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Trimethylsilylnitrene and its Surprising Rearrangement to *N*-(Dimethylsilyl)methanimine via Silaziridine and Silaazomethine Ylide

Curt Wentrup,* Holger Lüerssen, Hugo Santos Silva, Alain Dargelos, and Didier Bégué*

Abstract:

Photolysis of trimethylsilyl azide at 254 nm in Ar matrix at 15 K generates the triplet ground state trimethylsilylnitrene **2aT**, observed by ESR spectroscopy ($|D/hc| = 1.540 \text{ cm}^{-1}$; $|E/hc| = 0.0002 \text{ cm}^{-1}$). Calculations at the CASPT2(14,13) level reveal the open-shell singlet nitrene **2aS**(¹A") is a discrete intermediate lying ~38 kcal/mol above the triplet. The normally expected rearrangement of the nitrene **2aS** to dimethylsilanimine **3a** has a high calculated barrier (33 kcal/mol), which explains why this product has never been observed. Instead, the singlet nitrene **2aS** inserts into a methyl C-H bond to yield silaziridine **12** via an activation barrier of only 6 kcal/mol. Ring opening of **12** generates a 1-silaazomethine ylide **13**, in which a facile 1,2-H shift yields *N*-(dimethylsilyl)methanimine **5**, all with barriers well below the energy of the singlet nitrene.

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Introduction

Despite extensive experimental and computational investigations, our understanding of silylnitrenes 2 (eq 1) is still very limited, especially as regards the existence of a singlet state (open shell $2S(^{1}A'')$ or closed shell $2S(^{1}A'')$).

$$\begin{array}{ccc} R_{3}Si-N_{3} & \longrightarrow & R_{3}Si-N: \\ \mathbf{1} & -N_{2} & \mathbf{2} \end{array} \quad (1)$$

a: R = CH₃
b: R = Ph

Pyrolysis of triphenylsilyl azide **1b** in a vacuum system at 680 °C yields a cyclic dimer $[Ph_2SiNPh]_2$ and a linear polymer, suggesting the intermediacy of the silanimine $Ph_2Si=N-Ph$ **3b**,^[1] but pyrolysis of trimethylsilyl azide **1a** at 500 °C under nitrogen flow was reported to yield about 20 compounds with none identified. Evidence for the formation of silanimines $R_2Si=NR$ **3** was obtained by co-pyrolysis of trialkyl- and triphenylsilyl azides with trapping agents in an atmospheric pressure nitrogen flow system at 610 °C.^[2] The imines underwent Wittig-type reactions with aldehyde and ketones and were also trapped with (Me₂SiO)₃ and (Me₂SiNMe)₂ in co-pyrolysis reactions to form eight-membered ring systems **4** in moderate yields (eq 2). These products were also obtained by photolysis of the azides.^[3]

$$\begin{array}{c} \mathsf{RR'}_2\mathsf{Si}\mathsf{-N}_3 + (\mathsf{Me}_2\mathsf{SiO})_3 & \xrightarrow{\mathsf{FVP}} \left[\mathsf{R'}_2\mathsf{Si}\mathsf{=}\mathsf{NR}\right] \xrightarrow{(\mathsf{Me}_2\mathsf{SiO})_3} & \xrightarrow{\mathsf{R'}} \left[\stackrel{\mathsf{K'}}{\underset{i=N}{\mathsf{Si-N}}} \right] \xrightarrow{\mathsf{Ne}_2} \left[\mathsf{R'}_2\mathsf{Si}\mathsf{=}\mathsf{NR} \right] \xrightarrow{\mathsf{Me}_2\mathsf{Si}} \left[\stackrel{\mathsf{Ne}_2\mathsf{Si}}{\underset{i=N}{\mathsf{O}}} \right] \xrightarrow{\mathsf{O}} \left[\stackrel{\mathsf{Ne}_2\mathsf{Si}}{\underset{i=N}{\mathsf{Ne}_2}} \right] \xrightarrow{\mathsf{O}} \left[\mathsf{Ne}_2\mathsf{Si} \right] \xrightarrow{\mathsf{O}} \left[\stackrel{\mathsf{Ne}_2\mathsf{Si}}{\underset{i=N}{\mathsf{O}}} \right] \xrightarrow{\mathsf{O}} \left[\stackrel{\mathsf{Ne}_2\mathsf{Si}} \atop \\ \mathsf{O}} \right] \xrightarrow{\mathsf{O}} \left[\stackrel{\mathsf{Ne}2\mathsf$$

