Si-, Ge-, and Sn-Centered Free Radicals: From Phantom Species to Grams-Order-Scale Materials

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Keywords: Free radicals / X-ray diffraction / EPR spectroscopy / Silicon / Germanium / Tin

Recent developments in the field of the stable free radicals of heavier group 14 elements are reviewed, covering both neutral and charged radical species. The electronic and crystal structural features of these radicals, both in the solid state and in solution, are compared with each other. The most important parameters affecting the stability, geometry and electronic configuration of the radicals are discussed on the basis of the latest experimental and computational data.

1. Introduction

Free radicals, that is, compounds featuring a trivalent carbon atom having only seven valence electrons, have been known for more than one hundred years, since the groundbreaking discovery of the triphenylmethyl radical. Such a departure from the fundamental octet rule causes an intrinsic electronic unsaturation of the radical species expressed in the existence of the unpaired electron, resulting in the extremely high reactivity of free radicals compared with that of normal tetravalent carbon compounds.[1] Together with carbocations and carbanions (and later, carbenes), the most fundamental species in organic chemistry, free radicals were always among the most desired and challenging synthetic goals. The two most historically significant discoveries are worth mentioning in this review. The first one commemorates the starting point of free radical chemistry: in 1900 Gomberg provided convincing evidence for the existence of $Ph_3C^{\cdot}$ species obtained by the treatment of triphenylmethyl chloride with metallic silver.[2] This was the first representative of a new class of organic compounds, which were later named free radicals. At the beginning of the era of free radical chemistry, another fundamental breakthrough was achieved by Paneth, who reported in 1929 the first proof for the generation of the simplest methyl radical by the thermal decomposition of tetramethyllead.[3] Since then, and during the last one hundred years, a great deal of experimental information supporting the real existence and participation in chemical reactions of free radical species has been developed. In the early stage, free radicals were speculated to be reactive intermediates with

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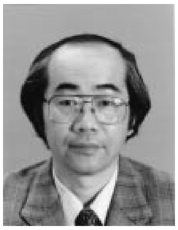

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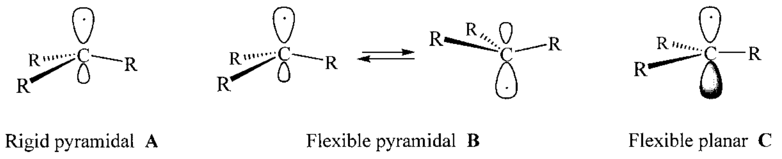
MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

DOI: 10.1002/ejic.200400999



Scheme 1. Geometry of organic free radicals.

very short lifetimes, often undetectable by physico-chemical methods. However, researchers quickly realized that such ephemeral radical species could gain extra stability through the electronic and steric effects of substituents. This greatly extended the lifetime of those radicals, enabling them to be detected and identified directly by means of spectroscopic methods, mainly by EPR and CIDNP techniques.[1] Many so-called persistent radicals have been prepared and characterized since then, and a review dealing with this topic has been published.[4] As a major development in this field, one should mention the synthesis of stable free radicals, whose isolation and structural identification has been possible in a limited number of cases in the past few years.[5]

One of the most fundamental characteristics of free radicals, directly associated with their ground-state electronic structure, is their geometry in the solid state and in solution. It is now well-established that free radicals can adopt one of three possible geometries, known as rigid pyramidal (**A**), flexible pyramidal (**B**), and planar (**C**) (Scheme 1).[1] Planar radicals are also flexible.

In the first two cases, the unpaired electron is accommodated in an orbital with some degree of s-character (tetrahedral configuration), whereas in the latter case the SOMO (singly occupied molecular orbital) is represented by an orbital with essentially p-character (trigonal-planar configuration). The arrangement of the odd electron in an orbital of either s- or p-character is totally governed by the substitution pattern at the radical center. For example, the structure of the methyl radical was found by EPR studies to be either planar or in the form of a very shallow pyramid,[6] whereas the trifluoromethyl radical was found to be markedly pyramidal.[7] The general tendency of the σ-accepting and π-donating substituents to favor the pyramidal structure is explained by the attractive interaction of the SOMO and the central element–electronegative substituent antibonding σ* orbital, increasing the electron density on the more electronegative atom. Accordingly, electropositive σ-donating and π-accepting substituents (such as silyl groups) have the opposite influence on the geometry of the radical center, causing a significant flattening of the radical structure. A great deal of information about the geometry and consequently the electronic structure of free radicals in solution can be obtained from their EPR spectra. The geometry of free radicals in solution can thus be reliably elucidated on the basis of the value of the hyperfine coupling constant (hfcc), since the latter arises from the spin density in the *n*s-orbitals, markedly increasing with increased s-character of the SOMO.[8] In other words, the higher the hfcc value, the more pyramidal is the radical (σ-type radical), the lower the hfcc value, the more planar is the radical (π-type radical).

