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Photoelectron spectra of vinyl- and 1-alkynylgermanes and stannanes[1]

Anna Chrostowska [a], Véronique Métail [a], Geneviève Pfister-Guillouzo [a,*], Jean-Claude Guillemin [b]

[a] *Groupe de Physicochimie Moléculaire, CNRS UMR 5624, Université de Pau, Avenue de l'Universitaire, 64000 Pau, France*
[b] *Groupe de Synthèses et Activations de Biomolécules, CNRS UMR 6052, ENSCR, 35700 Rennes, France*

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Abstract

Primary vinylic and acetylenic germanes and stannanes, synthesized by a chemoselective reduction of the corresponding trichloro derivatives, were investigated by ab initio quantum chemical methods and photoelectron spectroscopy. In particular, the PE spectra display very well-resolved bands which show the increasing destabilizing effect of 14 group heteroatom α-substitution of double or triple carbon–carbon bonds. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photoelectron spectroscopy; Vinylgermane; Vinylstannane; 1-Alkynylgermane; 1-Alkynylstannane

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1. Introduction

For a long time, numerous works have been devoted to the synthesis and the particular chemical or spectroscopic properties of α,β-unsaturated heterocompounds bearing one or several hydrogens on the heteroatom. The vinylalcohols and -amines have been extensively studied [2]. The presence of the unsaturated group leads to a dramatic increase of the acidity of the OH or NH function [2], and, although most of these compounds quickly rearrange into the corresponding carbonyl- or imines derivatives in the presence of traces of acid or base, the nature of the substituents on the carbon–carbon multiple bond can lead to kinetically stable compounds [3]. Only 11 elements of the periodic table (Hg [4], Si [5], Ge [6], Sn ([6]a, [7]), N [1,8], P [9], As [10], Sb [11], O [2,12], S [13], Se [14]) have such isolated primary α,β-unsaturated derivatives. The photoelectron spectra of some of these compounds have been recorded and, in the 15th and 16th groups, the role played by the set "unsaturated system (C=C or C≡C bond), lone pair or hydrogen(s) of the (XH_n) substituent" has been clearly shown ([9]b,e, [10]c, [11], [12]b, [13]b). However, the PE spectra of vinyl derivatives of the group 14 has been limited, up-to-now, to the carbon and silicon derivatives ([5]c). The recent improvement of the synthesis of vinylstannanes ([7]a) and the first preparation of primary ethynylstannanes ([7]b) by one of us, prompted us to develop a spectroscopic study devoted to the simple primary α,β-unsaturated germanes and stannanes. Such compounds present a good opportunity to determine the role played by the couple unsaturated system heteroatomic group without lone pair. We report here the photoelectron spectra of vinyl- **1a**, propenyl- **1b**, ethynyl- **2a** and propynylgermane **2b** and the corresponding stannanes **3a**,**b**, **4a**. We also present a comparative ab initio theoretical study of the molecular and electronic structures of the vinylsilane **5a** and vinylstannane **3a**. The ionization potentials are calculated for the vinylic derivatives with Koopmans approximation in order to corroborate the assignment of the PE spectra.

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[*] Corresponding author. Tel.: +33 05 59923019; fax: +33 05 59923029; ; e-mail: geneviève.pfister@univ-pau.fr

[1] See Ref. 1.

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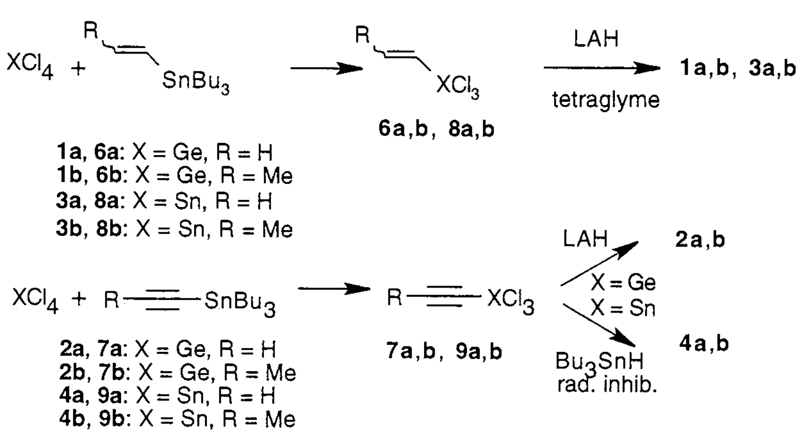
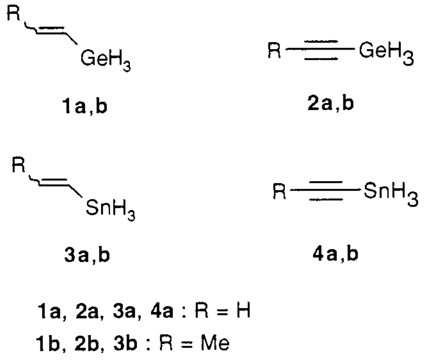


Scheme 1.



