Gas-Phase Characterization by Photoelectron Spectroscopy of Unhindered, Low-Coordinate Germanium Compounds: Germaimines, Germylenes, and Germaisonitriles[1]

Séverine Foucat,[†] Thierry Pigot,[†] Geneviève Pfister-Guillouzo,*,[†]
Hélène Lavayssière,[‡] and Stéphane Mazières[‡]

*Laboratoire de Physico-Chimie Moléculaire UMR CNRS 5624, Avenue de l'Université,
64000 Pau, France, and Laboratoire d'Hétérochimie Fondamentale et Appliquée, 118,
Route de Narbonne, F-31062 Toulouse, France*

Low-coordinate, unhindered germanium compounds, germaimines, germylenes, and germaisonitriles, have been generated and characterized by the combination of flash vacuum thermolysis (FVT) of appropriately substituted germacyclopentenes and ultraviolet photoelectron spectroscopy (UV−PES). These products have characteristic ionization potentials (IPs) at low energy consistent with their great kinetic instability and their high reactivity. The ionization potentials associated with the ejection of an electron from the $\pi_{Ge=N}$ orbital for germaimines and the n_{Ge} lone pair for germylenes are useful fingerprints of these compounds. At higher temperature these transient species lead to the formation of germaisonitriles that show two characteristic IPs associated with the $\pi_{Ge=N}$ and the n_{Ge} orbital ionizations. Characterization of these three unhindered species is supported by ab initio calculations of the geometrical and electronic structures by using the B3LYP density functional hybrid with LANL2DZ(d) and 6-311G(d) basis sets.

Group 14 low-coordinate element (Si, Ge, Sn) chemistry has been extensively studied for the last 30 years.[2] Contrary to early beliefs, these compounds have an intrinsic thermodynamic stability despite their high reactivity.[3−5] This stability has allowed their indirect characterization by chemical trapping. In recent years two different approaches to the study of such molecules became possible. In the early 1980s it was discovered that such reactive species could be kinetically stabilized by appropriate substitution with bulky groups, which permitted the study of their chemical reactivity and determination of their structure by standard methods. The other approach involves the use of well-established techniques for the study of short-lived species: matrix isolation and IR and/or UV spectroscopic characterization,[6−8] gas-phase generation by flash vacuum thermolysis (FVT), or vacuum gas−solid reactions (VGSR) coupled with mass spectrometry or UV−PES.[9−11]

Our laboratory has wide experience in the latter approach, and recent studies of the coupling of photoelectron spectroscopy with flash vacuum thermolysis were found to be particularly well-adapted to the study of low-coordinate, unhindered silicon (>Si=P−, >Si= N−)[12−14] species. Only few low-coordinate, unhindered germanium species have been characterized in the gas phase. For example, to our knowledge, only three gas-phase characterizations of germanium−nitrogen double bond (or triple bond) containing compounds[15−17] have been reported. We present here the results of our investigation of the thermal decomposition of appropriately substituted germacyclopentenes as a route to three low-coordinate germanium compound types: germaimines (>Ge=N−), germylenes (>Ge:), and germaisonitriles (:Ge≡N−). Scheme 1 shows the different decomposition processes involved. The course of these decompositions

*Corresponding author. E-mail: genevieve.pfister@univ-pau.fr.
Fax: +33 (0)5.59.80.83.44.

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Scheme 1
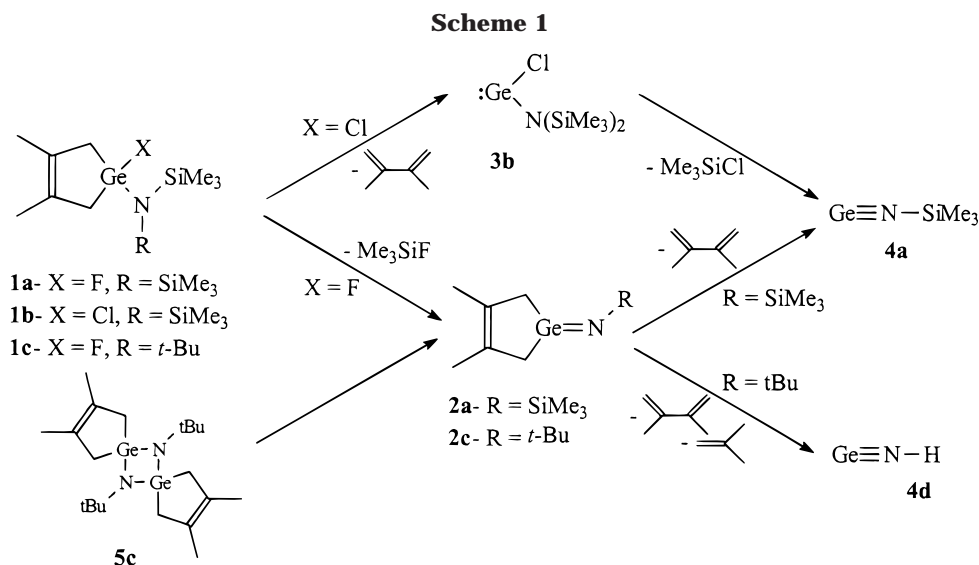
depends on the substituents on the germanium (F or Cl) and on the nitrogen (t-Bu or Me₃Si).

