Hetero π Systems, 28[◇]

Reaction of Silicon Atoms with Acetylene and Ethylene: Generation and Matrix-Spectroscopic Identification of C_2H_2Si and C_2H_4Si Isomers

Günther Maier*, Hans Peter Reisenauer, and Heiko Egenolf

Institut für Organische Chemie der Universität Gießen,
Heinrich-Buff-Ring 58, 35392 Gießen, Germany
Fax: (internat.) +49(0)641/99-34309

Received February 2, 1998

Keywords: Matrix isolation / Silicon atoms / Ab initio calculations / Photochemistry

Evaporation of silicon and consecutive cocondensation of the generated atoms with acetylene or ethylene in an argon matrix turnes out to be a new access to C_2H_2Si and C_2H_4Si isomers, respectively. In both cases the silicon atoms rather add to the π system than insert into C–H bonds, leading to cyclic silylenes as primary reaction products. In the Si/acetylene system the primary product is silacyclopropenylidene (**2**), which shows the already known photochemical interconversion into additional C_2H_2Si species. On the other hand, cocondensation of silicon atoms with ethylene and subsequent irradiation lead to the matrix-isolation of three new C_2H_4Si isomers [apart from the known silacyclopropene (**7**) and silylacetylene (**8**)], namely silacyclopropylidene (**10**), *s-trans*-vinylsilylene (**11**), and the unsubstituted 1-silaallene (**13**). These species can be identified by comparison of their experimental IR spectra and those obtained by ab initio calculations. In a second reaction path, SiH_2, which is formed as a byproduct from atomic silicon and hydrogen impurities, adds to the π system of acetylene, yielding silacyclopropene (**7**). Silacyclopropane (**16**), the analogous product of the reaction of SiH_2 with ethylene, could not be observed.

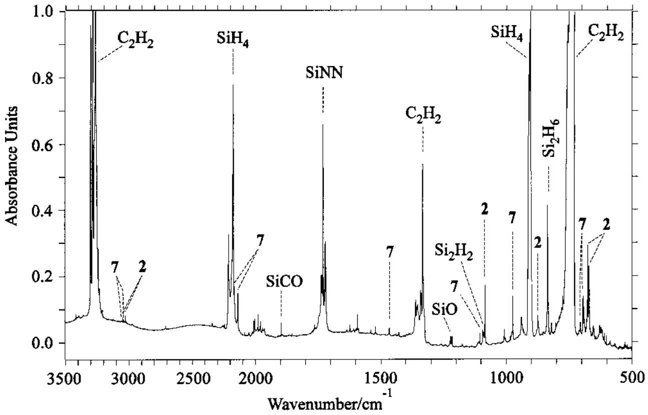
Reaction of Silicon Atoms with Acetylene

In 1990, Handy et al. predicted that the reaction of silicon atoms with acetylene could provide an access to the C_2H_2Si energy hypersurface[1]. According to UMP2(DZP) calculations, a distorted C_2H_2Si triplet structure can be formed without a barrier from atomic silicon and acetylene, which after rearrangement and intersystem crossing would lead to the formation of 1-silacyclopropenylidene (**2**), the global minimum of the C_2H_2Si singlet species. Kinetic measurements by Husain[2] indeed showed that the reaction of silicon atoms with acetylene proceeds with almost collision efficiency. However, it was the pulsed flash pyrolysis of 2-ethynyl-1,1,1-trimethyldisilane (**1**) that led to the matrix-isolation of **2** and three other C_2H_2Si isomers[3] for the first time.

Based on our knowledge about these species it was tempting to use the Si/acetylene system to refine our evaporation techniques[4]. In accordance with the theoretical predictions **2** is indeed the primary product after codeposition of atomic silicon and acetylene in an argon matrix (Figure 1). Obviously, addition of the silicon atom to the π system is preferred compared to the formation of insertion products. The photochemical interconversion of **2**[3] into the other C_2H_2Si isomers **3**−**6** could be reproduced.

