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Gas-Phase Characterization of Unhindered Silanimines by Photoelectron Spectroscopy: Experimental and Theoretical Study of the Si═N Double Bond[1]

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The coupling of flash vacuum thermolysis reactions (retro [2+2] cleavages) with photoelectron spectroscopy allowed the first direct characterization of several highly reactive N-alkylated silanimines. For the trimethylsilanimine **1b**, the IPs corresponding to the ejection of an electron from the nitrogen lone pair (n_N) and the $\pi_{Si=N}$ orbital are observed at 7.9 and 8.3 eV, respectively. In the case of the N-isopropylated and N-*tert*-butylated analogues **1c**,**d**, these characteristic ionizations are energetically closed (7.8 and 7.4 eV). These unexpected attributions have been corroborated by the *ab initio* calculations of the ionization energies using 6-31G(d) and LANL1DZ basis sets and MP2 level. Our results have been completed by the determination of the structural and electronic characteristics of these silanimines.

Introduction

The existence of π bonds involving overlap of p orbitals between silicon and other elements has been questioned for a long time: None of these multiple bonded systems had been isolated until 1966, when Gusel'Nikov proved the existence of dimethylsilene.[2]

Among these compounds, the silanimines **1**, which contain a silicon−nitrogen double bond, are of particular interest because of their role as material precursors.[3]

However, the simplest unhindered silanimines remain practically unknown in the monomeric state. In fact, they tend to undergo polymerization or other reactions such as oligomerization, hydrolysis, etc., and have only a fleeting existence under usual experimental conditions. Only very appropriate conditions could allow the direct detection of these reactive species.[4] In this context, our aim was to generate and characterize spectroscopically short-lived silanimines by using the coupling of flash vacuum thermolysis reactions with photoelectron spectroscopy (PES). This technique has been until now the most used and convenient method for real time gas-phase detection of unstable silicon and germanium low-coordinated compounds.[5]

At first, we had to choose some precursors of these silanimines that could be cleaved without thermal degradation or competitive reactions upon FVT conditions.

Hexamethylcyclodisilazane (**2b**) was susceptible to give specifically the trimethylsilanimine **1b** by thermal monomerization and seemed to us to be a promising candidate. We describe first the thermolytic behavior of this precursor.

The comparative study of the thermolysis of two azasilacyclobutanes **3c**,**d**[6] is also presented: These precursors are expected to undergo a retro [2+2] cleavage into propene and silanimines.

Finally, 2,4-di-*tert*-butyl-1,1,3,3-tetramethylcyclodisilazane (**2d**), another potential precursor of silanimine **1d**, has been also investigated.

In order to access a theoretical support for our experimental data and a better understanding of the nature of the Si═N double bond, we have undertaken quantum calculations of the molecular and electronic structures of simple N-alkylated silanimines.

Experimental Section

The photoelectron spectra were recorded on an Helectros 0078 spectrometer equipped with an 127° cylindrical analyzer and connected to a microcomputer system supplemented with a digital analogic converter. HeI 21.21 eV radiation is used as a photon source, and helium auto-ionization at 4.98 and nitrogen ionization at 15.59 eV are taken as references. The apparatus, including a short-path internal FVT oven (*ca*. 5 cm between oven exit and ionization head), has already been described.[7] The working pressure of about 10^{-5} mbar allows the detection of short-lived species (lifetimes of about 10^{-2} s).[8] Reported methods have been used for the synthesis of precursors **2b**,[9] **2c** and **2d**,[10] and **3d**[6]. 1-Isopropyl-2,2,3-trimethyl-1-aza-2-silacyclobutane (**3c**) has been prepared, in the way described for **3d**,[6] from *N*-allyl-*N*-isopropyl-1,1-dimethylsilanamine[11] and purified by GC at 120 °C on a SE30 column [^{1}H NMR ($CDCl_3$): $\delta = 0.20$ (s, 3 H), 0.25 (s, 3 H), 0.96 (d, $J = 6.3$ Hz, 6 H), 1.10 ((d, $J = 7.6$ Hz, 3 H), 1.53 (ddq, $J =$ 8.4, 7.6 and 5.2 Hz, 1 H), 2.80 (dd, $J = 6.3$ and 5.2 Hz, 1 H), 2.83

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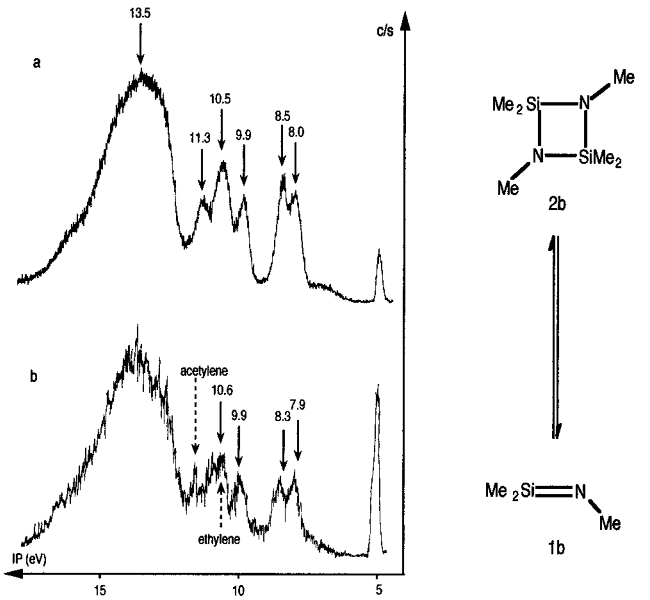