Study of *N*-Trimethylsilyl Species. Synthesis of the Precursors 1a and 1b. The monohalo-3,4-dimethylgermacyclopent-3-enes **1a** and **1b** were synthesized by reaction of the corresponding lithium amide with the respective dihalo-3,4-dimethylgermacyclopent-3-ene (eq 1).
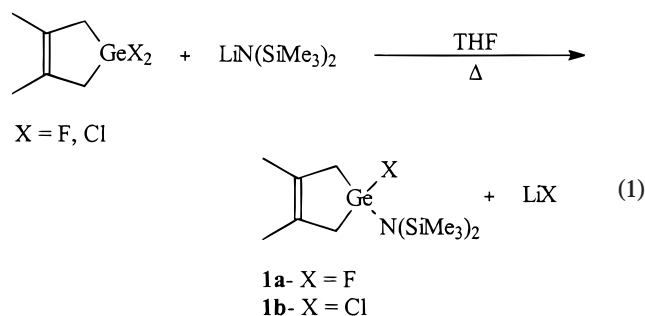
Thermolysis of Germacyclopentenes 1a and 1b. Figure 1 shows the PE spectra of the germacyclopent-3-ene **1a** at 293, 753, and 973 K. The PE spectrum (Figure 1a) of **1a** shows, first, a set of three bands at 8.7, 10.4, and 11.5 eV. The next band is broader and appears at higher ionization energy, around 13.5 eV. This spectrum can be assigned on the basis of known experimental data of the sila- and germacyclopentene series[18] and of HN(SiMe₃)₂.[19,20] The latter displays a first band at 8.8 eV characteristic of the ionization of a nitrogen lone pair electron. This clearly indicates that the first band of **1a**, at 8.7 eV, corresponds to the ejection of an electron from the n_N lone pair and from the $\pi_{C=C}$ orbital of the germacyclopentenic ring. The second band shows a shoulder at 10.0 eV, which is due to ionization of electrons in σ_{GeC} orbitals. The second and third bands at 10.4 and 11.5 eV arise from the ionizations of σ_{SiC} and σ_{GeN} electrons, respectively.

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At 753 K, this PE spectrum is different and indicates that **1a** is completely transformed (Figure 1b). During internal thermolysis, where the oven is inside the spectrometer, a new band appears at 7.3 eV. Moreover, Me₃SiF is the only volatile and stable compound generated during a separate product study of the pyrolysis. (In this case, the oven is external of the spectrometer and only long-lived molecules are detected; see Experimental Section for a detailed description of the thermolysis experiments.) The presence of Me₃SiF was demonstrated by its characteristic ionization at 10.9 eV (Figure 1b). Thus, according to Scheme 1, the spectrum in Figure 1b corresponds to that of the germaimine **2a** if the Me₃SiF bands are subtracted.

On further heating, the PE spectrum changes up to 973 K. The band at 7.3 eV disappears while characteristic ionizations of 2,3-dimethylbuta-1,3-diene (DMB) (8.7, 10.3, and 11.4 eV) are observed in addition to those of Me₃SiF (Figure 1c). The formation of these products of the thermal decomposition is confirmed by a separate product study. Moreover, in a pyrolysis experiment in which the products were identified by NMR spectroscopy DMB and Me₃SiF were present in 1:1 ratio. The PE spectrum at 973 K (Figure 1d) obtained after subtraction of the PE spectra of Me₃SiF and DMB displays a first band at 9.0 eV followed by two broader signals around 10.7 and 13.5 eV. These could be due to the germaisonitrile **4a** generated by loss of DMB and Me₃SiF in the thermolysis of **1a** (Scheme 1).

The PE spectra of the germacyclopentene **1b** at 293, 713, and 1023 K are depicted in Figure 2. The PE spectrum of **1b** (Figure 2a) is characterized by only one well-defined band at 8.5 eV followed by broad signals at 10.1, 11.0, 12.0, and 13.0 eV. The first band is assigned to the ionizations of the nitrogen atom lone pair and the $\pi_{C=C}$ double bond electrons of **1b** in line with the PES spectrum of **1a**. The ionizations of electrons in the exo σ_{SiC} and cyclic σ_{GeC} orbitals are seen around 10.1 eV. Ionization energies between 11.0 and 12.0 eV arise from ionizations of electrons mainly localized on the chlorine atom.

Up to 713 K, the following changes are observed: the band at 10.1 eV disappears and a new one at 9.2 eV appears (Figure 2b). In contrast to the thermolysis of
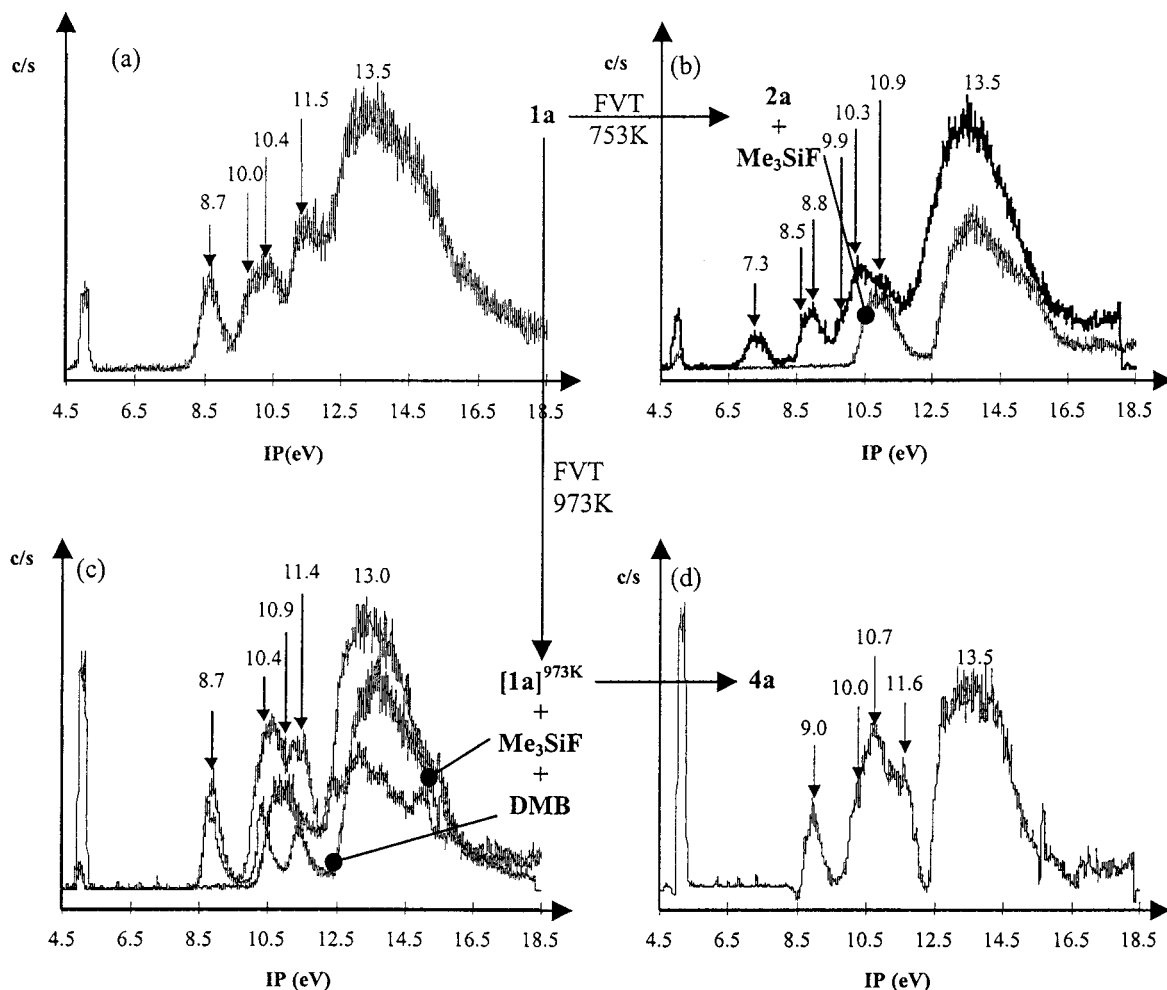
Figure 1. PE spectra of **1a** at (a) 293 K, (b) 753 K, and (c) 973 K and (d) **1a** at 973 K after subtraction of Me$_3$SiF and DMB spectra.