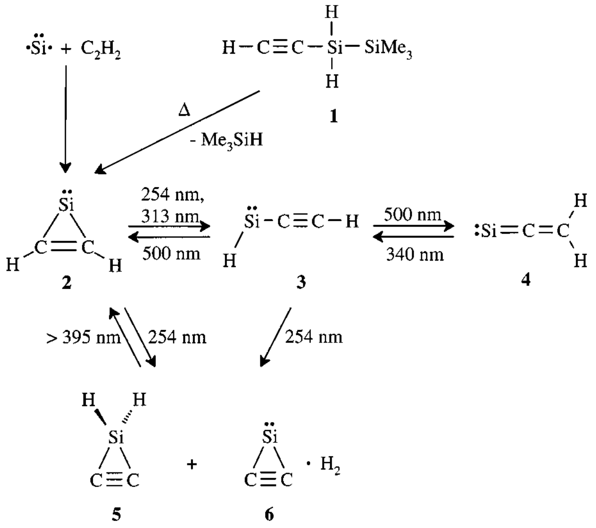
Interestingly, silacyclopropene (**7**)[5], a C_2H_4Si (two additional H atoms) species, can be observed after the cocondensation of atomic silicon and acetylene as well. The formation of **7** can be explained by addition of SiH_2 to the π system of acetylene. SiH_2 is formed as a byproduct in almost every cocondensation experiment; it is most likely emerging from reaction of the silicon atoms with hydrogen impurities contained in the metal surfaces of the apparatus. The reaction of SiH_2 and acetylene has been examined both theoretically and experimentally. Ab initio calculations reveal that this reaction proceeds without a barrier[6], and according to kinetic measurements its rate constant is in-

Figure 1. Matrix IR spectrum (Ar, 10 K) after codeposition of atomic silicon and a gaseous mixture of hydrogen, acetylene, and argon (1:12.5:1000)

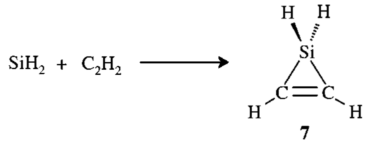


[◇] Part 27: Ref.[4a].

1434−193X/98/0707−1313 $ 17.50+.50/0



deed close to the gas kinetic maximum[7]. Hence, the observation of **7** in these experiments is intelligible.



The amount of **7** formed is about 15% of that of silacyclopropenylidene (**2**)[8]. It can be increased to about one third by adding molecular hydrogen (1−10 mbar) to the acetylene/argon mixture.

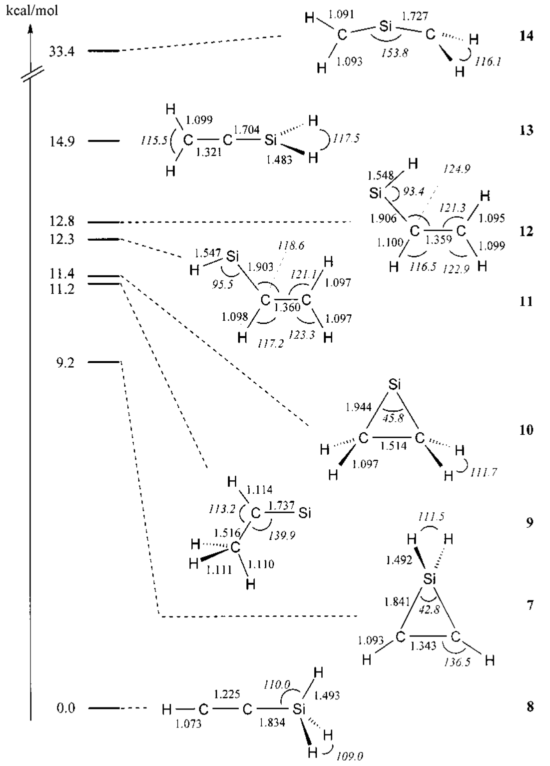
Reaction of Silicon Atoms with Ethylene

Scheme 1 shows the relative energies of eight C_2H_4Si singlet isomers (**7**−**14**) as calculated with the density functional method BLYP/6-31G**[9]. It is noteworthy that seven of these isomers lie within a very close energetic range, even ethylidenesilylene (**9**) and 1-silaallene (**13**), which contain a carbon-silicon double bond, belong to this group. Only 2-silaallene (**14**), containing two carbon−silicon double bonds, is of fairly high energy. The calculations predict for **14** a CSiC bond angle of 153.8°, whereas the linear structure of **14** is no minimum at both the MP2 and BLYP levels of theory.