The matrix photolysis of trimethylsilyl azide **1a** at 17 K was investigated by Ogilvie, who postulated a rearrangement of an initially formed but unobserved silanimine to a silylimine: **1a** \rightarrow [**3a**] \rightarrow **5** (eq. 3).^[4] Perutz also concluded that the matrix photolysis of trimethylsilyl azide at 10 K did not result in compounds containing Si=N bonds, but instead C=N and Si-H bonds ascribed to **5** or, less likely, Me₂Si(H)-CH=NH.^[5] Formation of **5** was confirmed by Ferrante, who also obtained **2a** by microwave discharge in N₂ and Ar.^[6]

$$(H_{3}C)_{3}Si-N_{3} \xrightarrow{h\nu} \begin{bmatrix} H_{3}C \\ Si=N \\ H_{3}C & CH_{3} \end{bmatrix} \xrightarrow{H_{3}C} \begin{array}{c} H_{3}C \\ SiH-N \\ H_{3}C & CH_{2} \end{array} (3)$$
1a 3a 5

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FVP of trimethylsilyl azide **1a** at 830 $^{\circ}$ C/10⁻² hPa with online photoelectron spectroscopic monitoring resulted in ionization peaks at 9.3 and 10.9 eV assigned to **5**, but the putative silanimine **3a** was not observed.^[7]

Yet, matrix photolysis experiments have clearly revealed the formation of other silanimines of the type RR'Si=NR" (e.g. 10 and 11, Scheme 1) and silylimine 9 from silyl azides $6^{[8,9]}$ but again, the *N*-methylsilanimine 8 was not observed. Silylnitrenes 7 were postulated, but neither triplets nor singlets were observed.



Scheme 1. Photochemical silyl azide rearrangements

Early calculations on trimethylsilylnitrene **2a** located the triplet state (³A"), but a singlet was not mentioned.^[10] Calculations on the unsubstituted silyl azide **6a** by Nguyen et al.^[11] indicated that the loss of N₂ is concerted with the rearrangement to silanimine H₂Si=NH **10**, and that a singlet nitrene H₃Si-N does not appear as a distinct intermediate, although it was mentioned that preliminary data suggested that the open-shell ¹A" singlet state might play a role in photolysis.

DFT calculations on **6b** by Kuhn and Sander confirmed the concerted nature of imine formation and the absence of a minimum for the singlet nitrene **7b**S.^[8] In a study of bicyclic compounds containing twisted Si=N bonds, Michl et al.^[12] also concluded that silanimine formation from silyl azides was most likely concerted with N₂ loss, and that discrete singlet silylnitrenes were not involved. However, Bertrand et al. concluded that there are two reaction paths in the photolysis of cyclic *Si*-azidosilanes in solution, one involving the triplet nitrene, which abstracts H from solvent and results in dimerization of the resulting free radicals, the other being the concerted formation of silanimine from the azide without the occurrence of a singlet silylnitrene.^[13]

Triplet silylnitrene **2aT** has been generated by microwave discharges in N_2 or Ar and investigated by ESR spectrosocopy in N_2 and Ar matrices at 10-20 K.^[6] A zero-field splitting

(ZFS) parameter |D/hc| = 1.57 cm⁻¹ in N₂ was measured, but the ESR signal was destroyed, if the sample was briefly exposed to the radiation of a Hg arc lamp or on annealing the matrix to temperatures of ~35 K. Therefore, the nitrene was reportedly not observable under UV irradiation due to rapid destruction.^[6]