1a at 753 K, trimethylchlorosilane is not formed; DMB is the only volatile product, as confirmed by a separate product study. Furthermore, a lower ionization energy at 7.3 eV characteristic of the nitrogen atom lone pair of the germaimine **2a** is not observed. Thus, the PE spectrum (Figure 2d) corresponds to that of the germylene **3b**, which is generated by DMB loss in the thermal decomposition of **1b** (Scheme 1).

A second decomposition takes place at higher temperatures (around 1023 K). The first band at 9.2 eV disappears, and three new bands at 8.7, 10.3, and 11.4 eV, characteristic of the DMB ionizations are observed (Figure 2c). Under these experimental conditions, only DMB and Me$_3$SiCl are detected in a separate product study. Subtraction of the PE spectra of DMB and Me$_3$SiCl from that observed at 1023 K (Figure 2e) gave a new PE spectrum, which is quite similar to that in Figure 1d, displaying a first band at 9.0 eV followed by two broader bands centered at 10.7 and 13.5 eV. It is likely that these bands correspond to the ionizations of the germaisonitrile **4a** (Scheme 1).

Assignment of the Thermolysis Spectra and Discussion. The scheme of decomposition presented in Scheme 1 is backed up by ab initio calculations of the first ionization energies of germaimine **2a′**, germylene **3b′**, and germaisonitrile **4a′** with less bulky substituents

than those of **2a**, **3b**, and **4a**.
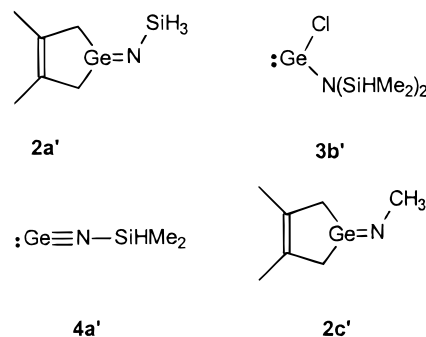
The calculated lengths of the Ge=N double bond and the N−Si single bond (respectively 1.683 and 1.704 Å) in **2a′** are in good agreement with experimental data previously obtained by single-crystal X-ray diffraction[21−24] ($R_{Ge=N}$ = 1.688−1.704 Å and $R_{Si−N}$ = 1.648−1.673 Å). Moreover, the evaluated GeNSi angle is around 136.0°, a value that Ando observed for an N-silylated dimesitylgermaimine.[24] The N-silylated germaimines remain