2. Results and discussion

2.1. Preparation of *α,β*-unsaturated compounds

The vinylic germanes **1a**,**b** ([6]a), alkynylgermanes **2a**,**b** ([6]b), vinylic stannanes **3a**,**b** ([7]a) and alkynylstannanes **4a**,**b** ([7]b) were prepared in a two-step sequence involving the synthesis of the trichloro derivatives **6a**,**b**–**9a**,**b** and their chemoselective reduction. The vinylic **6a**,**b** and 1-alkynyltrichlorogermanes **7a**,**b** ([7]c) and the corresponding stannanes **8a**,**b** and **9a**,**b** ([7]d) were synthesized by redistribution between the vinylic and 1-alkynyltributylstannanes and $GeCl_4$ or $SnCl_4$, respectively. The reduction of compounds **6a**,**b**–**8a**,**b** in the corresponding primary germanes **1a**,**b**, **2a**,**b** and stannanes **3a**,**b** was chemoselective even using a reducing agent as LAH in tetraglyme. To inhibit their decomposition, the products were quickly distilled off in vacuo from the reaction mixture and purified by trap-to-trap distillation. Primary alkynylstannanes **4a**,**b** were prepared in a similar procedure but using tributylstannane in the presence of small amounts of a radical inhibitor as reducing agent (Scheme 1). In the condensed phase, these two compounds in pure form decomposed at a temperature higher than − 100°C. A black material was slowly formed under these conditions. The half-life at room temperature of stannanes **4a**,**b** in benzene-d_6 is of about 1 h.

2.2. PE spectra of vinylic germanes and stannanes

To record the PE spectra, pure germanes **1a**,**b**, **2a**,**b** and stannanes **3a**,**b**, **4a** were frozen in a liquid nitrogen bath and slowly allowed to warm in vacuo to the temperature of revaporization (ca. − 100°C). Attempts to slowly revaporize pure 1-propynylstannane **4b** were unsuccessful.

The spectra of the vinylic germanes **1a**,**b** and stannanes **3a**,**b** are displayed in Fig. 1. The PES of the corresponding vinylsilane **5a** have also been recorded. The experimental IP's have been listed in Table 1 with the corresponding graphical presentation of molecular orbitals (MP2, LANL1DZ for **5a**, **3a**). According to these PE data, the band shapes and their number are quite similar for all these molecules, suggesting electronic similarity. The only noticeable differences concern the shift of all bands at lower energy from Si to Sn and their relative intensities.

The assignment of spectra is in agreement with the findings of Schweig and Bock et al. ([5]c,d, [15]) for the vinylsilane **5a**. The position of the first band, associated with the ejection of an electron from the asymmetric combination between the $\pi_{C=C}$ and the π_{XH_3} orbitals of same symmetry, is slightly higher than the corresponding one of the isoelectronic and isovalent propene. This band is seen to undergo a characteristic shift conform to the sequence: $SiH_3 > GeH_3 > SnH_3$. It is consistent with the increasing heteroatom sizes (bond lengths longer, diffuse character of the heteroatom more significant) taking into account that the electronegativity is nearly constant: 1.9 Si, 2.0 Ge, 1.95 Sn [16].

The stabilizing negative hyperconjugation effect [17] upon the system $(\pi \leftrightarrow \pi^*_{XH})$ is more important for SiH_3, GeH_3 than for SnH_3, while their inductive effect, expected to destabilize the $\pi_{C=C}$ orbital, is just slightly effective. The decrease in intensity of the remaining PE bands, on going from He(I) (21.21 eV) to He(II) (40.81 eV) excitating ionization energy, indicates that these ionizations arise from orbitals localized on silicon,

