# Applications of Photoelectron Spectroscopy to Molecular Properties, 52[+]

# Gas-Phase Characterization of an Unhindered Germaimine by UV-Photoelectron Spectroscopy

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

**Keywords:** Germacyclopentene / Germaimine / Photoelectron spectroscopy / Ab initio calculations / Germanium

An unhindered germaimine has been generated and characterized by the coupling of flash vacuum pyrolysis of two different precursors with UV-photoelectron spectroscopy. The Ge=N unit exhibits two ionizations in the low-energy region, corresponding to the ejection of an electron from the nitrogen atom lone pair and from the $\pi_{Ge=N}$ orbital, respectively.

## Introduction

The chemistry of low-coordinated group-14 and -15 elements of the third and fourth periods has undergone considerable development over the past 35 years. The first experimental characterizations of the C≡P triple bond[1] and of the Si=C double bond appeared in the 1960s.[2] Soon after, germanium compounds with multiple bonds were reported. These species showed greater overall kinetic instability when they were slightly sterically hindered.

The germaimines, compounds with a Ge=N double bond, were first characterized indirectly using various trapping reagents.[3] Only in the last ten years have sufficiently stable germaimines been synthesized to allow their analysis in the solid state (XR, IR) or in solution (IR, NMR).[4-7] However, there have been no reports of the characterization of germaimines in the gas phase, other than that by Lee[8] concerning $H_2Ge=NCF_3$. This latter exhibited a surprising stability and proved to be resistant to hydrolysis (!).

We present in this paper the first characterization of an unhindered germaimine by UV-photoelectron spectroscopy (UV-PES), specifically *N-tert*-butyl-3,4-dimethyl-1-germacyclopent-3-en-1-imine (**1**).

## Results and Discussion

The aforementioned germaimine was generated by flash vacuum thermolysis (FVT) of the fluorogermacyclopentene **2** and the cyclodigermazane **3**, and was analyzed by photoelectron spectroscopy (UV-PES). The coupling of FVT with UV-PES has turned out to be particularly well suited for the detection of highly reactive species and has recently been used in studies of *N*-alkylated and *N*-silylated silaimines.[9][10]

The precursor **2** was synthesized by condensation of the corresponding lithiated amine with germacyclopentene difluoride. After several weeks at ambient temperature under inert atmosphere, **2** had undergone spontaneous conversion into a white crystalline solid corresponding to the cyclodigermazane **3**, which was fully characterized by MS and NMR analysis.

The photoelectron spectrum of the precursor **2** (Figure 1a) features a first well-resolved band at 8.4 eV, corresponding to the ejection of an electron from the nitrogen atom lone pair[11] and the $\pi_{C=C}$ orbital.[12] The broader signal seen at 10.3 eV is associated with ionization from the $\sigma_{Si-C}$ orbitals. The latter signal shows an obvious shoulder at 9.7 eV, which corresponds to ionization from the $\sigma_{Ge-C}$ orbitals. The following ionization, which is attributed to the ejection of an electron from the $\sigma_{Ge-N}$ orbital, is poorly resolved (11.6 eV).

The PE spectrum of the cyclodigermazane **3** (Figure 1c) is characterized by two bands in the low-energy region, at 7.4 eV and 8.2 eV. We attribute the band at 7.4 eV to ionizations from the antibonding and bonding combinations of the nitrogen atom lone pairs. Ionizations of the antibonding and bonding $\pi_{C=C}$ orbital combinations are responsible for the broad signal at 8.2 eV. The bands above 9.0 eV correspond to the ejection of an electron from the $\sigma_{Ge-C}$ and $\sigma_{Ge-N}$ bonds.

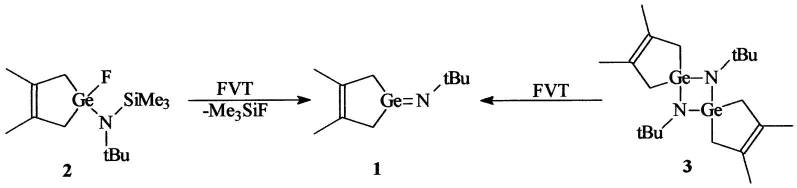
The short-path thermolysis spectrum of **2** at 673 K is displayed in Figure 1b. In the low-energy region, a broad signal at 7.0 eV, and an intense band at 8.7 eV with a marked shoulder at 8.1 eV can be seen. Beyond these signals, an ionization at 10.9 eV with a shoulder at 10.3 eV, and another signal at 11.4 eV can be noted. The ionization energy at 10.9 eV corresponds to $Me_3SiF$, formation of which was unambiguously proven when long-path thermolysis experiments were performed (520 K). An identical spectrum (lacking the band at 10.9 eV) was obtained upon