Apart from silylacetylene (**8**), the global minimum of this potential energy surface, the only C_2H_4Si isomer, which could be unequivocally matrix-isolated after vacuum flash pyrolysis of 1,1,1-trimethyl-2-vinyldisilane (**15**)[5], was silacyclopropene (**7**). Of the other isomers, only substituted derivatives are known, such as the vinyl-substituted silylenes that have been isolated in organic matrices by Sakurai et al.[10] or a highly substituted, air-stable 1-silaallene synthesized by West et al.[11]. Other 1-silaallenes[12], as well as the unsubstituted 2-silaallene (**14**)[13], have been claimed to be intermediates in various pyrolysis or photolysis experiments.

Similar to the C_2H_2Si system, the above mentioned UMP2(DZP) calculations by Handy et al.[1] let us expect a silacyclopropylidene-like C_2H_4Si triplet structure, which can be formed without a barrier from ethylene and atomic silicon. Hence, it was of interest to examine the aptitude of cocondensed silicon atoms and ethylene as an entry to C_2H_4Si isomers, especially since the analogous reaction with acetylene was so successful.

Scheme 1. Calculated (BLYP/6-31G**) relative energies [kcal mol^{-1}] (corrected by zero point vibrational energies) of eight singlet C_2H_4Si isomers



Apart from the usual byproducts[4] and ethylene, the IR spectrum after codeposition of silicon atoms and ethylene indeed shows absorptions, which − according to our BLYP calculations − can be assigned to 1-silacyclopropylidene (**10**, Table 1). There is no Si−H vibration observable, but an intense band at 593 cm^{-1} for the ring deformation vibration. In addition, this assignment can be corroborated by the analogy to the reaction of atomic silicon with acetylene, which leads to the formation of the corresponding cyclic silylene **2** instead of an insertion product. Upon irradiation of **10** with light of wavelengths >395 nm, ring opening occurs under breakage of a Si−C bond. A simultaneous hydrogen shift from a carbon to the silicon atom[14] leads to the formation of vinylsilylene (**11**), a previously unknown C_2H_4Si isomer, which shows an intense absorption for the Si−H vibration at 1979 cm^{-1} (Table 2, Figure 2). A careful comparison of experimental and calculated IR spectra and a consideration of the most probable atomic migrations within the isomerization of **10** into **11** suggest that the conformation in **11** is *anti* with regard to the Si−C bond. The *syn* conformer **12** is not observed, neither as a photoproduct of **10** nor upon irradiation of **11**. The obser-

Figure 2. Difference IR spectrum (Ar matrix, 12 K) of the photoreaction (λ >395 nm) **10** $\rightarrow$ **11**

