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Complex of Silylene with Nitrogen: A Combined Matrix-Spectroscopic and Density Functional Theory Study**

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Abstract: The quest for a new and productive route to matrix-isolated silylene **1** has led to the observation that the presence of nitrogen is favorable, as under such conditions **1** is stabilized by formation of a donor–acceptor complex **1**·N_2. Either matrix photolysis of diazidosilane or pulsed high-vacuum flash pyrolysis of 1,1,1-trimethyldisilane, followed by condensation of the products with nitrogen at 10 K, were applied as synthetic procedures. In a similar manner, complex **1**·CO can be generated. The results are supported by isotopic-labeling studies. The structural elucidation of the new species is based on the comparison of experimental IR and UV/Vis spectra with data from density functional theory calculations.

Keywords: cocondensation · donor–acceptor systems · matrix isolation · reactive intermediates · structure elucidation

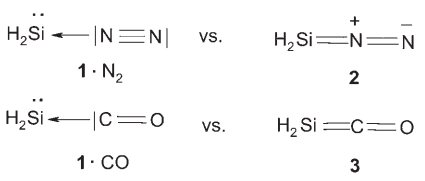
Introduction

Silylenes have been the subject of intensive investigations over decades. Gaspar and West gave a comprehensive survey on this field,[1] which contains, among other topics, a chapter describing the tendency of silylenes to form complexes with donor molecules. The adduct between water and hydroxysilylene, which was proposed by Margrave et al. in their study on the reaction of silicon atoms with water,[2] was mentioned as the first inorganic example for such an effect. The first direct observation of an organic complex is attributed to West and co-workers, who elaborated the interactions of hindered silylenes in a 2-methyltetrahydrofuran matrix.[3]

We took notice of such an influence of the surrounding medium soon after, when, in connection with the first detection of silaethene, the IR und UV/Vis spectra of matrix-isolated methylsilylene were recorded.[4] In particular, the astonishing hypsochromic shift of 150 nm (480 vs. 330 nm) in the UV/Vis spectrum in switching from an argon to a nitrogen matrix was a strong argument for a possible donor–acceptor relationship between nitrogen and methylsilylene. Also, the IR spectra were disturbing: in argon, instead of one theoretically expected signal, two absorptions in very different positions (2004 and 1935 cm^{-1}; unusually large matrix effect) was observed; in nitrogen, three bands even appeared in the Si–H region (1986, 1978, 1971 cm^{-1}).[4]

It was obvious that the most reliable information on the specific interaction between silylene and nitrogen would be achieved by working with the parent compound. Unfortunately, it is difficult to isolate in a matrix a sufficient amount of SiH_2.[5] On the other hand, the system SiH_2/N_2 would be ideally suited to elucidating the characteristics of the intermolecular attraction by comparison of the experimental results with theoretical calculations.

Our impetus to revisit this topic was enforced by two further sources. First, we observed several years ago that in a nitrogen matrix, methylene CH_2, which was generated by irradiation of diiodomethane, was attacked by nitrogen in the formation of diazomethane.[6] So we asked: is it possible to synthesize siladiazomethane (**2**) by a similar reaction between SiH_2 (**1**) and nitrogen? Second, we recently found that 2-silaketene (**3**) does not exist, and the compound in discussion is a complex between silylene and carbon monox-


$\ddot{S}iH_2 \leftarrow |N{\equiv}N|$ vs. $H_2Si{=}\overset{+}{N}{=}\overset{-}{N}$

1·N_2 **2**

$\ddot{S}iH_2 \leftarrow |C{\equiv}O$ vs. $H_2Si{=}C{=}O$

1·CO **3**

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ide, **1**·CO.[7] Will complex **1**·N_2 also be preferred relative to the bonded isomer **2**?

With this background, we started a project to clarify the similarities and/or differences in the behavior of silylene and methylene with nitrogen and carbon monoxide as reaction partners. Part of the results is presented in this report.[8]

Results and Discussion

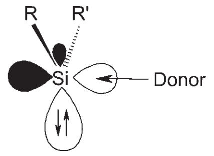
Silylenes are analogues of carbenes. They are very similar in the sense that both contain a formally divalent atom, which causes the high reactivity of both species. On the other hand, the two systems represent completely different worlds. Silylene **1** possesses a singlet, but methylene a triplet ground state. Since silylenes have a vacant p orbital and a doubly occupied n orbital, they should behave as strong electrophiles (attack at the empty p orbital), but can in principle also react as nucleophiles (by the free electron pair). Experience shows that in silylenes, as in carbenes, both options can operate. This dichotomy can only be understood in detail by applying theoretical studies. This is why quantum chemical calculations, which are now reaching chemical reality, always played an important role in rationalizing the chemistry of organosilicon compounds.[1,9] For instance, the above-mentioned hypsochromic shift in the UV absorption of methylsilylene in an argon and nitrogen matrix is in agreement with the calculations of Apeloig et al. concerning the influence of a donor substituent on the UV spectrum of silylenes.[10] Theory predicts that the transfer of electrons into the empty silicon 3p orbital in the ground state of silylene results in an increase in energy difference between n and p orbitals, thus causing a blue shift. This effect is expected to operate also in end-on donor–acceptor complexes, and has been confirmed experimentally in several cases, for example, in the study of alkyl- and aryl-substituted silylenes in 3-methylpentane and 2-methyltetrahydrofuran.[3]

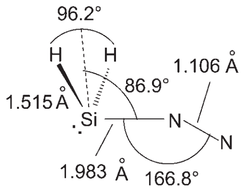
Abstract in German:
Silylen **1** wird in Gegenwart von Stickstoff durch Ausbildung eines Donor-Acceptor-Komplexes **1**·N_2 stabilisiert. Dieser Effekt zeigt sich bei der Matrix-Photolyse von Diazidosilan oder bei der Kombination von gepulster Blitzpyyrolyse von 1,1,1-Trimethyldisilan mit anschließender Co-Kondensation der Produkte zusammen mit Stickstoff bei 10 K. Auf ähnliche Weise kann auch Komplex **1·CO** dargestellt werden. Die Aussagen werden durch Studien an Isotopomeren der zur Diskussion stehenden Komplexe unterstützt. Die Strukturaufklärung der neuen Spezies basiert auf dem Vergleich der experimentellen mit berechneten (DFT-Methoden) IR- und UV/Vis-Spektren.