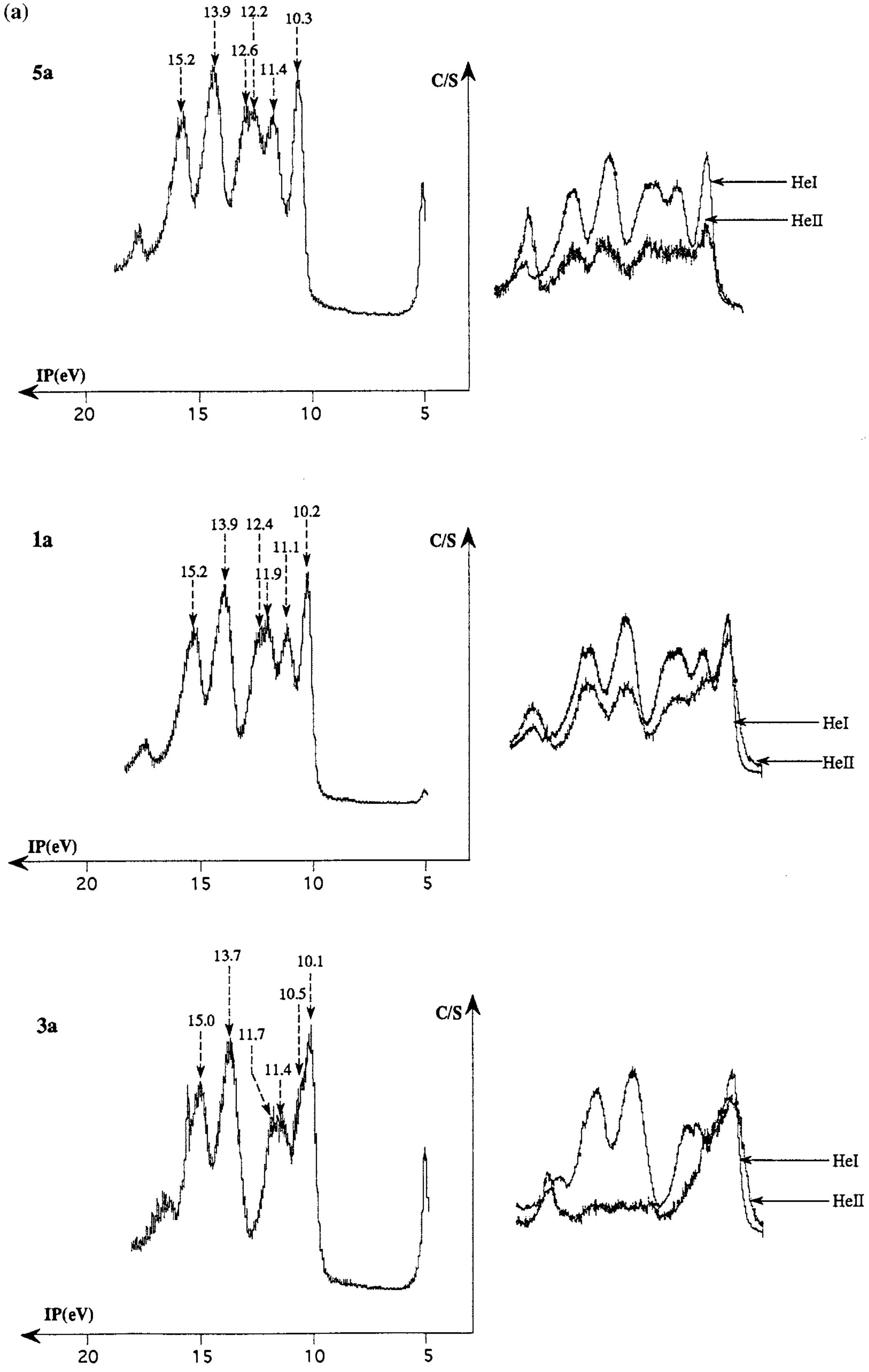


Fig. 1. The spectra of the vinylic germanes **1a**,**b** and stannanes **3a**,**b**.