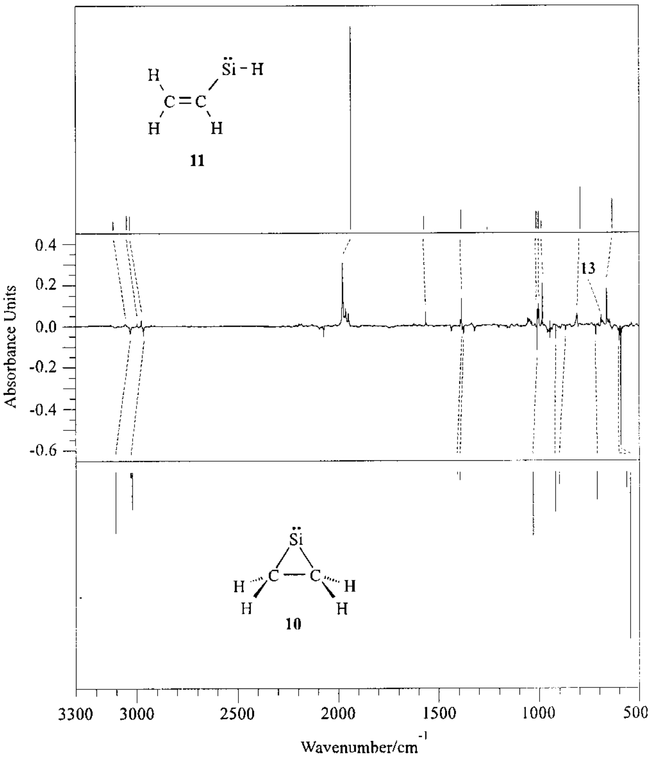


Table 1. Calculated (BLYP/6-31G**, C_{2v} symmetry, absolute intensities [km mol^{-1}] in parentheses) and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm^{-1}] of silacyclopropylidene (**10**)

		mode	$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{obs.}$
ν_8	a_2	CH_2 def	419.9(0)	–
ν_{15}	b_2	ring def	546.4 (47)	592.1 (100)
ν_5	a_1	ring def	562.6 (5)	601.4 (12)
ν_{11}	b_1	CH_2 def	647.1 (<1)	–
ν_{10}	b_1	CH_2 def	712.0 (8)	719.4 (6)
ν_4	a_1	CH_2 def	902.2 (4)	869.6 (4)
ν_{14}	b_2	CH_2 def	920.1 (11)	919.4 (10)
ν_3	a_1	CC str	1029.9 (18)	1011.9 (20)
ν_7	a_2	CH_2 def	1184.2 (0)	–
ν_{13}	b_2	CH_2 def	1394.4 (2)	1376.7 (7)
ν_2	a_1	CH_2 def	1407.6 (1)	1417.1 (3)
$2\nu_{15}+\nu_{14}$				2073.5
ν_{12}	b_2	CH str	3022.3 (11)	2966.3 (11)
ν_1	a_1	CH str	3027.9 (2)	–
ν_6	a_2	CH str	3080.3 (0)	–
ν_9	b_1	CH str	3102.4 (17)	3032.0 (23)

vation of **11** as the first photoproduct is another analogy to the C_2H_2Si system, where the cyclic primary product opens under breakage of a Si−C bond to ethynylsilylene (**3**) upon irradiation. The alternative cleavage of the C−C bond in **10** would lead to the energetically unfavoured 2-silaallene (**14**).

Prolonged irradiation of **11** with light of wavelengths >395 nm leads to a decrease of its IR absorptions and gives rise to many new IR bands that can be assigned to two different C_2H_4Si species. This photoreaction can be accelerated by using light of shorter wavelengths (> 310 nm). One of the products is silacyclopropene (**7**), formed by insertion of the silylenic centre into an adjacent C−H bond, the reaction that had made possible the observation of **7** in an argon matrix in our earlier study[5]. However, the IR absorptions of **7** observed here are slightly shifted from those observed upon vacuum flash pyrolysis of 1,1,1-trimethyl-2-vinyldisilane (**15**), presumably because of different surroundings of **7** in its respective matrix cage.

The other C_2H_4Si isomer concomitantly formed upon irradiation of **11** with light of wavelengths >395 nm is perhaps the unsubstituted 1-silaallene (**13**) (Table 3), which to the best of our knowledge was not known yet. Unfortunately, both the Si−H and the C−H stretching vibrations of **13** are calculated to lie in a range, where other reaction products or byproducts such as **7**, SiH_4 or C_2H_4 also show their corresponding absorptions. Thus the assignment of these bands to **13** is still speculative.