The chemistry of the heavy analogues of free radicals, centered on the Si, Ge, Sn, and Pb atoms, was developed much later than its carbon counterpart, although the participation of radicals of the type $R_3E^{\cdot}$ (E = heavier group 14 element) in a number of organometallic reactions was postulated and debated several decades ago.[9] Later, the right combination of both steric and electronic stabilizing effects of substituents enabled the preparation of heavier group 14 element centered radicals with lifetimes long enough to be detected directly by EPR spectroscopy.[10] Such compounds have been known since the important publication of the first EPR spectrum of the persistent stannyl radical $[(Me_3Si)_2CH]_3Sn^{\cdot}$ by Lappert et al. nearly 30 years ago.[11] The progress in this field, made after this first discovery, was thoroughly described in a most recent review, to which we refer our readers.[12] The culmination of this steady progress in the field of heavier group 14 element centered radicals was reached just in the past few years, expressed in the publication of the papers describing the first crystal structures of the Si-, Ge- and Sn-centered free radicals. In this review we will deal with the chemistry of such stable (that is, isolable) compounds only, leaving the vast area of the transient and limitedly stable radical species outside the framework of the present article.

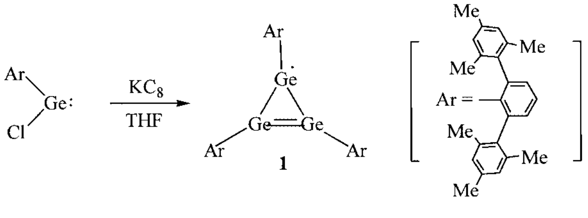
The chemistry of stable free radicals centered on the heavier group 14 elements (Si, Ge, Sn, Pb) can be divided into two main areas: the first one concerns the chemistry of the stable *neutral* radical species, whereas the second one is devoted to the *charged* radical species, that is, ion radicals (namely, anion radicals). Below, we will deal with the radicals of both groups, emphasizing the synthetic methods for each class as well as their structural peculiarities, first of all geometry and electronic structure. A remark concerning the terminology used throughout the text: In the literature two main terms for the long-lived radical species are currently used: **persistent** radicals, with a relatively long lifetime enabling them to be detected either by spectroscopic means or chemically, and **stable** radicals, which are indefinitely stable and isolable.[4,12] However, such confusing terminology, particularly with respect to the "relatively" or "indefinitely" long lifetime, may cause conflicting situations when the same radicals are sometimes treated as persistent ones, and sometimes as stable ones. In order to avoid such contradictions, in our review we will use only the term "stable" for those radical species that can be isolated and characterized as individual compounds, in the majority of cases by means of X-ray crystallography.

2. Neutral Si-, Ge- and Sn-Centered Radicals

The area of neutral radical species of heavier group 14 elements can be subdivided into the chemistry of cyclic and acyclic compounds. The electronic composition, structural features and stability of these two subgroups differ from each other greatly, since the cyclic radicals can gain extra stability from the cyclic π delocalization of the odd electron over the cyclic π-bond system, whereas the simple acyclic tricoordinate silyl-substituted radicals mainly take advantage of the stabilization through the σ delocalization of the odd electron over the σ* orbitals of the neighboring silyl substituents. The chemistry of both of these groups of neutral radicals will be considered below.

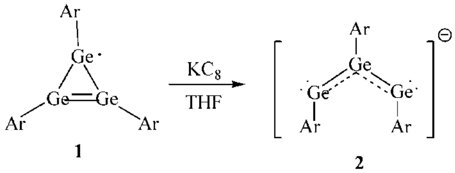
2.1 Cyclic Neutral Radicals

The first example of a stable compound featuring a radical center on a heavier group 14 element, the cyclotrigermenyl radical **1** stabilized by the very bulky 2,6-Mes_2–C_6H_3 groups, was reported by Power's group in 1996.[13] Compound **1** was synthesized by the reduction of chlorogermylene :Ge(Cl)(2,6-Mes_2–C_6H_3)[14] with KC_8 in THF (Scheme 2). Although the exact structural determination of **1** was prevented by skeletal disorder problems, its structure was reliably refined to reveal a Ge analogue of the cyclopropenyl radical, that is, a three-membered ring involving a double bond between the two Ge atoms and an odd electron on the remaining Ge atom.



Scheme 2. Synthesis of cyclotrigermenyl radical **1**.

