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Electronic Structure of Stable Radicals of the Heavy Group 14 Elements: UV-Photoelectron Spectroscopy Characterization

Anna Chrostowska,^{*,†} Alain Dargelos,[†] Alain Graciaa,[‡] Patrick Baylère,[†]
Vladimir Ya. Lee,^{*,§} Masaaki Nakamoto,[§] and Akira Sekiguchi^{*,§}

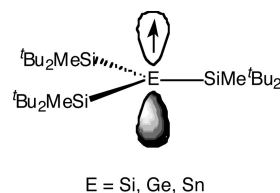
Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, UMR 5254, Université de Pau et des Pays de l'Adour, Avenue de l'Université, BP 1155, 64 013 Pau Cedex, France, Laboratoire des Fluides Complexes, UMR 5150, Université de Pau et des Pays de l'Adour, Avenue de l'Université, BP 1155, 64013 Pau Cédex, France, and Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

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Summary: A series of stable persilyl-substituted heavy group 14 element-centered radicals ($(\text{Bu}_2\text{MeSi})_3\text{E}^\bullet$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$)) was studied by UV-photoelectron spectroscopy in order to determine the values of the first ionization energies of the title species and to make a systematic comparison of their ease of oxidation.

UV-photoelectron spectroscopy (UV-PES) is one of the most important and informative experimental techniques to study the energy of the valence levels and chemical bonding, particularly the bonding character of molecular orbitals. It is now well-recognized that UV-PES is particularly well-suited for the study of a wide range of low-coordinate derivatives of group 14 organometallics.¹ However, to the best of our knowledge, until now the PES studies of the stable free radicals centered on the heavy group 14 elements were not reported due to the lack of starting compounds, which became synthetically accessible only very recently.² Taking into account the intrinsic electron deficiency of such free radicals featuring only seven valence electrons around the radical centers, one should expect their high electronic demand and, consequently, an enhanced tendency toward one-electron reduction to form anionic derivatives in which the octet rule will be satisfied. This is indeed the case, as was experimentally proved by the recent successful reduction of the stable persilyl-substituted planar π -radicals of the type $(\text{Bu}_2\text{MeSi})_3\text{E}^\bullet$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$)³ (Chart 1) with alkali metals to

Chart 1. Stable Persilyl-Substituted π -Radicals $(\text{Bu}_2\text{MeSi})_3\text{E}^\bullet$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$)



produce the corresponding anionic derivatives $(\text{Bu}_2\text{MeSi})_3\text{E}^\bullet \cdot \text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$).⁴ Even more exciting, however, was the surprising ease of one-electron oxidation of the $(\text{Bu}_2\text{MeSi})_3\text{E}^\bullet$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$) radicals by strong oxidizing reagents, such as $\text{Ph}_3\text{C}^+ \cdot \text{B}(\text{C}_6\text{F}_5)_4^-$, providing a straightforward access to the still more electron-deficient silylium,^{5a} germylum,^{5b} and stannylum^{3b} ion derivatives $(\text{Bu}_2\text{MeSi})_3\text{E}^+ \cdot \text{B}(\text{C}_6\text{F}_5)_4^-$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$).⁶ In view of the above-described experimental achievements, we decided to apply an efficient UV-PES method for the detailed investigation of the electronic structure of the isolable radicals of group 14. In this paper we report a UV-PES study of a series of stable persilyl-substituted radicals $(\text{Bu}_2\text{MeSi})_3\text{E}^\bullet$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$), which sheds light on the mechanism of their one-electron oxidation, reveals the reasons for such a smooth and highly selective oxidation process, and makes a systematic comparison of the ease of oxidation in the series silyl, germyl, and stannyl radicals.

The UV-PE spectra of tris(di-*tert*-butylmethylsilyl)silyl **1**, tris(di-*tert*-butylmethylsilyl)germyl **2**, and tris(di-*tert*-butylmethylsilyl)stannyl **3** radicals have been successfully recorded upon their ionization.⁷ As expected, the spectra of these three radicals are very similar, distinguished from each other mainly by the first two bands of markedly smaller intensity (Figures 1, 2, and 3).

The most fundamental low-energy region revealed a couple of diagnostic ionization bands for each radical species under

* Corresponding authors. E-mail: anna.chrostowska@univ-pau.fr; leevya@chem.tsukuba.ac.jp; sekiguchi@chem.tsukuba.ac.jp.

[†] Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux UMR 5254.

[‡] Laboratoire des Fluides Complexes, UMR 5150.

[§] University of Tsukuba.

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(6) Such ambiphilic (reductant/oxidant) behavior of the stable heavy group 14 element-centered radicals makes them unique organometallic reagents for the preparation of both anionic and cationic derivatives.

(7) The UV-PES spectra were recorded on a home-built, three-part spectrometer equipped with a spherical analyzer (Omicron), main body device (Meca2000), and He-I radiation source (Focus). For additional details, see the Supporting Information. It should be mentioned that all three radicals **1**, **2**, and **3** are thermally stable at the gas-phase conditions, since their mass spectra were successfully measured (see ref 3).

