

Photochemistry of Dimethylsilyl Azide: Formation and Reactivity of 1,1-Dimethylsilanimine

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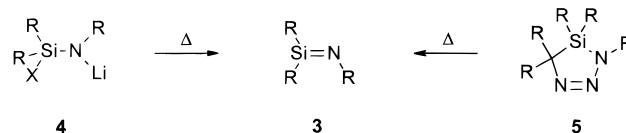
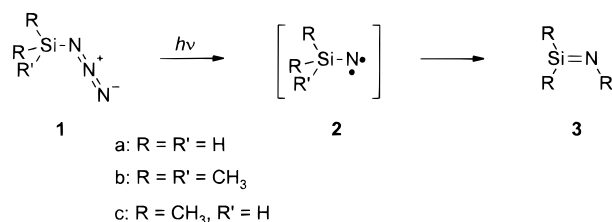
UV photolysis (248 nm) of matrix-isolated dimethylsilyl azide (**1c**) leads to the formation of 1,1-dimethylsilanimine (**3c**) and 1-(methylsilyl)methanimine (**6c**). The reactivity of the silanimine in the matrix was investigated. Thermal reaction at 50 K yields the *head-to-tail* dimerization product. Under the conditions of matrix isolation the silanimine proved to be stable toward oxidation and photooxidation with molecular oxygen and did not react with formaldehyde, carbon monoxide, and ammonia. (Dimethylsilyl)nitrene (**2c**) as the primary photoproduct of the azide could not be observed spectroscopically but was trapped with carbon monoxide or with molecular oxygen. Upon photolysis at $\lambda = 193$ nm methane and silyl isocyanide (**17**) are formed. The latter is the final product of a series of rearrangements of methyltrilosilane (**14**), which is postulated to be the primary product of the 193 nm photolysis of the silanimine.

Introduction

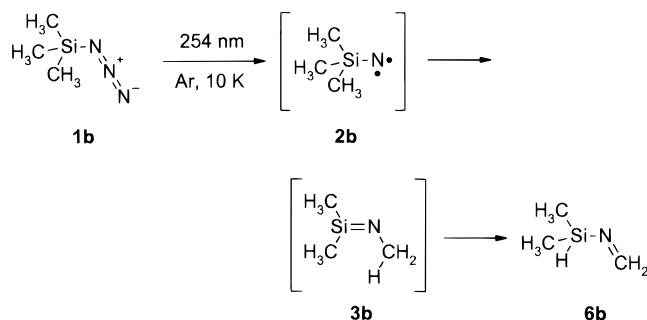
Silanimines **3** are highly reactive species¹ which can be generated photochemically from silyl azides **1** or thermally by elimination reactions, e.g. from lithiated aminohalogenosilanes **4** or triazasiloles **5** (Scheme 1). When carrying bulky substituents such as *tert*-butyl, silanimines can be isolated at ambient temperature.^{2,3} Transient silanimines can be trapped by suitable reagents such as alcohols and silyl ethers, which add across the Si=N double bond.^{1a} In the absence of trapping agents, silanimines in solution are known to yield 1,3-cyclodisilazanes, the formal *head-to-tail* dimerization products.⁴ However, if the salt-elimination method is used, the dimers are not necessarily the products of intermediate silanimines but may also result from other mechanisms.⁵

To investigate silanimines in cryogenic matrices, the photolysis of silyl azides is the preferred method. Maier et al.⁶ investigated the photolysis of the parent silyl azide ($R = R' = H$) **1a** and found, among other species, the unsubstituted silanimine **3a**. 1,1,2-Trimethylsilanimine (**3b**), however, which is the expected product of the photolysis of trimethylsilyl azide (**1b**; $R = R' = CH_3$), could not be observed directly, since it rearranges to 1-(dimethylsilyl)methanimine (**6b**) (Scheme 2).^{7,8}

Scheme 1



Scheme 2



[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

(1) (a) For a general review on multiple bonding to silicon see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) For a recent review on silanimines see: Hemme, I.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *39*, 159.

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Although much work has been done on the reactivity of silanimines in solution,^{1a} the knowledge of the reactivity of isolated silanimines at cryogenic temperatures is scarce. Here we report on the spectroscopic characterization of matrix-isolated 1,1-dimethylsilanimine (**3c**) and its photochemical and thermal reactivity.

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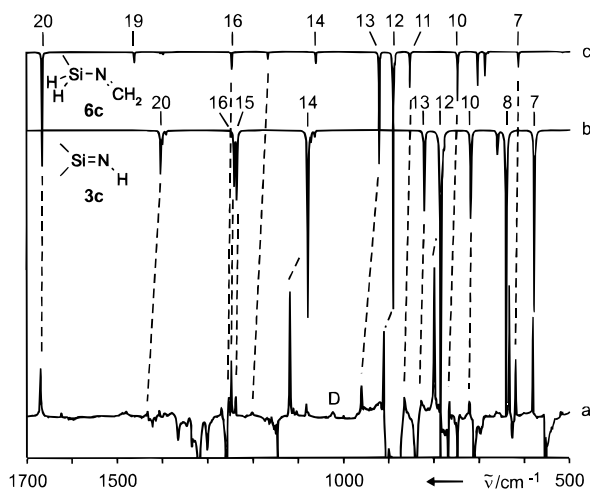


Figure 1. (a) IR difference spectrum showing the photolysis of dimethylsilyl azide (**1c**). (b) Calculated spectrum of **3c** (B3LYP/6-31G(d,p)). (c) Calculated spectrum of **6c** (B3LYP/6-31G(d,p)). Tentative assignments are based on band positions and intensities. The calculated spectra are scaled by a factor of 0.95 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 1. D = tetramethyldisiloxane impurity.