Irradiation of **7** and **13** with light of wavelength 254 nm leads to the formation of silylacetylene (**8**), the global minimum of the C_2H_4Si hypersurface, which is photostable. The interconversion of **13** into **8** is several times faster than that of **7**. This fact helps to distinguish the IR absorptions of these two species. But again, the very intense IR bands of **8** lie very close to those of **13** so that its Si−H and the C−H stretching vibrations are covered almost completely. Nevertheless, the identification of **13** can be supported by the fact that it fits well in a series of C_2H_4Si molecules, which show a successive migration of hydrogen atoms from carbon to silicon (note: the silicon atoms of **10**, **11**, **13**, and **8** bear 0, 1, 2, and 3 hydrogen atoms, respectively).

The different rates of the interconversions of **7** and **13** into **8** may be understood by considering the two reaction pathways. The isomerization **13** $\rightarrow$ **8** requires almost no geometrical change, but only a 1,3 hydrogen shift from carbon to silicon, and hence can be expected to be relatively fast. On the other hand **7** is probably not interconverted directly into **8**, but via silylene **11**, which then isomerizes to **13**, the direct precursor of **8**. This mechanism can be derived from the intermediate reoccurrence of the IR absorptions of **11** (about 10% of the intensity observed after irradiation of **10)** upon photochemical exitation of **7** with 254 nm light. The most intense band of **11** is found at 1979.4 cm^{-1} (Table 2). In this context it should be pointed out, that irradiation of **13**, which was generated separately by vacuum flash pyrolysis of 1,1,1-trimethyl-2-vinyldisilane (**15**)[5], led to the intermediate observation of a weak absorption at 1983 cm^{-1}, which may also be assigned to the Si-H stretching vibration of **11**. The shift of 3.6 cm^{-1} is again caused by the different precursor and is paralleled by similar shifts in the case of silacyclopropene (**7**) (see above).

Addendum

Two additional points are worth mentioning. First, analogous to the formation of silacyclopropene (**7**) from SiH_2 (originating from the Si atoms and hydrogen adsorbed on the metal surface) and acetylene, SiH_2 should also be able to react with ethylene yielding silacyclopropane (**16**), the corresponding cyclic addition product. Again, ab initio calculations reveal the absence of a barrier for this reaction[15]

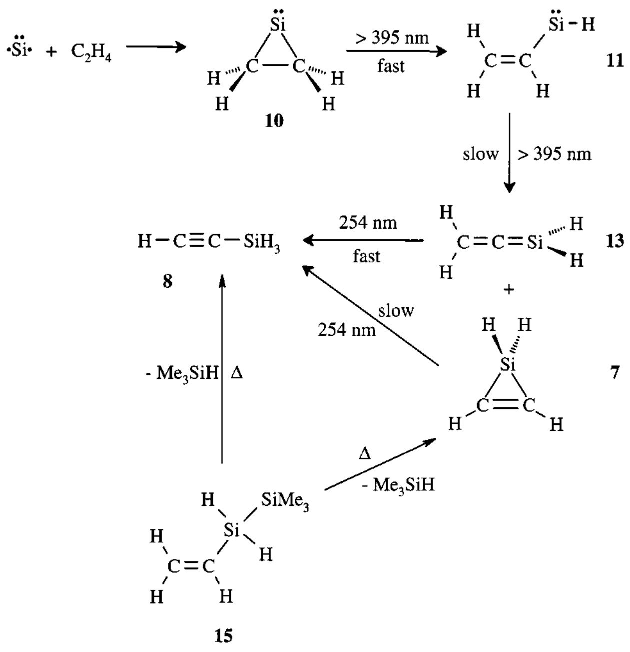
Table 2. Calculated (BLYP/6-31G**, C_S symmetry, absolute intensities [km mol^{-1}] in parentheses) and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm^{-1}] of *s-trans*-vinylsilylene (**11**) and *s-cis*-vinylsilylene (**12**)