Figure 1. PE spectra of (a) precursor **2b** and (b) FVT of **2b** at 1200 K after digital subtraction of starting compound spectrum.

(hept, $J = 6.3$ Hz, 1 H), 3.55 ppm (dd, $J = 8.4$ and 6.3 Hz, 1 H). ^{13}C NMR: $\delta = -0.84$, 2.84, 15.00, 17.57, 22.99, 48.52, 55.84 ppm].

Method of Calculation

Ab initio calculations were performed with the Gaussian 92[12] package of programs. The geometry and frequency calculations were performed at the MP2/6-31G(d)[13] and MP2/LANLD1Z (D95V on H, C, N,[14a] Los Alamos ECP+DZ on Si[14b]) levels. The latter application is justified by the necessity to compare IPs of monomeric species with those of their large dimers. For the ionic species, the unrestricted formalism (UMP2) is employed. The value of the spin-squared operator (S^2) is 0.75 for all ionic species. Vertical IPs have been calculated either within Koopmans' approximation or more precisely as differences between the ionic and ground-state energies, both obtained on the neutral ground state-optimized geometry (ΔE_v). Adiabatic IPs have been calculated as differences between the ionic and ground-state energies corresponding to the optimized geometries of each one (ΔE_a).

Thermolysis of Hexamethylcyclodisilazane (2b)

The PE spectra of **2b** and of its thermolysis products at 1200 K are displayed in Figure 1.

The photoelectronic spectrum of the starting compound (Figure 1a) is characterized by two well-resolved bands at 8.0 and 8.5 eV, followed by a broad signal comprising three ionizations at 9.9, 10.5, and 11.3 eV and a poorly resolved band around 13.5 eV.

This compound was found to be thermally stable, and the spectrum does not change up to 1100 K. Above this temperature, a progressive modification of the spectrum is observed, showing occurrence of a thermolysis product. We observe a broadening of the two first bands and a pronounced modification of the band at 10.5 eV. We note the presence of the characteristic ionization of acetylene at 11.4 eV showed the beginning of a thermal degradation process.

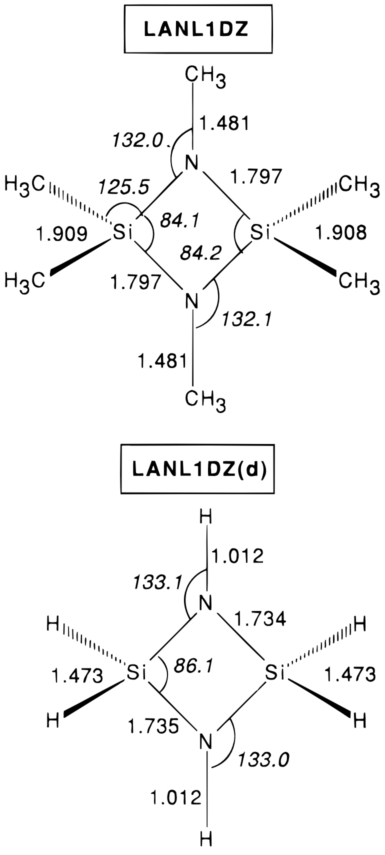

Figure 2. Geometrical parameters of dimer **2b** optimized with LANL1DZ at the MP2 level and unsubstituted cyclodisilazane optimized with LANL1DZ(d) at the MP2 level. Bond lengths are in Å, and bond angles are in deg.

After digital subtraction of the precursor spectrum from the spectrum obtained at 1200 K (Figure 1b), we observe two close bands at 7.9 and 8.3 eV and two ionizations at 9.9 and 10.6 eV.

Assignment of the Spectra and Discussion. For hexamethylcyclodisilazane (**2b**), a planar structure is obtained by optimization of the geometrical parameters with the LANL1DZ basis set at the MP2 level. A same planar structure is obtained for unsubstituted cyclodisilazane with introduction of d polarization orbitals ($\alpha^{d}_{Si} = 0.45$, $\alpha^{d}_{N} = 0.8$) (Figure 2). The energies of the two first molecular orbitals, calculated at 9.08 and 9.16 eV, correspond to the ejection of an electron from the asymmetric and symmetric combinations of the two nitrogen lone pairs n_{N}^{-} and n_{N}^{+}, respectively. The first ionization potential at 8.0 eV is thus associated with the ionization of the asymmetric combination n_{N}^{-} while the 8.5 eV ionization potential corresponds to the symmetric one n_{N}^{+}. The following ionizations at 9.9, 10.5, and 11.3 eV are associated with "Hartree–Fock" molecular orbitals mainly localized in the σ_{Si-C}, σ_{Si-N}, and σ_{Si-H} bonds.

