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Photochemistry of Bis(diazomethyl)silanes: A Novel Approach to 1*H*-Silirenes

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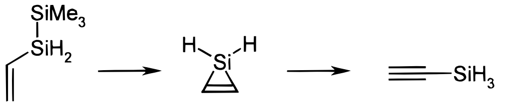
A novel synthesis of silirenes, starting from bis(diazomethyl)silanes **6**, is described. The diazo compounds **6** were obtained by treatment of the corresponding triflates with diazomethane. Irradiation of alkyl- or phenyl-substituted **6** in argon matrices or organic glasses at cryogenic temperatures produced 1,1-disubstituted silirenes **7** in high yields. The silirenes were characterized by comparison of the experimental IR spectra with DFT calculations and by their subsequent photochemistry. 1,1-Diphenylsilirene **7c** was stable enough in solution below −50 °C to be characterized by ^{1}H and ^{13}C NMR spectroscopy. UV irradiation of silirenes **7** results in ring-opening and formation of ethynylsilanes.

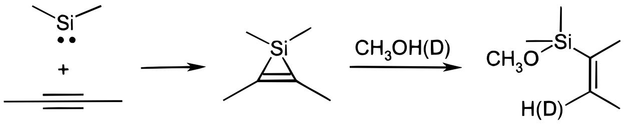
Introduction

Silirenes (silacyclopropenes) are reactive molecules that have been utilized as building blocks for the synthesis of organosilicon compounds.[1,2] Maier et al. synthesized the highly labile parent silirene **1** by flash vacuum pyrolysis of 1,1,1-trimethyl-2-vinyldisilane with subsequent trapping of the products in argon at 10 K.[3]



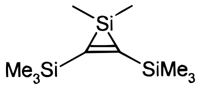
1

A general route to silirenes is the reaction of in-situ generated silylenes with substituted acetylenes.[1,4−8] The reaction of dimethylsilylene with 2-butyne was used by Conlin and Gaspar to synthesize tetramethylsilirene **2**, which at room temperature in the absence of air was stable for many weeks.[4] Methanolysis of **2** resulted in the cleavage of one of the SiC bonds and formation of (*E*)-1,2-(dimethylvinyl)dimethylmethoxysilane.



2

Seyferth et al. independently synthesized silirene **3**, which in benzene solution at 70−75 °C has a half-life of about 60 h.[5] Thus, substituted silirenes are thermally fairly stable, although highly reactive.[7] Belzner and Ihmels used cyclotrisilanes as a source of silylenes and were able to obtain silirenes **4** bearing one vinylic hydrogen atom.[9] The sterically highly congested silirene **5** is stable in the solid state and could be characterized by X-ray crystal structure analysis.[10]



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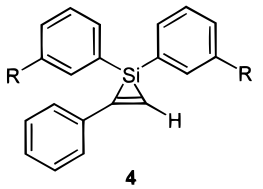

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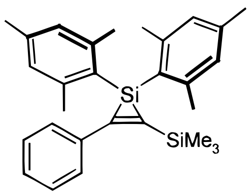
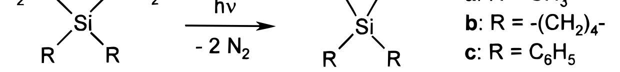


5

In 1994 we communicated on the matrix isolation and spectroscopic characterization of 1,1-dimethyl-1*H*-silirene **7a** (R = CH_3), the first silirene unsubstituted at the double bond.[11] This silirene was synthesized by a novel synthetic method via 2-sila-1,3-bis(diazo)propane **6a**. Here we report on the photochemistry of a series of α,α′-silylbis(diazomethyl)compounds **6**, which provides a general entry to silirenes of type **7**.



6 **7**

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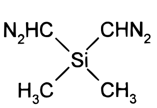
10.1021/om990120j CCC: $18.00

Table 1. Some Characteristic Spectroscopic Data of Silyldiazo Compounds 6

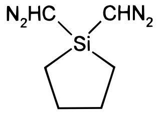
	^{1}H NMR (δ)	^{13}C NMR (δ)	IR (cm^{-1})
6a	2.72	19.8	2082.5 2073.3
6b	2.7	20.71	2086.4 2083.3 2077.7 2071.8
6c	3.18	18.79	2089.4 2081.9 2075.3
6d	2.67	16.00	2070.9 2051.2

Results and Discussion

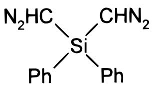
Synthesis of α,α′-Silylbisdiazo Compounds. The silylbisdiazo compounds **6** were synthesized by reaction of the corresponding silylbistriflates **8** with diazomethane in diethyl ether at low temperatures (−50 to −20 °C)[12,13] and purified by preparative gas chromatography as yellow liquids (Table 1). All compounds **6** were stable at −78 °C, but slowly decomposed at room temperature. The aliphatic diazo compounds **6a** and **6b** are considerably less stable than **6c** and **6d** with phenyl and trimethylsilyl groups attached to the silicon atom.



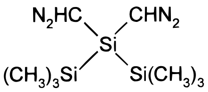
6a



6b

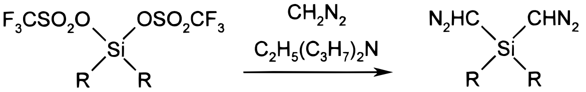


6c



6d

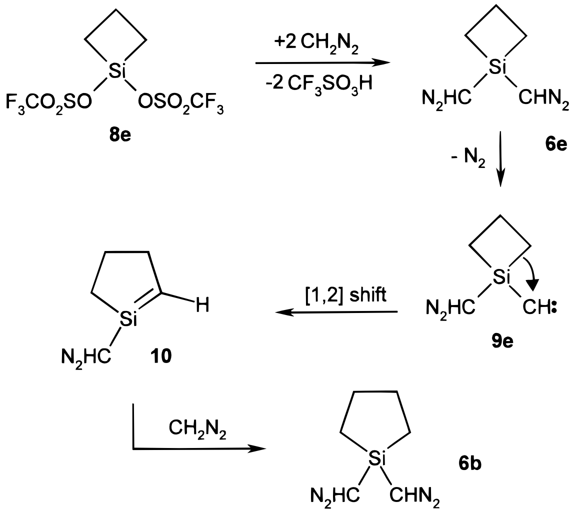
Bis(diazomethyl)silacyclopentane **6b** was synthesized in 32% yield by treating bistriflate **8b** with diazomethane. Other diazo compounds, and in particular bis(diazomethyl)silacyclobutane, were not formed. The formation of **6b** can be rationalized by assuming that silacyclobutane **6e** rapidly loses nitrogen to form carbene **9e**, which subsequently rearranges to silene **10** (Scheme 1). The silene is trapped by diazomethane to finally give **6b**. A similar ring-enlargement of silacyclobutyldiazo compounds was described by Oku et al.[14]

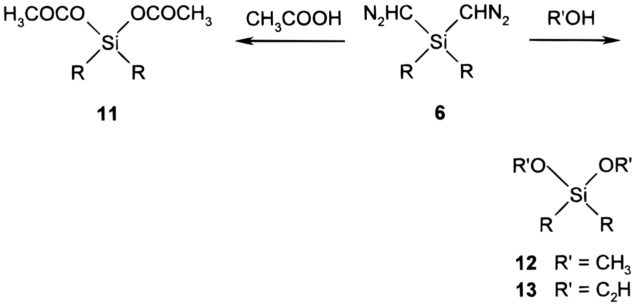


8 **6**

The yellow solutions of silylbisdiazomethyl compounds **6** are rapidly decolorized under evolution of nitrogen when exposed to light or treated with acidic compounds. The major products of the reactions of **6** with acetic acid are methyl acetate and silanediyl acetates **11**, while the reaction with alcohols (ethanol, methanol) at room temperature slowly leads to dialkoxysilanes **12** and **13**. The reaction of **6** with protic compounds under cleavage of a SiC bond is characteristic of silyldiazo compounds.[15]