The EPR spectrum of **1** displayed a resonance with a *g* value of 2.0069 and an hfcc, $a(^{73}Ge)$, of 1.6 mT, suggesting a location for the unpaired electron in an orbital of π symmetry, which in turn means essential planarity at the Ge radical centers. Further reduction of radical **1** resulted in the formation of the corresponding anion species accompanied with the ring-opening process to produce finally the acyclic trigermaallyl anion **2** (Scheme 3).[13]



Scheme 3. Synthesis of trigermaallyl anion **2**.

The cyclic silicon analogue of the delocalized allyl radical, cyclotetrasilenyl radical **3**, was recently reported by Sekiguchi et al.[15] This compound, representing the first stable Si-centered radical, was synthesized by the one-electron reduction of the precursor compound, cyclotetrasilenylium ion **4**,[16] with either silylsodium tBu_3SiNa or KC_8 in Et_2O (Scheme 4).

X-ray crystallography disclosed the free radical structure of **3** (Figure 1). As expected, the four-membered-ring core of **3** was nearly planar (folding angle 4.7°) in contrast to the precursor cation **4**,[16] which had a largely folded cyclic skeleton (folding angle 46.6°) due to the homoaromatic 1,3-

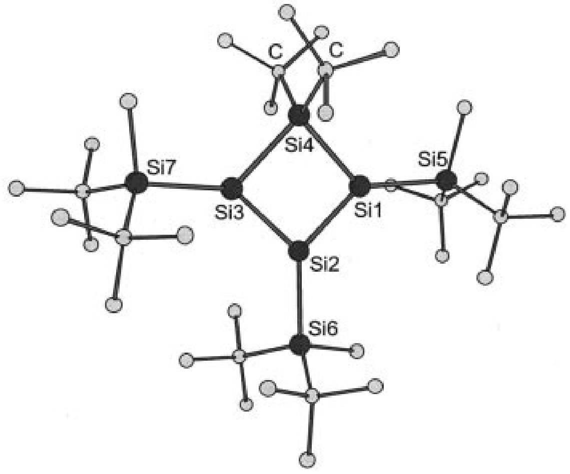
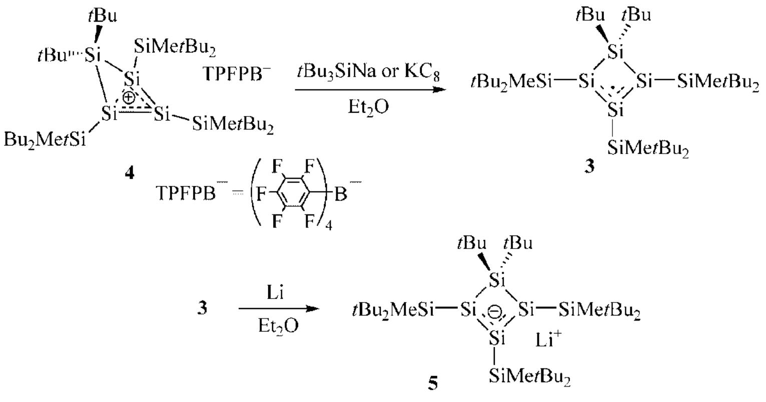


Figure 1. Crystal structure of cyclotetrasilenyl radical **3**.



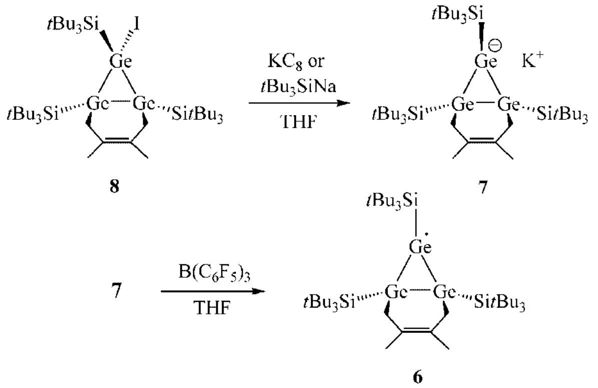
Scheme 4. Synthesis of cyclotetrasilenyl radical **3**.

orbital interaction. The Si1–Si2 and Si2–Si3 bond lengths were slightly different [2.226(1) and 2.263(1) Å, respectively]. This was consistent with some insignificant pyramidalization of the Si3 atom (the sum of the bond angles was 356.2°). However, the lengths of both the Si1–Si2 and the Si2–Si3 bonds were intermediate between those of the typical Si–Si single and Si=Si double bonds, which proved the allylic-radical-type structure of **3**.