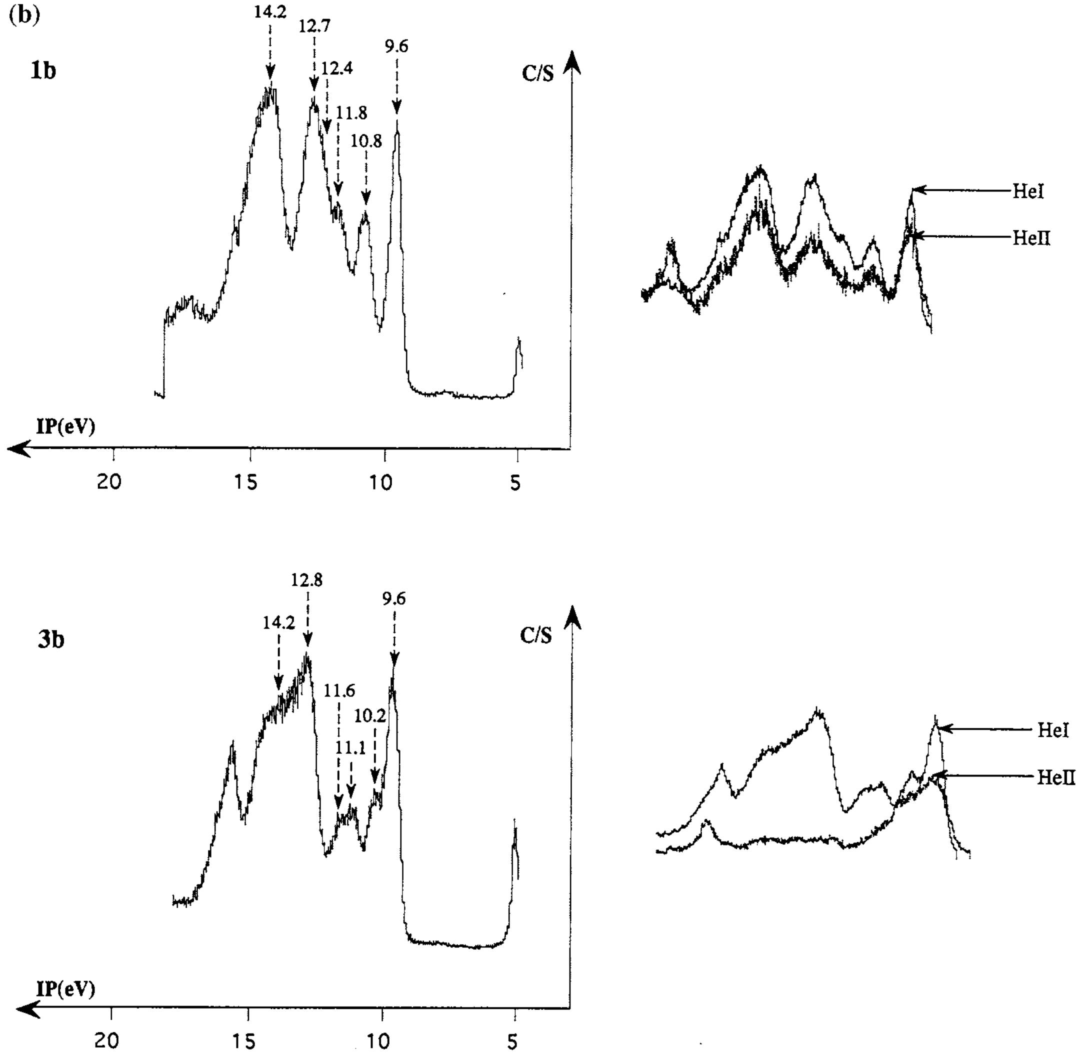


Fig. 1. (*Continued*)

manium or tin: the second and the third bands correspond to the ejection of one electron from σ_{C-X} and σ_{X-H} orbitals, respectively. The following ionization corresponds to the symmetric combination $\pi_{C=C}+\pi_{XH_3}$. The last two bands, at deeper energy, arise from σ_{C-C} and σ_{C-H} orbitals.

On the other hand, the introduction of a methyl group on the carbon atom of the double bond induces the destabilization of all IPs by a symmetry allowed admixture of the out-of-plane σ_{C-H} bond as well as by inductive effect. This reveals an electronic delocalisation on molecules framework due to numerous orbital interactions. The result of the He(II) experiment confirms this delocalization. The constancy of this first band intensity is in agreement with the description of the corresponding orbital, mainly localized on the $\pi_{C=C}$ system. The decrease in intensity of the other bands confirms their attribution to orbitals heavily localized on silicon in particular for the fourth ionization.

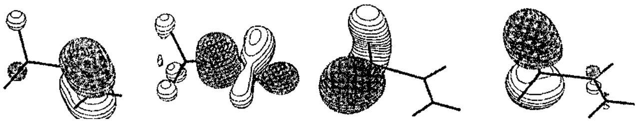
In order to further confirm our assignments, IPs evaluations have been performed for the vinylsilane **5a** and vinylstannane **3a** (Table 1). The ab initio results (Koopmans' approximation without taken into account the electronic reorganization) overestimate all IP's, expect the first one corresponding to a molecular orbital mainly localized on the $\pi_{C=C}$ bond.

2.3. PE spectra of acetylenic germanes and stannanes

The photoelectronic spectra of alkynylgermanes **2a** and **2b** are quite similar (Fig. 2). The first band is sharp, intense and followed by a broad and poorly resolved massif at the higher ionization energies. It should be pointed out that it was particularly difficult to obtain the spectrum of alkynylstannane **4a**. During the revaporization, the partial decomposition of stannane **4a** leads to the formation of SnH_4 and C_2H_2. The bands corresponding to these molecules were also observed. Attempts to record the PES of the propynylstannane **4b** were unsuccessful; this compound decomposes at a temperature

Table 1
Experimental and calculated values of ionization potentials (in eV) with graphical representationof the nature of the corresponding molecular orbitals