Parent Silylene

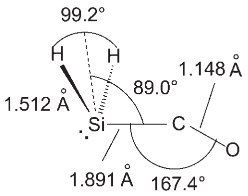
It is important to know, first of all, whether **1** will be stabilized by complexation with nitrogen. Early calculations of the H_2N_2Si energy hypersurface gave no hint of such an effect.[11] Parallel to our investigations on the SiH_2/nitrogen interaction, studies by Kawauchi et al.[12] and Walsh et al.[13] were published. Both groups predict an exothermic formation of complex **1**·N_2 from the starting components. For the structural identification of the expected species, it was necessary for us to have the calculated vibrational spectra of the involved species. Therefore, in addition to the earlier theoretical treatments,[1,9–13] we carried out some density functional theory (DFT) calculations on our own with the Gaussian package of programs.[14] The stationary points together with the corresponding vibrational spectra were calculated with the 6-311+G(d,p) basis set and the B3LYP functional. Scheme 1 shows the calculated relative energies of some minima.

The calculated stabilization energy of **1**·N_2, which represents the global minimum, relative to the free **1** and nitrogen amounts to 5.3 kcal mol^{-1}. This value (MP4SDTQ/6-31G**:[12] 5.3, G3 level:[13] 6.2 kcal mol^{-1}) should be sufficient to identify this species by matrix-isolation spectroscopy. Siladiazomethane **2** cannot be regarded as an isolable compound. It does not occupy a minimum on the energy surface, but is a transition state that lies 19 kcal mol^{-1} higher than the two fragments SiH_2 and N_2 (Scheme 1)



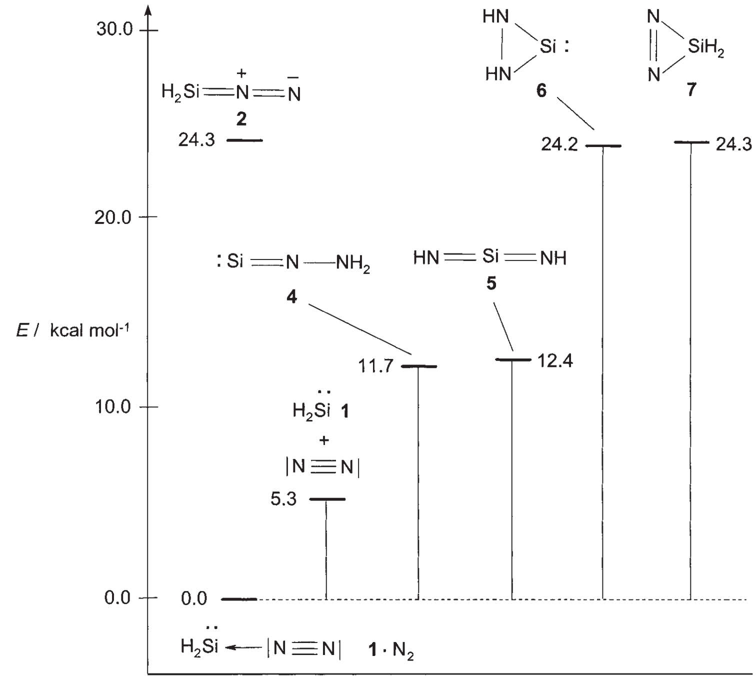


1 · N_2



1 · CO

The donor–acceptor-type interaction between silylene and a donor molecule demands that the donor is perpendicularly oriented relative to the plane of the SiH_2 moiety. Indeed, calculations show that for the N_2 complex of **1**, an end-on attachment of the nitrogen molecule has to be expected. The similarity between the calculated geometries of **1**·N_2 and the CO complex **1**·CO[7] is apparent. The Si–N bond length in **1**·N_2 is 1.983 Å, that is, longer than a normal Si–N single bond (experimental average: 1.71 Å[15]), and much longer than a Si–N double bond (experimental average: 1.59 Å[15]). The N–N bond length of 1.106 Å is slightly longer than in free nitrogen (experimental: 1.0976 Å). The Si–H bond



Scheme 1. Calculated [B3LYP/6-311+G(d,p)] relative energies of some H_2N_2Si isomers; zero-point energies included.

length of 1.515 Å in **1**·N_2 is also practically identical with the experimental value of 1.51 Å for free **1**.[16–18].

A side-on interaction between **1** and nitrogen is endothermic. An energy minimum for a side-on complex is not found computationally. The corresponding isomer with real Si–N bonds, siladiazirene **7**, lies 19 kcal mol^{-1} above the components (Scheme 1). But, as already shown by Walsh and coworkers,[13] **7** should open without any barrier to the end-on complex **1**·N_2. Consequently, only the latter compound can be expected to be isolated in a matrix experiment.

The isomers **4**–**6** can only be formed by secondary rearrangements of **1**·N_2 and therefore have not been taken into account.

The calculated IR spectra should allow, especially in connection with labeling experiments, the differentiation between free **1** and the end-on complex **1**·N_2 (Table 1). An essential feature in the spectrum of **1**·N_2 is the N–N vibration band at 2296 cm^{-1}, which arises from the fact that, upon interaction with the substrate **1**, the vibration of the attached nitrogen molecule becomes IR active.

As already mentioned above, calculated UV/Vis spectra should also be helpful in elucidating the structures of the involved compounds. The calculated [TD//B3LYP/6-311+G(d,p)] UV absorptions of **1**, **1**·N_2, and **1**·CO are given in Table 2. The HOMO→LUMO transition of **1** at 526 nm is surprisingly close to the value for the absorption maximum at 532 nm calculated by Apeloig et al. (UMP4SDTQ/6-31G*).[10b] Complexation with nitrogen is expected to cause a blue shift of the long-wavelength absorption; carbon monoxide has an even larger effect with a shift of 254 nm. In both cases, an additional strong absorption maximum at still shorter wavelength (**1**·N_2: 313 nm; **1**·CO: 273 nm) is expected.

Matrix Experiments

Silyene **1** is assumed to be the decisive intermediate in the industrially important chemical vapor deposition (CVD) of silicon films. As a result, most studies on SiH_2 to date deal with its reactivity and reaction dynamics in the gas phase. A concentration just sufficient for spectroscopic detection of the target molecule can be obtained with various methods, for instance, a) photolysis (UV, IR multiple-photon excitation) of phenylsilane, alkylsilanes, disilane, or silane, b) discharge in silane, or c) reaction of silicon atoms (laser ablation, thermal evaporation) with hydrogen.