The EPR spectrum of **3** displayed a strong signal with a *g* value of 2.0058 (typical for silyl-substituted silyl radicals: 2.0053–2.0063).[10i–10l] The three pairs of satellite signals with the largest spin densities [hfcc values: $a(^{29}Si)$ = 4.07, 3.74, and 1.55 mT] were assigned to the coupling of an unpaired electron with the terminal Si1, terminal Si3, and the central Si2 nuclei, respectively, which also agreed well with the delocalized-allylic-type structure of radical **3**. The small values of the hfcc's are consistent with the planarity of the radical unit, that is, the planarity of the four-membered ring of **3** is also retained in solution. The cyclic radical **3** can be smoothly reduced with metallic Li in Et_2O to form the corresponding cyclotetrasilenide ion **5**, which preserves the allylic-type structure of its predecessor (Scheme 4).[17] Such stability of the four-membered ring of **3** upon reduction is amazing, in contrast to the above-mentioned ring-opening reduction of the cyclotrigermenyl radical **1**.[13]

The first, and still the sole, example of a stable bicyclic radical of heavier group 14 elements was reported just recently by Sekiguchi et al.[18] Such a Ge-centered free radical, 1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl (**6**), was synthesized by the selective one-electron oxidation of the corresponding precursor, bicyclic anion **7**, generated by the reduction of iodide **8**, with tris(pentafluorophenyl)boron in THF (Scheme 5).

The crystal structure of **6** was determined by means of X-ray crystallographic analysis (Figure 2), which showed that the radical center was specifically accommodated on the Ge3 atom having a nearly planar geometry (sum of the bond angles: 357°). The bridgehead Ge1–Ge2 bond was slightly longer than the bridging Ge1–Ge3 and Ge2–Ge3 bonds: 2.4864(4) Å vs. 2.4254(5) and 2.4326(4) Å. A particularly important observation is that compound **6** has *endo* conformation, in contrast to all other structurally characterized compounds of this type, which have exclusively *exo* conformation.[19] This fact indicates some degree of intramolecular Ge radical–π(C=C) interaction in **6**; this is deduced from the relative proximity of the two species: the interatomic distance between the Ge radical and the C=C bond is 3.632 Å, which lies in the range of van der Waals interactions.



Scheme 5. Synthesis of bicyclic germyl radical **6**.

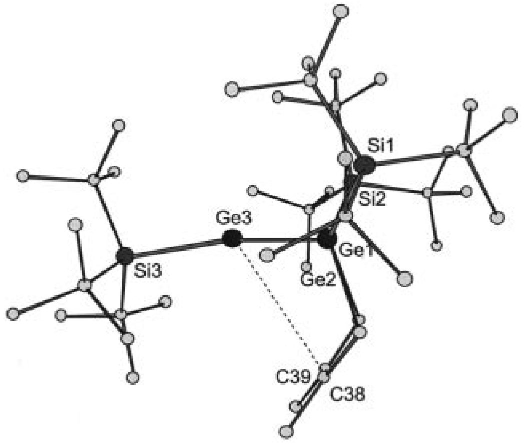


Figure 2. Crystal structure of bicyclic germyl radical **6**.

Surprisingly, the EPR spectrum of **6** revealed two signals of almost identical intensity, with *g* values of 2.0210 and 2.0223. Again, as in all of the above cases of cyclic radicals,

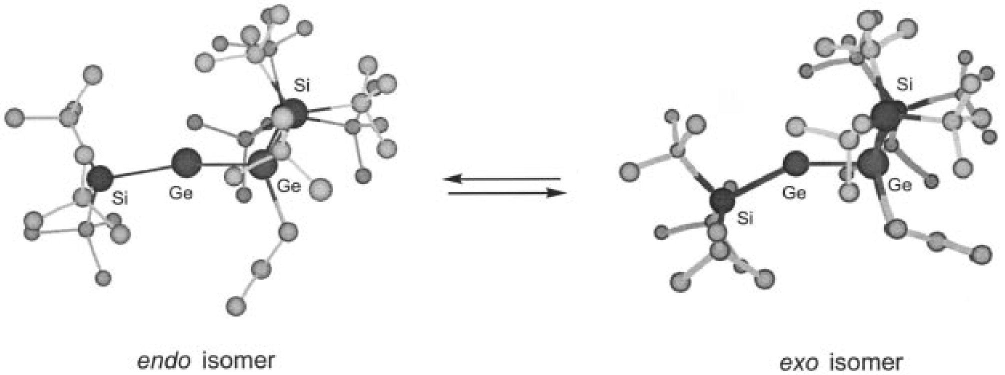


Figure 3. *endo*–*exo* isomerization of bicyclic germyl radical **6**.

the planarity of these Ge radical centers was maintained also in the condensed phase, which was clearly manifested by their small hfcc's (3.4 and 2.6 mT, respectively), indicating also the sp^2-type hybridization of the Ge radical center. The existence of two signals in the EPR spectrum was explained in terms of the *endo–exo* isomerization taking place in the solution of **6** on the EPR time scale (Figure 3).[18] Apparently, in the solid state such isomerization is suppressed in favor of the *endo* isomer, stabilized by the intramolecular Ge radical–C=C interaction, which was supported by theoretical calculations (the *endo* isomer is more stable than the *exo* isomer by 0.59 kcal/mol).