Graphical presentation of MO's



Attribution	$\pi_{C=C}-\pi_{XH_3}$	σ_{X-C}	σ_{X-H}	$\pi_{C=C}+\pi_{XH_3}$	$\sigma_{C-C}\sigma$	
CH_2=CH–SiH_3 **5a**	10.3[a], 10.18[b]	11.4[a], 12.52[b]	12.2[a], 13.14[b]	12.6[a], 13.37[b]	13.9[a], 15.36[b]	15.2[a], 17.02[b]
CH_2=CH–GeH_3 **1a**	10.2	11.1	11.9	12.4	13.9	15.2
CH_2=CH–SnH_3 **3a**	10.1[a], 10.17[b]	10.5[a], 11.51[b]	11.4[a], 12.14[b]	11.7[a], 12.27[b]	13.7[a], 15.2[b]	15.0[a], 16.75[b]
CH_3–CH=CH–GeH_3 **1b**	9.6	10.8	11.8	12.4	12.7	14.2
CH_3–CH – =CH–SnH_3 **3b**	9.6	10.2	11.1	11.6	12.8	14.2

[a] Expected value.
[b] Calculated value.

lower than the temperature of distillation in vacuo (10^{-3} mbar).

The experimental data of the ionization potentials of **2a**,**b**, **4a** are reported on Table 2, the first ionization potential of ethynylsilane reported by Schweig and Bock et al. ([5]c) is mentioned too. In the aim to compare the first ionization potentials (corresponding to the degenerated π_{CC} orbitals of the carbon–carbon triple bond) of the studied systems with their carbon analogs, we displayed also in Table 2, values corresponding to the acetylene and propyne molecules.

The photoelectronic spectra of **2a** and **2b** could be easily interpreted with attribution to: the first ionization potential to the ejection of an electron from the degenerated acetylenic $\pi_{C\equiv C}$ molecular orbitals, broad and poorly resolved massif observed beyond 12 eV to ionizations of different types of σ bonds like σ_{X-C}, σ_{X-H}, σ_{C-H} equate with this range of energy.

The values of the first ionization potentials (associated with carbon–carbon triple bond) are quite similar for ethynylsilane, ethynylgermane and ethynylstannane. The very weak destabilization observed for ethynylgermane **2a** and ethynylstannane **4a** is consistent with evolution of atomic and molecular properties going from silicon to tin. In particular the carbon–heteroatom bond lengths are longer, the diffuse character of the heteroatom orbitals are more significant and the negative hyperconjugation effect is weaker.

The substitution of hydrogen atom in the molecule of acetylene by SiH_3, GeH_3 and SnH_3 induces the $\pi_{C\equiv C}$ orbital destabilization more important than in the ethylenic derivatives, contrary to the ionizations associated with σ_{X-H} and σ_{X-C} molecular orbitals which are shifted to deeper energies.

It may be pointed out that the acetylenic derivatives are less stable than the ethylenic ones due to the more important destabilizing interactions between a XH_3 fragment and the two perpendicular π-systems. In fact, it was quite difficult to characterize experimentally ethynylstannane **4a**.

3. Conclusions

Considering the lengthening of σ_{X-C} bond and the more pronounced pyramidal character of the lone pair of the heteroatom for the vinylic derivatives of group 15, the destabilizing interactions between the $\pi_{C=C}$ orbital and the lone pair of the 15 group atoms decrease on going from nitrogen to arsenic. In the case of the vinylphosphine ([9]b,e) and vinylarsine ([10]c) the 'gauche' conformation is favoured because of the stabilizing interactions $\pi_{C=C}-\pi^{*}_{XH_2}$ and $\pi^{*}_{C=C}-\pi_{XH_2}$. In the same manner the destabilizing interaction $\pi_{C=C}-\sigma_{X-H}$ is observed for X belonging to group 14. The negative hyperconjugaison effect decreases on going from silicon to tin. We have shown for the acetylenic derivatives of group 15 (ethynylphosphine and ethynylarsine) the destabilizing interaction of four electrons ($\pi_{C\equiv C}$-lone pair) weaker for the arsenic atom than for phosphorus one which is added to the destabilizing inductive effect in both cases. But taking into account the respective energetic positions of the $\pi_{C\equiv C}$ and n_X orbitals this interaction appears roughly in the same range as the vinylic derivatives. On the other hand, the energetic proximity of the $\pi_{C\equiv C}$ and σ_{X-H} orbitals for the acetylenic derivatives of group 15 induces strong destabilizing interaction not counterbalanced by negative hyperconjugation effect. Considering that the thermodynamical stability of these systems depends on the importance of the possible stabilizing interactions it will be interesting to analyse the substitution by elements

