4776 *Organometallics* **1998,** *17,* 4776−4783

Photochemistry of Matrix-Isolated Phenylsilyl Azides

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Received February 23, 1998

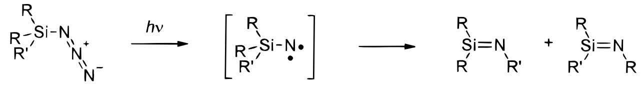
Triphenylsilyl azide (**1c**) and diphenylsilyl azide (**1d**) have been examined in cryogenic matrixes. In argon at 15 K both compounds exhibit intense blue phosphorescence upon excitation with the light of a KrF excimer laser (248 nm). The phosphorescence is completely quenched if the matrices are doped with 3% oxygen. UV photolysis ($\lambda = 248$ nm) of matrix-isolated triphenylsilyl azide (**1c**) yields 1,1,2-triphenylsilanimine (**3c**). The latter has been characterized by UV and IR spectroscopy and identified by comparison of the experimental spectrum with a calculated one. Diphenylsilyl azide (**1d**) yields two isomeric diphenylsilanimines **3d** and **4d** upon irradiation. Photochemical 1,2-elimination of benzene from the Si═N double bond leads to the formation of phenylsilanitrile (**6c**), which rearranges to phenylsilaisonitrile (**7c**).

Introduction

Multiply bonded silicon compounds[1] are, unlike their carbon analogues, highly reactive species and therefore have been intensively studied both theoretically[2−4] and experimentally. Silanimines containing a Si═N double bond can be prepared conveniently by UV photolysis of silyl azides (Scheme 1) and can be stabilized at cryogenic temperatures in solid noble gas matrixes and in organic glasses.[1]

Maier et al.[5] matrix-isolated the parent silanimine **3a** (R = R′ = H) by photolysis of silyl azide (**1a**) in solid argon and characterized the silanimine by IR and UV spectroscopy. The photolysis of trimesitylsilyl azide (**1e**) in an organic glass at 77 K was studied by West and Michl et al. and yielded 1,1,2-trimesitylsilanimine (**3e**) and a C−H insertion product.[6,7] The UV spectrum of **3e** is similar to that published by Ando et al.[8] for 1,1-dimesityl-2-(trimethylsilyl)silanimine (**3f**), obtained by photolysis of the corresponding azide **1f** in organic glasses or in argon. Michl et al. also photolyzed triphenylsilyl azide (**1c**) in argon and reported the UV maximum for 1,1,2-triphenylsilanimine (**3c**).[1a] The formation of **3c** upon irradiation of azide **1c** has also been proved by trapping experiments in solution.[9] After irradiating matrix-isolated di-*tert*-butylsilyl azide (**1g**) the products of both H (**3g**) and alkyl migration (**4g**) were obtained and identified by trapping experiments.[10] While there is ample UV spectroscopic evidence for matrix-isolated silanimines, only a few IR spectra were published, and the unequivocal assignment of the SiN stretching vibration of a silanimine was reported only for several small silanimines.[5,11] Silanimines with bulky substituents that are kinetically stable at room temperature were prepared by Wiberg et al.[12−14] and Klingebiel et al.[1b,15,16] The crystal structures of two free silanimines are known,[12,17] and the reactivity of such sterically hindered silanimines was studied in detail.[1b]

Scheme 1



1 2 3 4

a: R = R′ = H
b: R = CH_3, R′ = H
c: R = R′ = Ph
d: R = Ph, R′ = H
e: R = R′ = 2,4,6-$(CH_3)_3C_6H_2$
f: R = 2,4,6-$(CH_3)_3C_6H_2$, R′ = $Si(CH_3)_3$
g: R = $C(CH_3)_3$, R′ = H

Less is known about silanitriles **6**, which contain a SiN triple bond (Scheme 2), and only very few examples were characterized spectroscopically. Maier et al.[5] observed the unsubstituted parent silanitrile H−Si≡N (**6a**) after irradiating matrix-isolated silyl azide (**1a**) with the light of an ArF excimer laser ($\lambda = 193$ nm). The isomeric silaisonitrile **:**Si═N−H (**7a**) was

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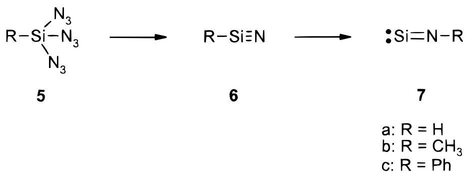
10.1021/om9801296 CCC: $15.00
Publication on Web 09/26/1998

Scheme 2



identified in an argon matrix[18] and as a transient species in neutralization–reionization mass spectrometry studies.[19] Attempts to generate phenylsilanitrile (**6c**) from gas-phase pyrolysis or matrix photolysis of phenyltriazidosilane (**5c**) yielded the isomeric phenylsilaisonitrile (**7c**), which was detected by photoelectron spectroscopy[20] and by matrix IR and UV spectroscopy.[21] Similarly, methylsilanitrile (**6b**) was postulated to be an intermediate in the photolysis of methyltriazidosilane (**5b**)[22] and also in the photochemical elimination of methane from 1,1-dimethylsilanimine (**3b**)[11] but could not be isolated in these experiments. Calculations of the parent system (**6a** → **7a**)[19,23] and of the methyl- (**6b** → **7b**)[23,24] and phenyl-substituted (**6c** → **7c**)[21,24] compounds predict that the silaisonitriles **7** are more stable than the silanitriles **6** by about 40–50 kcal mol^{-1}, depending on the substituent. The SiN bond length in silaisonitriles **7** is longer than in silanitriles **6**, in accordance with the description as a SiN double bond and a divalent silicon atom.

We here report on the photolysis of matrix-isolated tri- and diphenylsilyl azide (**1c** and **1d**, respectively) and on the spectroscopic characterization of the photoproducts.