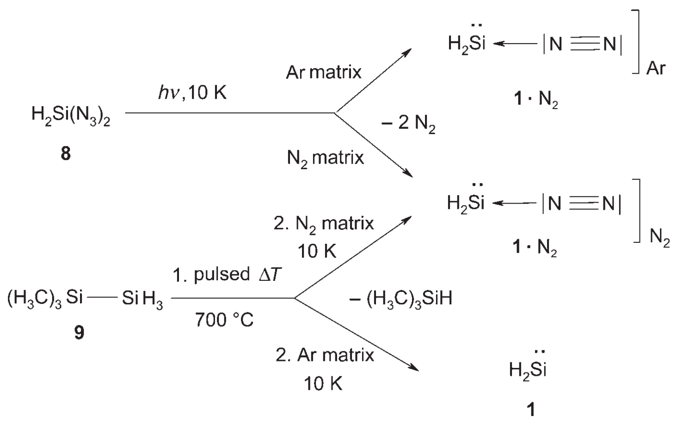
Investigations on **1** in the condensed phase (matrix isolation) were first carried out by Milligan and Jacox,[19] then by Margrave and co-workers,[20] and recently by Andrews and Wang.[21] A drawback in all these attempts was the low intensity of the signals ascribed to **1**. We hoped that matrix photolysis of diazidosilane **8** or flash pyrolysis of disilane **9** would open a route to higher concentrations of **1** or perhaps **1**·N_2 (Scheme 2)

Table 1. Calculated [B3LYP/6-311+G(d,p)] IR absorptions (wavenumbers in cm^{-1}, absolute intensities in km mol^{-1} in parentheses, and symmetries) of **1** and **1**·N_2 (including isotopomers).

Species	IR absorptions
1	2037 (290) A_1, 2036 (303) B_2, 1026 (110) A_1
1·N_2	2296 (255) A′, 2079 (214) A″, 2073 (156) A′, 960 (67) A′, 744 (32) A′, 729 (12) A″, 302 (1) A′, 260 (3) A′, 242 (1) A″
1·$^{15}N_2$	2220 (237) A′, 2081 (214) A″, 2074 (157) A′, 960 (67) A′, 741 (31) A′, 726 (13) A″, 294 (1) A′, 255 (3) A′, 235 (1) A″
[D]**1**·N_2	2297 (256) A″, 2077 (186) A″, 1494 (96) A″, 839 (49) A″, 734 (24) A″, 566 (12) A″, 294 (0) A″, 259 (3) A″, 232 (1) A′
[D_2]**1**·N_2	2296 (257) A′, 1500 (112) A″, 1487 (83) A′, 692 (3) A′, 579 (21) A′, 551 (5) A″, 285 (0) A′, 257 (3) A′, 225 (1) A″
[D_2]**1**·$^{15}N_2$	2219 (240) A′, 1500 (116) A″, 1487 (83) A′, 692 (33) A′, 574 (21) A′, 547 (6) A″, 278 (0) A′, 252 (3) A′, 220 (0) A″

Table 2. Calculated [TD//B3LYP/6-311+G(d,p)] UV absorptions (wavelengths in nm, oscillator strengths in parentheses) of **1**, **1**·N_2, and **1**·CO.

Species	UV maxima
1	526.3 (0.0203), 286.0 (0.0000), 206.0 (0.1966), 185.5 (0.1038)
1·N_2	404.0 (0.0014), 313.4 (0.1812), 252.2 (0.0280), 224.7 (0.1141), 197.0 (0.1931), 192.9 (0.0611)
1·CO	393.7 (0.0019), 272.5 (0.1911), 227.5 (0.1410), 211.2 (0.0045), 194.4 (0.0014), 187.3 (0.0413)



Scheme 2. Preparation of **1** and **1**·N_2 by matrix photolysis of **8** or flash pyrolysis of **9**.

In our attempts to isolate methylsilylene **13** in a matrix (see below), we learned that the combination with standard high-vacuum flash pyrolysis of disilane **16** is not suitable for the preparation of **13**.[22] Simple silylenes, in which the silicon bears a hydrogen atom, can only be detected if pulsed flash pyrolysis (energy transfer not by the hot surface but by collisions with hot Ar atoms or N_2 molecules) is applied.[23,24] Indeed, upon pulsed flash pyrolysis of **9** at 700 °C with Ar as carrier gas and condensation of the products on a spectroscopic window at 10 K, free **1** can be detected. Besides the bands of trimethylsilane, three absorptions at 1992.5, 1972.7, and 1963.9 cm^{-1} are registered. Comparison with the calculated and experimental values already reported illustrates that these absorptions have to be attributed to free **1** (Table 3). Unfortunately, the small intensities indicate that thermal fragmentation of **9** gives no better yield than reaction of silicon atoms with hydrogen.

A more-positive result is obtained when stabilization by complex formation with nitrogen is used. This effect is already observed during photolysis of **8** in an argon matrix. As the eliminated nitrogen molecules cannot escape the matrix cage, **1** formed is kept in the close vicinity of these molecules and can finally be captured by them. This results in a higher yield of the fragments formed, but with the disadvantage that, instead of free **1**, only complex **1**·N_2 is present in the matrix, even if argon is used as the carrier gas. This phenomenon is evidenced in the IR spectrum. Upon photolysis (254 nm) of **8** in argon at 10 K, instead of the bands of **1**, other new absorptions appear (Table 4). The band at 2253.0 cm^{-1} represents the N–N stretching vibration of complex **1**·N_2. The strong absorption at 2026.8 cm^{-1} can be attributed to the sum of the asymmetric and symmetric Si–H stretching vibration. The scissoring deformation vibration appears as a broad signal at 960.8 cm^{-1}, and the wagging deformation gives rise to a small band at 749.6 cm^{-1}. This characterization is in accord with theory (compare Table 1 and Table 4; see also Figure 4).

Table 3. IR spectroscopic (wavenumbers in cm^{-1}) identification of **1**, generated by the reaction of atomic silicon[19,20] with hydrogen or by pulsed flash pyrolysis of **9** with Ar as carrier gas.

Mode	Calcd[a]	Margrave[b]	Andrews[c]	**1** (from **9**/Ar)
ν_{as} (Si–H)	2037	1973.3	1976.2/1972.8	1972.7
ν_s (Si–H)	2036	1964.4	1964.9	1963.9
δ (Si–H)	1026	994.8	1007.6/994.6	–
$2\times\delta$ (Si–H)		1992.5	1992.8	1992.5

[a] See Table 1. [b] Thermal evaporation of silicon.[19] [c] Laser ablation of silicon.[20]

The spectrum changes only slightly if N_2 is used as the matrix host. The small shifts are due to the different environment. In this case, the two Si–H stretching vibration bands appear separately, and the paired splitting is caused by two different matrix sites (Table 4).