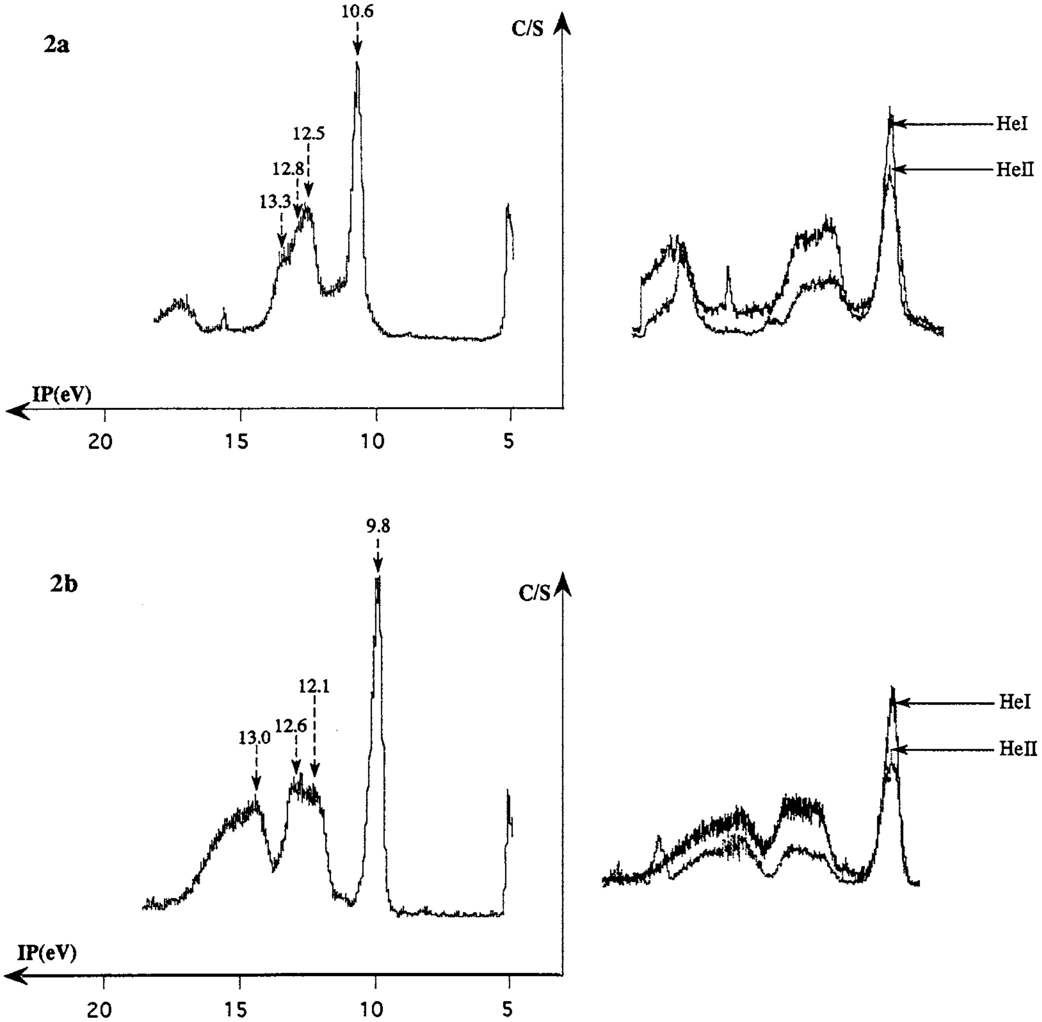


Fig. 2. The photoelectronic spectra of alkynylgermanes **2a** and **2b**.

having p-vacant orbitals (e.g. boron or aluminium derivatives). This study is currently under progress in our lab.

4. Experimental

4.1. Materials

^{1}H- (300 or 400 MHz) and ^{13}C- (75.5 or 100 MHz) NMR spectra were recorded on a Bruker AC-300P or Bruker AC 400 spectrometer and ^{119}Sn- (111 MHz) spectra on a Bruker AC 300C spectrometer. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^{1}H- and ^{13}C-spectra and external Me_4Sn for ^{119}Sn-NMR spectra. High resolution mass spectrometry experiments (HRMS) were performed on a Varian MAT 311 instrument. To record the mass spectra, stannanes **4a**,**b** were directly introduced from a cooled cell into the ionization chamber of the spectrometer. Stannanes **4a**,**b** are too reactive to be characterized by combustion analysis. The yields of the unstabilized derivatives were determined by ^{1}H-NMR spectroscopy with an internal reference. The half-life ($\tau_{1/2}$) of the unstabilized compounds was determined by ^{1}H-NMR spectroscopy for an about 5% concentration in $CDCl_3$.

4.2. Computational details

Ab initio calculations were carried out with the Gaussian 92 [18] package of programs. The geometries and frequency calculations were realized at MP2/LANL1DZ [19] (D95V on H, C, Los Alamos, ECP + DZ on Si and Sn) level.