Results and Discussion

Phosphorescence of Triphenylsilyl Azide (1c). The UV spectrum of matrix-isolated triphenylsilyl azide (**1c**, Figure 1; argon, 15 K) exhibits an intense band at 219 nm and a weaker band with a vibrational progression at 254, 259, 264, and 270 nm. Upon excitation with the light of a KrF excimer laser ($\lambda = 248$ nm) the azide shows intense blue phosphorescence ($\lambda_{max} = 413$ nm) with a lifetime of about 0.5 s (Figure 2). The phosphorescence intensity is proportional to the first power of the exciting laser intensity, and thus multiphoton excitation of **1c** can be excluded. Irradiation at 248 nm results slowly in the photochemical decomposition of the azide (vide infra), and thus the intensity of the phosphorescence is reduced in proportion to the azide concentration. After complete decomposition of the azide, phosphorescence is no longer observed. The phosphorescence excitation spectrum in EPA at 77 K agrees with the absorption spectrum of the azide **1c**, which reveals that the azide is indeed the source of the phosphorescence. At $\lambda = 335$ nm the intensity of the emission is 10% of its maximum at 413 nm. Taking 335 nm as the basis for calculating the triplet energy of the azide **1c**, a value of 85 kcal/mol is obtained.

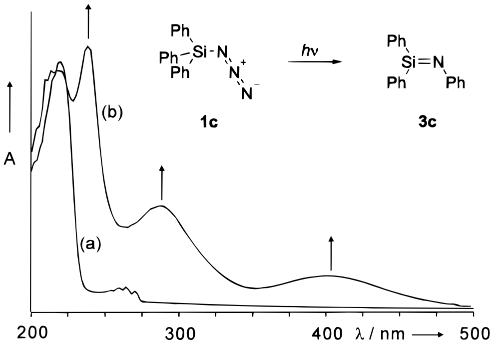


Figure 1. UV spectrum showing the photolysis ($\lambda = 254$ nm) of triphenylsilyl azide (**1c**), argon, 15 K: (a) triphenylsilyl azide (**1c**), $\lambda_{max} = 270$, 264, 259, 254, 219 nm; (b) appearing bands of 1,1,2-triphenylsilanimine (**3c**), $\lambda_{max} = 404$, 292, 271, 241, 220 nm.

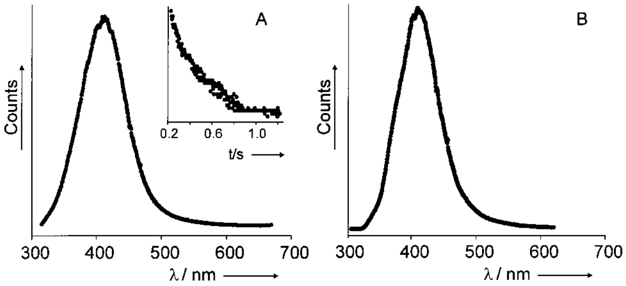


Figure 2. (A) Phosphorescence spectrum of triphenylsilyl azide (**1c**), in argon, 15 K; excitation with $\lambda = 248$ nm; $\lambda_{max} = 413$ nm. Inset: decay of the emission; $\tau = 0.5$ s. (B) Phosphorescence spectrum of triphenylsilyl chloride (**11**), argon, 15 K; excitation with $\lambda = 248$ nm; $\lambda_{max} = 408$ nm.

In an organic glass (methylcyclohexane) at 77 K the maximum of the emission is blue-shifted to 390 nm, while the half-life time is still on the same order of magnitude as in solid argon. In a 3% O_2-doped argon matrix the phosphorescence is completely quenched. Since triphenylsilyl chloride **11** shows very similar emission (λ_{max}, argon, 15 K: 408 nm; Figure 2), the phosphorescence is not linked to the azide group but rather to the silyl moiety. The intensity of the phosphorescence of **11** remains the same even after long irradiation times.

So far, luminescence has not been described for arylsilyl azides, although it was known for aryl-substituted silanes[25,26] as well as for aryl azides.[27] The phosphorescence spectrum of tetraphenylsilane in EPA glass exhibits a maximum at $\lambda = 370$ nm with a lifetime of the emission of $\tau = 1000$ ms.[25] In the crystalline state the emission is red-shifted to $\lambda_{max} = 430$ and 460 nm.[26]

Photolysis of Triphenylsilyl Azide (1c). If matrix-isolated triphenylsilyl azide (**1c**) is photolyzed with $\lambda = 254$ nm (low-pressure mercury arc lamp) or with the light of an excimer laser ($\lambda = 248$ nm), 1,1,2-triphenylsilanimine (**3c**) is formed (Scheme 3), indicated by a

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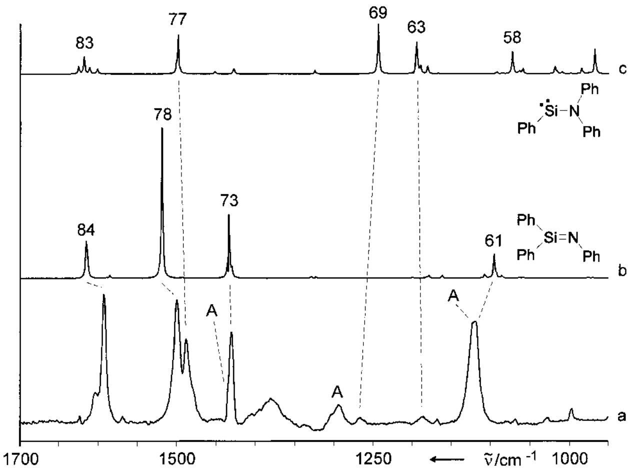
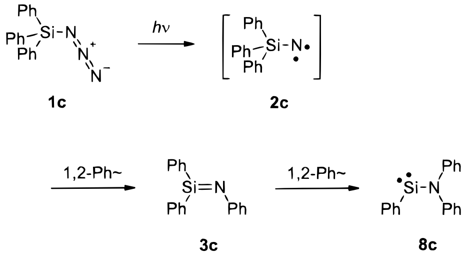


Figure 3. (a) IR spectrum showing the photolysis ($\lambda = 254$ nm) of triphenylsilyl azide (**1c**), argon, 10 K. Bands originating from vibrations of unphotolyzed azide are marked **A**. (b) Calculated spectrum of **3c** (RHF/6-31G(d)). (c) Calculated spectrum of **8c** (RHF/6-31G(d)). Tentative assignments are based on band positions and intensities. The calculated spectra are scaled by a factor of 0.90 to allow for the direct comparison with the experimental spectrum, and a Lorentz band shape is simulated with a half-width of 2 cm^{-1}. The numbers in the calculated spectra correspond to those in Table 1.