Scheme 1





12 R' = CH$_3$
13 R' = C$_2$H$_5$

Photochemistry of 2-Sila-1,3-bis(diazo)propane 6a. The primary step in the photolysis of bisdiazomethane **6a** is the loss of one N$_2$ molecule and formation of diazocarbene **9a**. Since diazomethylsilanes are known to photochemically rearrange to the corresponding diazirines, species such as **23a**, **24a**, and **25a** also have to be considered (Scheme 2). For the sake of simplicity we only discuss the diazo compounds, as long as there is no direct evidence for diazirines. Carbene **9a** can now rearrange to silene **15a** or to silirane **20** or can lose a second N$_2$ molecule to give biscarbene **14a**. From biscarbene **14a** there are pathways to silirene **7a** (direct coupling of the carbene centers), silene **16** ([1,2]-methyl shift), silaallene **17a** (two subsequent [1,2]-methyl shifts), silirane **21** (insertion into a CH bond), or 1-silaspiropentane **22** (two subsequent CH insertions). However, the formation of the intermediate **7a**, **16**, **17a**, **21**, or **22** does not prove the formation of **14a**, since all of these species can be formed in subsequent reaction steps, avoiding the formation of the energetically unfavorable biscarbene.

All of the intermediates containing a carbene center, a Si═C bond, or a three-membered ring are expected to be reactive toward ethanol. We thus investigated the photochemistry of **6a** in C$_2$H$_5$OH and C$_2$H$_5$OD at 273 K, 170 K (solution), and 77 K (glass), respectively (Table 2). The irradiation ($\lambda \geq 305$ nm) yielded four major products, which were isolated by preparative GC and

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[11] Trommer, M.; Sander, W.; Marquard, C. *Angew. Chem.* **1994**, *106*, 816; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 766.

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[13] Fronda, A.; Maas, G. *J. Organomet. Chem.* **1990**, *391*, 289.

[14] Oku, A.; Miki, T.; Ose, Y. *J. Phys. Org. Chem.* **1996**, *9*, 619.

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Scheme 2

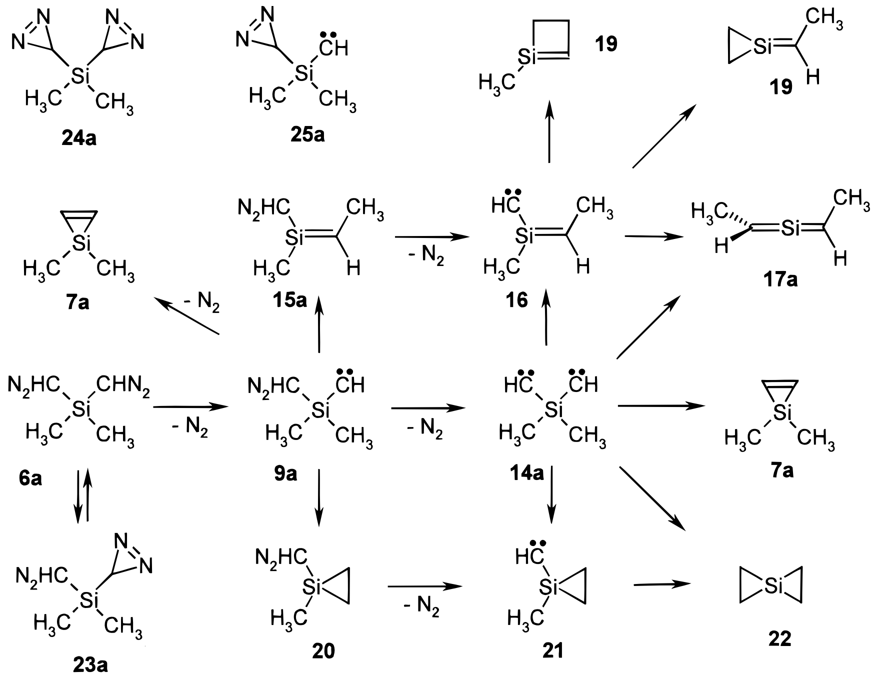
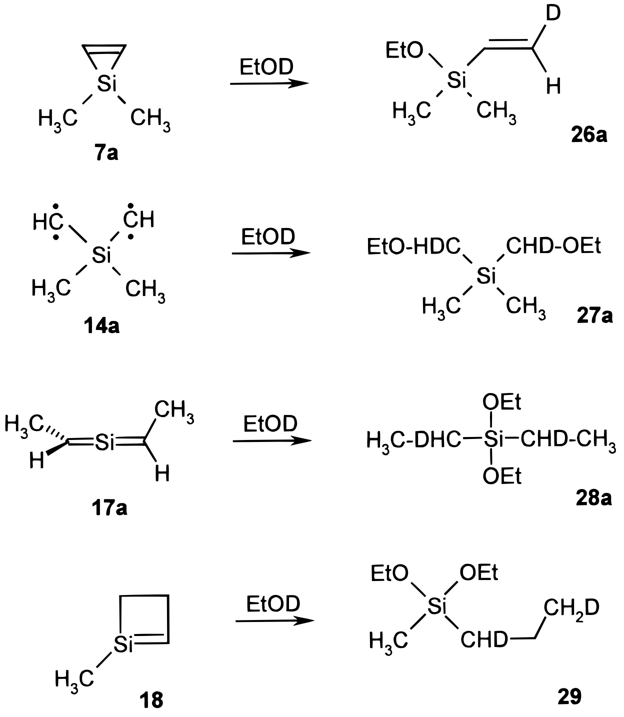


Table 2. Products Formed in the Photolysis of 6a in C_2H_5OH and C_2H_5OD at Various Temperatures

		yield		
formal precursor	trapping product	77 K	170 K	273 K
7a	**26a**	50%	47%	33%
14a	**27a**	13%	5%	3%
17a	**28a**	24%	26%	30%
18	**29**	13%	15%	19%
30a	**31a**		6%	13%

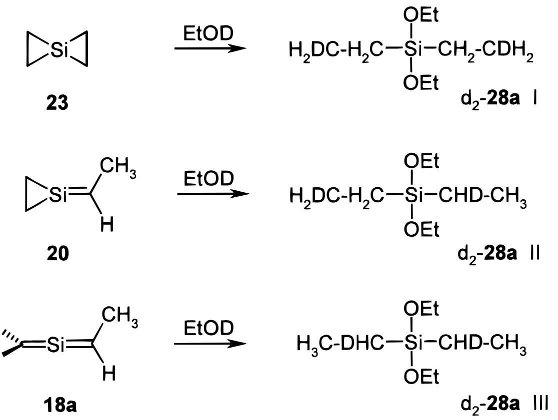
characterized by NMR and mass spectroscopy: ethenylethoxydimethylsilane **26a**, bis(ethoxymethyl)dimethylsilane **27a**, diethoxydiethylsilane **28a**, and diethoxymethylpropylsilane **29** (total yield > 95%, Table 2).



At all temperatures the main product of the photolysis is vinylsilane **26a**, the trapping product of silirene **7a**. Irradiation in C_2H_5OD results in deuterium labeling of the vinyl group. Increasing the photolysis temperature from 77 K to 0 °C results in a decrease of the yield of **26a** from 50% to 33%. Similar cleavages of Si−C bonds under formation of ethenylsilanes have been previously used to identify silirenes.[4,7]

Silane **27a** is the formal product of the addition of ethanol to biscarbene **14a**, although most likely nitrogen is released stepwise and the resulting monocarbene **9a** is trapped by ethanol. This primary trapping product loses the second N_2 molecule to give another carbene, which is trapped by ethanol. The yield depends much on the temperature and decreases from 13% in the ethanol glass at 77 K to only 3% at 0 °C (Table 2). With C_2H_5OD one deuterium atom is incorporated in each of the methylene groups adjacent to the Si atom.