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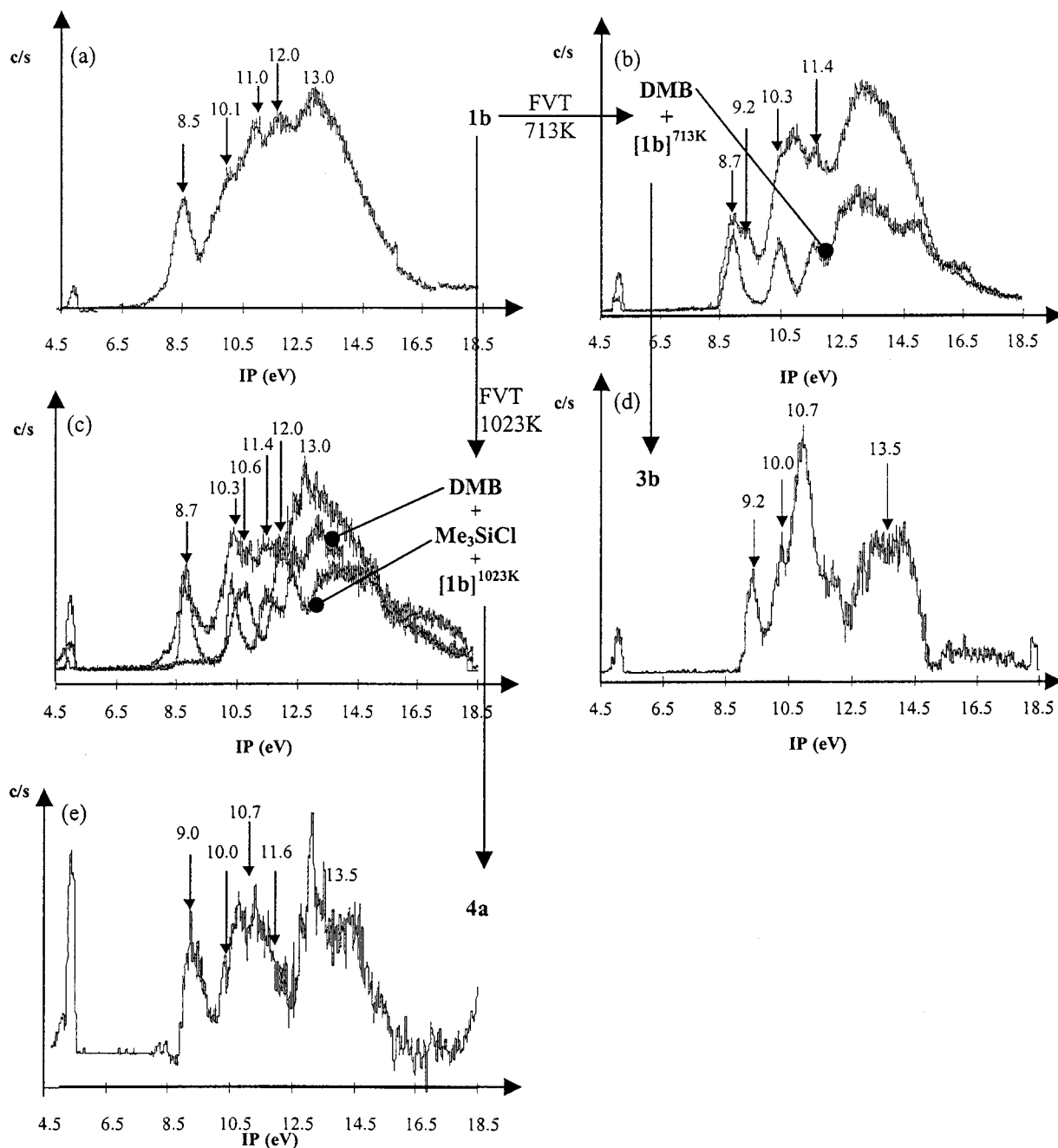(24) Ando, W.; Ohtaki, T.; Kabe, Y. *Organometallics* **1994**, *13*, 434.

Figure 2. PE spectra of **1b** at (a) 293 K, (b) 713 K, and (c) 1023 K, (d) **1b** at 713 K after subtraction of DMB, and (e) **1b** at 1023 K after subtraction of DMB and Me$_3$SiCl spectra.

Table 1. First Ionic State Energies (eV) of Germaimines (Me$_2$>Ge=N−SiH$_3$, Me$_2$>Ge=NSiHMe$_2$, 2a′, 2c′)

ionic state	^{2}A′(n$_N$)	^{2}A″($\pi_{C=C}$)	^{2}A″($\pi_{Ge=N}$)
Me$_2$Ge=NSiH$_3$	8.36		8.71
Me$_2$Ge=NSiHMe$_2$	8.06		8.31
2a′	8.08	8.29	8.67
2c′	7.71	7.93	7.78

bent in contrast to N-silylated silaimines, which are nearly linear.[13,25]

The evaluation of the first ionic state energies of **2a′** presented in Table 1 confirms the germaimine **2a** characterization and correlates the experimental bands with the corresponding ionic state energies. The first band at 7.3 eV of Figure 1b corresponds to the ^{2}A′ ionic state (n$_N$), which is estimated at 7.78 eV, considering the effect of a −SiHMe$_2$ group (about 0.3 eV) obtained by calculations on two less substituted N-silylated germaimines (Table 1). We suppose that the effects of −SiHMe$_2$ and −SiMe$_3$ groups are rather similar. The second band, at 8.5 eV, arises from the ionic state ^{2}A″ associated with the π electron ionizations of the Ge=N bond (calculated at 8.27 eV with the −SiHMe$_2$ group effect) and of the C=C double bond (evaluated at 8.29 eV). In accord with the higher energy of σ_{GeC} and σ_{SiC} electron ionizations, we assign the 9.9 and 10.3 eV bands to these orbitals, respectively.

In contrast to the results of Heinemann,[26] we char-

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Table 2. First Ionic State Energies (eV) of Germylenes (3b′, :GeClN(SiH₃)₂)

ionic state	$^2A''(n_N - n_{Cl})$	$^2A'(n_{Ge})$
3b′	9.10	
:GeClN(SiH₃)₂	9.78	9.73

Table 3. First Ionic State Energies (eV) of Germaisonitriles (4a′, 4d) and Germanitrile HGeN

ionic state	$^2\Pi(\Pi_{Ge=N})$	$^2\Sigma(n_{Ge})$
4a′	9.14	10.48
4d	9.93	11.69
HGeN	9.94	11.4

acterize only one minimum on the potential energy surface of the germylene **3b′**, which corresponds to a coplanar structure. The GeN bond length calculated (1.857 Å) is slightly shorter than those in :Ge(N(SiMe₃))₂ (R_{Ge-N} = 1.89 Å).[29] Conversely, the GeCl bond is longer (2.28 Å) than those in the symmetrical compound :GeCl₂ (R_{Ge-Cl} = 2.183 Å).[27,28]

The ionization energies evaluation is presented in Table 2. According to the number of heavy atoms in **3b′** and the large basis set used, we have only evaluated the first $^2A''$ ionic state energy. It corresponds to the ejection of an electron from the nitrogen and chlorine lone pair antibonding combination. The $^2A'$ ionic state is associated with the n_{Ge} orbital ionization and is calculated for the :GeClN(SiH₃)₂ germylene. This last value was evaluated at 9.73 eV; in fact, it is intermediate between the experimental ionization energies associated with the n_{Ge} orbital of :GeCl₂ (10.55 eV)[30] and :Ge(N(SiMe₃))₂ (8.68 eV).[31] This theoretical study confirms the characterization of germylene **3b**. The first band at 9.2 eV in Figure 2b is attributed to the ejection of an electron from the nitrogen and chlorine atom lone pair antibonding combination, while ionization of the germanium atom lone pair electron corresponds to the band at 10.0 eV. The higher energy bands around 10.7 eV are associated with the ionizations of chlorine atom lone pair electrons. The ionizations of electrons in the σ_{SiC} orbitals also occur within this energy range.