Scheme 3



bright yellow color of the matrix. In the UV spectrum new intense bands appear at $\lambda = 404$, 292, and 241 nm, characteristic of aryl-substituted silanimines[1,6,8] (Figure 1; this is in agreement with Michl's[1a] results that reported a UV maximum at $\lambda = 400$ nm for **3c** in an argon matrix). During the photolysis of **1c** the growing band of **3c** at 241 nm absorbs more and more of the incident light, and the photolysis slows down. Therefore, complete photolysis of the azide could only be achieved in matrixes with a low concentration of **1c**.

In the IR spectrum the intense stretching vibration of azide **1c** at 2147 cm^{-1} decreases and new intense bands at 1592, 1500, 1431, and 1120 cm^{-1} appear, which are assigned to 1,1,2-triphenylsilanimine (**3c**). A further intense band at 1488 cm^{-1} is tentatively assigned to phenyl(diphenylamino)silylene (**8c**). The spectrum of silanimine **3c** is reasonably reproduced by ab initio calculations (RHF/6-31G(d), Figure 3, Table 1). The expected primary photoproduct triphenylsilylnitrene (**2c**) could not be observed, and it therefore appears that it rearranges directly via 1,2-phenyl shift to the silanimine **3c**. In a second 1,2-phenyl shift, **3c** could undergo further rearrangement to silylene **8c** (Scheme 3). According to our calculations **8c** is only 6 kcal mol^{-1} higher in energy than **3c**. Similar photochemical rearrangements of silanimines to aminosilylenes have been described both experimentally[22] and theoretically[28] in the literature. In our experiments, however, it was not possible to show unequivocally the rearrangement of **3c** to **8c**.

Photolysis of Diphenylsilyl Azide (1d). Diphenylsilyl azide (**1d**) exhibits a UV spectrum similar to that of **1c** (argon, 15 K: intense band at $\lambda = 220$ nm, weaker bands at $\lambda = 252$, 259, 264, and 270 nm) and also shows phosphorescence ($\lambda = 412$ nm with two weak shoulders at 460 and 530 nm) upon excitation with the KrF excimer laser (248 nm). The phosphorescence has a lifetime of about 0.5 s and is completely quenched in oxygen-doped matrixes.

Upon photolysis of matrix-isolated diphenylsilyl azide (**1d**, KrF excimer laser, $\lambda = 248$ nm or low-pressure mercury arc lamp, $\lambda = 254$ nm), the clear colorless matrix changes to a bright yellow. In the UV spectrum new bands appear at $\lambda = 222$, 282, 288, 299, and 384 nm. In the IR spectrum the very intense band of the asymmetric stretching vibration of the azide at 2161 cm^{-1} decreases and new bands appear at 1499 and 1431 cm^{-1} and at 1141 and 1101 cm^{-1}. The spectral data are in accordance with the formation of two main photoproducts, 1,1-diphenylsilanimine (**3d**) and 1,2-diphenylsilanimine (**4d**, Scheme 4). In Figure 4 and Table 2 the experimental spectrum is compared with the calculated spectra of **3d** and **4d** (B3LYP/6-31G(d,p), Figure 4, Table 2). The observation of both the products of H and phenyl migration to the nitrene center indicates that there is hardly any discrimination in the migratory aptitudes of H and phenyl in silylnitrenes. This result is in accordance with earlier investigations on alkyl-substituted silyl azides where there is a similarly low selectivity between H and alkyl groups.[10,11]

Photochemistry of Diphenylsilanimines 3d and 4d. Analysis of the spectrum obtained after photolysis of diphenylsilyl azide (**1d**) shows that apart from **3d** and **4d** there are bands that belong to secondary photoproducts. As has been mentioned above, silanimines may undergo rearrangement to form silylenes **8**. The rearrangement of the isomeric diphenylsilanimines **3d** and **4d** could lead to two different silylenes **8d** and **9d** (Scheme 5). On the basis of the calculated IR spectra for silylenes **8d** and **9d** the band at 1271 cm^{-1} is tentatively assigned to the silylenes.

There is, however, still another set of bands in the experimental spectrum. The intensity of these bands relative to those of the silanimines is higher if the azide is photolyzed with the laser ($\lambda = 248$ nm) instead of the low-pressure mercury arc lamp. All the major bands of this set at 1598, 1528, 1482, 758, 690, and 677 cm^{-1} appear with an equal rate. By comparison with an authentic matrix-isolated sample the bands at 1482 and 677 cm^{-1} are assigned to benzene. The other bands of this set grow with the same rate as the benzene bands and are assigned to phenylsilaisonitrile (**7c**, Scheme 6) by comparison with literature data.[21]

Radziszewski and Michl[21] obtained **7c** by photolysis of matrix-isolated phenyltriazidosilane (**5c**, Scheme 2) or by gas-phase pyrolysis of **5c** and subsequent trapping of the products in an argon matrix. Phenylsilanitrile (**6c**), the expected primary product in the photolysis of