Results and Discussion

Photolysis of Dimethylsilyl Azide (1c). Dimethylsilyl azide (**1c**) is synthesized by heating dimethylchlorosilane with excess sodium azide in di-*n*-butyl ether and purified by preparative-scale gas chromatography. The IR spectrum of matrix-isolated **1c** is dominated by the very intense out-of-phase stretching mode of the azide group at 2151 cm⁻¹. The in-phase mode is found as a strong band at 1320 cm⁻¹. The characteristic bands of the Si–H stretching and deformation vibrations are observed at 2205 and 890 cm⁻¹, respectively.

UV irradiation of matrix-isolated **1c** (248 nm, KrF excimer laser) leads to the complete disappearance of the azide and formation of new IR absorptions. A characteristic band at 1118 cm⁻¹ shows two weak satellites shifted by 7 and 15 cm⁻¹, respectively, to the red (Figure 2). The splitting of the band and the relative intensities reflect the natural abundance of the three silicon isotopes ²⁸Si, ²⁹Si, and ³⁰Si. The isotopic shifts of the two less intense bands originate from the heavier isotopes ²⁹Si and ³⁰Si and allow us to assign this band to the Si=N stretching vibration. In combination with a band at 3406 cm⁻¹, characteristic of a N–H stretching vibration, the IR spectrum proves the formation of 1,1-dimethylsilanimine (**3c**) as a product of the photolysis of matrix-isolated **1c** (Figure 1, Table 1). As a second photoproduct 1-(methylsilyl)methanimine (**6c**) with bands at 1671 cm⁻¹ (characteristic of N=CH₂) and 2815 cm⁻¹ and weak absorptions in the Si–H stretching area is formed as well.

The spectral assignment is in accordance with calculated spectra of the two photoproducts. There is good agreement between experiment and theory for most of the bands; however, a larger deviation of 39 cm⁻¹ is found for the Si=N absorption at 1118 cm⁻¹. The experimental value for this vibration lies between that of the Si=O double bond in dimethylsilanone (1210

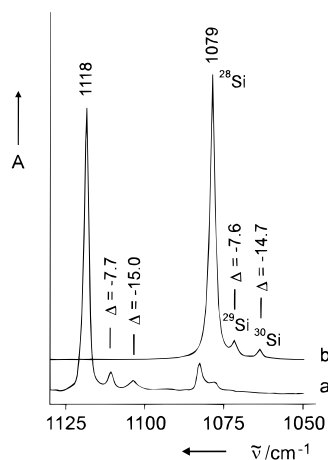
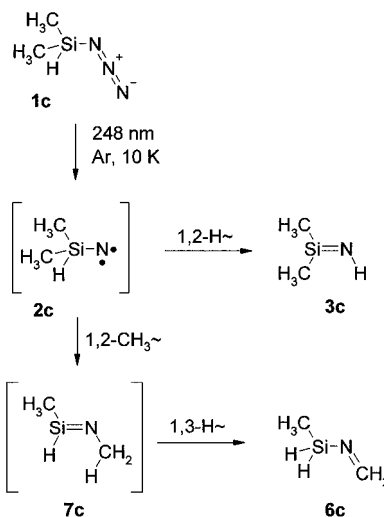


Figure 2. (a) IR spectrum after complete photolysis of dimethylsilyl azide (**1c**). (b) Calculated spectrum (B3LYP/6-31G(d,p)) of 1,1-dimethylsilanimine (**3c**). The calculated spectrum is scaled by a factor of 0.95, and a Lorentz band shape is simulated with a half-width of 2 cm⁻¹.

Scheme 3



cm⁻¹) and the Si=C double bond in 1,1-dimethylsilene (1004 cm⁻¹; Table 2). The pattern of the Si isotopic shifts can be very well reproduced by DFT calculations (Figure 2). Problems in the accurate calculation of Si=N stretching vibrations have also been reported by other authors.^{6,9} Three further isomers of **3c** (see below) were calculated at the same level of theory (B3LYP/6-31G(d,p)) and could clearly be excluded by comparison of the experimental and calculated spectra.

The formation of **3c** and **6c** during the photolysis of **1c** is in accordance with the reaction course given in Scheme 3. Upon photolysis of azide **1c** nitrogen is expelled and (dimethylsilyl)nitrene (**2c**) is formed as a highly reactive intermediate which is not stable under the conditions of the photolysis. 1,2-[H] or 1,2-[methyl] shifts result in the formation of 1,1-dimethylsilanimine (**3c**) and 1,2-dimethylsilanimine (**7c**), respectively.