The formation of diethoxydiethylsilane **28a** with two ethyl substituents at silicon indicates a major rearrangement in the precursor molecule with the formation of two new C−C bonds. The formal precursors of **28a** are 1-silaspiropentane **22**, 2-sila-2-ethylidenecyclopropane **19**, or dimethyl-2-silaallene **17a** (Table 2, Scheme 2), which are produced by [1,2] migration of the methyl groups to the carbene centers (**17a**), by insertion of the carbene centers into the methyl groups (**22**), or by a combination of both (**19**). More likely is a stepwise reaction with **16** or **21** as intermediates, which avoids the formation of these high-energy species. By using C_2H_5OD, the deuterium was found exclusively in the methylene groups of the two ethyl groups (isotopomer d_2-**28a** III) and not in the methyl groups (isotopomers I or II). This clearly demonstrates that Si=C bonds were trapped and not silirane rings (**22** or **19**). Trapping of a silirane ring system should result in ethyl groups labeled at the terminal methyl groups (isotopomer I or II).



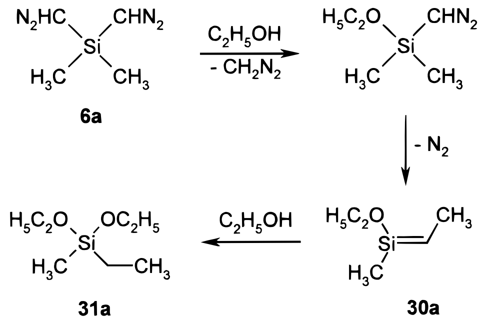
An interesting trapping product is the propylsilane **29**, which is produced in up to 19% yield (at 0 °C). The formation of a propyl substituent requires the formation of bonds between three carbon atoms not connected in **6a**! The best precursor for **29** is 1-methylsilacyclobutene **18**, which is formed by insertion of the carbene center of **16** into the ethylidene methyl group (Scheme 2).

As a byproduct of the photolysis in ethanol solution—but not in the glass at 77 K—diethoxymethylethylsilane **31a** was formed in up to 13% yield. Obviously, the partial solvolysis of **6a** results in the formation of silene **30a**, which is subsequently trapped by ethanol (Scheme 3). As expected, the yield of **31a** increases if the solution of **6a** in ethanol is allowed to stand in the dark prior to irradiation.

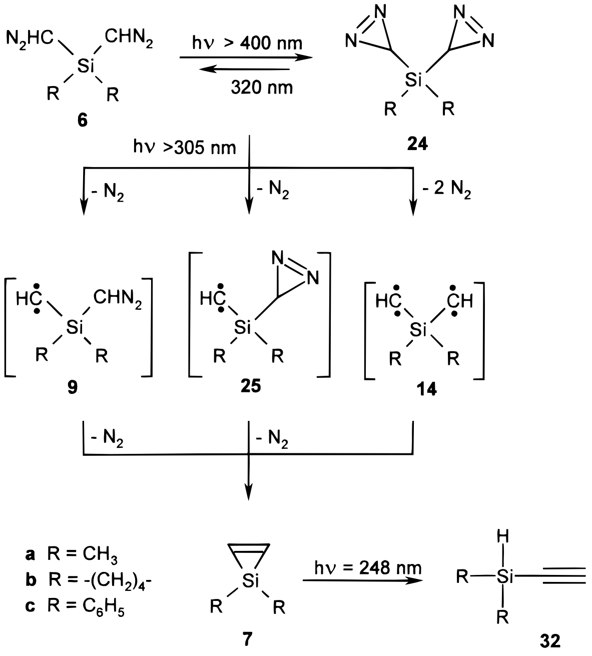
The photochemistry of diazo compound **6a** was also investigated under the conditions of matrix isolation, which allows the direct characterization of some of the reactive intermediates postulated in the trapping experiments. Diazo compound **6a** exhibits very strong IR absorptions at 2082.5 and 2073.3 cm^{-1}, characteristic of diazo CNN stretching vibrations. Visible light irradiation ($\lambda > 405$ nm) results in the disappearance of the IR absorptions of **6a** and formation of a diazirine with the N═N stretching vibrations at 1642, 1639, and 1636 cm^{-1} (Scheme 4). The diazo–diazirine isomerization is partially reversible, and shorter wavelength irradiation recovers small amounts of a diazo compound, most likely **6a**. However, the IR data do not allow one to distinguish between a mixture of **6a** and bisdiazirine **24a** and diazodiazirine **23a**.

Irradiation of **6a** or **24a**/**23a** with $\lambda > 305$ nm rapidly results in the disappearance of these compounds and formation of a new compound with strong absorptions at 884.1 and 788.4 cm^{-1} (Table 3, Figure 1). By comparison with the IR spectrum calculated at the B3LYP/6-311G(d,p) level of theory the newly formed compound was readily assigned to silirene **7a**. Both band positions and relative intensities of the IR spectrum of **7a** are nicely reproduced at this level of theory. The 305 nm photochemistry of **6a** is very clean, and no byproduct could be identified in the IR spectrum. Short wavelength UV irradiation ($\lambda = 254$ nm) of **7a** results in the ring-opening and formation of (dimethyl)ethynylsilane **32**, which was identified by comparison with an authentic matrix-isolated sample.

Scheme 3



Scheme 4



Photochemistry of Bis(diazomethyl)silacyclopentane 6b. Irradiation of diazomethane **6b** in ethanol ($\lambda \geq 305$ nm) at 77 K yields three major products (total yield > 81%), which were characterized as ethenylethoxysilacyclopentane **26b**, bis(ethoxymethyl)silacyclopentane **27b**, and diethoxysilacyclopentane **12b** (Scheme 5). The main product (almost 60% in typical experiments) is diethoxysilane **12b**, formed by loss of both diazo groups in a thermal reaction with ethanol prior to irradiation. Apparently **6b** is much more sensitive toward ethanolysis than **6a,** and a considerable fraction of **6b** is lost before the irradiation begins.

Vinylsilane **26b** is obtained in 14% yield as the trapping product of cyclotetramethylene-1*H*-silirene **7b**. Photolysis of **6b** in C_2H_5OD leads to **26b** with one deuterium atom incorporated at the vinyl group. Bis(ethoxymethyl)silane **27b** (12% yield) is the formal trapping product of biscarbene **14b**. Trapping with C_2H_5OD results in the expected deuterium labeling of the methylene groups adjacent to the silicon atom.

Irradiation of **6b** with $\lambda \geq 305$ nm in an argon matrix at 10 K rapidly leads to the disappearance of the very strong IR absorptions at 2086.4, 2083.8, 2077.7, and 2071.8 cm^{-1}, characteristic of diazo CNN stretching vibrations, and formation of one major compound with strong absorptions at 841.1 and 702.5 cm^{-1}. By comparison of the experimental and DFT calculated (B3LYP/6-311G(d,p)) IR spectra the new compound is assigned to cyclotetramethylene-1*H*-silirene **7b** (Figure 2, Table 4).