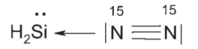
Table 4. IR spectroscopic (wavenumbers in cm^{-1}) identification of **1**·N_2 and **1**·$^{15}N_2$, generated by photolysis of **8** in argon or nitrogen, or by pulsed flash pyrolysis of **9** with N_2 or $^{15}N_2$ as carrier gas.

Mode	Calcd[a]	**1**·N_2 (from **8**/Ar)	**1**·N_2 (from **8**/N_2)	**1**·N_2 (from **9**/N_2)	Calcd[a]	**1**·$^{15}N_2$ (from **9**/$^{15}N_2$)
ν (N–N)	2296	2253.0[b]	2272.3/2266.5	2274.0/2271.1	2220	2198.5/2196.5
ν_{as} (Si–H)	2079	2026.8[c]	2017.4/2013.1	2014.2	2081	2014.1
ν_s (Si–H)	2073	2026.8[c]	2011.6/2009.7	2010.0	2074	2010

[a] See Table 1. [b] Two additional weak bands at 960.8 and 749.0 cm^{-1}. [c] No separation between ν_{as} and ν_s.

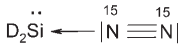
Practically the same IR spectrum is measured after pulsed flash pyrolysis of **9** at 700 °C with N_2 instead of Ar as carrier gas and condensation of the products at 10 K (Table 4). The correctness of our structural elucidation is supported by the spectrum measured in a run with $^{15}N_2$ instead of $^{14}N_2$ (Table 4). The N–N band shows the expected shift of 75 cm^{-1} to lower wavelengths, whereas the other absorptions remain constant.

Further proof of the correct analysis of the spectroscopic findings is based on additional isotopic-labeling studies. For instance, **[D$_2$]1·N$_2$** and **[D$_2$]1·^{15}N$_2$** were generated by photolysis of [D$_2$]**8** in nitrogen, or by pulsed flash pyrolysis (700 °C) of [D$_3$]**9** with N_2 or $^{15}N_2$ as carrier gas. The type of spectra is retained, except that the Si–H are replaced by Si–D stretching vibrations. Again the experimental and calculated values are similar (Table 5).

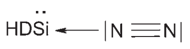


1 · $^{15}N_2$

[D$_2$]**1** · N_2



[D$_2$]**1** · $^{15}N_2$



[D]**1** · N_2

The list is completed by the monodeuterated isotopomer [D]**1**·N_2, which was prepared by pulsed flash pyrolysis

Table 5. IR spectroscopic (wavenumbers in cm^{-1}) identification of $[D_2]$**1**·N_2 and $[D_2]$**1**·$^{15}N_2$, generated by photolysis of $[D_2]$**8** in nitrogen, or by pulsed flash pyrolysis of $[D_3]$**9** with N_2 or $^{15}N_2$ as carrier gas.

Mode	Calcd[a]	$[D_2]$**1**·N_2 (from $[D_2]$**8**/N_2)	$[D_2]$**1**·N_2 (from $[D_3]$**9**/N_2)	Calcd[a]	$[D_2]$**1**·$^{15}N_2$ (from $[D_3]$**9**/$^{15}N_2$)
ν (N–N)	2296	2272.3/2266.9	2274.1/2272.0	2219	2198.5/2196.5
ν_{as} (Si–D)	1500	1468.1/1466.1	1466.5	1500	1466.6
ν_s (Si–D)	1487	1462.8/1460.8	1460.7	1487	1460.6

[a] See Table 1.

(700 °C) of $[2,2\text{-}D_2]$1,1,1-trimethyldisilane $[D_2]$**9**; this procedure furnished $[D_2]$**1**·N_2 as well as $[D]$**1**·N_2. As expected, the latter isotopomer shows, in addition to the N–N, both an Si–H and an Si–D stretching vibration in the expected positions (Table 6).

Table 6. IR spectroscopic (wavenumbers in cm^{-1}) identification of $[D]$**1**·N_2, generated by pulsed flash pyrolysis of $[D_2]$**9** with N_2 as carrier gas.

Mode	Calcd[a]	$[D]$**1**·N_2 (from $[D_2]$**9**/N_2)
ν (N–N)	2297	2274.1/2272.0
ν_s (Si–H)	2077	2013.6/2009.3
ν_s (Si–D)	1494	1466.6/1460.8

[a] See Table 1.

There is also chemical proof that **1** and nitrogen form a real new species with its own characteristic reaction potential. For instance, **1**·N_2 and its isotopomers undergo specific dehydrogenations upon longer irradiation with 254-nm light in the formation of the rather stable triplet-state molecule SiN_2 (or $Si^{15}N_2$) (**10**).[25] This observation allows the measurement of FTIR difference spectra during the photochemical hydrogen eliminations. For instance, by these means it is easy to extract clean spectra of **1**·$^{14}N_2$ and $[D_2]$**1**·$^{14}N_2$ (Figure 1 and Figure 2). Since pyrolysis of $[D_2]$**9** generates a mixture of $[D_2]$**1**·$^{14}N_2$ and $[D]$**1**·$^{14}N_2$, the bands of both isotopomers are present in the difference spectrum (Figure 3).

With regard to the history of **1**, the UV/Vis spectra of the involved species deserve special comment. The first detection of **1** goes back to Dubois et al., who observed upon flash photolysis of phenylsilane a strong gas-phase absorption in the region 650–480 nm.[26] Escribano and Campargue found experimentally that the (0,0,0)–(0,0,0) transition is situated near 640 nm.[16] In our experiments, we were unable to measure the electronic absorption of matrix-isolated free **1**. The accessible maximum concentration is too low for the observation of the UV spectrum of **1** in condensed phase.

As a result of complexation, the concentration of silylene in the matrix can be raised by the presence of nitrogen. In fact, under these conditions it is possible to observe a UV absorption, which in view of the IR study should not be assigned to free **1** but to **1**·N_2. Furthermore, the relevant experiment revealed that **1**·N_2 can undergo particular thermal chemical reactions, such as substitution of the nitrogen by other ligands (Scheme 3). For instance, if **8** is irradiated (254 nm) in an argon matrix that contains 1 % carbon monoxide, initially the IR spectrum of **1**·N_2 is registered. Upon annealing of the matrix for 20 min at 30 K, the signals of **1**·N_2 diminish, and the bands of **1**·CO appear (Figure 4). This thermal-substitution reaction can also be followed with UV/Vis spectroscopy. Before annealing, one observes a broad absorption between 300 and 350 nm (maximum near 300 nm), which has to originate from **1**·N_2. After annealing, when according to the IR spectrum the exchange **1**·$N_2 \rightarrow$ **1**·CO must have taken place, there is still a detectable absorption at 300–350 nm, which can be assigned to **1**·CO (in agreement with the maximum at 296 nm observed in the photoisomerization **12**→**1**·CO[7]). This means that both complexes have about the same electronic properties, and the blue shift by complexation of free **1** is dramatic (around 340 nm, compared with the experimental gas-phase absorption of **1** at 640 nm). This is in agreement with theory (**1**·N_2: $\Delta = 213$ nm (526 nm for the first transition of **1** minus