The thermolysis spectrum observed above 1200 K could correspond to the monomerization product of the cyclodimer **2b,** i.e. the trimethylsilanimine **1b**.

In order to confirm this hypothesis, vertical IPs evaluation have been performed for **1b**. Preliminary calculations have been realized on the unsubstitued silanimine **1e** to choose the best basis sets for the evaluation of the IPs of the substituted silanimines.

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Table 1. Vertical Ionization Potentials (in eV) of the Silanimine **1e** Calculated at the MP2 Theory Level Using Differents Basis Sets

	$^2A'$	$^2A''$		$^2A'$	$^2A''$
3-21G(d)	8.99	9.62	6-31G(d,p)	9.63	9.89
3-21G(d,p)	9.12	9.68	LANL1DZ	9.41	9.60
6-31G(d)	9.62	9.81			

Previously, Peyerimhoff et al.[15] calculated for **1e** the energies of the two first ionic states A′ and A″, using MRDCI computations with a double ζ basis and d polarization functions. The two first IPs calculated at 9.52 and 9.72 eV correspond to the ejection of an electron from the nitrogen lone pair and from the $\pi_{Si=N}$ orbital, respectively.

In Table 1, we present the calculated vertical ionization energies (ΔE_v) of **1e** using the different basis of Pople 3-21G(d), 3-21G(d,p) ($\alpha^{d}_{Si} = 0.45$, $\alpha^{d}_{N} = 0.8$), 6-31G(d), and 6-31G(d,p) and the LANL1DZ basis.

The values of IPs obtained with the 6-31G(d) and LANL1DZ basis are similar with those of Peyerimhoff.

So, it appears that these two basis sets would be of sufficient quality in order to complete the experimental results and to detail information concerning geometrical and electronic structures of the differently substituted silanimines.

Geometrical Parameters. The geometrical parameters of silanimine **1e** and of the methylated silanimines **1b,f**, optimized with the 6-31G(d) basis sets, are reported in Figure 3. For the unsubstituted silanimine **1e**, the length of the Si═N double bond is 1.619 Å and the SiNH angle 120.5°.

The N-methylation of **1e**, leading to **1f**, induces the shortening of the Si═N bond by about 0.01 Å ($d = 1.611$ Å), the angle SiNC being 132.6°. The decrease of the Si═N bond length and the opening of the angle is related to the decrease of the s character in the nitrogen lone pair: 30% in **1e** and 18% in **1f** calculated with natural bond orbital analysis (NBO).[16,17]

The methylations on the silicon atom have a slight influence on the geometry ($d_{Si=N} = 1.608$ Å and $\angle SiNC = 132.5°$).

The absence of the polarization functions in the LANL1DZ basis set explains the discrepancies in Si−N bond lengths and associated angles. The most significant changes involve the Si═N bond length and the SiNH angle. We note, for these three molecules, a Si═N distance of about 1.66 Å, namely a lengthening of ca. 0.05 Å, compared with those obtained with the 6-31G(d) basis. Whereas the SiNC angles remain similar, the SiNH angle of **1e** is more open by *ca.* 7°.

Ionization Potentials. Experimentally, we attempted to characterize the silanimines substituted either on the silicon or on the nitrogen atom. Thus, it seemed interesting to examine the influence of the N- and Si-methylations on the energies of these two first ionic states (Table 2).

The N-methylation of silanimine **1e** induces the destabilization of the orbital $\pi_{Si=N}$ (0.71 eV with 6-31G(d); 0.86 eV with LANL1DZ) and that of the n_N orbital (0.88 eV with 6-31G(d); 0.58 eV with LANL1DZ).

The increasing of the energy of the nitrogen lone pair can be explained by the donor inductive effect of the methyl group. However, this effect is counterbalanced by the hyperconjugative effect, i.e. the interaction between the n_N orbital and the antibonding σ^*_{C-H} orbital in the plane.