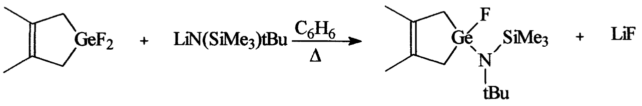
---

[+] For Part 51, see ref.[10]

[a] Laboratoire de Physico-Chimie Moléculaire, CNRS UMR 5624,
Avenue de l'Université, F-64000 Pau, France
Fax: (internat.) + 33-5/59808344
E-mail: genevieve.pfister@univ-pau.fr
[b] Laboratoire d'Hétérochimie Fondamentale et Appliquée,
118, route de Narbonne, F-31062 Toulouse, France

1434–1948/99/0707–1151 $ 17.50+.50/0





heating the cyclic dimer **3** at the same temperature. Thus, it seems as though the same species was generated in each case, namely the germaimine **1**.

In order to verify the assigned natures of the ionizations, we have theoretically evaluated the energies of the first three ionic states of a structurally similar germaimine, **1′** (*N*-methyl rather than *N*-*tert*-butyl). These calculations were performed using the density functional method with the hybrid functional B3LYP[13] and the LANL2DZ(d) basis set.[14][15] The optimized structure of this molecule is shown in Figure 2. The calculated Ge=N bond length (1.696 Å) is in excellent agreement with both the experimental[7] and a previous theoretical value.[16]

The magnitudes and assignments of the first three vertical ionization energies are summarized in Table 1. We note that the ionization energies of the nitrogen atom lone pair and $\pi_{C=C}$ double-bond orbitals of *N*-alkylated germaimine are very close (7.78 eV and 7.71 eV). Moreover, the destabilizing effect of a *tert*-butyl group on the nitrogen atom compared to a methyl group has previously been observed for ionization from the $n_N$ and $\pi_{Si=N}$ orbitals of dimethylsilaimines (0.5 eV and 0.9 eV, respectively).[9]

Table 1. Calculated [B3LYP/LANL2DZ(d), ΔSCF] and experimental first ionic states energies of **1** and **1′** [eV]

| Ionic states | Calculated energies of **1′** | Experimental energies of **1** |
|---|---|---|
| $^2A'$ ($n_N$) | 7.71 | 7.0 |
| $^2A''$ ($\pi_{Ge=N}$) | 7.78 | 7.0 |
| $^2A''$ ($\pi_{C=C}$) | 7.93 | 8.1 |

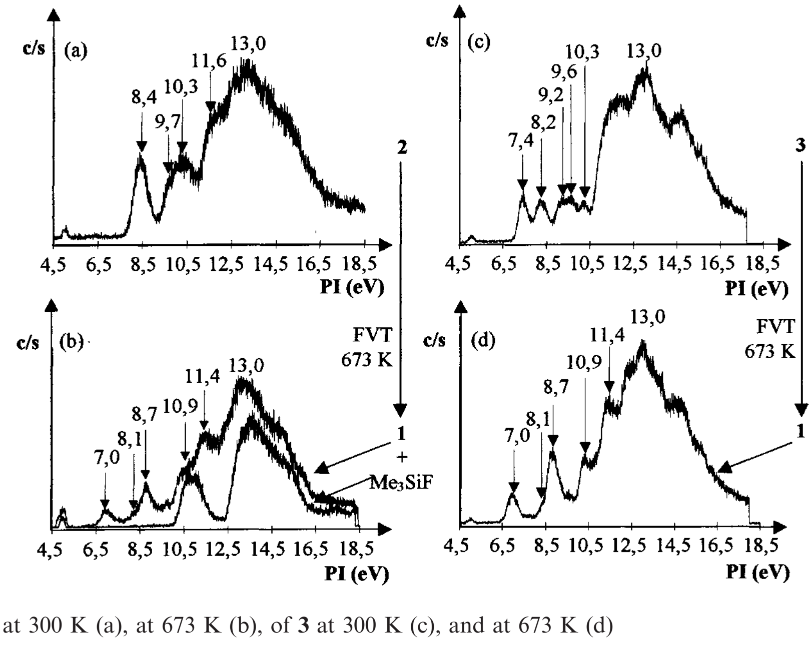


Figure 1. PE spectra of **2** at 300 K (a), at 673 K (b), of **3** at 300 K (c), and at 673 K (d)