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Table 1. IR Spectroscopic Data for Silanimine **3c and Silylimine **6c****

argon, 10 K		DFT (B3LYP/6-31G(d,p)) ^a						assignment
ν , cm ⁻¹	<i>I</i>	dimethylsilanimine (3c)			1-(methylsilyl)methanimine (6c)			
		no.	ν , cm ⁻¹	<i>I</i>	no.	ν , cm ⁻¹	<i>I</i>	
3404.3	11	27	3399	3				N-H str
2999.7	1	26	2999	1				C-H str
2982.1	1	25	2987	3				C-H str
					27	2979	2	C-H str
2967.3	0.5				26	2971	3	C-H str
		24	2960	5				C-H str
2954.6	2	23	2957	1				C-H str
					25	2906	23	C-H str
2855.3	9				24	2896	1	C-H str
		22	2895	1				C-H str
		21	2888	1				C-H str
2815.3	18				23	2811	24	C-H str
2171.5	5				22	2126	48	Si-H str
2137.4	55				21	2062	56	Si-H str
1670.4	37				20	1666	40	N=C str
1480.7	2				19	1462	3	HCH bend
1433.4	4							
1407.0	2	20	1404	10	18	1404	0	HCH bend
		19	1400	2				HCH bend
					17	1398	0	HCH bend
1379.3	0.5	18	1392	1				HCH bend
		17	1391	0				HCH bend
1254.2	14				16	1247	6	CH ₃ rock
1248.1	30	16	1242	13				CH ₃ rock
1238.7	10	15	1236	16				CH ₃ rock
1159.5	0.07				15	1167	2	
1118.6	77	14	1079	48				²⁸ Si=N str
1110.9	3		1072					²⁹ Si=N str
1103.9	2		1064					³⁰ Si=N str
1082.9	6				14	1061	4	HCH out of plane
961.2	18				13	922	42	HSiH bend
912.2	48				12	891	100	H- ²⁸ Si-H
						887		H- ²⁹ Si-H
					11	854	13	
865.9	12							
828.5	7	13	822	19				
800.0	100	12	786	100				²⁸ Si-N-H
795.6	5		782					²⁹ Si-N-H
790.9	4		779					³⁰ Si-N-H
779.4	3	11	780	0				HCH bend
766.7	8				10	749	18	
722.5	8	10	720	21				HCH bend
703.8	3				9	705	13	
					8	689	9	
662.7	1	9	662	6				
635.0	68	8	642	68				N-H bend
620.6	30				7	616	6	
582.6	53	7	580	43				
		6	579	0				
520.6	2				6	518	0	
495.3	3				5	490	4	
		5	264	14	4	264	2	
		4	215	2				
		3	204	0	3	193	2	
		2	98	0	2	137	0	
		1	72	0	1	98	1	

^a Frequencies are scaled by 0.95.**Table 2. Measured and Calculated IR Spectroscopic Data for Si=X Bands**

	$\nu(\text{Si=X})/\text{cm}^{-1}$			
	(H ₃ C) ₂ Si=O	(H ₃ C) ₂ Si=NH	H ₂ Si=NH	(H ₃ C) ₂ Si=CH ₂
experiment	1210 ^a	1118	1097 ^b	1004 ^c
theory	1218 ^a	1079 ^d	1061 ^d	991 ^e
difference	+8	-39	-36	-13

^a Reference 10. ^b Reference 6. ^c Reference 11. ^d B3LYP/6-31G(d,p), factor 0.95. ^e Reference 12.

Whereas **3c** is stable at 10 K in the matrix, **7c** is photochemically unstable under the conditions of its generation and rearranges via a 1,3-[H] shift to 1-(me-

thylsilyl)methanimine (**6c**). Thus, the system avoids the Si=N double bond by formation of the thermodynamically more stable N=C double bond.

The known matrix photochemistry of trimethylsilyl azide (**1b**) results in the formation of 1-(dimethylsilyl)methanimine (**6b**) as the only product, while 1,1,2-trimethylsilanimine (**3b**) was not observed.^{7,8} The formation of both the products of H and methyl migration from silicon to nitrogen in silylnitrene **2c** is surprising in view of the largely different migratory aptitudes of these groups in silylcarbenes. Thus, the rearrangement of dimethylsilylcarbene (**9c**) exclusively yields 1,1-dimethylsilene (**10c**) as the product of the migration of