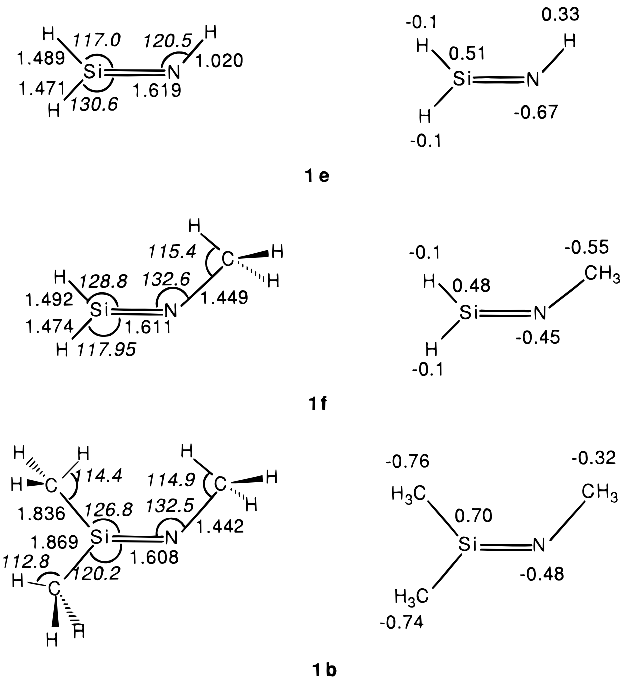

Figure 3. Geometrical parameters and total atomic charges of silanimines **1b,e,f** optimized with 6-31G(d). Bond lengths are in Å, and bond angles are in deg.

Table 2. Calculated Ionization Energies at the UMP2 Theory Level (in eV) of the Silanimine **1e**, the *N*-Methylsilanimine **1f,** and the Trimethylsilanimine **1b**

	$^2A'$		$^2A''$	
	6-31G(d)	LANL1DZ	6-31G(d)	LANL1DZ
		Compound **1e**		
Koopmans	10.95	10.77	10.02	10.14
ΔE_v	9.62	9.41	9.81	9.96
ΔE_a	8.89	8.52	9.62	9.74
		Compound **1f**		
Koopmans	10.07	10.19	9.31	9.28
ΔE_v	8.71	8.41	9.18	8.39
ΔE_a	8.18	7.81	9.08	9.15
		Compound **1b**		
Koopmans	9.41	9.42	8.83	8.78
ΔE_v	7.98	7.8	8.40	8.48
ΔE_a	7.53	7.26	8.23	8.0
expt	7.9		8.3	

The π system, less sensitive to the inductive effect (because of its delocalization), is destabilized by the interaction with the σ_{C-H} orbitals out of plane.

For the N-methylation with the two basis used, we observe, for the vertical calculated IP, a more important shift for the ionization of the lone pair (~1 eV) than for that of the π system (~0.7 eV). For the methylation on the silicon atom of **1f**, we notice that the energies of the $^2A'$ and $^2A''$ ionic states undergo the same type of variation.

The theoretical results for **1b**, presented in Table 2, are in excellent agreement with the experimental data and confirm our assignment. So, the observed ionizations at 7.9 and 8.3 eV arise from the ejection of an electron from the nitrogen lone pair (n_N) orbital and from the $\pi_{Si=N}$ orbital of the trimethylsilanimine, respectively.

We observe important polarization and correlation effects for the nitrogen lone pair ionization (1.4 eV using 6-31G(d), 1.6 eV using LANL1DZ) and weak effects for the π system ionization (0.4 eV with the 6-31G(d) basis; 0.3 eV with LANL1DZ). The distributions of the total atomic charges of the A′ and A″ cations show that the electronic reorganizations, and the polarization effects, are of the same order of magnitude

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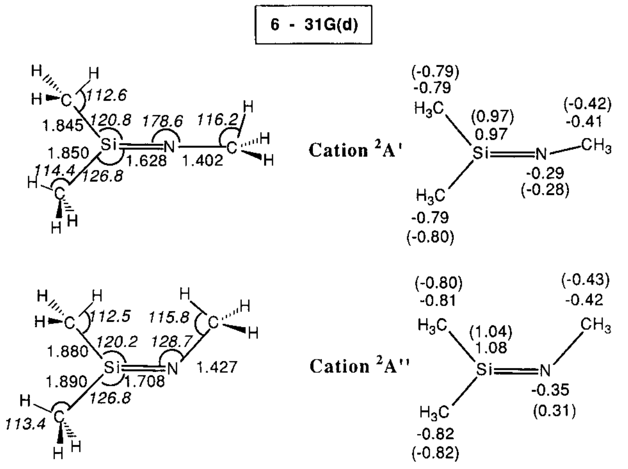

Figure 4. Geometrical parameters and total atomic charges of two cations (^{2}A′ and ^{2}A″) of trimethylsilanimine **1b** optimized with the 6-31G(d) basis set. Bond lengths are in Å, and bond angles in deg. (In parentheses: total atomic charges of the two cations obtained with the neutral ground-state optimized geometry.)

for the two cations. Thus, the correlation effect is more important in the cation A″. The energetic difference between the adiabatic and vertical ionization potentials (*ca.* 0.5 eV) indicates the strong geometrical reorganization of the two ionic states. Figure 4 displays the geometrical parameters and charges of the two cations optimized with 6-31G(d).

The cation of A′ symmetry is nearly linear with an SiNC angle of 178.6° and a Si=N double bond slightly longer than that of the neutral molecule: $d_{\mathrm{Si=N}} = 1.628$ Å. The cation A″ has a bent structure with an SiNC angle of 128.7°.