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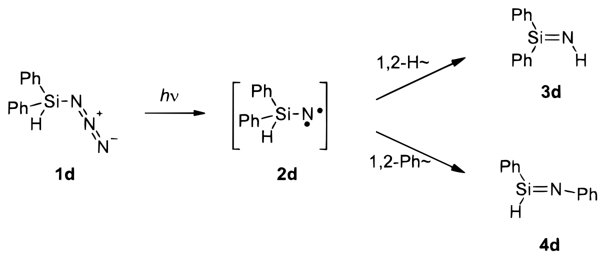
Table 1. IR Spectroscopic Data for the Products of the Photolysis of Triphenylsilyl Azide (1c)

argon, 10 K		ab initio (RHF/6-31G(d))						
		triphenylsilanimine (3c)			phenyl(diphenylamino)silylene (8c)			
ν/cm^{-1}	I[a]	no.[b]	ν/cm^{-1}[c]	I[a]	no.[b]	ν/cm^{-1}[c]	I[a]	assignm
3092	4	92	3034	5	96	3047	19	C−H str
3074	11	89	3029	4	95	3046	15	C−H str
3056	12				94	3042	31	C−H str
3031	5				93	3040	17	C−H str
					92	3039	27	C−H str
					91	3029	15	C−H str
1604	3				84	1625	15	skel ring vib
					83	1618	34	skel ring vib
					82	1611	12	skel ring vib
					80	1601	9	skel ring vib
1592	72	84	1615	24				skel ring vib
		83	1614	6				skel ring vib
		82	1613	5				skel ring vib
1569	2	79	1585	1				skel ring vib
1500	100	78	1519	100				N−C str + skel ring vib
1488 sh	12				78	1500	25	skel ring vib
					77	1499	65	skel ring vib
					73	1428	10	skel ring vib
		74	1435	4				
1431	42	73	1434	40				Si=N str + skel ring vib
		72	1430	5				
1267	3				69	1244	100	asym C−N−C
1185	4				67	1195	63	sym C−N−C
					65	1190	14	C−H in plane
1168	1				64	1181	15	C−H in plane
1120[d]		61	1096	16				Si−C str
1071	1				58	1073	44	C−H in plane
					55	1060	10	C−H in plane
1028	1				54	1019	14	C−H in plane
					52	1018	6	C−H in plane
					45	985	11	C−H out of pl
997	3				42	968	50	C−H out of pl
905	1				39	909	29	C−H out of pl
894	1	39	895	1				
889	1				37	862	19	in ph ring str
754	9	35	761	9	34	770	25	C−H out of pl
739	22	33	752	6	32	747	26	C−H out of pl
712	7	31	705	6	31	703	33	C−H out of pl
700	16				30	698	16	C−H out of pl
694	10	28	693	5	29	697	15	C−H out of pl
					28	678	12	
514	3				22	536	28	
					21	533	14	C−H out of pl
488	1	22	487	6				
475	1	21	475	7				
469	1				15	386	30	
461	2	20	463	10	14	380	6	

[a] Relative intensities based on the most intense band (100%). [b] Number of vibrational mode. The assignment of experimental to calculated vibrations is based on the comparison of band positions and relative intensities. [c] Calculated frequencies are scaled by 0.90. Only those calculated frequencies are listed that have a relative intensity > 5. [d] This band (1120 cm^{-1}) is overlaid by remaining unphotolyzed azide (1122 cm^{-1}) so that no intensity can be given.

Scheme 4



5c, could not be isolated. Calculations predict that **6c**, which contains a SiN triple bond, is considerably higher in energy than the isomeric isonitrile, which is formally described as a SiN double-bond system.[20,21,24] At the MP2/6-31G(d) level of theory the difference is 55.0 kcal mol^{-1}.[21]

The formation of **7c** in the photolysis of the silanimines **3d** and **4d** can be rationalized by a 1,2-elimination of benzene from the SiN double-bond system to form phenylsilanitrile (**6c**, Scheme 6). As the photochemical conditions of its generation are similar to those in Radziszewski's and Michl experiments, **6c** undergoes the same photochemical rearrangement to **7c**.

By integrating IR absorptions of the azide and the products relative concentrations of the compounds in the matrix can be monitored (Figure 5). The azide shows the expected continuous decrease, and at the beginning of the irradiation the concentration of the silanimine **4d** grows with a significantly higher rate than isonitrile **7c**. However, the experiments do not allow the determination of whether **7c** is formed in subsequent steps from **1d** via **3d** (1,2-elimination) or **4d** (1,1-elimination).

A 1,2-photoelimination reaction at a Si=N double

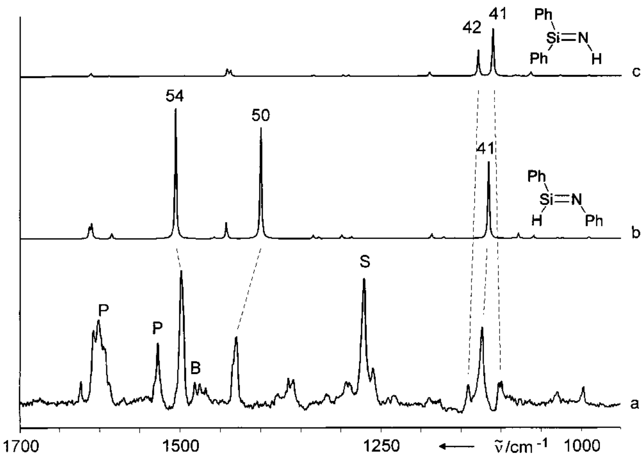


Figure 4. (a) IR spectrum showing the photolysis ($\lambda = 254$ nm) of diphenylsilyl azide (**1d**, appearing bands of the photoproducts, argon, 10 K); P, phenylsilaisonitrile (**7c**); B, benzene; S, tentative assignment to silylenes **8d** and **9d**. (b) Calculated spectrum of **4d** (B3LYP/6-31G(d,p)). (c) Calculated spectrum of **3d** (B3LYP/6-31G(d,p)). Tentative assignments are based on band positions and relative intensities. The calculated spectra are scaled by a factor of 0.98 to allow direct comparison with the experimental spectrum, and a Lorentz band shape is simulated with a half-width of 2 cm^{-1}. The numbers in the calculated spectra correspond to those in Table 2.

bond was observed for matrix-isolated 1,1-dimethylsilanimine.[11] UV irradiation of this silanimine with the light of an ArF excimer laser ($\lambda = 193$ nm) produced methane and silylisocyanide (**10**, Scheme 7), which is the final rearrangement product of the primarily formed methylsilanitrile.