The optimized GeN bond length of the germaisonitrile **4a′** (1.671 Å) is slightly shorter than that of a Ge=N double bond (about 1.69−1.70 Å[21−24]), in agreement with the formation of a Ge≡N triple bond.

By the calculations of the first ionic state energies (Table 3) and the decomposition pathway, we could associate the band at 9.0 eV (Figures 1d and 2e) with the ionizations of the electrons of the two $\pi_{Ge=N}$ orbitals of **4a**. The broad signal centered at 10.7 eV is due to ionization of the germanium atom lone pair electron. The σ_{Si-C} and σ_{Si-N} ionizations are also situated within this band.

Study of N-*tert*-Butyl Species. Thermolysis of Germacyclopentene 1c and Cyclodigermazane 5c.

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The syntheses of fluoro-3,4-dimethylgermacyclopent-3-ene **1c** and cyclodigermazane **5c** have been reported previously[15] (eq 2). We have thermolyzed separately
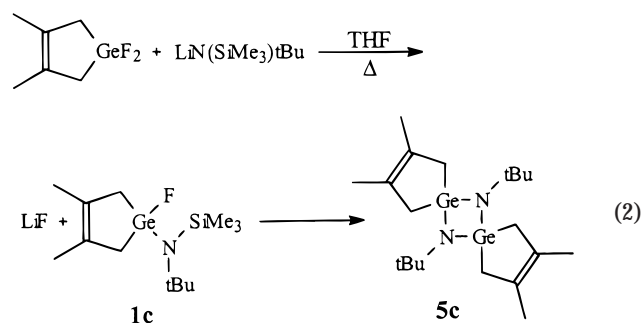
these compounds and analyzed if the same species were generated from these two different precursors.

The PE spectra of **1c** at 293, 673, and 1073 K are reported in Figure 3.

As for the precursor **1a**, we interpret the spectrum of **1c** from the germacyclopentene[18] and HN(t-Bu)SiMe₃ amine[19] PES studies. The latter shows a first band at 8.4 eV associated with the ionization of a nitrogen lone pair electron. According to these results, we attribute the first band of the Figure 3a PE spectrum at 8.4 eV to the ejection of an electron from the n_N lone pair and the $\pi_{C=C}$ germacyclopentenic ring. The next signals at 9.7 and 10.3 eV result, respectively, from the ionizations of the antibonding combinations of σ_{GeC} and σ_{SiC} electrons. The shoulder at 11.6 eV corresponds to the ejection of an electron from the σ_{GeN} orbitals.

On heating to 673 K, this spectrum is completely different. A new band is observed at 7.0 eV, followed by a second intense one at 8.7 eV with a shoulder at 8.1 eV. The next bands at 10.9, 11.4, and 13.0 eV are poorly resolved. The ionization at 10.9 eV is characteristic of Me₃SiF, whose formation is confirmed by a separate product study and NMR analysis of the thermolysis products. Then, the Figure 3b spectrum corresponds to the germaimine **2c**.

Up to 1073 K, the PE spectrum changes. The previous band at 7.0 eV disappears, while the second one at 8.7 eV widens (Figure 3c). In a separate product study we detect DMB, isobutene, and Me₃SiF by their characteristic ionizations at 8.7, 10.3, and 11.4 eV for the first, 9.4 and 11.8 eV for the second, and 10.9 eV for the third. The loss of isobutene (β-elimination) is often observed when thermolyzing compounds with *tert*-butyl groups. Subtraction of the PE spectra of DMB and Me₃SiF from that observed at 1073 K gives a new spectrum (Figure 3d). We have not undertaken a third subtraction, that of isobutene, in order to minimize the loss of resolution in the PE spectrum. The ionizations of this stable product are mentioned in Figure 3d. Then, we suppose that the bands at 9.9 and 11.4 eV correspond to those of the germaisonitrile **4d** ionizations.