In summary, the essential characteristic of the Si=N backbone, in comparison to its homologous imine (IP: 9.23 A′, 10.25 A″),[18] is the important destabilization of the ionization energy associated with the $\pi_{\mathrm{Si=N}}$ orbital (about 2 eV). This weaker energy relative to the $\pi_{\mathrm{C=N}}$ ionization originates from the diffuse character of the $\pi_{\mathrm{Si=N}}$ bond and explains the great reactivity of the silanimines.

This conclusive result providing a starting point for developing this approach toward other unhindered alkylated silanimines, the flash vacuum thermolysis of precursors **3c**,**d**, and **2d** has been undertaken.

Thermolysis of 1-Isopropyl-2,2,3-trimethyl-1-aza-2-silacyclobutane (3c)

Our aim was to generate from this precursor the *N*-isopropyl-1,1-dimethyl-silanimine **1c**. This unstable silanimine has been already generated by vacuum gas−solid dehydrochlorination of (chlorodimethylsilyl)isopropylamine.[11]

The PE spectrum of precursor **3c**, reported in Figure 5a, unchanged up to the FVT temperature of 1020 K, shows two distinct bands at 7.8 and 9.3 eV, followed by a broad signal centered around 13.6 eV with important shoulders at 11.0 and 12.0 eV.

Between 1020 and 1220 K, a clear loss of propene (10.0 eV) is observed, as indicated in Figure 5b. The new spectrum presents two bands at 7.8 and 8.4 eV and a shoulder at 9.5 eV.

Above 1220 K (Figure 5c), ethylene and acetylene loss is obvious (10.55 and 11.4 eV, respectively) along with the propene ionization at 10.0 eV. The previous ionizations at 7.8 and 9.5 eV are still present, and the 8.4 eV band has now disappeared.

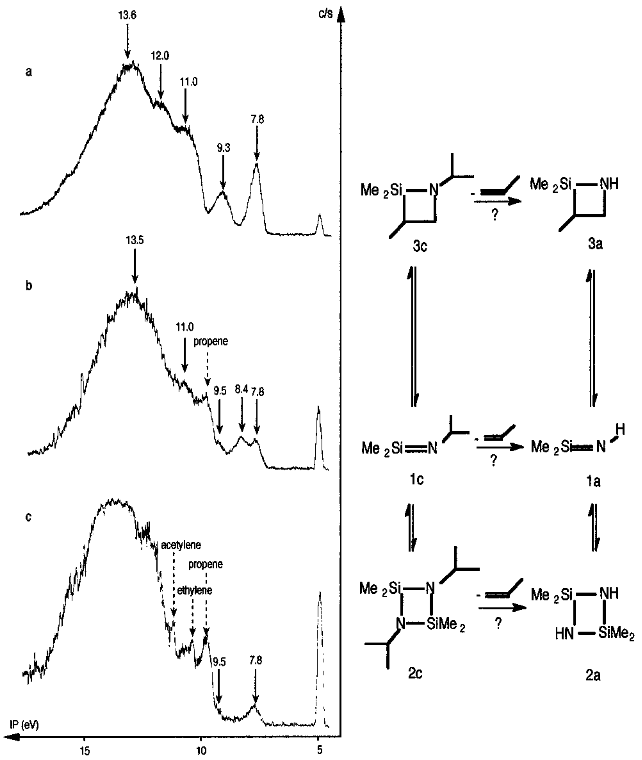

Figure 5. PE spectra of (a) precursor **3c**, (b) FVT of **3c** between 1020 and 1220 K, and (c) FVT of **3c** above 1220 K.

Assignment of Photoelectron Spectra. The assignment of the spectrum of azasilacyclobutane **3c** is supported by the AM1[19] calculation of IPs for the simple analogue possessing hydrogen atoms on both silicon and nitrogen atoms of the cycle. We note, as expected, that the IPs calculated values (9.04, 10.3, 10.5, 12.5 eV) are overestimated by about 1 eV, when compared with the experimental ones, the destabilization of the methyl substituents having not been considered.

The first band at 7.8 eV is associated with the ejection of one electron from the nitrogen lone pair. The second ionization at 9.3 eV is assigned to the ejection of an electron from the $\sigma_{\mathrm{Si-C}}$ orbitals. The ionization energies of the other MOs ($\sigma_{\mathrm{C-C}}$, $\pi_{\mathrm{Si-C}}$, $\sigma_{\mathrm{Si-C}}$, $\sigma_{\mathrm{Si-N}}$, ...) are observed above 10 eV.

Between 1020 and 1220 K the precursor is totally cleaved. Taking into account the clear observation of propene, we can propose three possible pathways for the thermolysis: In the first one, a N-unsubstituted azasilacyclobutane **3a** could be formed by the degradation of the isopropyl substituent of precursor **3c**. The second one could correspond to the cleavage into silanimine **1c** or its dimer **2c**. Finally, there is a possibility of double loss of propene. The detection of the resulting silanimine (**1a**, $\mathrm{Me_2Si{=}NH}$) seems improbable, due to its expected high instability, while the observation of its dimer **2a** could reasonably be envisaged.