Another possible pathway is 1,1-elimination of benzene in an excited state of the azide or nitrene (Scheme 8). Short-wavelength photolysis ($\lambda = 193$ nm) of matrix-isolated silyl azide H_3SiN_3 resulted in the elimination of both molecular nitrogen and hydrogen.[5]

As described above, in the photolysis of triphenylsilyl azide (**1c**) no elimination reaction is observed. Particularly, there is no spectroscopic evidence for the formation of either phenylsilaisonitrile or biphenyl, the expected products. Obviously, hydrogen atoms at the Si═N double bond are necessary for this kind of elimination.

Si═N Stretching Vibrations of Silanimines. In the unsubstituted silanimine **3a** the SiN stretching vibration absorbs at 1097 cm^{-1};[5] in 1,1-dimethylsilanimine (**3b**) it is shifted to 1118 cm^{-1}.[11] The phenyl groups cause a further blue shift of the band in 1,1-diphenylsilanimine (**3d**) to 1141 cm^{-1} (Table 2). An isotopic shift of 7 and 14 cm^{-1}, respectively, is predicted from the calculations of the naturally occurring silicon isotopes ^{29}Si and ^{30}Si in the SiN stretching vibration, but is not observed due to the comparatively broad IR absorptions of the phenyl-substituted silanimines. This line broadening is also found in other *gem*-diphenyl-substituted compounds and caused by the flat torsion potential of the phenyl rings, which results in a broad distribution of matrix-isolated molecules in slightly different conformations and matrix sites.

In the N-substituted silanimines **4d** (1,2-diphenylsilanimine) and **3c** (1,1,2-triphenylsilanimine) it is more difficult to assign one band to the SiN stretching vibration. The analysis of the calculated IR spectra indicates that there is no localized vibration of the SiN bonds but rather combination vibrations which include deformation of the phenyl rings. In the experimental spectra of **4d** and **3c** bands at 1431 cm^{-1} correspond to the calculated vibrations with the highest SiN stretching character. These vibrations are described best as combinations of the SiN stretching vibrations with deformation vibrations of the N-phenyl rings, while the Si-phenyl rings do not contribute (Table 3). As was shown previously, the accurate calculation of SiN double-bond stretching vibrations is difficult,[11] and it is thus not surprising that the calculated vibrations match the experiment better when the SiN contribution is smaller.

Geometries of Silanimines. The calculated structures of silanimines **3c**, **3d**, and **4d** reflect the expected dependence of the bond angles at silicon and nitrogen on the substitution (Table 4). In the planar, sterically unhindered silanimine **3a** the SiNH bond angle is calculated to be 127° (RHF/6-31G(d,p)). A very similar value is found in silanimine **3d** (Figure 6), which is also unsubstituted at the nitrogen atom. In the 1,2-substituted silanimines **4d** and **3c**, however, the angle opens to around 150°. In the sterically crowded compounds **3d** (Figure 6) and **3c** (Figure 7) the phenyl rings are twisted (**3c:** $d_{\mathrm{Si-N-C-C}} = 82°$) due to the steric repulsion of the *ortho* hydrogen atoms (Figure 7).

The calculated SiN double-bond lengths and RSiR angles are similar to those found in the crystal structures of the free uncoordinated silanimines **3h** (described by West et al.[12]) and **3i** (described by Klingebiel et al.[17]), showing the reliability of the calculations (Table 5). The experimentally observed SiNR angles for **3h** and **3i** are much larger than those calculated for **3a**–**4d**, but this is due to silicon substitution at the nitrogen atom, which results in a nearly linear arrangement of the SiNSi group in **3h**. This effect is reproduced by calculations on $H_2Si{=}N{-}SiH_3$, which does not carry any bulky groups and nevertheless has a SiNSi angle of nearly 176°.[29]

B3LYP calculations result in SiN double-bond lengths that are about 2% longer than the RHF values and in smaller SiNR angles. The influence of the substituents, however, leads to similar trends in the geometries.

Conclusion

Triphenylsilyl azide (**1c**) and diphenylsilyl azide (**1d**) have been matrix-isolated in argon at 10 K. Both compounds exhibit phosphorescence upon excitation with the light of an excimer laser (KrF, $\lambda = 248$ nm). From the emission spectra a triplet energy of 85 kcal mol^{-1} is calculated.

UV photolysis of **1c** and **1d** results in the formation of the corresponding silanimines, which have been characterized by IR and UV spectroscopy, and in the formation of silylenes as byproducts by rearrangement of the silanimines. In the case of hydrogen-substituted silanimines photochemical elimination from the SiN double bond and formation of silaisonitriles **7** is possible. Diphenyl-substituted silanimines eliminate benzene to form phenylsilaisonitrile. The reaction rates, however,

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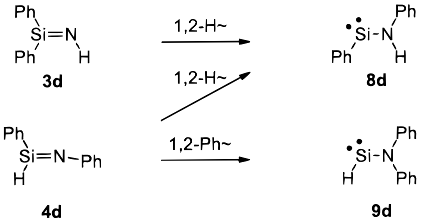
[29] Schleyer, P. v. R.; Stout, P. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1373–1374.