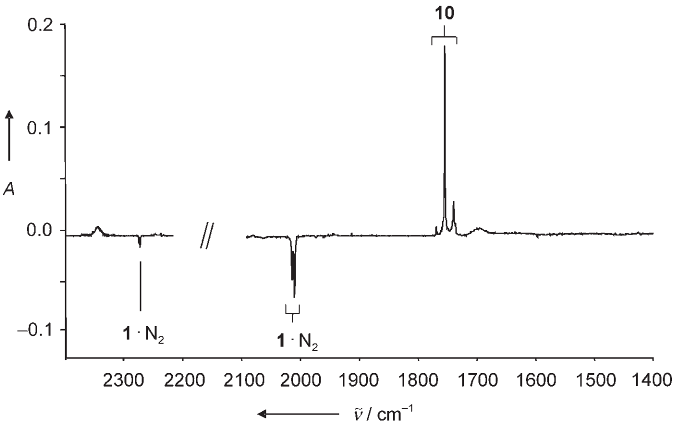


Figure 1. FTIR difference spectrum of the photochemical hydrogen elimination **1**·$N_2 \rightarrow$ **10** + H_2 in nitrogen at 10 K (obtained by subtraction of the spectra acquired after and before irradiation with 254-nm light).

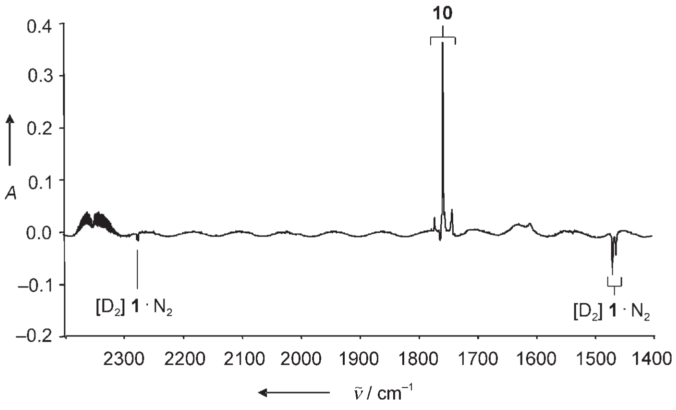


Figure 2. FTIR difference spectrum of the photochemical deuterium elimination $[D_2]$**1**·$N_2 \rightarrow$ **10** + D_2 in nitrogen at 10 K (obtained by subtraction of the spectra acquired after and before irradiation with 254-nm light from that before).

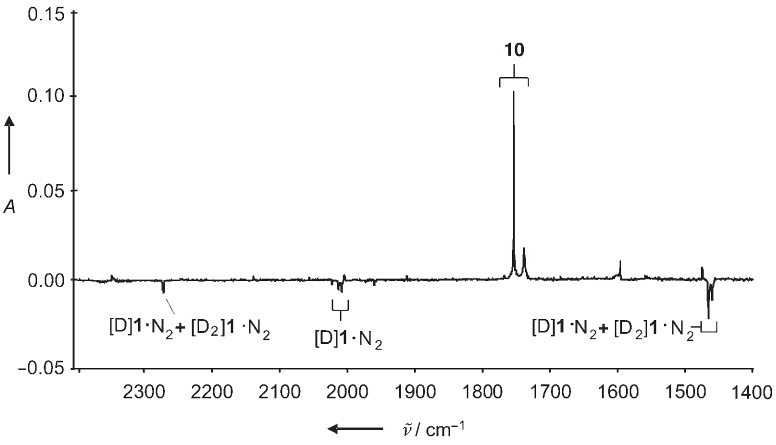
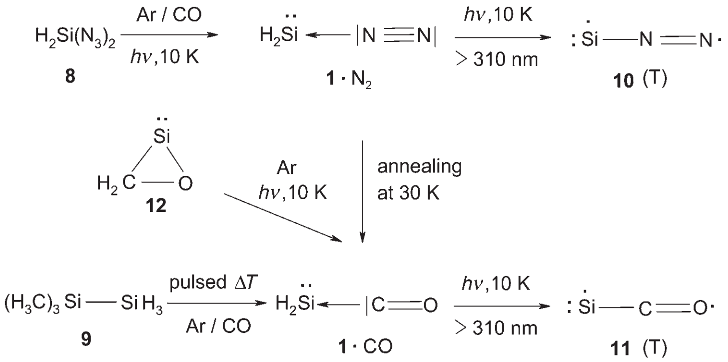


Figure 3. FTIR difference spectrum of the photochemical deuterium/hydrogen elimination [D]**1**·N_2+[D_2]**1**·N_2→**10**+HD/D_2 in nitrogen at 10 K (obtained by subtraction of the spectrum acquired after irradiation with 254-nm light from that before).



Scheme 3. Matrix photolysis of **8** in Ar/CO with subsequent conversion of **1**·N_2 into **1**·CO by annealing. Flash pyrolysis of **9** with Ar/CO as carrier gas. T = triplet state.

313 nm for the second transition of **1**·N_2); **1**·CO: Δ = 254 nm (526 nm minus 272 nm for the second transition of **1·CO**); Table 2).

It is no real surprise that the substitution **1**·N_2→**1**·CO occurs as soon as the matrix begins to soften. The calculated stabilization energy of **1**·CO relative to the partner molecules is 26.5 kcal mol^{-1}, the value for **1**·N_2 (5.3 kcal mol^{-1}) is much lower, and as a result of this, the replacement of nitrogen with carbon monoxide should be a strongly exothermic process. It also makes sense that **1**·CO, like **1**·N_2, suffers dehydrogenation and forms SiCO (**11**)[25] upon irradiation.

Last but not least, it should be mentioned that **1**·CO is also generated upon pulsed flash pyrolysis of **9** at 700 °C with N_2/CO as carrier gas and subsequent quenching to 10 K. The same procedure also allows the spectroscopic detection of [D_2]**1**·CO. The IR spectra of differently prepared samples of **1**·CO and [D_2]**1**·CO are compared in Table 7.