IPs associated with the ejection of an electron from the nitrogen lone pair of the postulated cyclic secondary amine **3a**, expected to be not very different from those of the methyl(trimethylsilyl)amine at 8.9 eV,[20] are not experimentally observed.

The observation of the tetramethylcyclodisilazane **2a** (obtained by dimerization of the unstable dimethylsilanimine **1a** formed by double loss of propene from the precursor **3c**) is possible.

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The experimental ionizations observed at 8.4 and 9.5 eV could eventually correspond to the characteristic IPs of this cyclodimer **2a**. However, this process is unlikely because the retro [2+2] cleavage generally takes place at a lower temperature than the β-elimination of propene. Moreover, the ionization potentials of this dimer are calculated at 9.6 and 9.8 eV within Koopmans' approximation, the through-bond interactions leading to the inversion of the last two occupied molecular orbitals. According to the corrections beyond Koopmans' for **1b**, these two ionization potentials are both expected around 8.7 eV.

Finally, it is more reasonable to interpret the first step of the thermolysis only by the predicted cleavage into the silanimine **1c** that could rapidly dimerize into **2c**.

Since the observed spectrum remained unchanged through a temperature range of 200 deg, it may presumably correspond to the thermally most stable compound **2c**.

In fact, this spectrum agrees perfectly, except for the presence of propene, with that obtained from a sample of **2c** prepared according to the reported method[10] (IP: 7.8, 8.4, 9.8 eV).

If we now consider the second step of thermolysis (above 1220 K), we note a progressive disappearance of the ionizations of cyclodisilazane **2c**. It seems likely that, at this higher temperature, the equilibrium is displaced from **2c** to **1c**. In this case, the N-isopropylated silanimine **1c** could be specifically observed with two energetically close IPs at 7.8 eV, associated with the n_N and $\pi_{Si=N}$ orbitals and an ionization at 9.5 eV.

A theoretical estimation of the ionic states energies of compound **1c** with the LANL1DZ basis set gives a good explanation of the weaker energetic gap between these two ionizations by the more significant destabilizing effect of isopropyl substituent on the $^2A''$ ionic state.

Thermolysis of 1-*tert*-Butyl-2,2,3-trimethyl-1-aza-2-silacyclobutane (3d)

We recently described the thermolysis of this compound:[6] The thermal decomposition at 970 K, monitored by ^1H NMR, leads to the formation of propene and cyclodisilazane **2d**. At 1070 K, isobutene is also formed. In the presence of *tert*-butanol, the addition product with 1,1-dimethylsilanimine **1a** is detected.

The monomeric silanimines **1a**,**d** are not directly observed, because of their too high reactivity, but the formation of their cyclodimers **2a**,**d** was definitely confirmed by FVT/HRMS coupling.

In addition, it should be stressed that the thermolysis of the *tert*-butylated cyclodimer **2d** shows, as main decomposition pathway at 1170 K, the loss of methane from the *tert*-butyl groups, leading to the unsaturated cyclodisilazanes **2g**,**h** identified by NMR and HRMS.[21]

Photoelectron Spectra. In the spectrum of precursor **3d** (Figure 6a), two well-resolved bands at 7.8 and 9.3 eV are observed as well as a broad signal with two shoulders at 10.5 and 10.8 eV and a maximum at 13.0 eV.

Above 970 K, we note a two-step thermolysis process: (i) Between 970 and 1120 K, the spectrum changes quickly with the formation of propene (10.0 eV). The new spectrum presents an ionization at 7.4 eV and a broad signal at 8.4 eV (Figure 6b). (ii) Above 1120 K, the 7.4 eV band disappears progressively. At the same time, we note the broadening of the 8.4 eV band and a shoulder around 9.5 eV attributed to a loss of isobutene (Figure 6c).

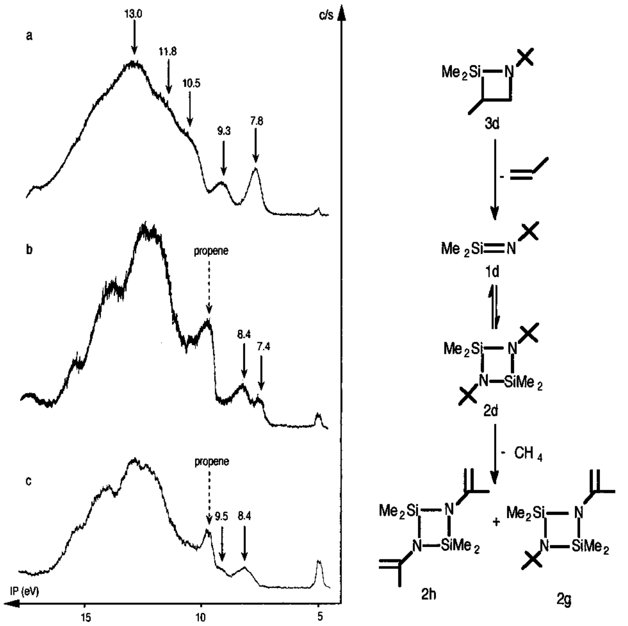

Figure 6. PE spectra of (a) precursor **3d**, (b) FVT of **3d** between 970 and 1120 K, and (c) FVT of **3d** above 1120 K.