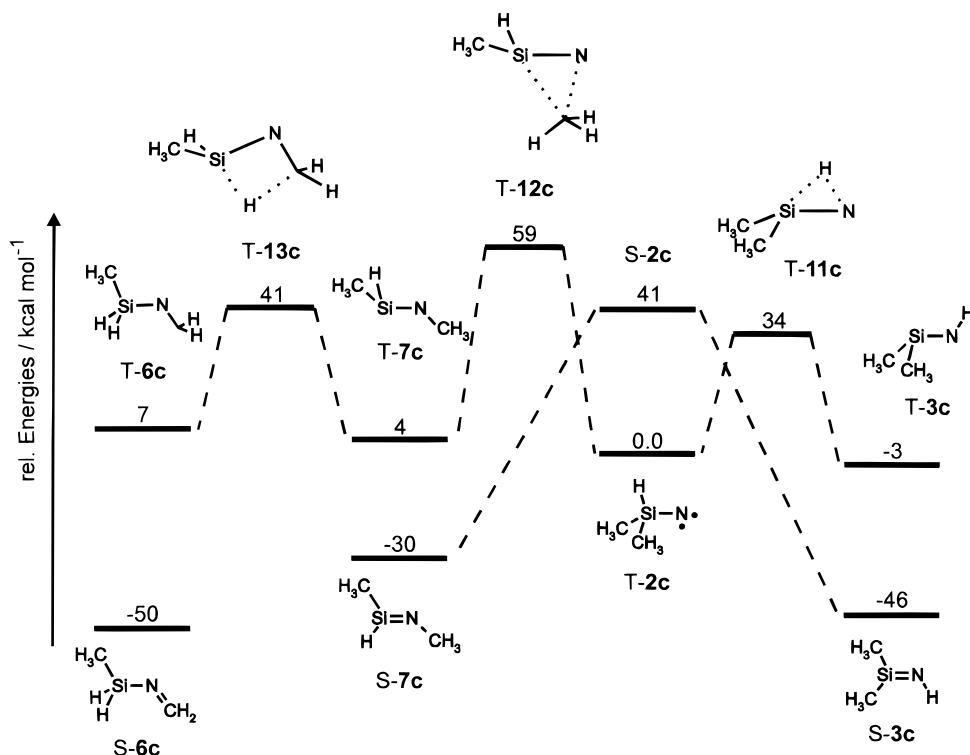
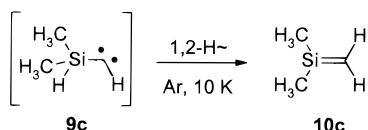


Figure 3. Schematic relative energies of singlet and triplet C_2H_7NSi species in kcal mol^{-1} , calculated at the B3LYP/6-31G(d,p) level of theory (UB3LYP for triplet species). The ground-state triplet nitrene T-2c is set to 0 kcal mol^{-1} . All energies have been corrected by zero-point vibrational energies.

Scheme 4



hydrogen (Scheme 4).¹³ The different selectivities of the rearrangements of **2c** and **9c** reflect the higher reactivity of silylnitrenes compared to silylcarbenes.

Calculations on the C_2H_7NSi Potential Energy Surface. The geometries of four isomeric species on the C_2H_7NSi potential energy surface ((dimethylsilyl)-nitrene (**2c**), 1,1-dimethylsilanimine (**3c**), 1,2-dimethylsilanimine (**7c**), and 1-(methylsilyl)methanimine (**6c**)) and three transition states connecting them (structures **11c** and **12c** for the isomerization of nitrene **2c** to silanimines **3c** and **7c**, respectively, and structure **13c** for the isomerization of **7c** to **6c**) have been calculated in their singlet (B3LYP/6-31G(d,p)) and triplet (UB3LYP/6-31G(d,p)) ground states (Figure 3, Table 3). As expected, the $^3A''$ ground state of the nitrene T-2c is higher in energy than the ground states of **3**, **6**, and **7**. Both experimentally observed species, 1,1-dimethylsilanimine (**3c**) and 1-(methylsilyl)methanimine (**6c**), are more stable than T-2c by about 50 kcal/mol. (A similarly large energy difference was found for the unsubstituted silylnitrene H_3SiN /silanimine $H_2Si=NH$ by Nguyen et al.).¹⁴ *trans*-1,2-Dimethylsilanimine (*trans*-**7c**) is still more stable than the nitrene T-2c but is considerably higher in energy than 1,1-dimethylsilan-

Table 3. Calculated Properties of C_2H_7NSi Species (B3LYP/6-31G(d,p))

	M^a	sc^b	sym	electronic state	rel E^c	$E(\text{uncor})^c$	ZPE c,d
2c	T	2.0056	C_S	$^3A''$	0	-266 446.1	52.6
3c	T	2.0051	C_S	$^3A''$	-3	-266 450.5	54.1
7c	T	2.0067	C_1		4	-266 442.3	53.5
6c	T	2.0058	C_S	$^3A''$	7	-266 436.7	50.8
11c	T	2.0147			34	-266 410.5	51.0
12c	T	2.0347			59	-266 385.4	51.5
13c	T	2.0099			41	-266 401.2	49.5
2c	S		C_S	$^1A'$	41	-266 404.6	52.5
3c	S		C_S	$^1A'$	-46	-266 494.6	55.2
7c	S		C_S	$^1A'$	-30	-266 477.9	54.6
6c	S				-50	-266 495.8	53.1

^a Multiplicity. ^b Spin contamination in s^2 . ^c kcal/mol. ^d Zero-point energy.

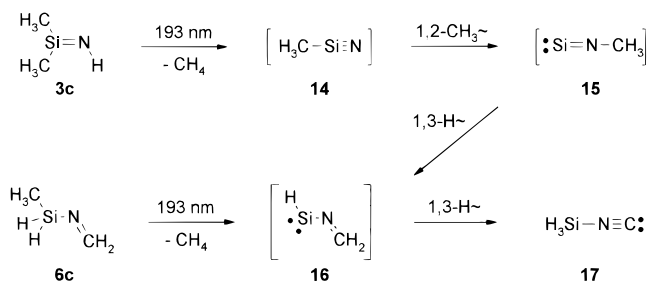
imine (**3c**). Obviously, 1,2-dimethylsilanimine (**7c**) is thermodynamically less favored than **3c**. No minimum was found for the isomeric *cis*-1,2-dimethylsilanimine (*cis*-**7c**).