Table 7. IR spectroscopic (wavenumbers in cm^{-1}) identification of **1**·CO and [D_2]**1**·CO, generated by photolysis of **8** and by pulsed flash pyrolysis of **9** or [D_3]**9** with N_2 as carrier gas.

Mode	Calcd[a]	**1**·CO (from **12**)[a]	**1**·CO (from **8**)	**1**·CO (from **9**)	Mode	Calcd[a]	[D_2]**1**·CO (from [D_2]**12**)[a]	[D_2]**1**·CO (from [D_3]**9**)
ν (C–O)	2129	2049.5	2051.2	2051.2	N (C–O)	2127	2043.9	2052.9
ν_{as} (Si–H)	2110	2046.8	2055.9	2054.4	ν_{as} (Si–D)	1521	1490.9	1459.9
ν_s (Si–H)	2100	2037.9	2054.4	2054.4	ν_s (Si–H)	1505	1479.1	1448.7
δ (SiH_2)	953	925.1	916.3		Δ (SiH_2)	699	689.0	

[a] See reference [7].

Methylsilylene

Following the same strategy as with the parent compound, we also studied the methylsilylene problem. Calculations on the CH_4N_2Si energy hypersurface confirm the assumed effect of a methyl group, namely, a reduction of the electrophilicity in methylsilylene **13**. The stabilization energy of **13**·N_2 relative to the components is lowered to 1.3 kcal mol^{-1}, so it may be difficult to differentiate experimentally between complex **13**·N_2 and free **13**. One should also keep in mind that the application of DFT calculations to weak interactions of this type has to be regarded with caution.

We began our numerous experiments with the interconversion between silaethene **15** and **13** (Scheme 4).[4a] Next, we found that **13** is formed upon pyrolysis of 1,2-dimethylsilane (**16**) and can be trapped with 2,3-dimethylbutadiene.[4c] Nevertheless, we still cannot close this chapter. At least several points have been clarified: whether synthesized through a) photochemical nitrogen elimination in methyldiazidosilane **14**, b) photoisomerization of **15**, c) pulsed high-vacuum

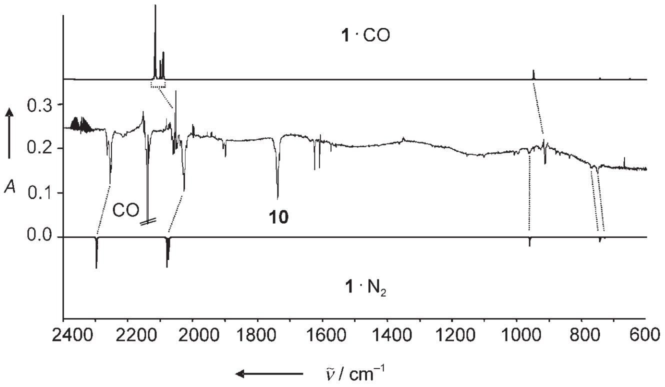
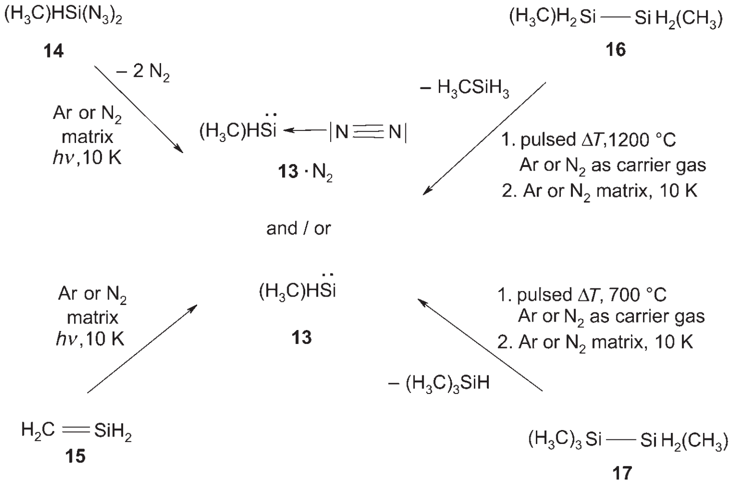


Figure 4. Top: calculated [B3LYP/6-311+G(d,p)] IR spectrum of **1**·CO. Middle: difference spectrum of the transformation **1**·N_2→**1**·CO upon annealing of the matrix (Ar, 1% CO) at 30 K (obtained by subtraction of the spectra acquired after and before annealing). Bottom: calculated [B3LYP/6-311+G(d,p)] IR spectrum of **1**·N_2.



Scheme 4. Preparation of **13** and/or **13**·N_2.

flash pyrolysis of **16** at 1200 °C, or d) pulsed flash pyrolysis of 1,1,1,3-tetramethyldisilane **17** at 700 °C, methylsilylene is formed in all cases, regardless of whether argon or nitrogen is applied as matrix material or carrier gas. But the spectral data do not allow a clear-cut answer concerning the precise nature of the product. It is tempting to argue that the difference in the UV spectra (480 nm in Ar, 330 nm in N_2) may arise from the presence of free **13** in the one or **13**·N_2 in the other case. We mentioned previously the photochemical fragmentation of **14** and argued that the spectral bands (UV: 330 nm; IR: 1981, 1975, 1966 cm^{-1}) should be attributed to **13**·N_2.[27] But even today, after many further experiments, two factors make a final answer difficult. First, in the methyl series the number of disturbing bands in the spectra is much higher, and an N–N absorption cannot be identified. Second, the Si–H stretching vibration is extremely sensitive to the nature of the matrix holes. Therefore, different matrix sites cause complex spectra in the Si–H region. Our present view is that the two signals at 2005 and 1935 cm^{-1}, observed upon photoisomerization of **15** in argon at 10 K,[4c] may result from such a matrix splitting of free **13**. IR spectra cannot be used to detect separately **13** and **13**·N_2. The details are described elsewhere.[28]

Conclusions

Our conclusions are as follows. a) There is no effective way to isolate free **1** in condensed phase in sufficient concentration (argon matrix) for UV/Vis spectroscopic detection. Therefore, its identification is restricted to IR measurements in combination with quantum-chemical calculations. b) Silylene can be stabilized by reaction with nitrogen under formation of a donor–acceptor complex. This effect can be used to generate a higher yield of silylene in form of **1**·N_2. c) There is a close resemblance between the system SiH_2/N_2 and SiH_2/CO. Complexation with carbon monoxide is stronger than with nitrogen. Consequently, **1**·N_2 is transformed into **1**·CO by thermal substitution. d) Siladiazomethane **2** does not exist; only **1**·N_2 is detectable. The situation is the same as that of the preference for **1**·CO rather than **3**. e) Photochemical dehydrogenation is a typical example of an intrinsic reaction of the silylene complexes. f) The results of matrix studies can even shed some light on the behavior of **1** in the gas phase. The higher stability of **1**·CO relative to **1**·N_2 mirrors kinetic reports of Walsh and co-workers, who showed that **1** reacts in the gas phase rapidly with CO[29] but not with nitrogen.[13]