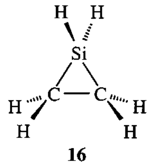
		mode	$\tilde{\nu}_{calc.}$ (**11**)		$\tilde{\nu}_{obs.}$		$\tilde{\nu}_{calc.}$ (**12**)	
ν_{15}	a''	HSiC/CCH def oop	140.4	(1)	–		122.3	(1)
ν_{11}	a'	CCSi def ip	281.0	(<1)	–		323.8	(1)
ν_{14}	a''	CCSi def oop	468.6	(2)	–		484.5	(<1)
ν_{10}	a'	HSiC/SiCC def ip	636.6	(48)	665.2	(14)	623.6	(66)
ν_9	a'	SiH/CH_2 def	797.4	(66)	812.7	(13)	813.1	(41)
ν_{13}	a''	CH_2 def oop	990.5	(14)	985.2	(10)	992.7	(11)
ν_8	a'	CH_2 def ip	1004.4	(29)	1004.8	(3)	1014.4	(11)
ν_{12}	a''	CH def oop	1014.9	(29)	1009.3	(7)	1020.3	(25)
ν_7	a'	CH def ip	1259.4	(4)	–		1271.3	(1)
ν_6	a'	CH_2 def ip	1390.2	(31)	1388.2	(15)	1396.8	(44)
ν_5	a'	CC str/CH_2 def ip	1574.1	(22)	1566.9	(4)	1575.5	(62)
ν_4	a'	SiH str	1937.8	(319)	1979.4	(100)	1925.0	(272)
ν_3	a'	CH str	3032.3	(22)	2976.5	(3)	3021.9	(24)
ν_2	a'	CH str	3048.1	(22)	2997.0	(2)	3038.1	(41)
ν_1	a'	CH_2 str	3114.8	(16)	3056.1	(3)	3123.1	(15)

Table 3. Calculated (BLYP/6-31G**, C_{2v} symmetry, absolute intensities [km mol^{-1}] in parentheses) and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm^{-1}] of 1-silaallene (**13**)

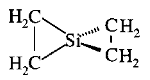
		mode	$\tilde{\nu}_{calc.}$		$\tilde{\nu}_{obs.}$
ν_{11}	b_1	CCSi def/SiH_2 def	80.8	(4)	–
ν_{15}	b_2	CCSi def	254.3	(3)	–
ν_{10}	b_1	CCSi def	359.6	(5)	–
ν_7	a_2	SiH_2/CH_2 def (rot)	647.9	(0)	–
ν_{14}	b_2	$CSiH_2$ def	649.8	(59)	656.2 (100)
ν_6	a_1	SiC str	746.9	(<1)	–
ν_{13}	b_2	CH_2 def oop	903.6	(36)	917.6 (98)
ν_5	a_1	SiH_2 def ip	918.8	(68)	930.3 (84)
ν_9	b_1	CH_2/CCSi def	983.8	(<1)	–
ν_4	a_1	CH_2 def ip	1407.2	(2)	1371.0 (4)
ν_3	a_1	CC str/CH_2 def	1757.8	(2)	–
ν_2	a_1	SiH str	2225.1	(31)	2205.9 (–)[a]
ν_{12}	b_2	SiH str	2250.9	(83)	2221.6 (–)[a]
ν_1	a_1	CH str	3007.6	(25)	3008.2 (–)[a]
ν_8	b_1	CH str	3065.6	(7)	3069.1 (–)[a]

[a] Bands are partially covered by those of other products, see text.





16



17

(as with silicon atoms; see above), and experimental kinetic studies result in a rate constant close to the collisional maximum[7]. However, silacyclopropane (**16**) could not be observed after codeposition of silicon atoms and ethylene. Nevertheless, the presence of **16** cannot be excluded completely, for its characteristic IR absorptions are calculated to lie close to those of the above mentioned C_2H_4Si isomers or reaction byproducts and to be very weak. Thus it may be difficult to observe **16** at all.