The $^3A''$ nitrene T-2c is a minimum, separated from T-3c and T-7c by the transition states T-11c and T-12c, which are 34 and 59 kcal/mol higher in energy than the nitrene. In contrast to that, the $^1A'$ singlet nitrene S-2c (vertical excitation from $^3A''$ 40 kcal/mol) is no minimum at the B3LYP level of theory but rearranges without activation barriers to 1,2- or 1,1-dimethylsilanimine (S-3c and S-6c, respectively). A similar observation was reported for the silylnitrene-silanimine rearrangement ($H_3SiN \rightarrow H_2Si=NH$).¹⁴ It is thus obvious that the nitrene **2c** cannot be trapped even in an argon matrix at 10 K as long as it is generated in its singlet state, since the rearrangement to the imines will be faster than intersystem crossing to the triplet nitrene. Nev-

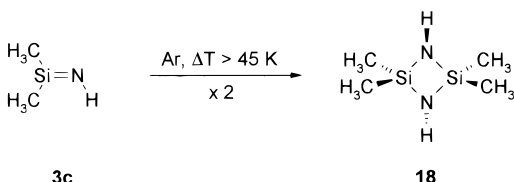
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Scheme 5



Scheme 6



ertheless, the nitrene **T-2c** is expected to be stable if it is generated in its triplet ground state (Figure 3).

Photochemistry of 1,1-Dimethylsilanimine. On prolonged irradiation of a matrix containing **3c** and **6c** with the light of an ArF excimer laser ($\lambda = 193$ nm), the bands of **3c** and **6c** decrease and new bands appear in the IR spectrum. By comparison with literature data the new products have been identified as methane¹⁵ and silyl isocyanide (**17**).¹⁶

As **17** cannot be formed in a one-step process from dimethylsilanimine (**3c**), several intermediates which could not be directly observed have to be postulated (Scheme 5). Loss of methane from silanimine **3c** results in the formation of methylnitrilosilane (**14**). Nitrilosilanes, which formally contain a silicon–nitrogen triple bond and an sp -hybridized silicon atom, are known to isomerize easily to iminosilenes with an sp^2 -hybridized silicon atom.^{1b} Calculations (CCD/6-31G(d,p)) show that (methylimino)silene (**15**) should be more stable than methylnitrilosilane (**14**; $\text{H}_3\text{CSi}\equiv\text{N}$) by about 57 kcal/mol. The next step is the rearrangement of (methylimino)silene (**15**) via a 1,3-H shift to yield the N-substituted carbon imine **16**. After two more 1,3-H shifts, imine **16**, which could also be formed by splitting off methane from 1-(methylsilyl)imine **6c**, gives the stable silyl isocyanide (**17**). The intermediates **14** and **15** have already been postulated by Maier et al.¹⁶ to explain the formation of silyl isocyanide in the photolysis of triazidomethylsilane.

Reactivity of 1,1-Dimethylsilanimine. The silanimine is stable in solid argon up to 42 K. A thermal reaction of the silanimine could be achieved by annealing the matrix to higher temperatures after capping the matrix with a layer of xenon, which prevents the evaporation of argon. At temperatures of about 49 K the silanimine dimerizes to form the head-to-tail dimer **18** (Scheme 6). The IR spectrum of **18** exhibits new bands at 3519 (N–H str), 1252, 1246 (Si–CH₃), and 1020 (N–H bend) cm^{-1} and is well-reproduced by DFT calculations (Table 4, Figure 4). The calculated structure has C_{2h} symmetry (Figure 5) and contains a planar cyclodisilazane ring with one amine hydrogen bent

Table 4. IR Spectroscopic Data for Cyclodisilazane **18**

no. ^b	argon, 10 K		DFT (B3LYP/6-31G(d,p)) ^a		sym	assignt
	ν , cm^{-1}	<i>I</i>	ν , cm^{-1}	<i>I</i>		
60	3519	7	3493	8	B	N–H str
37	1252	56	1244	10	A	CH ₃
36	1246	42	1242	15	B	CH ₃
34	1020	100	1014	100	A	N–H def

^a Scaled by 0.95. ^b Number of vibrational modes from the calculation.

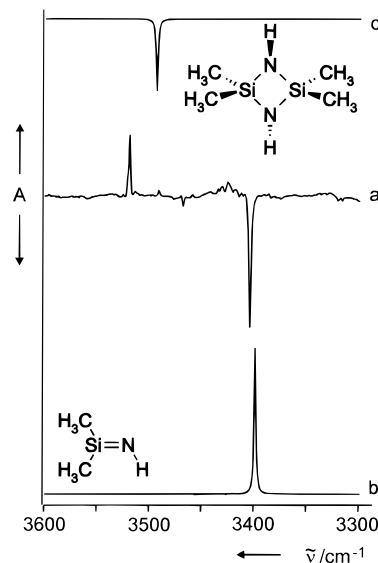


Figure 4. (a) IR difference spectrum of the formation of cyclodisilazane **18** on annealing the matrix containing **3c** to 49 K (top part: emerging band of **18**, bottom part: disappearing band of **3c**). (c) Calculated spectrum of **18**. (b) Calculated spectrum of **3c**. Both (b) and (c) were calculated at the B3LYP/6-31G(d,p) level of theory. The calculated spectra are scaled by a factor of 0.95 to allow direct comparison with the experimental spectrum, and a Lorentz band shape is simulated with a half-width of 2 cm^{-1} .