Silylnitrenes were also generated by γ -irradiation of trimethylsilyl azide **1a**, triphenylsilyl azide **1b**, and mixed methyl(phenyl)silyl azides using a ⁶⁰Co source and investigated by ESR spectroscopy in solid solution at 77 K. For **2aT** the ZFS parameters |D/hc| = 1.54 cm⁻¹ and |E/hc| = 0.0035 cm⁻¹ were determined.^[14] Methyl(phenyl)silyl azides and diazides PhSiMe(N₃)₂ and PhSi(N₃)₃, also yielded ESR spectra with |D/hc| close to 1.5 cm⁻¹ when the azides were irradiated in solid solution at 4 K (λ >350 nm), but trimethylsilylnitrene **2aT** was not observed under these conditions, and no nitrenes were observable at 77 K under photolysis conditions. The ¹⁴N hyperfine splitting was observable under the γ -irradiation conditions, but not when the azides were photolyzed at 4 K in solid solution. It was theorized that the silylnitrenes abstract H from solvent even at 40 K.

Experimental

Trimethylsilyl azide was deposited together with Ar (ratio ~1:1000) on a Cu rod at 15 K in a closed-cycle liquid helium cryostat. No signals were observable by ESR spectroscopy (9.3285 GHz, Varian X-band spectrometer). Irradiation of the matrix at 254 nm for 2 h generated the transition shown in Figure 1, $X_2 = 8178$ G, $Y_2 = 8187$ G, $H_0 = 3374.4$ G, |D/hc| = 1.540 cm⁻¹; |E/hc| = 0.0002 cm⁻¹. FVP of the azide at 500 °C and deposition of the product with Ar at 10 K did not result in any observable ESR absorption.

Computational Methods

Ground-state geometries and energies were determined at the DFT level using the B3LYP exchange-correlation functional with the 6-311G(d,p) basis set. The UB3LYP approach was used for systems capable of existing in open-shell states. In order to obtain reliable energies of the open-shell singlet (OSS) nitrenes and the transitions states connecting them to isomeric molecules, calculations were carried out at both the CASPT2(9,8)/6-311+G(d,p) and CASPT2(14,13)/SP/6-311+G(d,p) levels. Calculations were performed using the Gaussian 09 and the Molpro program packages.^[15,16] The transition state optimizations and IRC calculations are carried out at both DFT and CASPT2 levels. Excited-state calculations were performed using ORCA.^[17] Harmonic and anharmonic frequencies were calculated at the

B3LYP/6-311++G(3df,3pd) level. Natural spin densities calculated at the B3LYP/6-311g(dp) level for Me₃Si-N (**2aT**) were 1.93 on N and -0.049 on Si (see Supporting Information). Spin-spin (SS) and spin-orbit (SO) contributions to the zero-field slitting (ZFS) parameters were calculated with the BP86 exchange-correlation functional in UKS mode using the Resolution of the Identity approximation and with the def2-TZVPP basis set. Convergence criteria were set to very tight. SO coupling was calculated by solving the spin Hamiltonian in coupled perturbed form, and SS was calculated directly from the canonical orbitals for the spin density. All calculations of ZFS parameters were performed using the ORCA 3.0.3 software.^[17]

Results and Discussion

The Triplet Nitrene.

Although previous researchers had reported that the ESR spectrum of the triplet nitrene **2aT** was not obtainable under matrix UV photolysis conditions, we found that photolysis of trimethylsilyl azide **1a** in Ar matrix at 254 nm for 2 h generated a transition at 8187 G ascribed to Me₃Si-N **2a**T with ZFS parameters |D/hc| = 1.540 and |E/hc| = 0.0002 cm⁻¹ (Figure 1) in excellent agreement with the data from γ -irradiation.^[6]



Figure 1. ESR spectrum of trimethylsilylnitrene **2aT** (³A") in Ar at 15 K. $X_2 = 8178$ G, $Y_2 = 8187$ G, |D/hc| = 1.540 cm⁻¹; |E/hc| = 0.0002 cm⁻¹ ($H_0 = 3374.4$ G). Inset: repeated scan.