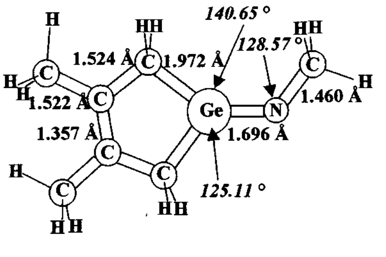


Figure 2. Geometrical parameters of the *N*-methylated germaimine **1′** [B3LYP/LANL2DZ(d)]

Thus, it seems reasonable to attribute the broad signal centered at 7.0 eV to ionizations from the nitrogen atom lone pair and $\pi_{Ge=N}$ bond, and the third ionization energy at 8.1 eV, the shoulder of the band at 8.7 eV in the PE spectrum, to the ejection of an electron from the $\pi_{C=C}$ cyclic bond (calculated at 7.93 eV). The ionizations of the antibonding and bonding combinations of the Ge−C bonds are observed at higher energies of 9.7 and 10.3 eV, respectively.[12] The intense signal at 8.7 eV is characteristic of the first ionization of 2,3-dimethylbuta-1,3-diene. Thus, at this temperature we observed the onset of the loss of 2,3-dimethylbuta-1,3-diene, corresponding to a second decomposition process (confirmed when long-path thermolysis experiments were conducted at 673 K).

## Conclusion

To the best of our knowledge, this work constitutes the first gas-phase characterization of a germaimine generated by flash vacuum thermolysis. This compound displays two characteristic ionizations in the low-energy region, corresponding to electron abstraction from the nitrogen atom lone pair and the Ge=N double bond. As in the case of silaimines, a $\pi_{Ge=N}$ orbital destabilization relative to the imines is in evidence. This stems from the kinetic instability and higher reactivity of the germaimines.

## Experimental Section

**Photoelectron Spectroscopy:** Photoelectron spectra were recorded with a Helectros 0078 spectrometer, monitored by a microcomputer system supplemented by a digital analog converter (DAC). The spectra were built up from 2000 points and are accurate to within ±0.1 eV. They were recorded with 21.21 eV HeI radiation as the photon supply and were calibrated against the well-known helium ionization at 4.98 eV and nitrogen ionizations at 15.59 eV and 16.98 eV. Two types of pyrolysis experiments were performed, in combination with photoelectron spectroscopy. In short-path pyrolyses, the furnace was placed inside the ionization chamber of the UV spectrometer. The pressure in the ionization chamber was $10^{-5}$ mbar prior to introduction of the sample, and less than $10^{-4}$ mbar when the product was present. This first experimental procedure permitted analysis of species of short lifetime as well as their decomposition products. The second thermolysis system was external from the spectrometer. Thermolysis was performed in a vacuum device (oven pressure: $10^{-3}$ mbar without sample) connected to the spectrometer. In this case, only the stable species could be characterized after cryogenic distillation. Unstable compounds decompose and/or polymerize because of the considerable distance between the oven and the ionization head (around 1 m).

### Synthesis of Precursors 2 and 3

**1-[*tert*-Butyl(trimethylsilyl)amino]-1-fluoro-3,4-dimethyl-1-germacyclopent-3-ene (2):** Germacyclopentene difluoride (6.65 g, 34.5 mmol) was added to a solution of LiN(*t*Bu)SiMe$_3$ (5.21 g, 34.5 mmol) in 20 mL of dry THF. The resulting yellow solution was stirred for 2 h at ambient temperature. Then, the THF was evaporated and pentane was added. LiF was eliminated by centrifugation and the organic layer was purified by vacuum distillation to yield 4.39 g (40%); b.p. 88°C/0.04 Torr. − MS (70 eV); *m*/*z*: 319 [M$^+$]. − $^1$H NMR (CDCl$_3$): $\delta$ = 0.22 [s, 9 H, Si(CH$_3$)$_3$], 1.34 [s, 9 H, C(CH$_3$)$_3$], 1.74 (m, 6 H, cyclic CH$_3$), 1.84 (m, 2 H, cyclic CH$_2$), 1.92 (m, 2 H, cyclic CH$_2$). − $^{19}$F NMR (CDCl$_3$): $\delta$ = −85.6 (m).