Second, the Si/ethylene system was also taken as a test for the concentration dependence of the cocondensation reactions. The ethylene/argon ratio was varied from 1:1000 up to 1:0, i. e. pure ethylene. For ratios up to 1:10, the species described above can be observed and interconverted. If the concentration of ethylene in the gaseous mixture is further increased, or if atomic silicon is cocondensed with pure ethylene, the bands of **10** are successively replaced by new absorptions. One could well assume that at these high concentration of ethylene the addition reaction of the silicon atoms takes place twice, thus leading to the formation of 3-sila[2,2]spiropentane (**17**). Absorptions at 655.2, 679.8, 742.3, and 845.8 cm^{-1} are close to the calculated (BLYP/6-31G**) values for **17** (657.4, 680.1, 726.8, and 858.9 cm^{-1}). But this assignment has to be made very cautiously, since all IR bands are very broad because of the high ethylene concentrations, resulting in rather poor spectra.

Conclusion

Silicon atoms react in an argon matrix at 10 K with acetylene to silacyclopropenylidene (**2**) and with ethylene to silacyclopropylidene (**10**). Upon subsequent irradiation the adducts **2** and **10** undergo ring opening reactions. For instance, vinylsilylene (**11**) and 1-silaallene (**13**) could be generated by photoisomerization of **10** for the first time.

Support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental Section

Equipment Used for Matrix Isolation and Photolyses: See Ref.[16].

General: See Ref.[16].

---

[1] M. D. Su, R. D. Amos, N. C. Handy, *J. Am. Chem. Soc.* **1990**, *112*, 1499−1504.

[2] D. Husain, P. E. Norris, *J. Chem. Soc. Faraday Trans. 2* **1978**, *74*, 106−114.

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

[4] [4a]G. Maier, H. P. Reisenauer, H. Egenolf, J. Glatthaar, *Eur. J. Org. Chem.*, **1998**, 1307−1311, preceding paper. − [4b] Preliminary report: G. Maier, H. P. Reisenauer, H. Egenolf, *Organosilicon Chemistry III − From Molecules to Materials*, (Eds. N. Auner, J. Weis), VCH, Weinheim **1998**, pp 31 − 35.

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

[6] J. A. Boatz, M. S. Gordon, L. R. Sita, *J. Phys. Chem.* **1990**, *94*, 5488−5493.

[7] J. O. Chu, D. B. Beach, J. M. Jasinski, *J. Phys. Chem.* **1987**, *91*, 5340−5343.

[8] The product ratio is obtained by integrating the most intense IR bands of **2** and **7**, respectively, taking into account the ab initio calculated absolute intensities of these bands.

[9] *GAUSSIAN 94*, *Revision B*. 1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomberts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, Gaussian, Inc. Pittsburgh, PA, **1995**.

[10] M. Kira, T. Maruyama, H. Sakurai, *Tetrahedron Lett.* **1992**, *33* 243−246.

[11] G. E. Miracle, J. L. Ball, D. R. Powell, R. West, *Am. Chem. Soc.* **1993**, *115*, 11598−11599.

[12] [12a] M. Ishikawa, Y. Yuzuhira, T. Horio, A. Kunai, *Organomet. Chem.* **1995**, *402*, C20−C22. − [12b] M. Ishikawa, D. Kovar, T. Fuchikama, K. Nishimura, M. Kumada, T. Higuchi, S. Miyamoto, *J. Am. Chem. Soc.* **1981**, *103*, 2324−2328. − [12c] M.Ishikawa, J. Ohshita,, Y. Ito, *Organomet.* **1986**, *5*, 1518−1519.

[13] [13a] G. Bertrand, G. Manuel, P. Mazerolles, *Tetrahedron* **1978**, *34*, 1951−1956. − [13b] M. Urbanova, E. A. Volnina. L. E. Gusel'nikov, Z. Bastl, J. Pola, *J. Organomet. Chem.* **1996**, *509*, 73−76.

[14] For a similar reaction in the case of silacyclopropenylidene compare: G. Maier, H. P. Reisenauer, J. Jung, H. Pacl, H. Egenolf, *Eur. J. Org. Chem.* **1998**, 1297−1305, Part 26 of this series.

[15] D. Sengupta, M. T. Nguyen, *Mol. Phys.* **1996**, *89*, 1567−1576.

[16] G. Maier, H. P. Reisenauer, A. Meudt, *Eur. J. Org. Chem.* **1998**, 1285−1290, Part 24 of this series.

[98046]