We have reported an excellent linear correlation between observed |D/hc| values and natural spin densities on the nitrene-N for a large number of nitrenes, calculated at the B3LYP/EPR-III level.^[18,19,20] This would require a spin density on N of 1.83 for a *D* value of 1.54. The calculated natural spin densities in Me₃Si-N **2aT** are 1.93 on N and -0.049 on Si at the B3LYP/6-311g(dp) level. Although the value for N is overestimated by 5%, which is below the computational accuracy, the high *D* value (1.54) demonstrates that there is little or no delocalization of a nitrene electron onto Si. This is clearly seen in the total calculated electron density projected on the spin density (Figure 2).



Figure 2. Total electron density of 2aT projected on the spin density. Blue = high spin density.

The relatively high *D* value of 1.54 cm⁻¹ is similar to those of alkylnitrenes, which again indicates little or no delocalization of electron spin onto Si. There is only a modest calculated contribution of spin-orbit coupling (SOC) to *D* by 0.10 cm⁻¹. Similarly, a SOC contribution to *D* of 0.15 cm⁻¹ was calculated for H₃SiN.^[21] In contrast, very strong SOC causes high *D* values in triplet silylenes ($D \sim 1.64 \text{ cm}^{-1}$).^[22] Since SOC is inversely proportional to the energy difference between the mixing states,^[23] the large S-T gap in silylnitrene (~38 kcal/mol) as well as the fact that the singlet state is an open shell may be responsible for the low level of SOC in silylnitrenes. Other examples of deviation from the linear correlation of *D* values with spin densities due to SOC have been summarized.^[20]

Ferrante obtained the IR spectrum of 2aT in N₂ matrix at 10 K by depositing the product of the microwave discharge.^[6] This only produced small amounts of the silylimine 5, but a better yield of 5 was obtained by matrix photolysis. The silanimine 3a was not characterized. We have confirmed Ferrante's assignments by calculating the IR spectra of 2aT, 3a, and 5 (see Supporting Information) at the B3LYP/6-311++G(d,p) level, which has given excellent results for a variety of nitrenes.^[24,25] The experimental IR spectra ascribed to 2aT and 5 are in excellent agreement with the calculations.

Reaction Mechanism.

In order to gain more clarity on the nature of the singlet nitrene Me₃Si-N 2aS and its possible involvement in the pyrolysis and photolysis of trimethylsilyl azide 1a, we carried out calculations at DFT as well as CASPT2 (10,9) and CASPT2(14,13) levels.

At the DFT level, the lowest energy path to the silanimine Me₂Si=NMe **3aS1** is clearly the concerted reaction of the azide (Figure 3); the transition state (A) resembles a distorted silylnitrene, where one Me group is already tilted toward the N atom (Figure 3). This transition state has a large degree of closed-shell singlet nature. The activation energy, which is largely the barrier for loss of N₂ from azide **1a** is high, ~61 kcal/mol.



Figure 3. The mechanisms of formation and rearrangements of triplet and singlet trimethylsilylnitrenees **2aT** and **2aS** at the DFT level. The triplet (T) and two different conformers (S1 and S2) of the singlet silanimine **3a** can form. Energies in kcal/mol.

However, there are two non-concerted paths as well, via the singlet and triplet nitrenes, but these have very much higher activation energies (Figure 3) and would not be expected to play any role, if the results of the DFT calculations were accepted.