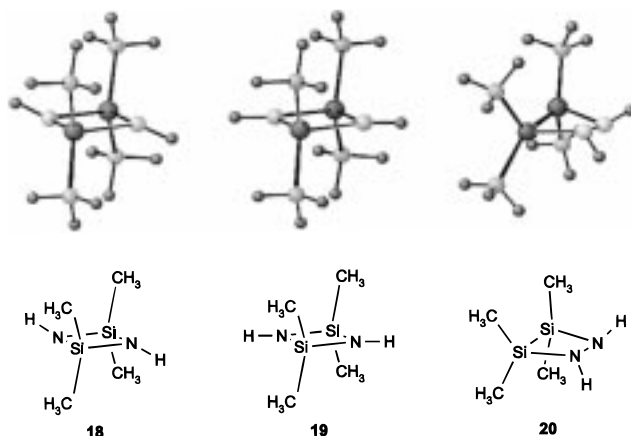


Figure 5. Calculated structures of cyclodisilazanes (B3LYP/6-31G(d,p)).

above and the other below the plane of the ring by 22°. The planar structure **19** (D_{2h}) was calculated to be the transition state for inversion at both nitrogen atoms, whereas no minimum was found for a structure with both hydrogen atoms on one side of the ring. The head-to-head dimer **20** (C_2) is about 75 kcal/mol higher in

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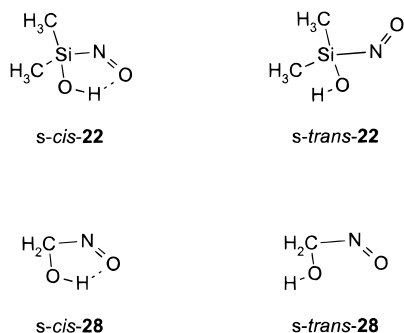
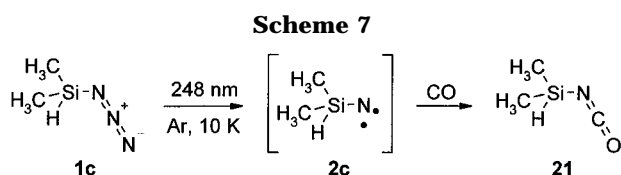


Figure 6.



energy and has been ruled out by comparing the calculated with the experimental spectrum.

Photocarbonylation of (Dimethylsilyl)nitrene (2c). Irradiation of dimethylsilyl azide in argon matrices containing 3–10% CO yields dimethylsilyl isocyanate (**21**) (Scheme 7), which was identified by comparison of the IR spectrum with that of an authentic sample. The isocyanate stretching vibration at 2295 cm^{-1} is the most intense band in the spectrum. In a 10% CO-doped argon matrix this absorption is slightly red-shifted to 2292 cm^{-1} .

Reactions with Molecular Oxygen. If **1c** is photolyzed in 1% O_2 -doped argon matrices, silanimine **3c** is still the main product. When the matrix was annealed at 45 K, the silanimine proved to be stable toward thermal oxidation and photooxidation ($\lambda > 305\text{ nm}$). Similarly, a reaction of **3c** with formaldehyde or ammonia (1% in argon) was not observed. This stability of a compound containing a silicon double bond is unexpected. Methylated silenes react readily with molecular oxygen¹³ as well as with formaldehyde¹⁷ under the conditions applied here. The relatively high temperature necessary for thermal dimerization also shows the low reactivity of this $\text{Si}=\text{N}$ double-bond system. The less polar 1,1-dimethylsilaethene (**10c**) dimerizes thermally in an argon matrix at about 35 K.¹¹

Irradiation ($\lambda = 248\text{ nm}$) of dimethylsilyl azide (**1c**) in 3–10% O_2 -doped argon matrices results in the formation of oxidation products and only traces of silanimine **3c**. New IR bands at 3555 cm^{-1} ($\text{Si}-\text{OH}$) and at 1516 and 1524 cm^{-1} ($\text{Si}-\text{NO}$) are assigned to dimethylnitrososilanol (**22**). The red shift of the $\text{Si}-\text{OH}$ band compared to a free hydroxy group indicates an intramolecular hydrogen bond to the oxygen of the nitroso group. DFT calculations show that the hydrogen bond in *s-cis*-dimethylnitrososilanol is part of a planar five-membered ring with an $\text{H}-\text{O}$ distance of about 217 pm (Figure 6). The calculated frequency for the $\text{O}-\text{H}$ stretching vibration at 3544 cm^{-1} and that of the nitroso group at 1523 cm^{-1} correspond well with the observed bands (Table 5).