Table 2. IR Spectroscopic Data for the Products of the Photolysis of Diphenylsilyl Azide (1d)

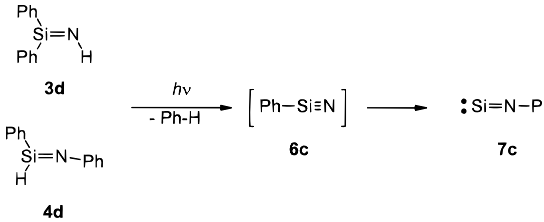
		density functional theory B3LYP/6-31G(d,p)							
argon, 10 K		1,2-diphenylsilanimine (**4d**)			1,1-diphenylsilanimine (**3d**)				
ν, cm^{-1}	I^a	no.^{b}	ν, cm$^{-1\,c}$	I^a	no.^{b}	ν, cm$^{-1\,c}$	I^a		assignm
					69	3520	8		N−H str
3144	2	69	3144	15	68	3144	12		C−H str
3096	3	68	3143	13	67	3141	23		
3076	14	67	3137	14	66	3137	16		C−H str
3066	2	66	3135	25	65	3131	21		C−H str
		65	3128	8					C−H str
3046	5	64	3123	18	64	3129	16		C−H str
3019	8	61	3106	7					C−H str
2155	95	59	2151	100					Si−H str
1601	9	58	1613	8	58	1612	5		skel ring vib
		57	1610	9					skel ring vib
1598	4							PhNSi:	skel ring vib
1569	3								skel ring vib
1529	33							PhNSi:	skel ring vib
1499	100	54	1506	87					N−C str + ring vib
1482	5							C_6H_6	
1476	3								
1468	1								
		51	1443	11					skel ring vib
					52	1442	15		skel ring vib
1431	49	50	1400	74					Si=N str +
					51	1438	10		skel ring vib
1365	2								
1359	5								
1271	69							8d/9d ?	asym C−N−C
1260	9							8d/9d ?	sym C−N−C
					45	1190	8		skel ring vib
1141	9				42	1129	53		Si=N str
1124	61	41	1116	51					N−C str
1101	12				41	1111	95		Si−C str + ring
1030	7								
998	8							PhNSi: ?	
902	19								
831	6	26	827	81					Si−H bend
781	5								
758	5	24	763	31				PhNSi:	
		23	744	16	25	746	22		C−H out of pl
					24	741	26		C−H out of pl
					23	727	98		C−N−H bend
734	39	22	738	10					in plane ring def
699	40	21	695	16					C−H out of pl
		20	693	5	21	697	28		C−H out of pl
		19	687	8					C−H out of pl
690	7							PhNSi:	
677	6							C_6H_6	
					20	676	19		N−H bend + ring def
668	4				19	661	100		N−H bend
					16	615	48		N−H out of pl
517	6								
477	21	15	497	12	15	468	33		C−H out of pl
		14	482	13	14	454	11		
		12	422	31	13	452	49		

[a] Relative intensities based on the most intense band (100%). [b] Number of vibrational mode. The assignment of experimental to calculated vibrations is based on the comparison of band positions and relative intensities. [c] Calculated frequencies are scaled by 0.98.

Scheme 5



Scheme 6



do not reveal the mechanism. In a similar reaction methane is extruded from matrix-isolated 1,1-dimethylsilanimine, while 1,1,2-triphenylsilanimine is stable, showing that a hydrogen atom at the SiN double bond is essential for this kind of elimination.

The stretching vibrations of the Si=N double bonds in the silanimines strongly depend on the substituents. In 1,1,2-triphenylsilanimine (**3c**) the Si=N stretching vibration is blue-shifted by some 330 cm^{-1} compared to the parent silanimine **1c**. Calculations show that this

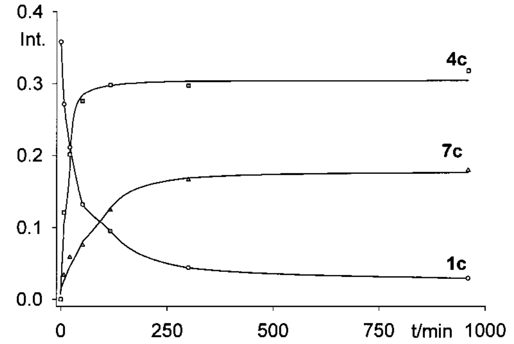
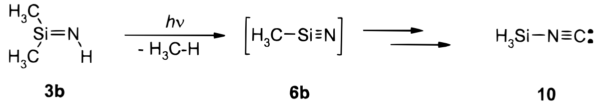


Figure 5. Course of the 254 nm photolysis of diphenylsilyl azide (**1d**), measured from the integration of IR bands, argon, 10 K. **1d**: Disappearing diphenylsilyl azide. **4d**: Appearing 1,2-diphenylsilanimine. **7c**: Appearing phenylsilaisonitrile.

Scheme 7



Scheme 8

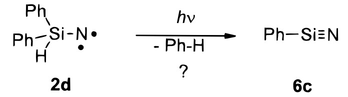


Table 3. Comparison of Si═N Stretching Vibrations in Various Silanimines

		$\nu_{Si=N}/cm^{-1}$		
		expt[a]	RHF[b]	B3LYP[c]
$H_2Si{=}NH$	**3a**	1097[d]	1120	1094
$(H_3C)_2Si{=}NH$	**3b**	1118[e]	1130	1113
$Ph_2Si{=}NH$	**3d**	1141	1142	1129
$PhHSi{=}NPh$	**4d**	1431	1413	1400
$Ph_2Si{=}NPh$	**3c**	1431	1434	

[a] Matrix-isolated in argon, 10 K. [b] RHF/6-31G(d,p) for **3a**,**b**,**d** and **4d**, RHF/6-31G(d) for **3c**. RHF frequencies are scaled by 0.90. [c] B3LYP/6-31G(d,p). B3LYP frequencies are scaled by 0.98. [d] Reference 5. [e] Reference 11.