A major difference at the CASPT2 levels is that the open-shell singlet trimethylsilylnitrene 2aS (A") is a discrete intermediate (Figure 4). The activation barrier for

its formation by N₂ loss from the azide is 60 kcal/mol, very close to the 61 kcal/mol at the DFT level. Activation energies for decomposition of silyl azides have not been reported, but the azides are said to be surprisingly stable.¹ Azide **1a** has been pyrolysed in flow systems at atmospheric pressure at temperatures of 350-430 $^{\circ}C^{[26]}$ and 500-600 $^{\circ}C^{,[1,2]}$ and in an FVP system at 800 $^{\circ}C/10^{-2}$ mm.^[7a]

The calculated singlet-triplet splitting in **2a** is high, ~38 kcal/mol (Figure 4). The high value agrees with previous calculations for H₃Si-N **7a**, 42.3 kcal/mol (MCSCF/6-3lG(d))^[27] and 39.7 kcal/mol (MP4SDQ),^[9] and for Me₂Si(H)-N **7b** 41 kcal/mol at the B3LYP/6-31G(dp) level.^[6] For consistency, we calculated the S-T splitting in H₃SiN **7a** (see below) at the CASPT2(8,9) level as 41 kcal/mol, very close to the value for **2a**.

The singlet nitrene **2aS** can rearrange to the silanimine **3aS2** (Figure 4), but again the barrier is high, ca. 33 kcal/mol above the singlet nitrene, or 94 kcal/mol above the azide. It is not surprising then, that there is no experimental evidence for formation of Me₂Si=NMe **3aS2** in the reaction.



Figure 4. Formation of singlet Me₃Si-N S(A") **2aS** and (potentially) silanimine **3aS2** at the CASPT2(9,8)/6-311+G(d,p) (upright numbers) and CASPT2(14,13)/SP/6-311+G(d,p) (*numbers in italics*) levels. Energies in kcal/mol.

However, there is an alternate and much more favourable route to the observed reaction product $Me_2Si(H)-N=CH_2$ 5 (Figure 5). Here, the singlet nitrene 2aS inserts into a

methyl group to form a silaziridine^[7a] **12** (Scheme 2, Figure 5 and Figure 6) via a transition state lying only 6 kcal/mol above the nitrene.



Figure 5. Formation of trimethylsilylnitrene 2aS and the silaaziridine 12 at the CASPT2(9,8)/6-311+G(d,p) (upright numbers) and CASPT2(14,13)/SP/6-311+G(d,p) (*italics*) levels. Energies in kcal/mol.

Silaziridine 12 can easily rearrange to the methanimine 5 by ring opening to a zwitterionic intermediate 13, $Me_2Si^{(-)}-NH^{(+)}=CH_2 \leftrightarrow Me_2Si=NH^{(+)}-CH_2^{(-)} \leftrightarrow Me_2Si^{(+)}-NH-CH_2^{(-)}$, which is in fact a 1-silaazomethine ylide (Scheme 2 and Figure 6). It is well known that aziridines undergo ring opening to azomethine ylides both thermally and photochemically.^[28] This takes place in thermal reactions well below the temperatures required for decomposition of silyl azides.



Scheme 2. The silazirine 12 – silazomethine ylide 13 route to *N*-silylimine 5.

If the postulated, thermally relaxed silanimine **3aS1** were formed, it would need to overcome a barrier of nearly 60 kcal/mol and undergo two hydrogen shifts to yield **5** (Figure 6). Activation barriers for direct 1,3-H shifts are usually very high, because they are thermally forbidden by the Woodward-Hoffmann rules.^[29] Therefore, such reactions commonly proceed by different, lower-energy mechanisms.^[30,31] In our case, the formal 1,3-H shift **3a** \rightarrow **5** takes place in the form of two consecutive 1,2-H shifts via the silaazomethine ylide **13** (Figure 6).



Figure 6. Two paths for formation of *N*-silylmethanimine Me₂Si(H)-N=CH₂. Numbers in upright font: CASPT2(10,9); *italics*: CASPT2(14,13); in parentheses: DFT (kcal/mol). Blue: triplets; black: singlets; orange: the singlet silaziridine – silaazomethine vlide route.