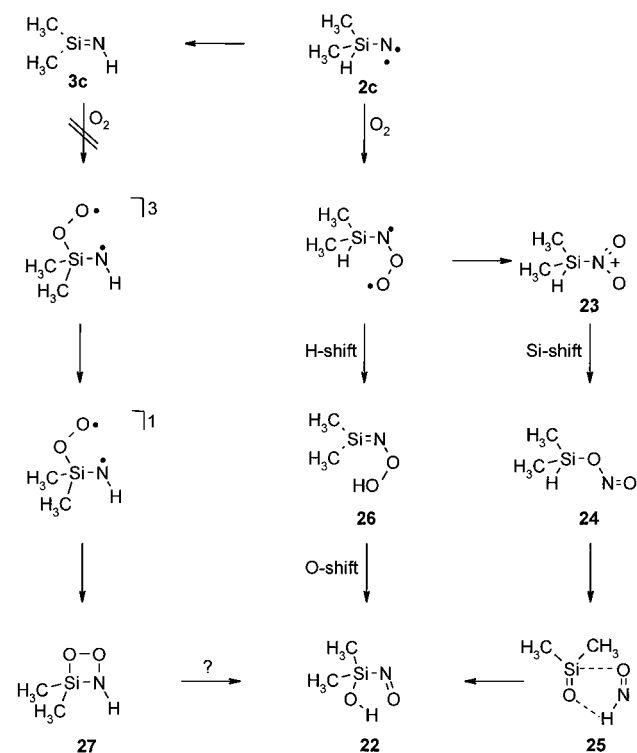
In the IR spectrum of *s-cis*-nitrosomethanol (**28**)

Table 5. IR Spectroscopic Data for *cis*- and *trans*-Dimethylnitrososilanol (**22**)

	ν, cm^{-1}	
	argon, 10 K	DFT (B3LYP/6-31G(d,p)) ^a
$\nu(\text{O}-\text{H}, \text{tr})$	3705 (?)	3699
$\nu(\text{O}-\text{H}, \text{cis})$	3555	3544
$\Delta\nu(\text{O}-\text{H}, \text{tr-cis})$	150	155
$\nu(\text{N}=\text{O}, \text{tr})$	1524	1528
$\nu(\text{N}=\text{O}, \text{cis})$	1516	1523
$\Delta\nu(\text{N}=\text{O}, \text{tr-cis})$	8	5

^a Scaled by 0.95.

Scheme 8



(Figure 6) reported by Müller and Huber¹⁸ and Jacox¹⁹ a similar red shift of the $\text{O}-\text{H}$ stretching vibration due to intramolecular hydrogen bonding is observed. Compared to the hydrogen-bonded *cis* rotamer, the free $\text{O}-\text{H}$ bond of *s-trans*-**28** is blue-shifted by 160 cm^{-1} , whereas there is only a small difference of 4 cm^{-1} for the $\text{N}=\text{O}$ stretching vibration.¹⁸

The second observed nitroso band at 1524 cm^{-1} in the spectrum of **22** indicates similar rotamers of the silanol with no hydrogen bonds. The corresponding free $\text{O}-\text{H}$ stretching vibration is expected around 3700 cm^{-1} but, due to strong absorptions of contaminations (water) and aggregates of substrate molecules with oxygen, is not observed.

An analogous pathway for the formation of **22** is outlined in Scheme 8 and involves the formation of the nitrosilane **23** from the reaction of nitrene **2c** with oxygen. The unstable nitrosilane rearranges to the more stable silyl nitrite **24** and to the van der Waals complex **25** between dimethylsilane and $\text{HN}=\text{O}$. A second possible pathway is the intermediate formation of the *N*(hydroperoxy)silanimine **26**. The reaction via the silaazadioxetane **27** can be excluded, since the

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silanimine was shown not to react with oxygen under these conditions.

Conclusion

Photolysis of dimethylsilyl azide (**1c**) in argon matrices at 10 K produces 1,1-dimethylsilanimine (**3c**) and 1-(methylsilyl)methanimine (**6c**). The primary photoproduct is (dimethylsilyl)nitrene (**2c**), which rapidly rearranges via hydrogen or methyl migration. Thus, the selectivity for the migration of hydrogen versus methyl from silicon to nitrogen is low. This is in contrast to the photolysis of (dimethylsilyl)diazomethane (**8c**), where only hydrogen migration and no methyl migration to the carbene center is observed.¹³ The intermediate nitrene **2c** can be trapped in matrices containing molecular oxygen or carbon monoxide.

1,1-Dimethylsilanimine (**3c**) is remarkably stable toward oxidation and photooxidation in the matrix. The only thermal reaction observed is the dimerization at temperatures higher than 45 K. On UV irradiation ($\lambda = 193$ nm) methane and silyl isocyanate (**17**) are formed, the isocyanate **17** being the final product in a series of rearrangements.

Experimental Section

Calculations. The ab initio and density functional theory calculations were carried out using Gaussian 94²⁰ and standard basis sets on an IBM RS/6000 workstation. With the known difficulties in the frequency calculation of Si=N compounds taken into account, geometry optimizations and frequency calculations were first performed at different levels of theory on the silanimine H₂Si=NH. The results were compared to the known experimental data and the method working best was then applied to the dimethyl compound. We are obliged to G. Maier and J. Glatthaar for private communications concerning the silanimine.

The geometries of the singlet species were optimized at the B3LYP/6-31G(d,p) level of theory. For the triplet species and transition states UB3LYP was used with the same basis set. The isomers on the CH₃NSi potential energy surface were optimized using CCD/6-31G(d,p).

