures of 1490−1550 °C by means of a tungsten wire wound around the alumina tube.

Monomeric formaldehyde was generated by heating paraformaldehyde in vacuo and stored as a gaseous mixture with argon in a flask coated with paraffin to prevent repolymerization.

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[21] (a) Maier, G.; Reisenauer, H. P.; Jung, J.; Pacl, H.; Egenolf, H. *Eur. J. Org. Chem.* **1998**, *1297*, 7−1305. (b) Summary: Maier, G.; Meudt, A.; Jung, J.; Pacl, H. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Chapter 19, pp 1143−1185.

[22] Hochstrasser, R.; Wirz, H. *Angew. Chem.* **1988**, *101*, 183−185; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181.

[23] Maier, G.; Reisenauer, H. P.; Meudt, A. *Eur. J. Org. Chem.* **1998**, 1285−1290.