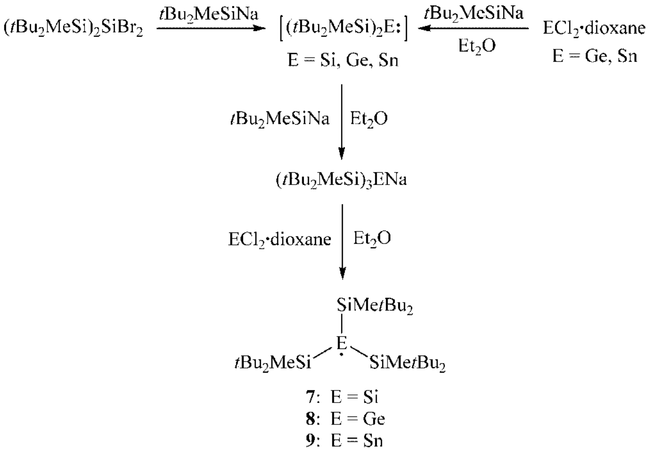
One can easily notice that, in contrast to the allylic-type cyclotrigermenyl radical **1**[13] and cyclotetrasilenyl radical **3**,[15] the bicyclic radical **6**[18] has a localized structure caused by the absence of the π bond in the proximity necessary for effective through-bond interaction and by the insufficiency of the through-space interaction with the C=C double bond to enable the remarkable delocalization of the odd-electron density.

2.2 Acyclic Tricoordinate Neutral Radicals

Although the above-mentioned cyclic Si- and Ge-centered radicals were synthesized as the remarkable first representatives of this class of organometallic compounds, their structural features were significantly affected by their particular and unique cyclic skeletons. However, the properties and stability of the acyclic radicals of the type $R_3E^{\cdot}$ (E = heavier group 14 element) without stabilization through cyclic π delocalization were expected to be greatly different and even more challenging. Therefore, despite the evident progress in the development of the stable-free-radical chemistry described in the previous section, the search for stable, tricoordinate, acyclic radicals of heavier group 14 elements turned out to be a problem of great importance.

The first breakthrough in the development of such chemistry was achieved just a couple of years ago by Sekiguchi et al., who reported the synthesis and structural identification of the first stable acyclic silyl, germyl, and stannyl radicals lacking conjugation with π bonds. Of particular importance was the fact that all compounds were prepared by a similar and very simple method, which demonstrated the generality of the synthetic approach. All synthesized $R_3E^{\cdot}$ (E = Si, Ge, Sn) radicals had the same silyl substituents (R = SiMe*t*Bu$_2$), which provided a unique possibility to prepare a homologous series of the compounds and trace the regularities and tendencies inside this series, on descending group 14.

The tris(silyl)substituted silyl radical **7** was synthesized by the oxidation of the in situ generated silylsodium derivative $(tBu_2MeSi)_3SiNa$, prepared by the reaction of dibromosilane $(tBu_2MeSi)_2SiBr_2$ and silylsodium $tBu_2MeSiNa$ with dichlorogermylene–dioxane complex $GeCl_2$·dioxane in Et_2O (Scheme 6).[20]



Scheme 6. Synthesis of tris(di-*tert*-butylmethylsilyl)-substituted silyl-, germyl-, and stannyl radicals **7**, **8**, and **9**.

Radical **7** has a trigonal-planar configuration of the Si radical center, implying that the odd electron is accommodated in the $3p_z$ orbital of the Si atom (Figure 4). Both steric and electronic factors contribute significantly to the planarity of the radical center: Sterically, for example, all methyl substituents at the peripheral Si atoms are arranged in a clockwise manner exactly in the Si1–Si2–Si3–Si4 plane, thus minimizing the steric repulsion of the bulky *t*Bu groups. Electronically, electropositive silyl substituents significantly lower the inversion barrier at the Si radical center, also resulting in its planarization. On the other hand, the bulky substituents sterically protect the free-radical species, enabling it to be isolated. Another important factor enhancing the stability of **7** is the possibility of delocalization of the unpaired-electron density over the antibonding σ* orbitals of the Si–C(*t*Bu) bonds (hyperconjugation effects).