Experimental Section

General

The cryostat for matrix isolation was a helium closed-cycle refrigeration system (compressor unit RW2 with coldhead base unit 210 and extension module ROK, Leybold). The matrix IR spectra were recorded with an FTIR instrument (IFS 85 or IFS 55, Bruker), the UV/Vis spectra were recorded with a diode-array spectrophotometer (HP 8453, Hewlett Packard). The light sources used were a mercury high-pressure lamp (HBO 200, Osram) with a monochromator (Bausch and Lomb) and a mercury low-pressure spiral lamp with a Vycor filter (Gräntzel). Equipment for the combination of pulsed high-vacuum pyrolysis with matrix isolation has been described previously.[23,24]

Starting materials

Diazides of type **8** or **14** are dangerous substances, and we had to develop special procedures for their safe preparation and handling. The method of choice was an azide-transfer reaction between the corresponding halosilane and tri-*n*-butyltin azide. Detailed information is given in reference [28].

8: This compound was prepared as described before.[30] To prepare [D_2]**8**, dideuteriodiiodosilane (1.14 g, 4.0 mmol) was treated with tri-*n*-butyl tin azide (3.30 g, 10 mmol) by applying the same procedure.

13: This compound was also prepared as described before.[30]

Disilanes

The strategy for the synthesis of the disilanes used herein consists of the coupling of monosilyl halides by salt elimination, subsequent exchange of phenyl or methyl groups in the disilane formed with halogen atoms, and final reduction of the halogenated disilanes with lithium aluminum hydride or deuteride.

9: 1,1,1-trichloro-2,2,2-trimethyldisilane (2.06 g, 10 mmol) [31] were reduced with excess $LiAlH_4$ (500 mg) in THF at 0 °C. After purification with preparative GC (4 m × 6 mm column, OV 101, 60 °C, isotherm), **9** (1.04 g) was isolated as a colorless liquid. The spectroscopic data are as reported.[32] [D_3]**9** was prepared by an analogous procedure with $LiAlD_4$ and obtained as a colorless liquid: ^1H NMR (C_6D_6): $\delta = 0.10$ ppm (s, 9 H); ^{13}C NMR (C_6D_6): $\delta = -0.4$ ppm; ^{29}Si NMR (C_6D_6): $\delta = -17.4$ ($SiMe_3$), -98.9 ppm (SiD_3); IR (gas phase): $\tilde{\nu} = 2961.1$, 2905.8, 1561.6, 1255.0, 842.4, 748.4, 695.6, 663.3, 617.4 cm^{-1}; MS (70 eV): *m/e* (%) = 103 (3) [$M^+ - D_2$], 92 (6) [$M^+ -$Me], 73 (100) [$SiMe_3$]; HRMS calcd for $C_3H_9D_3Si_2$: 103.038; found: 103.007. For the preparation of [D_2]**9**, HBr (25 mL) was condensed with 1,1,1-trimethyl-2,2-diphenyldisilane (2.4 g, 9.3 mmol)[24] in a flask (100 mL) at −196 °C. After 7 days at −78 °C, the crude product, which represents mostly highly reactive 1,1-dibromo-2,2,2-trimethylsilane, was directly reduced with $LiAlD_4$ under standard conditions. After purification by preparative GC, only a small amount of pure [D_2]**9** was isolated as a colorless liquid: IR (gas phase): $\tilde{\nu} = 2967.2$, 2906.5, 2137.7, 1561.7, 1254.9, 1142.6, 943.1, 786.2, 748.1, 695.5, 669.4, 663.3, 617.5 cm^{-1}; MS (70 eV): *m/e* (%) = 103 (5) [$M^+ -$HD], 91 (4) [$M^+ -$Me], 88 (6), 73 (100) [$SiMe_3$].

16: This compound was prepared as in our earlier work[4c] as a colorless liquid (b.p. 41 °C) and identified by comparison with published spectroscopic data:[33] ^{1}H NMR (CDCl$_3$): $\delta = 4.28$–4.60 (m, 4H, SiH), 0.23 ppm (t, 6H, 2CH$_3$, $^{3}J = 4$ Hz); ^{13}C NMR (CDCl$_3$): $\delta = -11.5$ ppm.

17: In the same manner as for [D$_2$]**9**, 1,1,1,2-tetramethyl-2,2-diphenyldisilane (6.7 g, 24.8 mmol)[34] was dephenylated with HBr. Pure 1,1-dibromo-1,2,2,2-tetramethyldisilane was obtained by preparative GC as colorless crystals: ^{1}H NMR (CDCl$_3$): $\delta = 0.15$ (s, 9H, SiMe$_3$), 0.98 ppm (s, 3H, SiMe); ^{13}C NMR (CDCl$_3$): $\delta = -3.6$ (SiMe$_3$), 7.5 ppm (SiMe); MS (70 eV): *m*/*e* (%) = 274 (1) [M^+], 137 (5), 107 (3) [SiBr], 73 (100) [SiMe$_3$]; HRMS calcd for $C_4H_{12}Si_2Br_2$: 273.884; found: 273.883. Because of its high sensitivity to moisture, the dibromosilane was directly reduced with LiAlH$_4$. Routine workup, which included preparative GC, gave **17** as a colorless liquid: IR (gas phase): $\tilde{\nu} = 2964.6$, 2906.1, 2359.1, 2118.4, 1253.8, 937.4, 836.0, 700.9, 622.9 cm^{-1}; MS (70 eV): *m*/*e* (%) = 118 (10) [M^+], 103 (13) [M^+−Me], 85 (3), 73 (100) [SiMe$_3$]; HRMS calcd for $C_4H_{14}Si_2$: 118.064; found: 118.063. To prepare [D$_2$]**17**, 1,1-dibromo-1,2,2,2-tetramethyldisilane was similarly reduced with LiAlD$_4$. After preparative GC, [D$_2$]**17** was isolated as a colorless oil: ^{1}H NMR (CDCl$_3$): $\delta = 0.69$ (s, 3H, SiMe), 0.74 ppm (s, 9H, SiMe$_3$); ^{13}C NMR (CDCl$_3$): $\delta = -12.4$ (SiMe), 30.3 ppm (SiMe$_3$); ^{29}Si NMR (CDCl$_3$): $\delta = -17.6$ (SiMe$_3$), -66.4 ppm (SiMe); IR (gas phase): $\tilde{\nu} = 2964.6$, 2906.4, 2362.0, 1540.0, 1253.4, 868.5, 839.9, 803.0, 744.4, 704.8, 669.2 621.9, 546.3 cm^{-1}; MS (70 eV): *m*/*e* (%) = 120 (9) [M^+], 105 (11) [M^+−Me], 73 (100) [SiMe$_3$]; HRMS calcd for $C_4H_{12}D_2Si_2$: 120.076; found: 120.076.