The silaziridine 12 - silazomethine ylide 13 path (orange path in Figure 6) is clearly favored energetically with its maximum transition state lying only ~45 kcal/mol above the triplet and 6 kcal/mol above the singlet nitrene, 2aT and 2aS, respectively. This route explains why the silanimine Me₂Si=NMe 3a has never been observed experimentally. Silanimine 3a may not even be formed as an intermediate; the conformer 3aS1 should be relatively stable and observable, whereas the unstable conformer 3aS2 is a very transient species, which can proceed to the product 5S with virtually no activation barrier (Figure 6). Also the triplet nitrene 2aT can rearrange to the final product, 5aT, which would then undergo intersystem crossing to the ground state 5aS. Moreover, 3aS2 and 3aT are nearly degenerate, and their energy profiles cross at a point close to the 3aS2 and 3aT minima, thereby allowing the reaction to pass easily from the triplet to the singlet energy surface. In addition, the singlet and triplet profiles also cross close to the transition states for the rearrangement $2aT \rightarrow 3aT$ and $2aS \rightarrow 3aS2$ (the crossing points are marked in Figure 6; see also Supporting Information).

In contrast, the simpler silanimines Me₂Si=NH **10b** and PhSi(H)=NPh **11** (Scheme 1) are observable^[8,9] – probably because here there is no *N*-methyl group, which could form a silaziridine, a silazomethine ylide, and hence a silylmethanimine. We calculated the transition state for the simplest 1,2-H shift H₃Si-N \rightarrow H₂Si=NH (**7a** \rightarrow **10a**) which lies only 4 kcal/mol above the singlet nitrene, and 41 kcal/mol above the triplet, at the CASPT2(8,9) level (Figure 7). Notably, the transition states for the singlet and triplet paths are nearly degenerate, and the reaction can easily pass from one to the other at this point. Once either **10aS2** or **10aT** is formed, simple rotation or intersystem crossing will generate the ground state silanimine **10aS1**.



Figure 7. Reaction paths for the 1,2-H shift in silvlnitrene H₃Si-N 7a to H₂Si=NH 10a calculated at the CASPT2(8,9)/6-311+G(d,p) level of theory (values in parenthesis are calculated at the B3LYP/6-311G(d,p) level of theory). Energies in kcal/mol.

Conclusion

Triplet ground state trimethylsilylnitrene **2aT** is generated by UV-photolysis of trimethylsilyl azide in Ar matrix at 10-15 K. CASPT2(14,13) calculations indicate that the open-shell singlet nitrene **2aS**(1 A") is a discrete intermediate lying 38 kcal/mol above the triplet. The rearrangement of singlet nitrene **2aS** to *N*-(dimethylsilyl)methanimine **5** takes place by a new reaction mechanism, whereby nitrene **2aS** inserts into a methyl C-H bond to form a silaziridine **12**. Ring opening of **12** generates a 1-silaazomethine ylide **13**, in which a facile 1,2-H shift yields the final product, **5**. This process is considerably easier than the usually expected 1,2-shift of a methyl group to yield a silanimine **3a** (6 versus 33 kcal/mol). The singlet and triplet energy surfaces overlap at the level of **3aS2** and **3aT**, thus implying facile interchange between the singlet and triplet energy surfaces. The mechanism described in Figure 6 may apply whenever *Si*-methyl groups are present in silylnitrenes. The 1,2-H shift in

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the unsubstituted singlet silylnitrene 7a to silanimine 10a also has a very low calculated barrier of 4 kcal/mol, and again the singlet and triplet energy surfaces overlap near the transition state.

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Graphical Abstract and Entry for Table of Contents:

Unusual rearrangement of trimethylsilylnitrene: Rather than the widely assumed 1,2methyl migration, the open-shell singlet trimethylsilylnitrene **2a** inserts into a methyl C-H bond to yield silaziridine **12** over an activation barrier of only 6 kcal/mol. Ring opening of **12** generates the 1-silaazomethine ylide **13**, in which a facile 1,2-H shift yields the final product, *N*-(dimethylsilyl)methanimine **5**.



Silylnitrene Rearrangement C. Wentrup,* H. Lüerssen, H. S. Silva, A. Dargelos, D. Bégué*

Trimethylsilylnitrene and its Surprising Rearrangement to *N*-(Dimethylsilyl)methanimine via Silaziridine and Silaazomethine Ylide