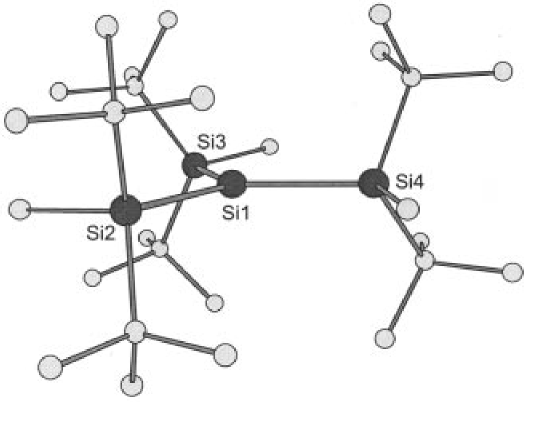


Figure 4. Crystal structure of tris(di-*tert*-butylmethylsilyl)silyl radical **7**.

Radical **7** exhibited an intense signal in the EPR spectrum with a *g* value of 2.0056 and two pairs of satellite signals with the hfcc's $a(^{29}Si)$ = 5.80 mT (α-Si) and 0.79 mT (β-Si) (Figure 5). The small coupling with the central Si atom of 5.80 mT definitely manifests the arrangement of the unpaired electron in an orbital of predominantly p-character, implying that the Si radical center is sp^2-hybridized and planar. Thus, both in the solid state and in solution the persilyl-radical **7** behaves as a π radical, whose SOMO is mainly represented by the $3p_z$(Si) orbital.

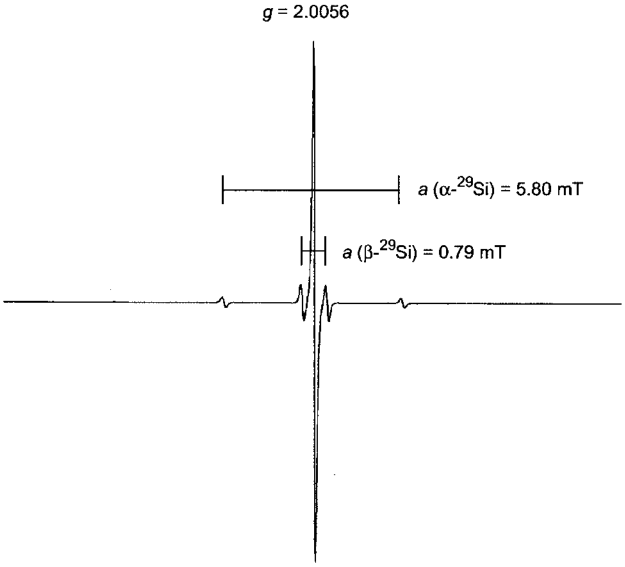


Figure 5. EPR spectrum of tris(di-*tert*-butylmethylsilyl)silyl-radical **7**.

The corresponding Ge analogue ($(t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Ge}^{\cdot}$ (**8**) was prepared in a similar, and even simpler, procedure: by the direct reaction of $t\mathrm{Bu}_2\mathrm{MeSiNa}$ with GeCl_2·dioxane in $\mathrm{Et}_2\mathrm{O}$ (Scheme 6).[20] At first, the intermediate germylene ($(t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{Ge}$: was generated in situ, followed by the formation of the germylsodium derivative $(t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{GeNa}$, and its subsequent oxidation with a second equivalent of GeCl_2·dioxane. It is worth mentioning that in the above reactions the GeCl_2·dioxane complex behaved as a very mild and selective oxidizing reagent, whose high oxidizing ability was documented in the previous electrochemical studies [$E_{1/2}$(red) = –0.41 V].[21]

Being a heavy homologue of silyl radical **7**, germyl radical **8** exhibited quite similar structural and electronic features. Its crystal structure was isomorphous to that of **7**: an absolutely planar configuration of the Ge center with the same in-plane and clockwise arrangement of the methyl groups.[20] The EPR spectrum of **8** displayed a strong central signal (*g*-factor = 2.0229) with the very characteristic picture of ten satellite signals with the hfcc $a(^{73}\mathrm{Ge})$ = 2.00 mT (Figure 6). Again, one should recognize that Ge radical **8** is a planar π radical, parallel to the above case of silyl radical **7**.

Employing the same synthetic approach, Sekiguchi et al., recently succeeded in the preparation of the first stable Sn-centered radical, $(t\mathrm{Bu}_2\mathrm{MeSi})_3\mathrm{Sn}^{\cdot}$ (**9**), by the reaction of $t\mathrm{Bu}_2\mathrm{MeSiNa}$ with SnCl_2·dioxane in $\mathrm{Et}_2\mathrm{O}$ (Scheme 6).[22] The crystal structure of **9** is identical to those of the silyl and germyl radicals **7** and **8** discussed above: a planar Sn radical center with the same orientation of the silyl substituents. The EPR spectrum of **9** revealed a central signal with a *g* value of 2.0482 and two pairs of satellite signals with the hfcc $a(^{119,117}\mathrm{Sn})$ = 32.9 mT (Figure 7).