Table 3. IR Spectroscopic Data of Dimethyl-1*H*-Silirene 7a

argon, 10 K				B3LYP/6-311G(d,p)		
ν [cm^{-1}]	I[a]	no.[b]	sym[c]	ν [cm^{-1}][d]	I[a]	assignment[c]
3023.1	9	33	A1	3168.8	13	sym. =C−H str.
2992.5	10	29	B2	3085.5	16	asym. C−H str.
2959.1	9	26	B1	3020.6	5	asym. C−H str.
1447.1	10	25	A1	1522.0	10	sym. C=C str.
1444.2	10	24	B2	1468.3	10	CH_3 def.
1438.1	12	23	A1	1465.3	5	CH_3 def.
1400.2	7	22	B1	1458.2	3	CH_3 def.
		21	A2	1454.9	0	CH_3 def.
1250.2	32	20	A1	1298.3	9	
1216.1	7	19	B1	1293.6	25	
1132.0	12					
1129.8	12	18	B2	1142.1	18	asym. H−C= bend.
1127.7	10					
		17	A2	985.4	0	sym. H−C= out of plane
991.6	10					
922.1	17	16	A1	936.4	17	sym. H−C= bend.
884.1	71	15	A1	900.8	81	
		14	B2	814.2	16	
788.4	100	13	B1	799.9	100	
784.9	31	12	A1	792.2	9	
		11	A2	761.4	0	
694.1	17	10	B1	697.9	13	asym. Si−C str.
691.1	21	9	B2	685.2	26	asym. Si−C str.
616.1	39	8	B1	626.0	49	asym. H−C= out of plane
613.7	28					

[a] Relative intensities, based on the most intense band (100%). [b] Number of vibrations according to the DFT calculation. [c] Symmetry and assignment of vibrations from the calculated spectrum. The assignment of the experimental and the calculated vibrations is based on the comparison of band position and relative intensities and is—particularly in the range of the C−H stretching vibrations—only tentative. [d] Calculated frequencies are not scaled (cf. Figure 1).

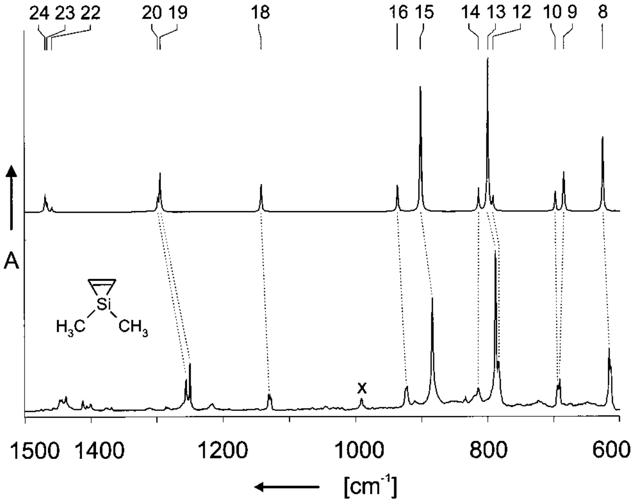


Figure 1. IR spectrum of dimethyl-1*H*-silirene **7a**, matrix-isolated in argon at 10 K (bottom) and ab initio-calculated at the B3LYP/6-311G(d,p) basis set (top). Tentative assignment based on the band position and band intensity. The calculated spectrum is not scaled, and a Lorentz band shape was simulated with a half-value width of 2 cm^{-1}. The bands labeled X are assigned to traces of remaining solvent.

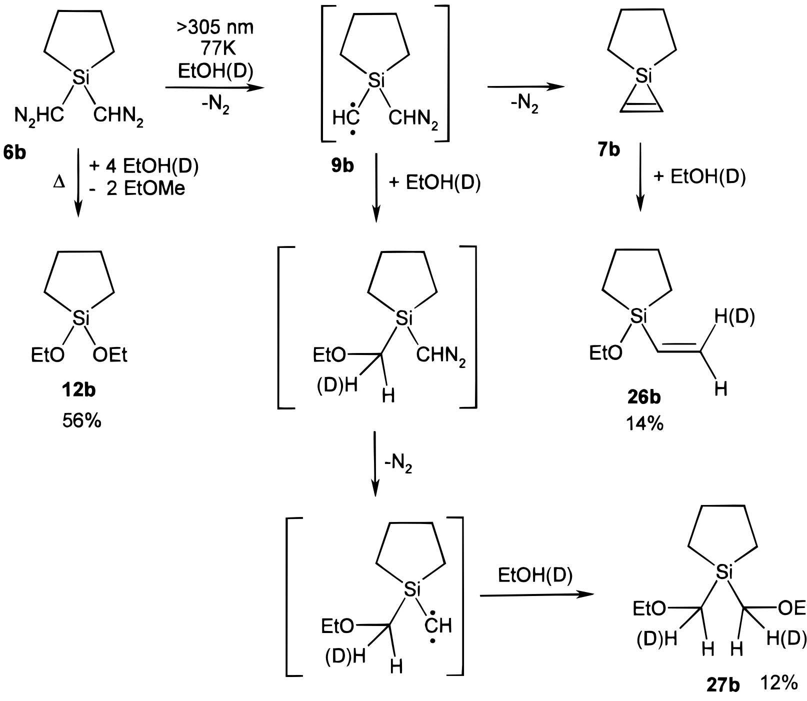
Visible light irradiation ($\lambda \geq 400$ nm) of **6b** produces a diazirine with the characteristic N=N stretching vibration at 1631 cm^{-1} [16] and only small amounts of silirene **7b**. UV irradiation ($\lambda \geq 305$ nm) of the diazirine mainly yields **7b**, but small amounts of a diazo compound are also formed. Since no CNN stretching vibrations are observed in the IR spectrum of the diazirine, we suggest that bisdiazirine **24b** rather than diazodiazirine **23b** is formed by the long-wavelength irradiation of **6b**. Prolonged UV irradiation of **7b** finally yields ethynylsilacyclopentane **32b**, which was characterized by comparison with an authentic matrix-isolated sample.

Photochemistry of Diphenylbis(diazomethyl)silane 6c. Irradiation ($\lambda \geq 305$ nm) of bisdiazomethane **6c** in ethanol at 77 K produces four major products in 94% total yield: ethenylethoxydiphenylsilane **26c**, bis(ethoxymethyl)diphenylsilane **27c**, diethoxydibenzylsilane **28c,** and diethoxybenzylphenylsilane **31c** (Scheme 6). The main product formed in up to 52% yield is ethenylsilane **26c**, the trapping product of diphenyl-1*H*-silirene **7c**. With C_2H_5OD as trapping reagent one deuterium atom is incorporated into the vinyl group. Bis(ethoxymethyl)silane **27c** is formed in 15% yield as the formal ethanol trapping product of biscarbene **14c**. With C_2H_5OD one deuterium atom is incorporated into each of the methylene groups, in accordance with the proposed mechanism. However, as discussed previously, a stepwise reaction is more plausible.

Dibenzylsilane **28c** is formed in 12% yield as the formal trapping product of 2-silaallene **17c**, again, most likely formed in a stepwise reaction without **17c** as an intermediate. Using C_2H_5OD as solvent results in the labeling of both benzylic positions with one deuterium each. Finally, as with the other bisdiazomethanes, **6c** slowly reacts with ethanol under loss of a diazomethyl group. This leads to diethoxysilane **31c** (up to 16% in a typical experiment) after irradiation of the glass. With C_2H_5OD the expected labeling pattern is obtained.