Assignment of the Spectra and Discussion. The interpretation of the photoelectron spectrum of compound **3d** is the same as already described for its N-isopropyl analogue **3c**: The first band at 7.8 eV is associated with the ejection of an electron from the nitrogen lone pair. The second one at 9.3 eV corresponds to the σ_{Si-C} orbitals ionization. Then, the poorly resolved bands at higher energy are attributed to other MOs such as σ_{C-C}, σ_{N-C}, and σ_{Si-N}.

Between 970 and 1170 K, propene loss is noticed (10.0 eV). The total absence of isobutene (9.45 eV) means that the formation of the N-unsubstituted azasilacyclobutane **3a** can be ruled out. In fact, the IP attributed to the ionization of the nitrogen lone pair of **3a** is expected to occur at 8.9 eV.

Accordingly, the first step of the thermolysis could correspond to a [2+2] cycloreversion of the starting azasilacyclobutane **3d,** leading to the formation of propene and the *N*-*tert*-butylsilanimine **1d**, in agreement with the HRMS/FVT coupling and FVT/NMR results.

The spectrum evolution above 1120 K indicates that the observed ionizations cannot be attributed to an unique product. The disappearance of the 7.4 eV band while that at 8.4 eV is only broadened provides evidence for this conclusion.

We have previously proposed for silanimine **1c** the close coincidence around 7.8 eV of the ionizations corresponding to the n_N and $\pi_{Si=C}$ orbitals and can thus assign the 7.4 eV band to the ejection of electrons from the n_N and $\pi_{Si=C}$ orbitals of the *N*-*tert*-butylsilanimine **1d**. In addition, due to the broadening of the band at 8.4 eV we cannot exclude the presence of its cyclodimer **2d**, characterized by two ionizations at 7.8 and 8.3 eV.

Subtraction of the spectrum of **2d** from that of the thermolysis at 1120 K yields the spectrum shown in Figure 7 with three distinct ionizations at 8.1, 8.5, and 9.1 eV. Above 9.1 eV, characteristic bands of propene (10.0 eV) and ethylene (10.55 eV) are also observed.

Assuming that the first thermolysis step leads to the silanimine **1d** and to its dimer **2d**, the products expected to be formed hereafter could be, according to the MS and NMR results, the three cyclodimers **2a**,**g**,**h**.

For the N-unsubstituted cyclodisilazane **2a**, we have estimated that the ionizations of the characteristic MOs $n_{N}+$ and n_N- will be energetically close to 8.7 eV: The band observed at 8.5 eV could correspond to this compound.

However, the orbital energies values, calculated for the analogues of **2g**,**h** unsubstituted on the silicon atoms by using

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(21) Systermans, A.; Dat, Y.; Ripoll, J. L. *Tetrahedron Lett.* **1996**, *37*, 3317−3318.

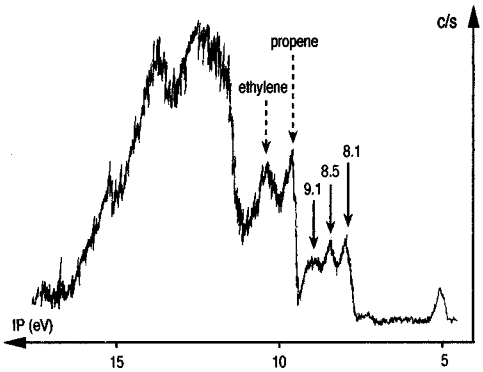

Figure 7. PE spectrum after digital subtraction of cyclodimer **2d** spectrum from the spectrum recorded during the thermolysis above 1120 K.

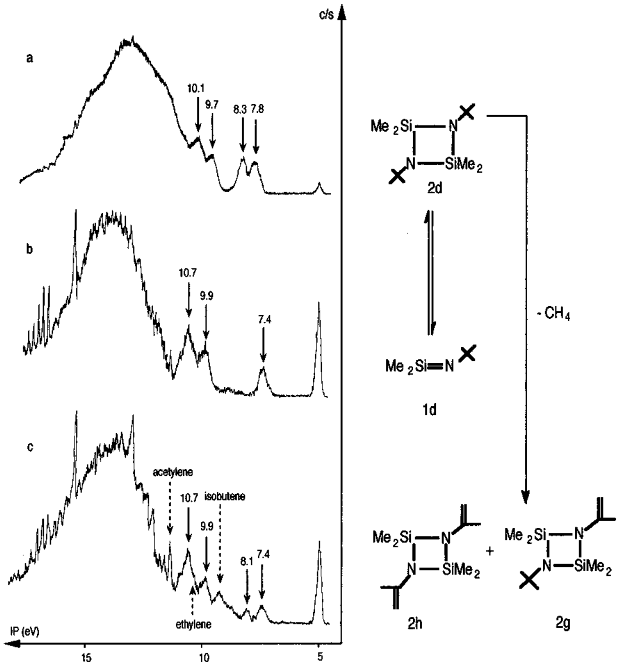

Figure 8. PE spectra of (a) precursor **2d**, (b) FVT of **2d** between 1120 and 1200 K, and (c) FVT of **2d** above 1200 K.