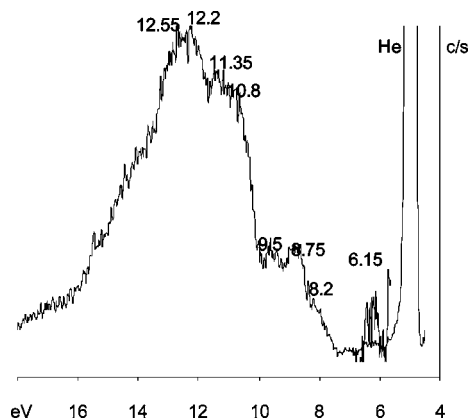


Figure 1. UV-PES of tris(di-*tert*-butylmethylsilyl)silyl radical **1** (the first IE band at 6.15 eV is magnified by a factor of 6).

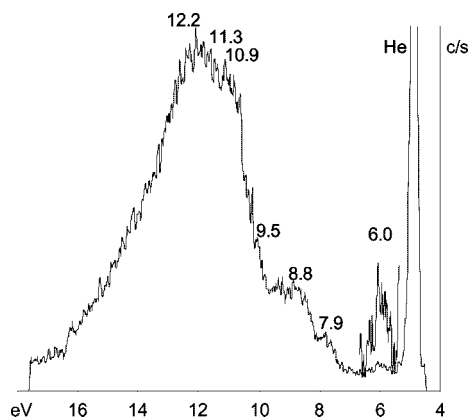


Figure 2. UV-PES of tris(di-*tert*-butylmethylsilyl)germyl radical **2** (the first IE band at 6.0 eV is magnified by a factor of 6).

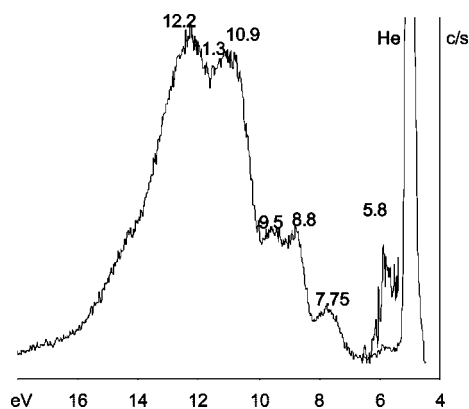


Figure 3. UV-PES of tris(di-*tert*-butylmethylsilyl)stannyl radical **3** (the first IE band at 5.8 eV is magnified by a factor of 6).

investigation: 6.15 and 8.2 eV (for silyl radical **1**), 6.0 and 7.9 eV (for germlyl radical **2**), and 5.8 and 7.75 eV (for stannyl radical **3**). These first UV-PES bands were followed by others around 8.8 eV (8.75 eV for **1** and 8.8 eV for **2** and **3**) and 9.50 eV (for **1**, **2**, and **3**). The UV-PE spectra were completed by very intense, broad ionization bands with several well-distinguished peaks centered at 10.8 and 11.35 eV (for **1**), 10.9 and 11.3 eV (for **2** and **3**), and 12.2 eV (for **1**, **2**, and **3**).

Interpretation of the UV-PES data was performed with the support of the first ionization energy (IE) DFT calculations.⁸

(8) All computational details are given in the Supporting Information.

Table 1. Selected Calculated Geometric Parameters of **1**, **2**, and **3** (experimental values are shown in square brackets; bond lengths in Å and bond angles in deg)

$\begin{array}{c} \text{Si}^2 \cdots \text{E} - \text{Si}^3 \\ \text{Si}^1 \nearrow \end{array}$	E = Si	E = Ge	E = Sn
E-Si ¹	2.434 [2.4195(7)]	2.471 [2.4537(4)]	2.712 [2.6146(5)]
E-Si ²	2.435 [2.4196(7)]	2.465 [2.4514(4)]	2.708 [2.6193(5)]
E-Si ³	2.440 [2.4239(7)]	2.477 [2.4553(4)]	2.710 [2.6189(5)]
Si ¹ -E-Si ²	119.17 [119.49(3)]	120.00 [119.546(14)]	119.08 [119.684(16)]
Si ¹ -E-Si ³	120.08 [120.08(2)]	119.82 [120.094(14)]	119.66 [120.229(16)]
Si ² -E-Si ³	120.72 [120.43(3)]	120.08 [120.357(14)]	119.63 [119.988(16)]

Table 2. Experimental PES Band Assignments of **1**, **2**, and **3**, as Well as Δ SCF (for the first IE, in parentheses) and TD-DFT¹⁵ (for the second IE, in parentheses) Values Calculated at the B3LYP/6-311G(d,p) (for Si and Ge radicals) and B3LYP/SDB-cc-pVTZ (for Sn radical) Levels (all values are given in eV)

MO	1	2	3
$n\text{p}_z(\text{E}^*)$ (SOMO)	6.15 (6.18)	6.0 (5.92)	5.8 (5.69)
σ (E-Si)	8.2 (S 8.19; T 7.73) ^a	7.9 (S 7.99; T 7.54) ^a	7.75 (S 7.73; T 7.23) ^a
σ (Si-C)	8.75	8.8	8.8
σ (other bonds)	9.5	9.5	9.5

^a TD-DFT calculations of transitions to singlet (S) or triplet (T) states.