Silirene **7c** is stabilized by two phenyl groups, and in contrast to **7a** and **b** stable enough at −80 °C to be observed by NMR spectroscopy. The photolysis of **6c** was carried out in an evacuated quartz NMR tube using a 1:1 mixture of $CFCl_3$ and $C_2F_4Br_2$ as solvent, which forms an optically transparent glass at 77 K. A solution of **6c** in this Freon mixture was irradiated ($\lambda \geq 305$ nm) at 77 K for 2 h and subsequently warmed to −80 °C. From the NMR spectra recorded at this temperature a yield of **7c** of 21% was estimated. Silirene **7c** has a half-life of about 46 min at −50 °C in $CFCl_3/C_2F_4Br_2$ and rapidly decomposes at −30 °C. The assignment of NMR signals to **7c** is based on the thermal lability during warmup of the sample. The ^{1}H NMR spectrum of **7c** shows a singlet at $\delta = 8.62$, attributed to the vinylic hydrogen atoms, and a complex signal at $\delta = 7.21−7.50$, assigned to the phenyl hydrogen atoms. The ^{13}C NMR spectrum reveals a resonance at $\delta = 151.84$ of the olefinic carbon atoms and the expected four resonances ($\delta = 136.38, 131.69, 130.77, 128.34$) of the phenyl carbon atoms. The assignment of ^{1}H and ^{13}C resonances was confirmed by a C−H−COSY spectrum. The ^{1}H and ^{13}C chemical shifts of the silirene ring occur at an unusually low field, which is in accordance with previous reports,[4,5,9] and provide further evidence for the electron delocalization and π-bonding involving participation of the vacant silicon 3d orbitals.[5] When the irradiation is carried out in $CFCl_3$ solution at −100 or −80 °C, no silirene is detected in the NMR spectra even at −80 °C, although in $CFCl_3/C_2F_4Br_2$ **7c** is stable at this temper-

Scheme 5



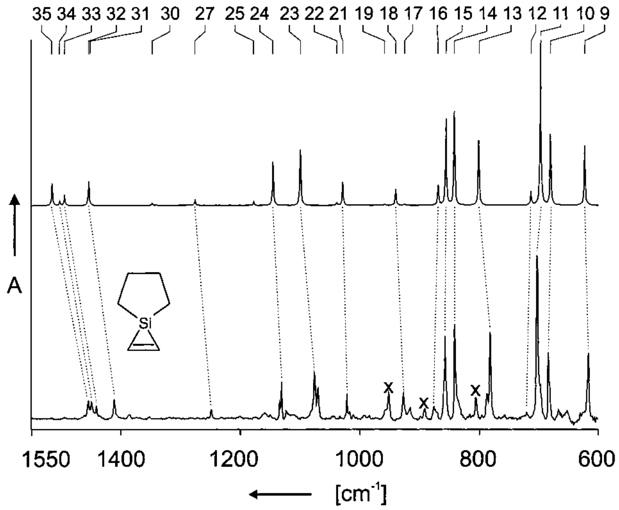


Figure 2. IR spectrum of cyclotetramethylene-1*H*-silirene **7b**, matrix-isolated in argon at 10 K (bottom) and ab initio-calculated at the B3LYP/6-311G(d,p) basis set (top). Tentative assignment is based on the band position and band intensity. The calculated spectrum is not scaled, and a Lorentz band shape was simulated with a half-value width of 2 cm^{-1}. The bands labeled X are assigned to traces of remaining solvent.

ature. Thus, the synthesis of **7c** requires the photolysis of **6c** in an organic glass.

UV photolysis ($\lambda \geq 305$ nm, Ar, 10 K) of matrix-isolated **6c** leads to the disappearance of the very strong IR absorptions at 2089.4, 2081.9, and 2075.3 cm^{-1}, characteristic of diazo CNN stretching vibrations, and formation of a new compound with strong absorptions at 814.8, 737.4, and 698.5 cm^{-1}, assigned to silirene **7c**. UV irradiation (248 nm, KrF Excimer-Laser) results in rearrangement to ethynylsilane **32c**, which was characterized by comparison with an authentic matrix-isolated sample.

Irradiation of **6c** with $\lambda \geq 400$ nm yields a diazirine (1631 and 959 cm^{-1}), which on 305 nm irradiation is converted to silirene **7c**. Again, a photostationary equilibrium between a diazo compound and a diazirine is observed; however, the spectroscopic data do not distinguish unequivocally between a mono- and bisdiazirine.

Photochemistry of 1,1,1,3,3,3-Hexamethyl-2,2-bis(diazo)trisilane 6d. The photochemical behavior of matrix-isolated bis(diazomethyl)trisilane **6d** turned out to be very complex. By changing the wavelength of the light source from the visible to the UV in small steps at least nine different products were observed. Presumably not only the elimination of nitrogen and rearrangements discussed above but also cleavage of Si–Si bonds and formation of radicals occur. We were not able to identify photoproducts unequivocally in this complex mixture.

When **6d** is irradiated ($\lambda \geq 400$ nm) in ethanol at 77 K, the photochemistry is much cleaner and two main products are identified: diazo compound **33** and diethoxysilane **28d** (Scheme 7). Compound **33** is most probably the ethanol trapping product of diazosilene **15d** formed after the release of only one nitrogen molecule from **6d** and subsequent [1,2] shift of a trimethylsilyl group. Prolonged irradiation results in the complete photolysis of **33** and formation of **28d** in 90% yield. This clearly demonstrates the stepwise formation of **28d**, the formal trapping product of silaallene **17d**.

Calculated Structures of Silirenes 7. Since the IR spectra of silirenes **7** are nicely reproduced by calculations at the B3LYP or MP2 level of theory, we expect that the geometric data are also well represented by these methods. This is confirmed by comparison of the calculated structures of silirenes **7a**–**7c** with X-ray crystal structures of silirenes kinetically stabilized by bulky substituents.[10,17–20] The C1C2 bond lengths (double bonds in the three-membered rings) in stable silirenes were determined to be 1.332–1.355 Å, and the CSiC bond angles in the three-membered rings, 43.1–43.7°.[17–20] Our calculations show C1C2 bond lengths of

Table 4. IR Spectroscopic Data of Cyclotetramethylene-1*H*-Silirene 7b

argon, 10 K				B3LYP/6-311G(d,p)		
ν [cm^{-1}]	I[a]	no.[b]	sym[c]	ν [cm^{-1}][d]	I[a]	assignment[c]
3039.4	9	45	A	3167.3	18	sym. =C−H str.
3020.6	8	44	B	3144.1	19	asym. =C−H str.
2967.5	7	43	B	3089.5	35	asym. C−H str.
		42	A	3089.1	1	sym. C−H str.
2954.8	67	41	B	3061.0	58	asym. C−H str.
2928.9	55	40	A	3056.4	58	sym. C−H str.
2918.2	10	39	A	3027.0	14	sym. C−H str.
2915.6	Schulter	38	B	3026.9	19	asym. C−H str.
2870.5	17	37	B	3013.7	41	asym. C−H str.
2860.3	40	36	A	3008.0	23	sym. C−H str.
1454.9	11	35	A	1515.8	14	sym. C=C str./ CH_2 scis.
1449.7	10	34	A	1502.7	3	sym. CH_2 scis.
1441.6	7	33	B	1494.6	7	asym. CH_2 scis.
1411.6	13	32	B	1454.7	15	asym. CH_2 scis.
1386.5	2	31	A	1453.6	1	sym. CH_2 scis.
1352.1	1	30	A	1347.8	1	
		29	B	1340.6	0	CH_2 wag.
		28	B	1283.0	0	CH_2 twist.
1248.7	4	27	A	1275.7	3	CH_2 twist./wag.
		26	A	1219.9	0	CH_2 twist./rock.
1160.0	6	25	B	1178.5	2	CH_2 wag.
1131.3	16	24	B	1146.3	27	asym. =C−H rock.
1076.2	46	23	A	1100.5	34	
		22	B	1038.9	2	CH_2 twist.
1021.7	11	21	A	1028.9	14	C−C str.
		20	A	987.6	0	=C−H wag.
		19	B	959.4	1	
926.8	11	18	A	939.9	10	sym. =C−H rock.
916.0	5	17	A	925.3	1	
875.9	12	16	B	869.0	12	
857.4	45	15	A	855.6	53	ring-breathing
841.4	50	14	A	841.7	57	
781.6	48	13	B	801.2	40	
720.5	2	12	A	712.7	9	CH_2 rock.
702.3	100	11	B	697.4	100	
683.6	33	10	B	679.7	43	
616.5	28	9	B	623.1	36	cis =C−H wag.

[a] Relative intensities, based on the most intense band (100%). [b] Number of vibrations according to the DFT calculation. [c] Symmetry and assignment of vibrations from the calculated spectrum. The assignment of the experimental and the calculated vibrations is based on the comparison of band position and relative intensities and is—particularly in the range of the C−H stretching vibrations—only tentative. [d] Calculated frequencies are not scaled (cf. Figure 2).