a AM1 semi-empirical procedure, led us to propose, above 1120 K, the formation of these two compounds, in agreement with the NMR and MS investigations of the FVT of **2d**.[21] More precisely, the theoretical values of the IPs of these related compounds (for **2g**, 8.4 and 9.3 eV; for **2h**, 8.4 and 8.5 eV) are slighly overestimated because the methyl groups destabilizing effects have not been taken into account.

In conclusion we observe, between 970 and 1120 K, the silanimine **1d** and its cyclodimer **2d** and, above 1120 K, the cyclodimers **2d**,**g**,**h**.

Thermolysis of 1,3-Di-*tert*-butyl-2,2,4,4-tetramethylcyclodisilazane (2d)

We have carried out the investigation of the thermolysis of N-*tert*-butyl cyclodisilazane **2d** in order to verify our above conclusions.

As reported in Figure 8a, the photoelectron spectrum of precursor **2d** displays, at 7.8 and 8.3 eV, the two usual bands characteristic of the asymmetric and symmetric combinations n_N- and $n_N{}^+$ of the nitrogen lone pairs.

The first modification of this spectrum takes place at 1120 K; we observe a new ionization at 7.4 eV. By digital subtraction of the remaining starting compound, a quite simple spectrum is detected with three well-resolved bands at 7.4, 9.9, and 10.7 eV preceding a broad signal with a maximum at 14.5 eV.

Above 1200 K (Figure 8c), the spectrum changes radically with formation of isobutene (9.45 eV) and products of thermal decomposition: ethylene (10.55 eV) and acetylene (11.40 eV). One can also notice the presence of remaining starting compound **2d**. By subtracting its spectrum, we obtain (in addition to the ionization already quoted) four well-resolved bands at 7.4, 8.1, 9.9, and 10.7 eV, followed by a broad and structureless component centered at *ca.* 14 eV.

Assignment of Photoelectron Spectra. The evident absence of isobutene, during the step of thermolysis between 1120 and 1200 K, suggests that the thermal fragmentation proceeds through the [2+2] cycloreversion of the precursor into the *N*-*tert*-butylsilanimine **1d**.

The 7.4 eV band could thus be assigned to the energetically close ionizations $\pi_{Si=N}$ and n_N-. In addition, the following bands at 9.9 and 10.7 eV, respectively, results from the σ_{Si-C} and σ_{Si-N} MOs ionizations. These findings corroborate the conclusions drawn from the above described thermolysis of the *N*-*tert*-butylazasilacyclobutane **3d** and confirm that, at high temperature, [2+2] cleavages take place for the N-alkylated dimers.

The presence of isobutene above 1200 K indicates that a supplementary step of thermolysis has taken place. Whether the isobutene loss occurs from the silanimine **1d** or its cyclodimer (the precursor **2d**), we will probably observe only cyclodisilazane **2a** since the corresponding silanimine **1a** is certainly too unstable to be observed in the monomeric state.

The poor resolution of the spectrum around 9.0 eV cannot permit us to rule out the hypothesis of **2a** formation.

On the other hand, the 8.1 eV band is well separated. As we did previously for compound **3d**, we assign this ionization to derivatives **2g**,**h**, formed by loss of a methane molecule from the precursor **2d**. The second characteristic ionization of this former compound (expected at 9.1 eV) is localized in the complex and poorly resolved part of the spectrum above 8.3 eV.

Conclusion

To our knowledge, this work constitutes the first experimental characterization of reactive, unhindered N-alkylated silanimines generated by FVT in the gas phase.

Two major characteristics of these compounds can be drawn from the observed ionization potentials: (i) Similarly to the homologous imines, the first ionization energy originates from the ejection of an electron from the nitrogen lone pair orbital. The position of this band, definitively lower than the corresponding one of imines, indicates for silanimines a more pronounced p-character of the nitrogen lone pair. (ii) The second important feature is that the second ionization potential, arising from the $\pi_{Si=N}$ orbital, is strongly destabilized when compared to the homologous imines (2 eV). This result explains the high kinetic instability of the silanimines and their ability to dimerize.

The here-investigated retro [2+2] cleavages under FVT conditions of azasilacyclobutanes and cyclodisilazanes constitute a general method to access reactive double-bonded silicon−heteroatom species and is presently being enlarged to the generation of silaphosphimines and silathiones.

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