4.3. Preparation of silane *5a*, germanes *1a*,*b*, *2a*,*b* and stannanes *3a*,*b*, *4a*,*b*

The vinylsilane **5a** has been synthesized by reduction of the vinyltrichlorosilane with LAH [5,15]. The vinylic germanes **1a**,**b** [6], the stannanes **3a**,**b** ([7]a), the ethynyl- and propynyltributylstannane [20] have been prepared as previously reported.

Table 2
Experimental ionization potentials (in eV) of acetylene and its XIVth group derivatives

	H–C≡C–H	H–C≡C–CH_3	H–C≡C–SiH_3	H–C≡C–GeH_3	CH_3–C≡C–GeH_3	H–C≡C–SnH_3
				2a	**2b**	**4a**
$\pi_{C\equiv C}$	11.40	10.4	10.7	10.6	9.8	10.6
σ_{X-C}				12.5	12.1	11.8
σ_{X-H}				12.8	12.6	12.4
σ				13.3	13.0	12.8

4.4. Synthesis of the ethynyl- ***2a*** *and propynylgermane* ***2b***

4.4.1. General procedure

Germanium tetrachloride (2.2 g, 10 mmol) and the ethynyl- or propynyltributylstannane (10 mmol) were heated 3 h at 80°C. Distillation in vacuo of the volatile part led to the corresponding alkynyltrichlorogermane **7a**,**b** ([7]c) in the presence of residual $GeCl_4$. Crude germanes **7a**,**b**, which were used without purification in the following step, can be purified by trap-to-trap distillation.

In a 50-ml two-necked flask were introduced LAH (0.4 g, 10 mmol) and tetraglyme (20-ml). The flask, cooled to − 20°C, was fitted on a vacuum line equipped with a stopcock, a cold trap and a cold finger. The flask was degassed. The crude alkynyltrichlorogermane **7a**,**b** (10 mmol) diluted in tetraglyme (10 ml) was slowly transferred through a flex-needle onto the reducing mixture. Alkynylgermane **2a**,**b** was distilled off from the reaction mixture during the course of the addition of germane **7a**,**b**. The high boiling impurities were selectively removed in a first trap cooled at − 80°C and germane **2a**,**b** was trapped on a cold finger cooled to − 196°C (GeH_4, which was not condensed at this temperature, was thus removed). To record the NMR spectra, a cosolvent was added at this step. After disconnecting from the vacuum line, the apparatus was filled with dry nitrogen and the cold finger was allowed to warm to room temperature. Alkynylgermane **2a**,**b** was collected in a Schlenk flask or an NMR tube and kept at low temperature (< − 50°C).

Ethynyltrichlorogermane (**7a**). b.p.$_{20}$ ca. 37°C. Yield: 59%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.99 (s, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 80.3 (d, $J = 45.5$, *C*≡C–H); 95.4 (d, $J = 251.7$, C ≡ *C*–H) [21].

1-Propynyltrichlorogermane (**7b**). b.p.$_{20}$ ca. 54°C. Yield: 62%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.05 (s, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 4.9 (q, $J = 133.1$, CH_3); 75.9 (s, *C*–Ge); 107.6 (s, *C* ≡ C–Ge) ([6]b).

Ethynylgermane (**2a**). b.p.$_{0.1}$ ca. − 110°C. Overall yield: 47%. ^{1}H-MR (300 MHz, $CDCl_3$): δ 2.30 (q, 1 H, $J = 1.2$, H–C); 4.07 (d, 1 H, $J = 1.2$, GeH_3) ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 78.3 (d, $J = 44.6$, *C*–Ge); 95.2 (d, $J = 236.6$, H–*C*) ([6]b).

1-Propynylgermane (**2b**). b.p.$_{0.1}$ ca. − 95°C. Overall yield: 42%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.86 (q, 3H, $J = 1.4$, CH_3); 3.96 (q, 3 H, $J = 1.4$, GeH_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 5.2 (q, $J = 131.7$, *C*H_3); 70.9 (s, *C*–Ge); 105.0 (q, $J = 17.6$, *C*≡C–Ge).

4.5. Synthesis of the ethynyl- ***4a*** *and propynylstannane* ***4b***

4.5.1. Synthesis of the ethynyl- ***9a*** *([7]d) and propynyltrichlorostannane* ***9b*** *precursors. General procedure*

Tin tetrachloride (2.2 g, 10 mmol) was frozen to − 80°C and the ethynyl- or propynyltributylstannane (10 mmol) was quickly added. The mixture was allowed to warm and shaken for a few minutes until only a liquid phase was observed (ca. − 20°C). The flask was then quickly fitted on a vacuum line and the solution was distilled in vacuo. The volatile part condensed on a cold finger (− 196°C). A mixture containing the alkynyltrichlorostannane **9a**,**b** and residual $SnCl_4$ was thus obtained.