Materials and General Methods. ¹H and ¹³C NMR spectra were taken at 200.1 and 50.3 MHz, respectively, in CDCl₃ as solvent. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7 instruments. All reactions involving moisture-sensitive silicon reactants were performed under an atmosphere of dry argon. All matrix-isolated compounds were purified by preparative-scale GLC using a Siemens RGC 202 gas chromatograph with a 4 m DC 200 column.

Dimethylsilyl Azide (1c). Dimethylchlorosilane (0.053 mol, 5.0 g) was heated with sodium azide (0.075 mol, 4.85 g) in 30 mL of dry di-*n*-butyl ether to 100 °C for 40 h. After the mixture had cooled to room temperature, the white precipitate was filtered off and the filtrate distilled until the head temperature reached 115 °C. The distillate contained the azide **1c** and siloxane impurities. It was finally purified by preparative GLC (48 °C, detector/injector 60 °C) before each experiment. The yield after GLC is about 1.5 g (28%). ¹H NMR (CDCl₃, 200 MHz): δ 4.66 (sept, 1 H, Si-H), 0.33 (d, 6

H, CH₃). ¹³C NMR (CDCl₃, 50 MHz): δ 2.63. EI-MS (*m/e* (%)): 101 (18) [M⁺], 100 (27) [M⁺ - H], 86 (55) [M⁺ - CH₃], 70 (10), 59 (37), 56 (44), 45 (37), 44 (21), 43 (100), 42 (28), 31 (68), 29 (59), 28 (32). IR (Ar, 10 K): 2987.0 (0.3), 2974.6 (0.5), 2205.5 (0.8), 2200.6 (0.1), 2197.0 (0.05), 2151.5 (100), 1431.2 (0.2), 1422.2 (0.3), 1415.0 (0.1), 1365.6 (1), 1334.9 (0.1), 1320.0 (10), 1301.2 (2), 1257.9 (6), 905.6 (9), 890.4 (10), 883.5 (3), 839.5 (8), 769.0 (0.01), 748.7 (2), 712.6 (5), 698.2 (0.3), 627.8 (0.4), 621.5 (0.2), 582.9 (0.5), 555.4 (1), 551.6 (0.5) cm⁻¹ (relative intensity). Anal. Calcd: C, 23.74; H, 6.97; N, 41.53. Found: C, 23.87; H, 7.03; N, 41.36.

Dimethylsilyl Isocyanate (21). The isocyanate was prepared by following a general literature procedure.²¹ Dimethylchlorosilane (4.72 g, 0.05 mol) was added slowly to lead cyanate (8 g, 0.027 mol) in 35 mL of dry xylene at -40 °C. The mixture was then refluxed for 10 h and filtered and the filtrate distilled. Preparative GLC yielded the isocyanate.

¹H NMR (CDCl₃, 200 MHz): δ 4.57 (sept, 1 H, Si-H), 0.31 (d, 6H, CH₃). ¹³C NMR (CDCl₃, 50 MHz): δ 0.5. EI-MS (*m/e* (%)): 101 (8) [M⁺], 100 (77) [M⁺ - 1], 86 (100) [M⁺ - CH₃], 70 (30), 43 (23). IR (Ar, 10 K): 2972.4 (2), 2295.6 (100), 2175.1 (6), 1448.7 (1), 1258.0 (6), 909.0 (6), 894.8 (3), 883.4 (2), 841.4 (5), 778.5 (5), 755.6 (2), 682.5 (2), 628.0 (1), 613.3 (1), 551.9 (1) cm⁻¹ (relative intensity).

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) or mixtures of argon and oxygen (Messer Griesheim, 99.998%), ammonia (99.99%), carbon monoxide (99.997%), or formaldehyde on top of a CsI 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 of 400–4000 cm⁻¹. Irradiations were carried out using an excimer laser (248 or 193 nm), a mercury low-pressure lamp (Graentzel), or Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR radiation from the lamps was absorbed by a 10-cm path of water.

1,1-Dimethylsilanimine (3c) and N-(Methylsilyl) Imine 6c. Irradiation of matrix-isolated dimethylsilyl azide (**1c**) with the light of a KrF excimer laser (248 nm) produced 1,1-dimethylsilanimine **3c** and 1-(methylsilyl)methanimine **6c**. IR data: Table 1.

1,1,3,3-Tetramethylcyclodisilazane (18). Annealing of matrix-isolated 1,1-dimethylsilanimine (**3c**) (Ar, coated with Xe) from 10 to 49 K produced the cyclodisilazane **18**. IR data: Table 4.

Silyl Isocyanide (17). Irradiation of a mixture of matrix-isolated silanimine **3c** and imine **6c** with the light of an ArF excimer laser (193 nm) produced methane and silyl isocyanide (**17**). IR (Ar, 10 K): 3025.9 (CH₄), 2201.4 (3), 2184.4 (2), 2097.8 (100), 1305.6 (CH₄), 952.1 (7), 941.2 (29), 900.2 (13), 871.8 (3), 868.4 (6), 725.2 (2), 685.9 (2), 603.0 (1) cm⁻¹ (relative intensity).

Dimethylsilyl Isocyanate (21). Irradiation of matrix-isolated dimethylsilyl azide (**1c**) in Ar containing 10% carbon monoxide produced dimethylsilyl isocyanate (**21**). IR (Ar, 10 K): 2292.3 cm⁻¹.

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