In Figure 4 are depicted the **5c** spectra at 293, 673, and 1173 K. The spectrum of Figure 4a is very similar to that of the cyclodigermazane [(CH₃)₂GeN-t-Bu]₂ previously studied in our laboratory (two bands at 7.4 and 7.7 eV in the low-energy area associated with the ionizations of the antibonding and bonding combinations of the nitrogen atom lone pair electrons, respectively, followed by three bands at 9.3, 9.7, and 10.1 eV). In **5c**,
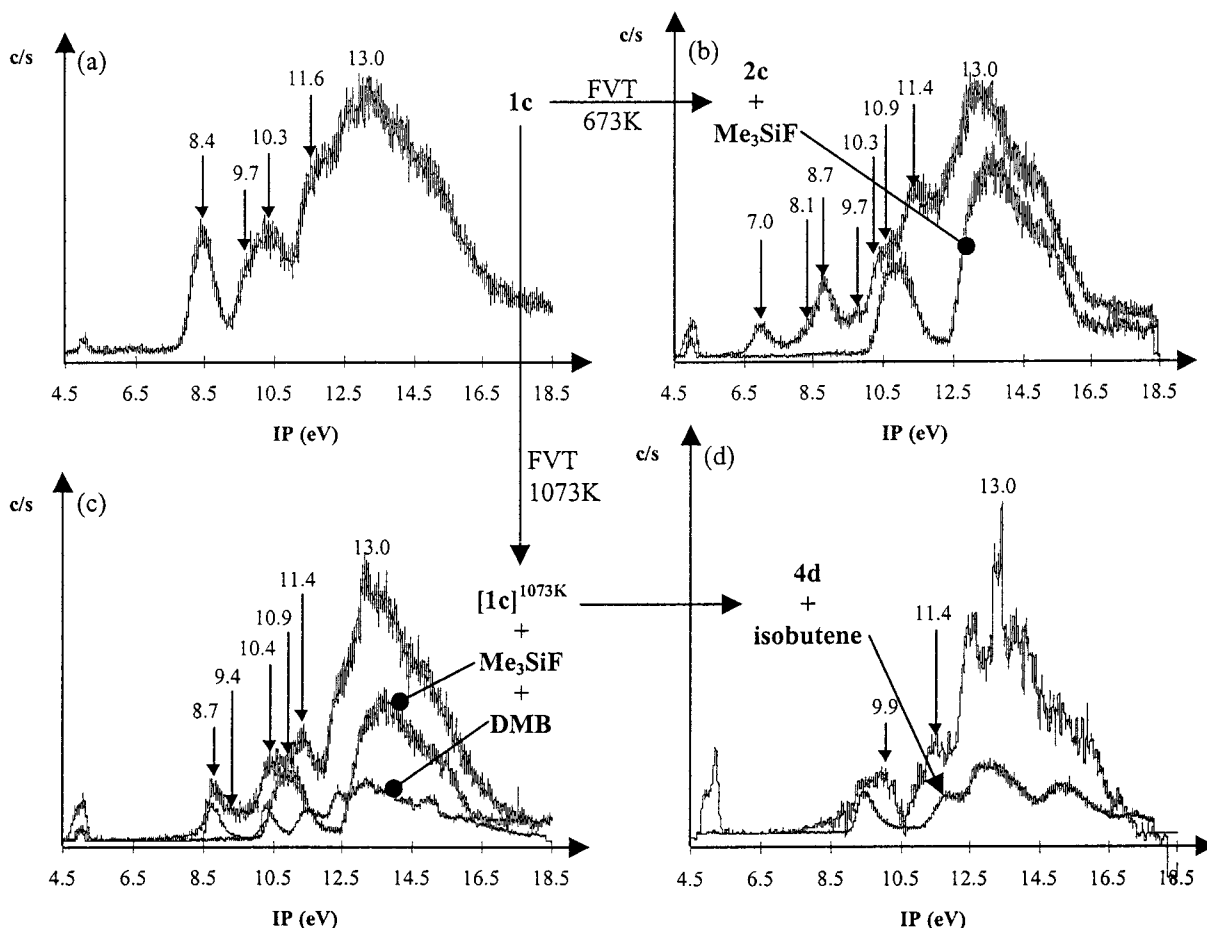
Figure 3. PE spectra of **1c** at (a) 293 K, (b) 673 K, and (c) 1073 K and (d) **1c** at 1073 K after subtraction of DMB and Me₃SiF spectra.

the germacyclopentene rings are perpendicular to the molecular plane formed by the Ge₂N₂ ring. That could induce different interactions and especially the destabilization of the bonding combination of the nitrogen atom lone pairs. So, the band at 7.4 eV is associated with the two ionizations of the antibonding and bonding combinations of the nitrogen atom lone pair electrons, while the ejection of an electron from the antibonding and bonding combinations of the $\pi_{C=C}$ orbitals of germacyclopentenic rings is observed at 8.2 eV. The next bands, above 9.0 eV, correspond to the ejection of an electron from the asymmetric and symmetric combinations of GeC and GeN bonds.

From 673 to 873 K this spectrum changes and shows a band at 7.0 eV (Figure 4b), followed by a second one, more intense, at 8.7 eV. The other ionizations are found at 9.7, 10.3, and 11.4 eV. The last broader signal is centered around 13.0 eV. We notice that this spectrum is identical to that of **1c** at 673 K without Me₃SiF ionizations. Thus we confirm the formation of germaimine **2c** generated by thermal decomposition of **1c** by loss of Me₃SiF and of **5c** by symmetrical cleavage of the cyclodigermazane.

At 1173 K, the band at 7.0 eV characteristic of germaimine **2c** disappears, while we observe the DMB (8.7, 10.3, 11.4 eV) and isobutene (9.4, 11.8 eV) ionizations (Figure 4c). The loss of these stable and volatile compounds was confirmed by a separate product study coupled with PES. The new spectrum, obtained after the subtraction of the DMB and isobutene spectra

(Figure 4d), is identical to that of **1c** at 1073 K without the DMB, Me₃SiF, and isobutene ionizations. In fact, it shows at 9.9 and 11.4 eV two bands, followed by another broad one at 13.5 eV. So, we attribute these experimental ionization energies to the germaisonitrile **4d**, identically synthesized by flash thermolysis of **1c** and **5c**.

Assignment of the Spectra of the Thermolysis Products and Discussion. Ab initio calculations on germaimine **2c′** and germaisonitrile **4d** confirm the previous assignment.

The lengths of Ge=N and N−C bonds of **2c′**, calculated at 1.696 and 1.460 Å, respectively, are close to the experimental values obtained by single-crystal X-ray diffraction of cyclic germaimine N-arylated ($R_{Ge=N}$ = 1.691−1.703 Å and R_{N-C} = 1.399−1.411 Å).[32] The GeNC angle is slightly smaller than that of the *N*-methylated silanimine (SiNC 114° for **2c′**, 137° for (CH₃)₂Si=N− CH₃).