**3**: Compound **3** was obtained by spontaneous transformation of **2**. After one month under inert atmosphere, **2** was transformed into yellow crystals of **3** as Me$_3$SiF was given off; m.p. 174−176°C. − MS (70 eV); *m*/*z*: 452 [M$^+$]. − $^1$H NMR (CDCl$_3$): $\delta$ = 1.15 [s, 18 H, C(CH$_3$)$_3$], 1.71−1.75 (m, 10 H, cyclic H).

**Calculation Method:** The theoretical evaluations were performed by means of an ab initio molecular orbital calculation method as implemented in the Gaussian 94 program package.[15] The geometrical parameters of neutral species were optimized by functional density theory using the B3LYP analytical function in conjunction with the LANL2DZ (D95 on H, C, N,[13] Los Alamos ECP plus DZ on Si, Ge[14]) basis set, extended with d orbitals (exponents: 0.8 for C and N; 0.202 for Ge). Ionization potentials (IPs) were evaluated at the ΔSCF level (IPs = $E_{\text{neutral}} - E_{\text{ion}}$).

## Acknowledgments

Financial support of this work by the CNRS (France) is gratefully acknowledged. We also thank the Institut du Développement des Ressources Scientifiques (IDRIS, Orsay, France), under the administration of the CNRS, for use of the calculation facilities, and Dr. Gijs Schaftenaar for allowing us to use his graphics program Molden.

---

[1] T. E. Gier, *J. Am. Chem. Soc.* **1961**, *83*, 1769.
[2] L. E. Gusel′nikov, M. C. Flowers, *Chem. Commun.* **1967**, 864−865.
[3] J. Barrau, J. Escudié, J. Satgé, *Chem. Rev.* **1990**, *90*, 283−319.
[4] M. Rivière-Baudet, J. Satgé, F. El-Baz, *J. Chem. Soc., Chem. Commun.* **1995**, 1687−1688.
[5] T. Tsumuraya, W. Ando, *Chem. Lett.* **1989**, 1043−1046.
[6] C. Glidewell, D. Lloyd, K. W. Lumbard, J. S. McKechnie, *Tetrahedron. Lett.* **1987**, *28*, 343−344.
[7] A. Meller, G. Ossig, W. Maringgele, D. Stalke, R. Herbst-Irmer, S. Freitag, G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.* **1991**, 1123−1124.
[8] H. G. Ang, F. K. Lee, *J. Chem. Soc., Chem. Commun.* **1989**, 310−311.
[9] V. Metail, S. Joanteguy, A. Chrostowska-Senio, G. Pfister-Guillouzo, A. Systermann, J. L. Ripoll, *Inorg. Chem.* **1997**, *36*, 1482−1487.
[10] V. Metail, S. Joanteguy, A. Chrostowska-Senio, G. Pfister-Guillouzo, A. Systermann, J. L. Ripoll, *Main Group Chem.* **1997**, *2*, 97−106.
[11] [11a] D. H. Harris, M. F. Lappert, J. B. Pedley, G. J. Sharp*, J. Chem. Soc., Dalton Trans.* **1976**, 945−950. − [11b] K. A. O. Starzewski, H. T. Dieck, H. Bock, *J. Organomet. Chem.* **1974**, *65*, 311−325.
[12] C. Guimon, G. Pfister-Guillouzo, G. Manuel, P. Mazerolles, *J. Organomet. Chem.* **1978**, *149*, 149−159.
[13] T. H. Dunning, Jr., P. J. Hay, *Modern Theoretical Chemistry* (Ed.: H. F. Schaefer III), Plenum, New York, **1976**, p. 1−28.
[14] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270−283; W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284−298; P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299−310.
[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Bingley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94* (Revision D.1), Gaussian, Inc., Pittsburgh PA, **1995**.
[16] G. Trinquier, J. C. Barthelat, J. Satgé, *J. Am. Chem. Soc.* **1982**, *104*, 5931−5936.

Received December 14, 1998
[I98421]