1.338 (**7a**) to 1.342 Å (**7b**) and 43.1° (**7a**) to 43.3° for the internal CSiC bond angles (Table 5). Thus, the structures of **7** show the expected small C−Si−C bond angles, which are not much effected by variation of the substituents at the silicon atom (Tables 1 and 2, Figure 3). The largest changes are observed for the spiro silirene **7b**, which due to the five-membered ring system exhibits a remarkable small external C3SiC6 bond angle of 96.5° compared to 111.1° of C3SiC4 in **7a**.

Conclusion

The irradiation of bisdiazocompounds **6** in inert gas matrices or organic glasses provides a novel route to silirenes **7**, unsubstituted at the double bond. Irradiation in the solid state is required, since in solution the highly reactive intermediates, particularly carbenes, are trapped with high efficiency by the solvent. Good yields are obtained for alkyl and phenyl substituents at the silicon atom, while trimethylsilyl with a high migratory aptitude results in the formation of a complex product mixture. All the silirenes **7** are highly reactive, which clearly demonstrates that substitution at the double bond is required for a kinetic stabilization. Even two phenyl substituents at the silicon atom are not sufficient for the stabilization in solution at temperatures above −50 °C.

Experimental Section

Warning: Although in our laboratory an explosion never occurred, bisdiazo compounds **6** are potentially explosive and should be handled with care.

All operations were carried out under exclusion of moisture and under inert gas in glass apparatus with silylated surfaces (through treatment of the glass surfaces with hexamethyldisilazane).

Matrix isolation experiments were performed by standard techniques with an APD DE-204SL and an APD DE-202 Displex closed cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) on top of a CsI (IR) or sapphire (UV/vis) window with a rate of approximately 0.15 mmol/min. To obtain optically clear matrices, the spectroscopic window was retained at 30 K during deposition, and the matrix was subsequently cooled to 10 K.

Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 or 0.5 cm^{-1} in the range 400−4000 cm^{-1}. UV/vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water. For broad-band irradiation Schott cutoff filters were used (50% transmission at the wavelength specified). For narrow-band irradiation interference filters in combination with dichroic mirrors ("cold mirrors") were used.

Bisdiazo compounds **6** were synthesized by treatment of silylbistriflates with diazomethane in analogy with a procedure described by Maas et al.[12,13]

Dimethylbis(diazomethyl)silane 6a. A solution of 4.0 g of dimethylsilanediylbis(trifluoromethanesulfonate) **8a** (12 mmol) in 50 mL of dry pentane was added slowly to a solution of 1 g of diazomethane (23.8 mmol) in 80 mL of Et_2O and 5 g of ethyldicyclohexylamine (27 mmol) at −50 °C and stirred vigorously for 1 h. The ammonium salt, which precipitated during the reaction, was separated from the yellow solution by rapid filtration. The solution was subsequently concentrated under vacuum to about 6 mL at −45 °C, and **6a** was separated by gas chromatography (Shimadzu GC-8a, column: 3m SE 30 10%, $\phi = 8$ mm, 80 °C). **6a** was obtained as yellow liquid, which was stable for several weeks in $CDCl_3$ at −10 °C. The yield determined by gas chromatography was 14%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.29$ (s, 6H, CH_3), 2.72 (s, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.14$, 19.8. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 2082.5 (100, C=N=N), 2073.3 (99, C=N=N) 1267.5 (36), 1263.6 (34), 1262.3 (28), 840.8 (23), 837.4 (9), 832.1 (35), 828.8 (15), 822.5 (6), 810.9 (7), 794.1 (14), 727.0 (4), 518.2 (4), 514.1 (13), 480.9 (3). MS: *m/z* (rel intensity) 140 (4) [M^+], 125 (8) [$M^+ - CH_3$], 112 (2) [$M^+ - N_2$], 99 (5) [$M^+ - CHN_2$], 84 (24) [$M^+ - 2N_2$], 58 (60) [$SiC_2H_6^+$], 43 (100), [$SiCH_3^+$].

Bis(diazomethyl)silacyclopentane 6b. A 4.41 g sample of bis(trifluoromethanesulfonyl)silacyclobutane **8b** (12 mmol) was added slowly to a solution of 1 g of diazomethane (23.8

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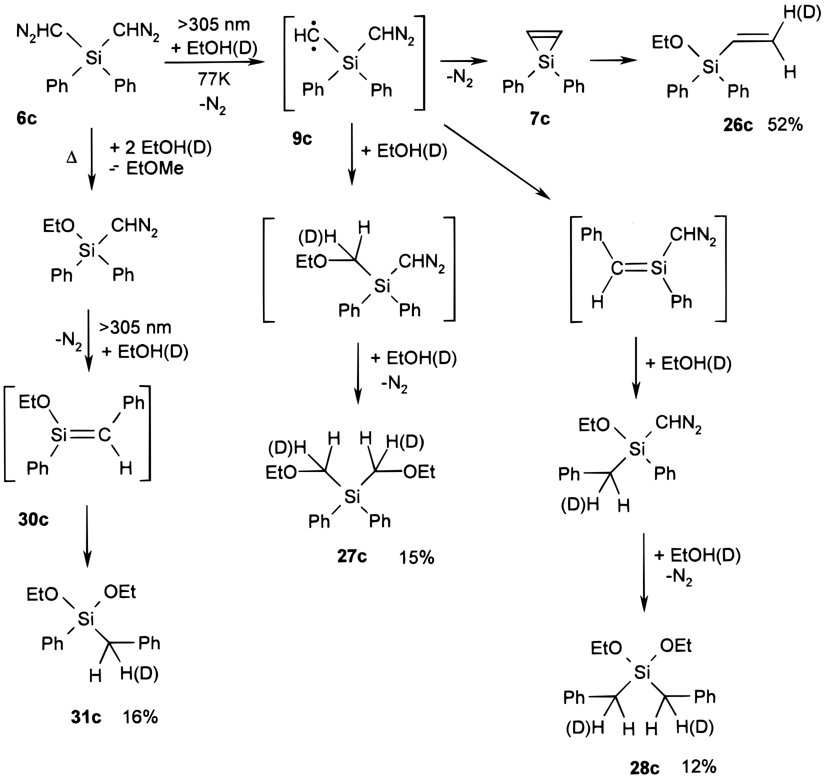
Scheme 6



Scheme 7

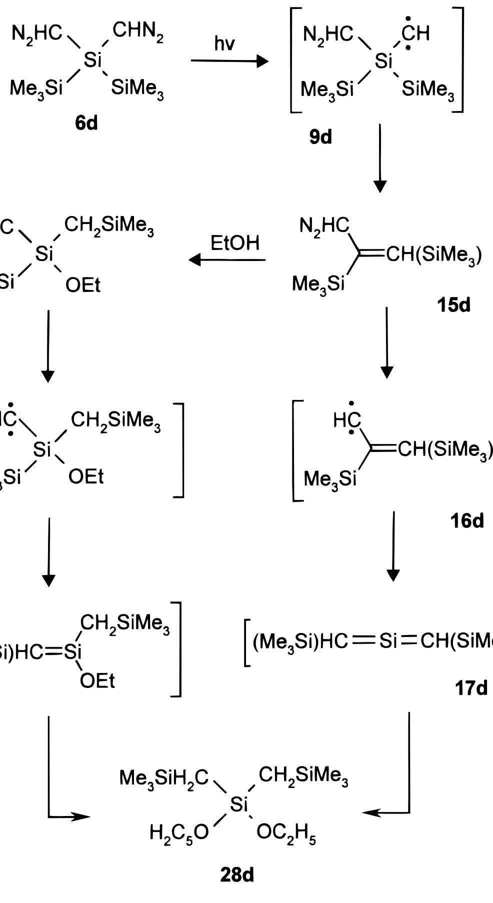


Table 5. Structural Parameters of 1*H*-Silirenes Calculated with DFT and ab Initio Methods