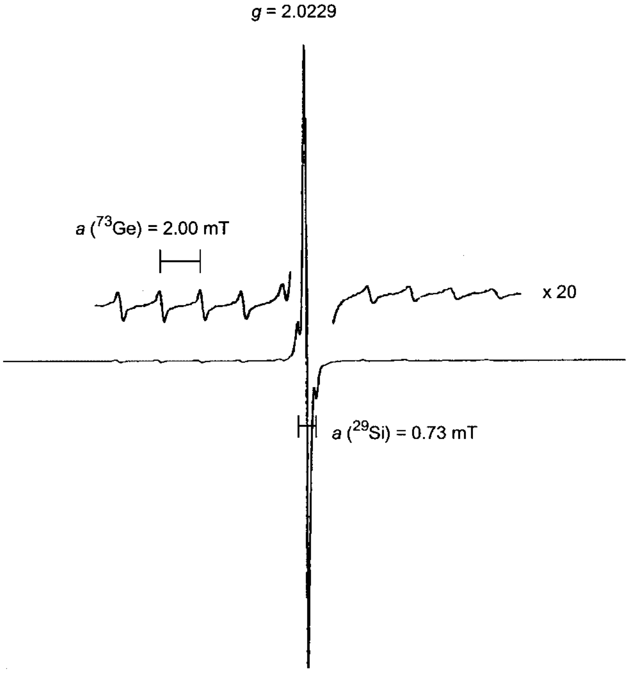


Figure 6. EPR spectrum of tris(di-*tert*-butylmethylsilyl)germyl radical **8**.

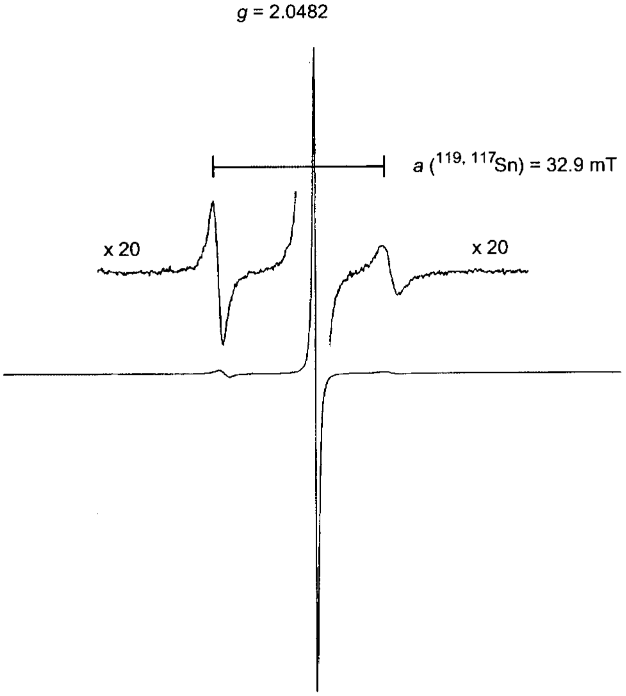
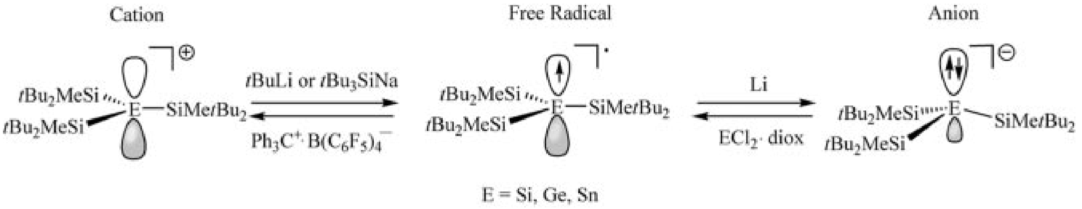


Figure 7. EPR spectrum of tris(di-*tert*-butylmethylsilyl)stannyl-radical **9**.

Most importantly, in the series of silyl, germyl and stannyl radicals **7**, **8**, and **9** the structural features are absolutely identical both in the solid state and in solution, that is, all radicals should be described as truly π radicals with the characteristic sp^2-hybridization and trigonal-planar configuration of the central element. Since the substitution



Scheme 7. Reversible redox system of the $(t\mathrm{Bu_2MeSi})_3\mathrm{E}$ (E = Si, Ge, Sn) species: cations–free radicals–anions.

pattern is the same in all cases, one should attribute such uniform behavior of the $(t\mathrm{Bu_2MeSi})\mathrm{E}^{\cdot}$ (E = Si, Ge, Sn) radical homologues to the determining influence of the bulky electropositive silyl substituents, in contrast to simple alkyl and aryl substituents causing a highly pronounced pyramidalization around the metal radical centers, in which the unpaired electron occupies the orbital with a high degree of s-character (σ radicals).