Table 4. Selected Calculated Parameters for Silanimines

		RHF/6-31G(d,p)[a]			B3LYP/6-31G(d,p)		
		$r_{(SiN)}$/ pm	$a_{(SiNR)}$/ deg	$a_{(RSiR)}$/ deg	$r_{(SiN)}$/ pm	$a_{(SiNR)}$/ deg	$a_{(RSiR)}$/ deg
$H_2Si{=}NH$	**3a**	157.1	126.9	111.7	160.7	120.3	112.5
$(H_3C)_2Si{=}NH$	**3b**	157.6	126.4	111.7	160.9	120.5	112.5
$Ph_2Si{=}NH$	**3d**	157.4	127.6	114.8	161.0	121.1	115.1
$PhHSi{=}NPh$	**4d**	155.7	149.6	110.6	159.6	143.7	111.6
$Ph_2Si{=}NPh$	**3c**	155.3	153.5	116.0			

[a] RHF/6-31G(d) for **3c**.

is due to a change in the nature of the vibrational mode. In small silanimines it is a simple stretching vibration, whereas it is mixed with deformation vibrations of the phenyl rings in the 1,2-disubstituted silanimines. The calculations also reflect the dependence of the silanimine geometry on the substituents.

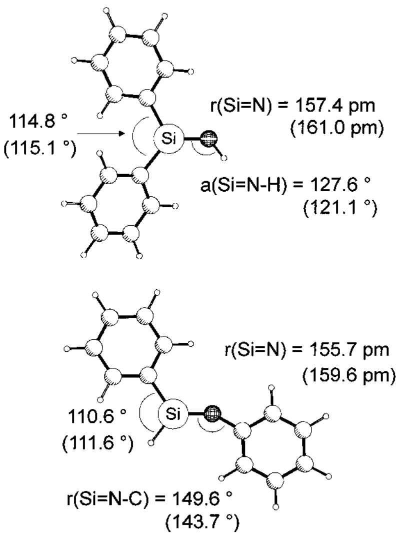


Figure 6. Calculated geometries (RHF/6-31G(d,p)) of 1,1-diphenylsilanimine (**3d**, top) and 1,2-diphenylsilanimine (**4d**, bottom). In parentheses, B3LYP/6-31G(d,p) values are given.

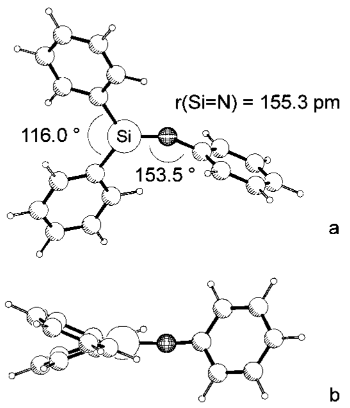


Figure 7. Calculated geometry (RHF/6-31G(d)) of 1,1,2-triphenylsilanimine (**3c**): (a) top view; (b) side view.

Table 5. Literature Data for Silanimines

		$r_{(SiN)}$/pm	$a_{(SiNSi)}$/deg	$a_{(RSiR)}$/deg
$t\text{-}Bu_2Si{=}N{-}Si(t{-}Bu)_3$	**3h**[a,b]	156.8	177.8	117.2
$t\text{-}Bu_2Si{=}N{-}Si(t{-}Bu)_2Ph$	**3i**[a,c]	157.2	168.3	115.1
$H_2Si{=}N{-}SiH_3$	**3j**[d]	154.9	175.6	110.1

[a] Data from crystal structure. [b] Reference 12. [c] Reference 17. [d] Data from calculation, 6-31/G(d), ref 29.

Experimental Section

Calculations. The ab initio and density-functional theory calculations were carried out using Gaussian 94[30] and standard basis sets on an IBM RS/6000 workstation. For **3c** and **8c** 6-31G(d) basis sets were used; for all other structures 6-31G(d,p) was used. RHF frequencies were scaled by 0.90, and B3LYP frequencies by 0.98.

Materials and General Methods. ^1H and ^{13}C NMR spectra were taken at 200.1 and 50.3 MHz, respectively, in $CDCl_3$ as solvent. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7. Phosphorescence excitation spectra were recorded in EPA at 77 K with a xenon high-pressure arc lamp in combination with a monochromator as excitation source. All reactions involving moisture-sensitive silicon reactants were performed under an atmosphere of dry argon.

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(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

Triphenylsilyl Azide 1c. **1c**[31] and **1d**[32] were prepared following general procedures. Triphenylchlorosilane (6.8 mmol, 2.0 g) was refluxed with sodium azide (9.2 mmol, 0.60 g) in 30 mL of dry tetrahydrofuran for 2 days. The white precipitate was filtered off, the solvent removed in vacuo, and the residue dried. For matrix experiments the substance was sublimed. Yield: 0.63 g (31%) after sublimation. Mp: 78 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.62 (m, 6 H, Ph), 7.42 (m, 9 H, Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.21, 135.15, 130.86, 128.26. EI-MS (*m*/*e* (%)): 303 (10), 301 (39) [M^+], 261 (8), 260 (28), 259 (100) [$M^+ - Ph$], 224 (11) [Ph_2SiN_3], 181 (17), 147 (25), 105 (25), 77 (8), 53 (10). IR (argon, 10 K): 3142.9 (2), 3096.0 (3), 3076.7 (9), 3060.9 (2), 3032.3 (2), 3017.3 (2), 3006.9 (1), 2147.2 (100), 1960.5 (1), 1892.1 (1), 1823.9 (2), 1592.9 (5), 1571.4 (1), 1487.4 (5), 1432.4 (35), 1381.8 (2), 1344.0 (7), 1323.4 (18), 1263.8 (3), 1188.8 (5), 1159.2 (1), 1122.1 (81), 1108.6 (8), 1069.5 (1), 1030.5 (2), 998.4 (8), 801.7 (2), 741.5 (6), 715 (70), 699.0 (57),620.5 (2), 578.9 (34), 510.8 (63), 505.2 (5), 486.1 (3) cm^{-1} (relative intensity). UV (argon, 15 K): $\lambda_{max} = 219, 254, 259, 264, 270$ nm. Phosphorescence (argon, 15 K): $\lambda_{max} = 413$ nm, $\tau = 0.5$ s; (methylcyclohexane, 77 K): $\lambda_{max} = 390$ nm, $\tau = 0.7$ s.