silirene	method	*r*(C=C) [Å]	*r*(Si−C)	α- (C−Si−C) [deg]	*β*- (R−Si−R) [deg]
1	B3LYP/6-311G(d,p)	1.332	182.2	42.9	111.4
	MP2/6-31G(d,p)	1.346	181.9	43.4	110.9
7a	B3LYP/6-311G(d,p)	1.338	182.2	43.1	111.1
	MP2/6-31G(d,p)	1.352	181.9	43.6	110.6
7b	B3LYP/6-311G(d,p)	1.342	181.7	43.3	96.5
	MP2/6-31G(d,p)	1.354	181.5	43.8	96.2
7c	B3LYP/6-*31*G(d,p)	1.341	182.3	43.2	112.8

mmol) in 120 mL of Et_2O and 3.5 g of *N*-ethyldiisopropylamine (27 mmol) at −50 °C. The reaction temperature was maintained between −50 and −40 °C over a period of 2 h. After filtration from the ammonium salt the yellow solution was concentrated under vacuum to about 10 mL at −45 °C and purified by gas chromatography (Siemens RGC 202, column: 70 cm OV 101 3%, $\phi = 8$ mm, 60 °C). **6b** was obtained as a yellow liquid, which decomposes at −30 °C. The yield determined by gas chromatography was 10%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.73$ (m, 4H, CH_2), 1.57 (m, 4H, CH_2), 2.70 (s, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.30$, 18.82, 20.71. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 2954.9 (3), 2950.6 (3), 2946.0 (5), 2936.7 (4), 2927.1 (5), 2899.7 (4), 2866.8 (3), 2856.6 (4), 2086.4 (36, C=N=N), 2083.8 (17, C=N=N), 2077.7 (100, C=N=N), 2071.8 (11, C=N=N), 1462.9 (2), 1454.7 (3), 1403.9 (5), 1307.2 (2), 1271.3 (7), 1267.5 (5), 1264.1 (12), 1256.9 (3) 1158.9 (3), 1155.3 (3), 1076.8 (8), 1030.3 (3), 1026.6 (2), 1021.2 (2), 860.8 (3), 820.3 (2), 814.2 (2), 808.5 (5), 799.6 (3), 774.7 (2), 768.0 (2), 761.2 (2), 758.6 (3), 749.1 (2), 744.9 (3), 723.1 (2), 712.8 (2), 685.3 (2), 668.7 (4), 626.8 (2), 525.6 (7), 508.6 (2). MS: *m*/*z* (rel intensity): 166 (1) $[M^+]$, 138 (0.5) $[M^+ - N_2]$, 110 (15) $[M^+ - 2N_2]$, 84 (100) $[M^+ - 2CHN_2]$, 83 (58), 67 (28), 56 (75) $[Si(CH_2)_2{}^+]$, 55 (53), 53 (49) $[SiC{\equiv}CH^+]$. HRMS: 166.068.

Diphenylbis(diazomethyl)silane 6c. A solution of 5.76 g of diphenylsilanediylbis(trifluoromethanesulfonate) **8c** (12 mmol) in 25 mL of dry benzene was added slowly to a solution of 1 g of diazomethane (23.8 mmol) in 100 mL of Et_2O and 3.5 g of *N*-ethyldiisopropylamine (27 mmol) at −20 °C. The mixture was stirred for 1 h at −20 °C, allowed to warm slowly to 10 °C, and kept at this temperature for an additional 6 h under stirring. The yellow solution was filtered from the

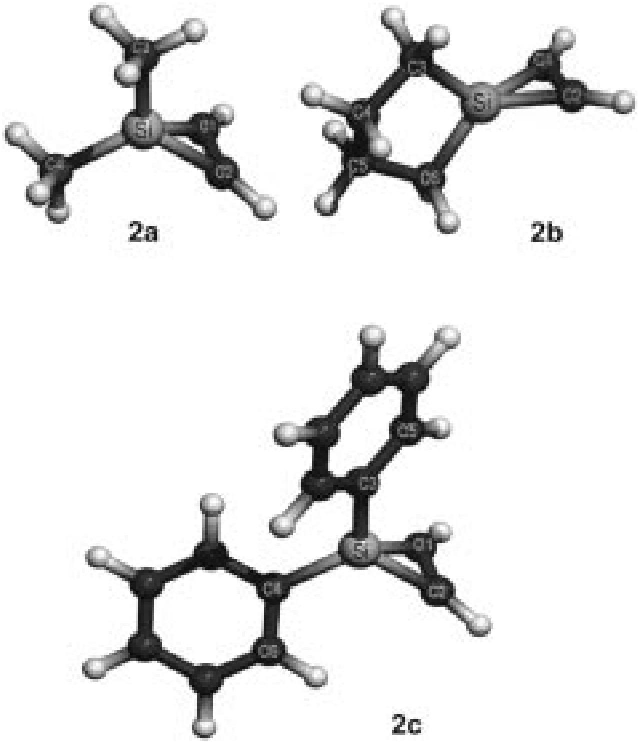


Figure 3. Structures of silirenes **7a**−**c**, calculated at the B3LYP/6-31G(d,p) level of theory.

ammonium salt which precipitated during the reaction and concentrated under vacuum to about 10 mL at −40 °C. After purification by gas chromatography (Siemens RGC 202, column: 15 cm OV 101 3%, $\phi = 3$ mm, 130 °C) **6c** was obtained as a yellow oil, which was stable for several days at room temperature. The yield determined by gas chromatography was 25%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.18$ (s, 2H, CH), 7.44−7.52 (c, 6H, Ph), 7.66−7.71 (c, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.79$, 128.24, 130.44, 132.31, 134.69. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 3095.0 (1), 3077.3 (2), 3063.0 (2), 3054.1(2), 3028.9 (2), 3018.1 (1), 3007.9 (1), 2089.4 (100, C=N=N), 2081.9 (32, C=N=N), 2075.3 (28, C=N=N), 1432.0 (4), 1277.1 (3), 1269.4 (3), 1267.2 (3), 1263.3 (5), 1260.0 (5), 1189.8 (1) 1157.4 (3), 1120.1 (6), 1112.4 (3), 768.5 (3), 753.1 (3), 733.3 (5), 725.6 (2), 709.7 (6), 698.7 (8), 568.3 (1), 560.1 (1), 552.4 (1), 547.3 (3), 542.8 (2), 537.9 (2), 531.2 (3), 524.0 (2), 491.2 (1), 486.5 (1), 481.8 (1), 476.9 (1) 448.8 (1). MS: *m*/*z* (rel intensity): 264 (1.5) [M$^+$], 208 (20) [M$^+$ − 2N$_2$], 207 (32), 182 (75) [SiPh$_2^+$], 181 (88), 130 (100), 105 (88) [SiPh$^+$], 79 (24), 53 (60) [SiC≡CH$^+$]. HRMS: 264.083.