The evaluation of the first ionic state energies of germaimine **2c′** (Table 1) confirms the germaimine **2c** characterization. Following our recent study on N-alkylated silaimines,[12] we estimate the destabilizing effect of a *tert*-butyl group on the nitrogen atom compared to that of the methyl group as 0.5 eV for the n_N orbital and 0.9 eV for $\pi_{Si=N}$. Assuming that substituent effects on the Ge=N and Si=N patterns are close, we

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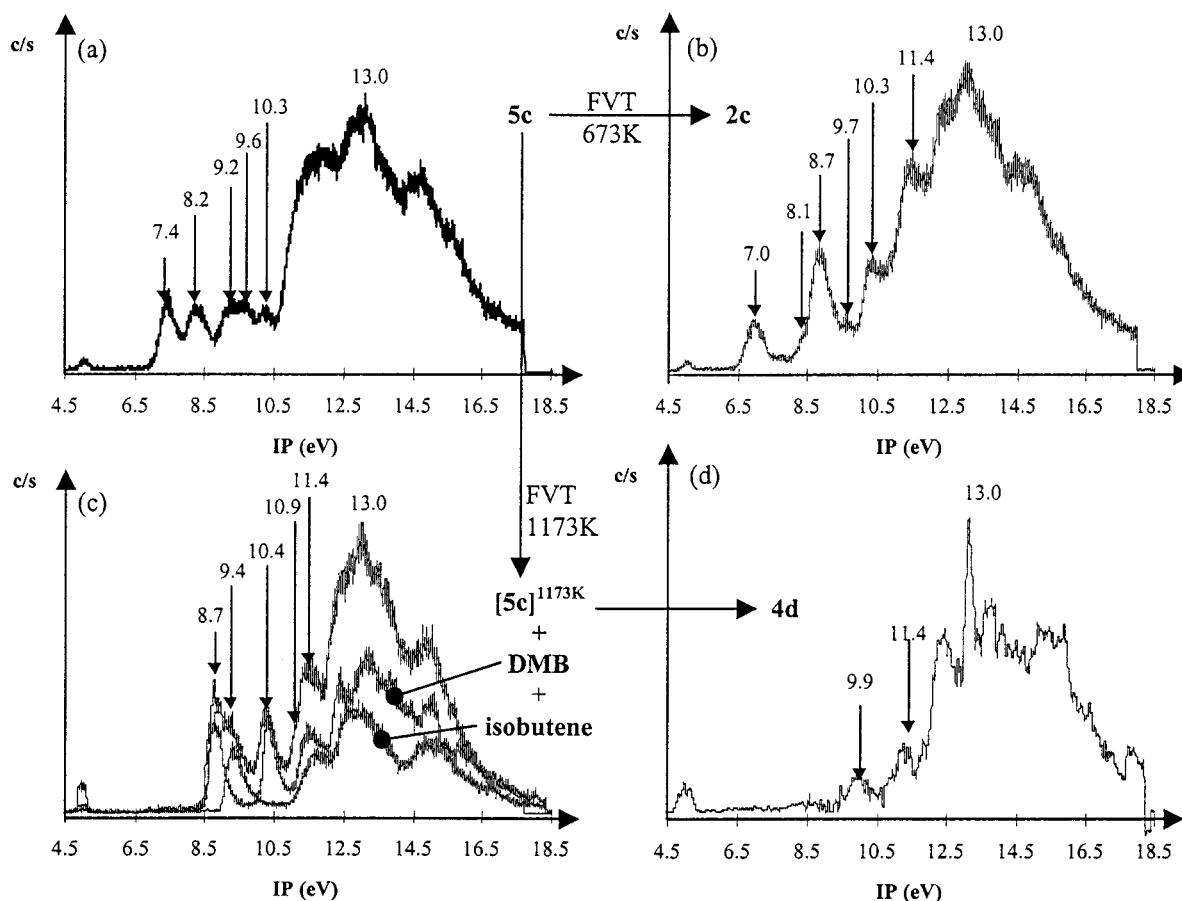
Figure 4. PE spectra of **5c** at (a) 293 K, (b) 673 K, and (c) 1173 K and (d) **5c** at 1173 K after subtraction of DMB and Me$_3$SiF spectra.

attribute the first broad band at 7.0 eV (Figures 3b and 4b) to the ionizations of the $\pi_{Ge=N}$ and n$_N$ electrons. The signal at 8.1 eV is associated with the ejection of an electron from the $\pi_{C=C}$ orbital. The ionizations of the combinations of asymmetric and symmetric σ_{GeC} electrons are located at higher energy, 9.7 and 10.3 eV, respectively. The intense band at 8.7 eV is characteristic of the first ionization of DMB. It seems that the second decomposition process, corresponding to the loss of a DMB molecule, has begun at this temperature during internal thermolysis.

The confirmation of the germaisonitrile **4d** formation by thermal decomposition of two different precursors is backed up by an ab initio study of the first ionization energies of **4d** (Table 3). This linear molecule contains, like germaisonitrile **4a′**, a triple GeN bond (about 1.653 Å), shorter than a double bond (about 1.71 Å). We have also evaluated the first ionic state energies of the germaisonitrile structural isomer, germanitrile, HGeN (Table 3).

The analysis of the electronic structure of HGeN indicates that this species posseses a "real" triple bond (σ bond and two π bonds), while germaisonitrile should be considered a nitrene in the triplet state in interaction with a nonhybridized germanium atom.

The energies of the first two ionic states of the two isomers are very close (Table 3). However, as for the silicon analogues silaisonitriles,[33,34] we find that the germaisonitrile is much more stable than the germanitrile (70.7 kcal/mol). So, given the decomposition pathway and the high isomerization barrier (83.7 kcal/mol),

we assign the PE spectrum in Figure 4d to germaisonitrile **4d**. The band at 9.9 eV is assigned to the two $^2\Pi$ ionic states corresponding to ionization of the $\pi_{Ge=N}$ electrons. The next band at 11.4 eV corresponds to the $^2\Sigma^+$ ionic state associated with the ionization of a germanium lone pair electron.