Triphenylsilyl Chloride 11. Phosphorescence (argon, 15 K): $\lambda_{max} = 408$ nm; (methylcyclohexane, 77 K): $\lambda_{max} = 357, 385$ nm, $\tau = 0.6$ s.

Diphenylsilyl Azide 1d. Diphenylchlorosilane (0.010 mol, 2.25 g) was refluxed with sodium azide (0.015 mol, 0.97 g) in 25 mL of dry tetrahydrofuran for 2 days. The white precipitate was filtered off, and the filtrate distilled in vacuo. Yield: 1.1 g (49%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.66 (d of mult, 4 H, Ph), 7.49 (m, 6 H, Ph), 5.57 (s, 1 H, Si−H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 134.67, 131.19, 130.45, 128.39. EI-MS (*m*/*e* (%)): 226 (7), 225 (40) [M^+], 184 (8), 183 (42) [$M^+ - N_3$], 148 (15), 147 (100) [$PhSiN_3$], 118 (17), 105 (32), 93 (22), 77 (17), 53 (19). IR (argon, 10 K): 3095.9 (1.5), 3080.3 (6.2), 3064.5 (2.4), 3034.6 (1.0), 3019.6 (0.8), 3010.4 (1.8), 2962.8 (1.3), 2874.9 (1.2), 2622.1 (0.9), 2339.5 (0.8), 2286.3 (2.9), 2186.5 (2.1), 2161.4 (100.0), 2156.4 (5.3), 2149.6 (1.8), 2144.7 (24.9), 2120.0 (1.3), 2039.8 (1.1), 1975.3 (0.8), 1958.9 (1.3), 1907.3 (0.8), 1890.7 (1.0), 1822.6 (1.5), 1593.9 (6.3), 1573.5 (0.6), 1491.0 (1.2), 1485.9 (4.4), 1433.3 (25.7), 1403.0 (1.1), 1362.6 (1.7), 1329.2 (5.6), 1326.0 (4.6), 1323.0 (40.8), 1320.2 (1.5), 1272.1 (2.7), 1267.1 (0.9), 1263.5 (1.1), 1190.1 (1.9), 1129.3 (38.2), 1121.1 (2.3), 1115.4 (7.0), 1068.3 (1.5), 999.4 (3.7), 959.3 (0.9), 943.0 (0.8), 938.1 (1.3), 926.7 (1.5), 853.8 (3.3), 851.9 (1.1), 845.7 (1.1), 838.3 (24.5), 831.7 (9.5), 824.2 (12.2), 810.9 (15.0), 804.2 (15.0), 799.9 (4.0), 794.9 (5.2), 791.9 (65.9), 740.3 (16.8), 734.8 (6.5), 732.2 (39.2), 722.2 (17.9), 698.3 (45.9), 680.8 (4.5), 581.2 (3.3), 571.5 (22.2), 491.3 (1.4), 486.9 (16.8), 469.0 (11.3), 466.3 (1.3), 463.7 (3.3), 441.1 (7.8) cm^{-1} (relative intensity). UV (argon, 15 K): 220, 252, 259, 264, 270 nm. Phosphorescence (argon, 15 K): $\lambda_{max} = 412$, 460 (sh), 530 (sh) nm, $\tau = 0.5$ s.

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrixes were produced by deposition of argon (Linde, 99.9999%) or mixtures of argon and oxygen (Messer Griesheim, 99.998%) on top of a CsI (IR experiments) or sapphire (UV−vis experiments) window at a rate of approximately 0.15 mmol/min at 30 K. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range 400−4000 cm^{-1}. UV spectra were recorded by using a HP 8452-A diode array spectrophotometer with a resolution of 2 nm. For phosphorescence spectra the spectroscopic window was replaced by a polished metal block which reflected the direct excitation light away from the detector. To record the spectra, an optical multichannel analyzer (OMA) was connected to the outer window of the cryostat. The OMA system consisted of a Princeton Applied Research OMA II system and Jobin Yvonne HR320 polychromator. The resolution was 0.5 nm/channel. Irradiations were carried out using an excimer laser (248 or 193 nm) or a mercury low-pressure lamp (Graentzel).

1,1-Diphenylsilanimine (3d) and 1,2-Diphenylsilanimine (4d). Irradiation of matrix-isolated diphenylsilyl azide (**1d**) with the light of a KrF excimer laser (248 nm) produced 1,1-diphenylsilanimine (**3d**) and 1,2-diphenylsilanimine (**4d**). IR data: Table 1.

Phenylsilaisonitrile (7c). Photochemical elimination of benzene from silanimines **3d** and **4d** ($\lambda = 248$ nm) produced phenylsilaisonitrile (**7c**). IR data: Table 2.

1,1,2-Triphenylsilanimine (3c). Irradiation of matrix-isolated triphenylsilyl azide (**1c**) produced 1,1,2-triphenylsilanimine (**3c**). IR data: Table 1.

Acknowledgment. This work was financially supported by the Deutsche Forschungsgemeinschaft ("Spezifische Phänomene in der Siliciumchemie") and the Fonds der Chemischen Industrie. We are obliged to Dr. H. Görner from the Max-Planck-Institut für Strahlenchemie in D-45413 Mülheim for phosphorescence measurements at 77 K. We also thank Prof. W. Schoeller for helpful discussions on the theoretical description of SiN double-bond systems.

OM9801296

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(32) Ettenhuber, E.; Rühlmann, K. *Chem. Ber.* **1968**, *101*, 743−750.