Hexamethylbis(diazomethyl)trisilane 6d. A 5.9 g sample of hexamethylbis(trifluoromethanesulfonyl)trisilane **8d** (12.5 mmol) was added slowly to a solution of 1.13 g of diazomethane (26.9 mmol) in 100 mL of Et_2O and 3.88 g of *N*-ethyldiisopropylamine (30 mmol) at −45 °C. After the addition was complete, the mixture was stirred vigorously for 1 h at −35 °C. After filtration from the ammonium salt the yellow solution was concentrated to about 6 mL and purified by gas chromatography (Siemens RGC 202, column: 0.5 m SE 30 20%, $\phi =$ 8 mm, 130 °C). **6d** was obtained as yellow liquid, which was stable in a $CDCl_3$ solution at 0 °C for several weeks. The yield determined by gas chromatography was 18%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.18$ (s, 18H, CH_3), 2.67 (s, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.92$, 16.0. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 3200.4 (2), 3047.5 (2), 2967.6 (5), 2956.6 (5), 2465.1 (2), 2387.0 (2), 2070.9 (100, C=N=N), 2054.2 (100, C=N=N), 1444.8 (2), 1409.5 (1), 1262.2 (5), 1250.7 (100), 1240.8 (20), 1235.5 (12), 1156.2 (3), 861.0 (10), 743.5(6), 727.9 (6), 706.4 (4), 624.5 (2), 546.8 (9), 539 (3), 510 (4), 437.5 (3), 432.1 (6). MS: *m*/*z* (rel intensity) 228 (0.1) [M$^+$], 185 (45) [M$^+$ − (CH_3 + N_2)], 157 [M$^+$ − (CH_3 + 2N_2)], 73 (100) [SiMe$_3^+$].

Synthesis of Silirenes 7a−**c in an Argon Matrix.** A mixture of diazirines **24a**−**c** and silirenes **7a**−**c** was obtained by irradiation ($\lambda \geq 400$ nm) of the corresponding bisdiazo compounds **6a**−**c** in argon at 10 K; irradiation at $\lambda \geq 305$ nm afforded silirenes **7a**−**c** quantitatively. Monochromatic irradiation at 248 nm led finally to the formation of ethynylsilanes **32a**−**c**.

Diphenyl-1*H*-silirene 7c. Diphenylbis(diazomethyl)silane **6c** was irradiated in organic glass consisting of $CFCl_3$ and $C_2F_4Br_2$ (1:1) (0.01mol/L) with $\lambda \geq 305$ nm at 77 K for 2 h in a quartz NMR tube. After the photolysis was complete the glass was warmed to −80 °C, and the NMR spectrum was recorded at this temperature. ^{1}H NMR (400 MHz, $CFCl_3$/$C_2F_4Br_2$, −80 °C): $\delta = 7.21$−7.50 (c, Ph), 8.62 (s, =CH silirene ring). ^{13}C NMR (100 MHz, $CFCl_3$/$C_2F_4Br_2$, −80 °C): $\delta = 136.38$, 131.69, 130.77, 128.34, 151.84 (C=C silirene ring).

Dimethylethynylsilane 32a. A 27 g sample of an 18% sodium acetylide slurry in xylene (101 mmol) was added dropwise to a solution of 8.63 g of dimethylchlorosilane (91 mmol) in 150 mL of dry xylene at 0 °C. The reaction mixture was brought to 50 °C for 20 min, and the subsequent distillation directly out of this mixture yielded 3.45 g of **32a**, bp 37−38 °C/760 Torr). The yield was 45%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.21$ (d, 6H, $SiCH_3$), 2.36 (d, 1H, C≡CH), 4.07 (d sept., 1H, SiH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -3.3$, 87.1, 94.5. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 3318.4 (11), 3316.1 (10), 3312.6 (9), 3306.6 (5), 2983.7 (4), 2159.9 (11), 2142.5 (32), 2052.9 (17), 2050.7 (10), 2048.9 (11), 1340.3 (2), 1336.3 (7), 1257.9 (7), 1253.9 (31), 959.4 (4), 899.4 (55), 889.4 (69), 886.1 (100), 843.2 (50), 775.1 (35), 773.1 (38), 745.2 (12), 739.6 (26), 684.0 (14), 678.5 (21), 675.8 (43), 623.9 (6), 584.2 (14). MS: *m*/*z* (rel intensity) 84 (46) [M$^+$], 69 (110) [M$^+$ − CH_3], 58 (62), [M$^+$ − HC≡CH], 43 (32).

Ethynylsilacyclopentane 32b. A 5.5 g sample of cyclotetramethylenechlorosilane (46 mmol) was added dropwise to 92 mL of a 0.5 M solution of ethynylmagnesium bromide (46 mmol) in THF at room temperature. The mixture was stirred for 2 h and refluxed for 3 h after the addition was completed. After cooling to room temperature, ether and water were added, and the ether layer was separated, washed well, and dried over $MgSO_4$. The solvent was evaporated and the ethynylsilane purified by gas chromatography (Siemens RGC 202, column: 280 cm DC 200 20%, $\phi = 8$ mm, 70 °C). The yield was 56%.^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (m, 4H, CH_2), 1.62 (m, 4H, CH_2), 2.45 (d, 1H, C≡CH), 4.19 (quint, 1H, Si−H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 10.31$, 26.92, 86.06, 95.66. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 3318.0 (23, ≡C−H), 3304.4 (13, ≡C−H), 2972.3 (12), 2964.6 (14), 2949.8 (30), 2930.0 (24), 2870.6 (17), 2861.5 (14), 2858.6 (10), 2165.0 (23), 2154.2 (34), 2149.7 (38, Si−H), 2146.9 (21) 2051.6 (C≡C, 18), 2046.9 (C≡C, 14), 1455.7 (5), 1409.9 (10), 1334.8 (17), 1250.4 (4), 1077.9 (46), 1034.7 (27), 1021.4 (8), 934.7 (7), 873.2 (43), 856.1 (79), 850.4 (100), 785.5 (23), 779.9(80), 746.7 (12), 709.3 (34), 682.9 (60), 675.5 (53), 642.8 (15), 639.0 (8), 636.1 (9), 585.9 (23). MS: *m*/*z* (rel intensity) 110 (17) [M$^+$], 95 (21), 82 (100), [M$^+$ − C_2H_4], 67 (43), 53 (62) [SiC≡CH$^+$]. HRMS: 110.055.

Diphenylethynylsilane 32c. A 3.35 g sample of diphenylchlorosilane (15 mmol) was added slowly to 31 mL of a 0.5 M solution of ethynylmagnesium bromide (15 mmol) in THF at room temperature. The mixture was stirred for 4 h and refluxed for an additional 6 h. After cooling to room temperature, ether and water were added, causing the precipitation of magnesium halide. The ether layer was separated, washed well, and dried over $MgSO_4$. Fractional distillation of the solution gave the colorless product boiling at 64 °C at 0.001 Torr. The yield was 62%. Diphenylethynylsilane was further purified by gas chromatography (Siemens RGC 202, column: 280 cm SE 30 20%, $\phi = 8$ mm, 200 °C). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.69$ (s, 1H, C≡CH), 5.15 (s, 1H, Si−H), 7.33−

7.46 (c, 6H, Ph), 7.59−7.68 (c, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 83.48, 97.77, 128.19, 130.29, 131.30, 135.13$. IR (Ar, 10 K): $\tilde{\nu}$ (rel intensity) = 3314.0 (5, ≡C−H), 3309.5 (5, ≡C−H), 3297.3 (4, ≡C−H), 3096.7 (2), 3080.7 (4), 3062.6 (1), 3057.8 (1), 2162.5 (3), 2158.2 (4, Si−H), 2053.3 (7, C≡C), 2047.3 (8, C≡C), 1490.2 (1), 1433.1 (14), 1339.3 (3), 1190.9 (1), 1121.6 (22), 1113.9 (11), 999.4 (1), 838.1 (2), 822.7 (14), 818.0 (31), 813.7 (22), 800.1 (100), 789.9 (2), 739.5 (2), 731.9 (31), 722.6 (3), 698.0 (33), 682.0 (9), 673.7 (9), 631.7 (6), 612.0 (1). MS: *m*/*z* (rel intensity) 208 (32) [M^+], 181 (12), 130 (100) [Si(Ph)C≡CH^+], 105 (22) [$SiPh^+$], 53 (31), [SiC≡CH^+]. HRMS: 208.070.

Cyclotetramethylenechlorosilane. This compound was prepared by the reaction of the Grignard reagent formed from 1,4-dibromobutane and trichlorosilane.[21]

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