Ethynyltrichlorostannane (**9a**). b.p.$_{0.1}$ ca. 20°C. Yield: 75%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 81.3 (d, $J = 42$, $^1J_{^{119}SnC} = 1519$, *C*–Sn), 100.8 (d, $J = 250.2$, $^2J_{^{119}SnC} = 317$, H–*C*). ^{119}Sn-NMR (111 MHz, $CDCl_3$): δ − 152.7 ([7]b).

1-Propynyltrichlorostannane (**9b**). b.p.$_{0.1}$ ca. 30°C. Yield: 79%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 5.79 (q, $J = 133.4$, $^3J_{^{119}SnC} = 27.0$, *C*H_3), 75.5 (s, $^1J_{^{119}SnC} = 1668$, *C*–Sn), 113.3 (d, $J = 40.8$, $^2J_{^{119}SnC} = 172.1$, CH_3–*C*). ^{119}Sn-NMR (111 MHz, $CDCl_3$): δ − 150.0 ([7]b).

4.6. Preparation of the primary alkynylstannanes ***4a***,***b***

The synthesis of ethynyl-stannane **4a** and 1-propynylstannane **4b** starting from the corresponding alkynyltrichloro-stannanes **9a**,**b** and their ^{1}H-, ^{13}C- and ^{119}Sn-NMR data have already been reported ([7]b).

Ethynylstannane (**4a**) ([7]b). Yield: 37%, $\tau_{1/2}$ (5% in C_6D_6): 1 h at room temperature. HRMS Anal. Calc. for $[M–H]^+$ ($C_2H_3\,^{120}Sn$)$^+$: 146.9257; Anal. found: 146.926. MS. *m*/*z* (%): 147 (51) ($C_2H_3\,^{120}Sn$)$^+$, 145 (43) ($C_2H_3\,^{118}Sn$)$^+$, 144 (20) ($^{120}SnC_2$)$^+$, 143 (27) ($C_2H_3\,^{116}Sn$)$^+$, 142 (14) ($^{118}SnC_2$)$^+$, 141 (19) ($C_2H\,^{116}Sn$)$^+$, 124 (19) (^{124}Sn)$^+$, 122 (28) (^{122}Sn)$^+$, 121 (30) (^{120}SnH)$^+$, 120 (100) (^{120}Sn)$^+$, 119 (35) (^{119}Sn)$^+$, 118 (75) (^{118}Sn)$^+$, 117 (26) (^{117}Sn)$^+$, 116 (44) (^{116}Sn)$^+$, 26 (20) (C_2H_2)$^+$, 25 (14) (C_2H)$^+$.

1-Propynylstannane (**4b**) ([7]b). Yield: 33%, $\tau_{1/2}$ (5% in C_6D_6): 1 h at room temperature. HRMS calc. $[M-H]^+(C_3H_5\,{}^{120}Sn)^+$: 160.9413; found: 160.942. MS. *m/z* (%): 161 (28) $(C_3H_5\,{}^{120}Sn)^+$, 159 (20) $(C_3H_5\,{}^{118}Sn)^+$, 157 (13) $(C_3H_5\,{}^{116}Sn)^+$, 123 (12) $({}^{120}SnH)^+$, 121 (24) $({}^{120}Sn)^+$, 120 (62) $({}^{120}Sn)^+$, 119 (27) $({}^{119}Sn)^+$, 118 (41) $({}^{118}Sn)^+$, 117 (12) $({}^{117}Sn)^+$, 116 (13) $({}^{116}Sn)^+$, 40 (100) $(C_3H_4)^+$, 39 (64) $(C_3H_3)^+$, 38 (21) $(C_3H_2)^+$.

4.7. UV photoelectron spectroscopy

PE spectra were recorded on a Helectron 0078 spectrometer equipped with a 127° cylindrical analyser using 21.21 eV He(I) and 40.81 eV He(II) radiations as a photon source and monitored by a microcomputer system supplemented by a digital analogic converter. Helium autoionization at 4.98 eV and nitrogen at 15.59 eV were used as references.

To record the PE spectra, one cold trap was fitted on a vacuum line (ca. 10^{-3} mbar) directly connected to the PES inlet. The precursor was added slowly (10 min) to the reducing agent solution cooled at 273 K. All the volatile products (**1**–**4**) were continuously distilled in vacuo from the reaction mixture, during and after the addition, and condensed onto a cold finger (−196°C). At the end of the reaction the cold trap was allowed to warm to 140, 150 or 165 K to remove traces of SiH_4, GeH_4 and SnH_4, respectively. Subsequent heating of the trap to suitable temperatures removed desired compounds, directly analyzed by PES (160 K for **5a**, 170 K for **1a**, **2a**, 180 K for **1b**, **2b**, **3a**, and **4a**, 200 K for **3b**, 210 K for **2b**).

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