Conclusion

This study shows the potential of PES to characterize low-coordinate germanium compounds. Germacyclopentenes are a useful source of these reactive species. This work constitutes a simultaneous characterization in the gas phase of three classes of low-coordinate germanium compounds: germaimines, germylenes, and germaisonitriles. Each species exhibits characteristic low-energy ionizations which allow their unambiguous identification. The observed ionization potentials allow some general observations: (1) Ionization potentials arising from the germaimine or germaisonitrile $\pi_{Ge=N}$ orbital are strongly destabilized when we compare them to those of the analogous carbon compounds. This result explains the high kinetic instability of the germanium species. (2) We note the ability of the germanium analogue of carbenes to be electronically stabilized by adjacent heteroatom lone pairs.

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Experimental Section

FVT−PES Couplings. Photoelectron spectra were recorded on an Helectros 0078 spectrometer, monitored by a microcomputer system supplemented by a digital analogic converter (DAC). The spectra were constructed with 2000 points and were accurate within 0.1 eV. They were recorded with 21.21 eV HeI radiation as the photon source and calibrated on well-known helium ionization at 4.98 eV and those of nitrogen at 15.59 and 16.98 eV.

Two types of pyrolysis experiments, coupled with photoelectron spectroscopy, were performed. First, a flash pyrolysis was effected inside the ionization chamber of a UV−PES spectrometer equipped with an internal heating device. The pressure of the ionization chamber was 10^{-5} mbar without sample. This first experiment, called "internal thermolysis", allowed the analysis of both the species with short lifetime and their decomposition products. The second system was an apparatus external to the spectrometer which allowed a separate product study. Thermolysis was performed in a vacuum device (pressure in the oven: 10^{-3} mbar without sample) connected to the spectrometer. In this case, only the stable and volatile species were characterized after cryogenic distillation. Unstable compounds decomposed and/or polymerized because of the long distance between the oven and the ionization head.

During external thermolysis, the pyrolysate could also be condensed and analyzed by ^{1}H NMR spectroscopy. The spectra were recorded on Bruker 400 MHz or on Hitachi R-1200 60 MHz spectrometers.

Synthesis of 1a, $C_{12}H_{28}NFSi_2Ge$, 1-Bis(trimethylsilyl)-amino-1-fluoro-3,4-dimethyl-1-germacyclopent-3-ene. In a 250 mL flask, a solution of $(Me_3Si)_2NLi$ (30.6 mmol, 4.9 g, 19 mL of n-BuLi 1.6 M in hexane) was added dropwise to a solution of 1,1-difluoro-3,4-dimethyl-1-germacyclopent-3-ene[35] (5.85 g, 30.4 mmol) in 25 mL of dry benzene at room temperature. After the addition, the mixture was heated at reflux for 2 h. Lithium fluoride was removed by centrifugation and washed twice with benzene. Solvents were evaporated, and the residue was distilled under vacuum. Bp: 76 °C/0.07 mmHg. Yield: 3.95 g, 39%. MS [EI, *m/z* (%): 335 [M$^{+•}$],(9); 316 (5); 253 (4); 238 (100). ^{1}H NMR (C_6D_6) δ (ppm): 0.24 (s, 18H); 1.53 (s, 6H), 1.80 (m, 4H). ^{19}F NMR (C_6D_6) δ (ppm): −88.2 (m). ^{13}C NMR (C_6D_6) δ (ppm): 4.32 (*C*H$_3$Si); 18.94 (*C*H$_3$); 29.91

(CH$_2$); 129.94 (C=). Anal. Calcd for $C_{12}H_{28}NFSi_2Ge$: C, 43.16; H, 8.39. Found: C, 42.89; H, 8.59.

Synthesis of 1b, $C_{12}H_{28}NClSi_2Ge$, 1-Bis(trimethylsilyl-amino)-1-chloro-3,4-dimethyl-1-germacyclopent-3-ene. In a 100 mL flask 2 g of 1,1-dichloro-3,4-dimethyl-1-germacyclopent-3-ene[35] was added to 25 mL of anhydrous THF. Then 8.9 mL of a 1 M $(Me_3Si)_2NLi$ solution was added dropwise. The mixture was stirred for 2 h. Solvents were evaporated, and 40 mL of hexane was added. The LiCl precipitate was filtered and the hexane evaporated. Vacuum distillation provided 1.96 g of a colorless liquid. Bp: 60 °C/0.01 mmHg. Yield: 1.96 g, 63%. MS [EI, *m/z*] (%): 351 [M$^{+•}$,4]; 269 (8); 254 (100); 146(22). ^{1}H NMR (C_6D_6) δ (ppm): 0.26 (s, 18H); 1.56 (s, 6H), 1.98 (m, 4H). ^{13}C NMR (C_6D_6) δ (ppm): 4.43 (CH$_3$Si); 16.66 (CH$_3$); 36.64 (CH$_2$); 129.14(C=). Anal. Calcd for $C_{12}H_{28}NClSi_2Ge$: C, 41.13; H, 8.00. Found: C, 40.78; H, 8.24.

The syntheses of **1c** and **5c** have been described[15] previously.

Calculation Methods. The theoretical evaluations were performed with an ab initio molecular orbital calculation method contained in the Gaussian 94 program package.[36] The geometrical parameters of neutral species were optimized with the density functional theory using the B3LYP hybrid analytical function and LANL2DZ(d) (D95 on H, C, N,[37] Los Alamos ECP plus DZ on Si, Ge[38]) basis set for **2a′** and **2c′**, the 6-311G-(d) basis set for **3b′** and **4a′**, and the 6-311G(d,p) basis set for **4d**. Ionization energies (IPs) were evaluated at ΔSCF (IPs = $E_{\text{neutral}} - E_{\text{ion}}$) level.

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