To verify the reliability of the selected basis sets for the calculation of electronic properties, the experimental crystal structure parameters were compared with those of the optimized geometries. The experimental and calculated values agreed well with each other. Both experimentally observed and calculated E-Si bonds become more stretched as E descends group 14, whereas the Si-E-Si bond angles remain essentially the same, thus pointing to a good correspondence of the experimental planar configuration of the π -radical centers to those of calculated structures (Table 1).

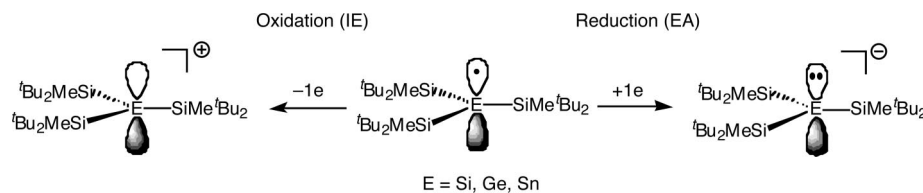
The first UV-PES bands at 6.15 eV (for **1**), 6.0 eV (for **2**), and 5.8 eV (for **3**) correspond to the removal of an electron from the easily accessible SOMO of silyl, germlyl, and stannyl radicals, respectively. In terms of the established planar ground-state geometry for both neutral radicals³ and their corresponding cations,⁵ no vibrational fine structure would be expected. The same tendency was observed for the planar⁹ methyl radical CH_3^\bullet ,¹⁰ although the analogous study of the silyl radical SiH_3^\bullet ,¹¹ for which a pyramidal structure has been proposed on the basis of EPR and UV spectroscopy data,¹² revealed an extensive vibrational structure associated with the SiH_3^+ symmetric

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Chart 2



bending deformation ($820 \pm 40 \text{ cm}^{-1}$ for the umbrella mode in the ion, $\text{IP}_v = 8.74 \text{ eV}$). The first ionization energy values for **1–3** decrease on going from silicon to germanium to tin radicals, in complete accord with the trend in ionization energies of isolated atoms (Si 8.15, Ge 7.90, and Sn 7.34 eV)¹³ albeit with smaller energy gaps. The second ionization energy values correspond to the removal of an electron from the E–Si_{subst.} σ -bonds (E = Si, Ge, and Sn), and the trend in changes of these values clearly reflects the increase in energy levels of σ -orbitals of the bonds in the sequence Si–Si > Ge–Si > Sn–Si. Higher energy parts of the UV-PE spectra of radicals **1–3** are, as expected, nearly identical and correspond to the ionization of different σ -bonds of the molecules. The remarkably good agreement between the experimentally determined values of IE for radicals **1–3** and the corresponding values calculated for the two first ionic states provides solid support for the correct assignment of the PES bands (Table 2).

Our UV-PES characterization of the electronic structure of tris(di-*tert*-butylmethylsilyl)silyl, germyl, and stannyl radicals **1**, **2**, and **3** through IE measurements confirms that the order of the first IE values, corresponding to the removal of an unpaired electron from the SOMO of each radical, is in complete accord with the expected trend of ease of oxidation based on difference

in the ionization energies of isolated Si, Ge, and Sn atoms. Thus, the stannyl radical **3** is the most easily oxidizable species, followed by germyl and silyl radicals. Similarly, the first ionization energies of a series of permethylated derivatives $\text{Me}_3\text{E–EME}_3$ (E = Si, Ge, Sn), corresponding to the removal of one electron from HOMOs, which are largely localized on the E–E σ -bonds, decrease in the order Si–Si (8.68 eV) > Ge–Ge (8.60 eV) > Sn–Sn (8.20 eV), in accord with the decrease in the E–E bond dissociation energy and IE of the isolated atoms.¹⁴

Thus, the overall redox behavior of the stable radicals of the heavy group 14 elements can be summarized as follows (Chart 2):

Comparing the experimental first IE⁷ and calculated electron affinity (EA)⁸ values for the silyl, germyl, and stannyl radicals **1**, **2**, and **3**, one can note that the steady decrease in the IE values (6.15, 6.0, and 5.8 eV) is manifested in an increase in the ease of oxidation and strengthening of reduction power in the order **1** < **2** < **3**, whereas the decrease in the EA values (1.120, 0.929, and 0.858 eV) gives evidence for a decrease in oxidation power: **1** > **2** > **3**. These tendencies are in line with those observed for the experimentally determined IE and EA values of isolated silicon, germanium, and tin atoms: 8.15, 7.90, and 7.34 eV (for IE) and 1.389, 1.233, and 1.112 eV (for EA), respectively.¹³

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Supporting Information Available: UV-PES and computational details, tables of atomic coordinates for optimized geometries of the radicals **1**, **2**, and **3**, and values of total energies and plots of the SOMOs of radicals **1–3** are available free of charge via the Internet at <http://pubs.acs.org>.

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