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[1] P. P. Gaspar, R. West in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 43, pp. 2463–2568; see also earlier reviews on silylene chemistry cited therein.

[2] Z. K. Ismail, R. H. Hauge, L. Fredin, J. W. Kauffman, J. L. Margrave, *J. Chem. Phys.* **1982**, *77*, 1617–1625.

[3] G. R. Gillette, G. H. Noren, R. West, *Organometallics* **1987**, *6*, 2617–2618.

[4] a) H. P. Reisenauer, G. Mihm, G. Maier, *Angew. Chem. Suppl.* **1982**, 1785–1792; H. P. Reisenauer, G. Mihm, G. Maier, *Angew. Chem.* **1982**, *94*, 864–865; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 854–855; b) G. Maier, G. Mihm, H. P. Reisenauer, *Chem. Ber.* **1984**, *117*, 2351–2368; c) G. Maier, G. Mihm, H. P. Reisenauer, D. Littmann, *Chem. Ber.* **1984**, *117*, 2369–2381.

[5] L. Fredin, R. M. Hauge, Z. F. Kafafi, L. Margrave, *J. Chem. Phys.* **1985**, *82*, 3542–3545.

[6] G. Maier, H. P. Reisenauer, *Angew. Chem.* **1986**, *98*, 829–831; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 819–822; G. Maier, H. P. Reisenauer, J. Hu, L. J. Schaad, B. A. Hess, *J. Am. Chem. Soc.* **1990**, *112*, 5117–5122.

[7] G. Maier, H. P. Reisenauer, H. Egenolf, *Organometallics* **1999**, *18*, 2155–2161.

[8] Presented at the PACIFICHEM 2005 meeting in Honolulu, December 15–20, **2005**.

[9] Survey: Y. Apeloig in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, chap. 2, pp. 57–225.

[10] a) Y. Apeloig, M. Karni, *J. Chem. Soc. Chem. Commun.* **1985**, 1048–1049; b) Y. Apeloig, M. Karni, R. West, K. Welsh, *J. Am. Chem. Soc.* **1994**, *116*, 9719–9729; c) Y. Apeloig, M. Karni, Th. Müller in *Organosilicon Chemistry II: From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **1996**, pp. 263–288.

[11] C. Thomson, C. Glidewell, *J. Comput. Chem.* **1983**, *4*, 1–8.

[12] S. Kawauchi, A. Tachibana, M. Mori, Y. Shibusa, T. Yamabe, *J. Mol. Struct.* **1994**, *310*, 255–267.

[13] R. Becerra, J. P. Cannady, R. Walsh, *J. Phys. Chem. A* **2003**, *107*, 9588–9593.

[14] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, **1998**..

[15] Survey: M. Kaftory, M. Kapon, M. Botoshansky in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, chap. 5, pp. 181–265.

[16] R. Escribano, A. Campargue, *J. Chem. Phys.* **1998**, *108*, 6249–6257.

[17] W. D. Allen, H. F. Schaefer III, *Chem. Phys.* **1986**, *108*, 243–274.

[18] I. Dubois, *Can. J. Phys.* **1968**, *46*, 2485–2490.

[19] D. E. Milligan, M. E. Jacox, *J. Chem. Phys.* **1970**, *52*, 2594–2608.

[20] L. Fredin, R. H. Hauge, Z. H. Kafafi, J. L. Margrave, *J. Chem. Phys.* **1985**, *82*, 3542–3545; see also: A. Lloret, L. Abouat-Marguin, *Chem. Phys.* **1986**, *107*, 139–143.

[21] L. Andrews, X. Wang, *J. Phys. Chem. A* **2002**, *106*, 7696–7702.

[22] G. Mihm, Dissertation, University Giessen (Germany), **1982**.

[23] G. Maier, H. Pacl, H. P. Reisenauer, A. Meudt, R. Janoschek, *J. Am. Chem. Soc.* **1995**, *117*, 12712–12720.

[24] G. Maier, H. P. Reisenauer, A. Meudt, *Eur. J. Org. Chem.* **1998**, 1285–1290.

[25] R. R. Lemke, R. F. Ferrante, W. Weltner, Jr., *J. Am. Chem. Soc.* **1977**, *99*, 416–423.

[26] I. Dubois, G. Herzberg, R. D. Verma, *J. Chem. Phys.* **1967**, *47*, 4262–4263.

[27] G. Maier, J. Glatthaar in *Organosilicon Chemistry I: From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **1994**, pp. 131–138.

[28] J. Glatthaar, Dissertation, University Giessen (Germany), **2003**; urn:nbn:de:hebis:26-opus-13278; http://geb.uni-giessen.de/geb/volltexte/2003/1327/.

[29] R. Becerra, J. P. Cannady, R. Walsh, *J. Phys. Chem. A* **2003**, *107*, 9588–9593.

[30] G. Maier, H. P. Reisenauer, J. Glatthaar, *Organometallics* **2000**, *19*, 4775–4783.

[31] a) K. Tamao, M. Kumada, *J. Organomet. Chem.* **1971**, *30*, 339–347; b) Y. Matsumoto, T. Hayashi, Y. Ito, *Tetrahedron* **1994**, *50*, 335–346.

[32] a) E. Amberger, A. Mülhofer, *J. Organomet. Chem.* **1968**, *12*, 55–63; b) D. P. Paquin, M. A. Ring, *J. Am. Chem. Soc.* **1977**, *99*, 1793–1797.

[33] M. A. Ring, R. B. Baird, M. D. Sefzik, *Inorg. Chem.* **1971**, *10*, 883–886.

[34] a) H. Gilman, G. D. Lichtenwalter, *J. Am. Chem. Soc.* **1958**, *80*, 608–611; b) M. Ishikawa, T. Fuchikami, M. Kumada, *J. Organomet. Chem.* **1978**, *162*, 223–238; c) G. Maier, H. P. Reisenauer, J. Jung, H. Pacl, H. Egenolf, *Eur. J. Org. Chem.* **1998**, 1297–1305.

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