In addition to the evident simplicity of the preparation and hence the easy accessibility of radicals **7**, **8**, and **9**, another striking peculiarity of these compounds is their reactivity. All these radicals easily and quantitatively undergo one-electron oxidation or reduction to form the corresponding cation and anion species (Scheme 7).[23,24] This allowed the synthesis of the first stable free germyl and stannyl cations $(t\mathrm{Bu_2MeSi})_3\mathrm{Ge}^+$ and $(t\mathrm{Bu_2MeSi})_3\mathrm{Sn}^+$, recently described by Sekiguchi et al.[23b,23c]

3. Charged Si-, Ge-, and Sn-Centered Radicals

Another name for charged radicals is ion radicals, either anion radicals or cation radicals of the heavier group 14 elements. Although the existence of such molecules as transient species has been discussed for a long while, being sometimes experimentally demonstrated by special spectroscopic techniques such as low-temperature EPR spectroscopy,[25] significant progress in this field has been achieved only in the last few years, with the synthesis of stable representatives of this class of highly reactive compounds. In reviewing these latest developments, we will also subdivide these radicals into two groups: cyclic and acyclic ones.

3.1 Cyclic Ion Radicals of Heavier Group 14 Elements

Only one example of a stable cyclic anion radical of heavier group 14 elements has been reported very recently, the cyclotetrasilane anion radical **10**.[26] This compound was formed, together with the more extensively reduced species, the cyclotetrasilane dianion **12**, upon reduction of the heterocyclic dichlorosilane precursor **11** with metallic potassium in THF (Scheme 8).

In the crystal state of **10** the potassium ion is solvent-separated from the anion radical part (Figure 8). The four-membered $\mathrm{Si_4}$ ring is square-planar with endocyclic Si–Si bond lengths of 2.347(2) Å, which are slightly shorter than those of known cyclopolysilanes.[27] The EPR spectrum of **10** showed a multiplet signal with $g = 2.0025$ and $a(^{14}\mathrm{N}) = 0.35$ mT, consisting of 15 of the expected 17 lines due to

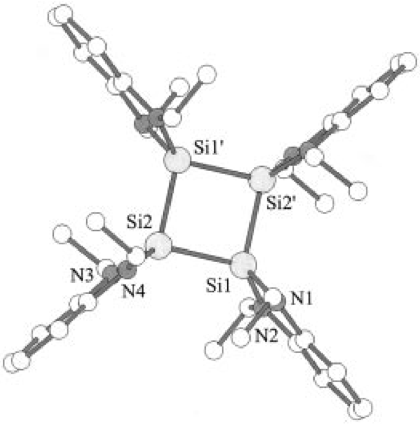
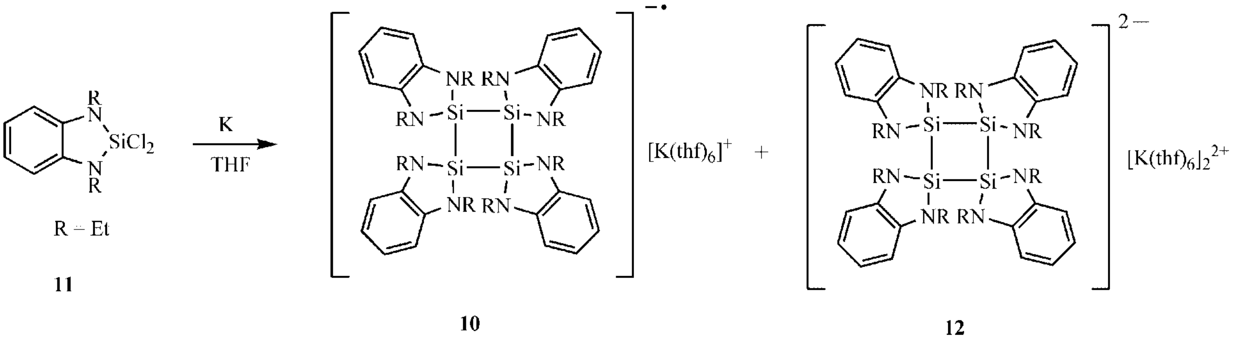


Figure 8. Crystal structure of cyclotetrasilane anion radical **10** (only the anionic part of the molecule is shown).



Scheme 8. Synthesis of the cyclotetrasilane anion radical **10**.

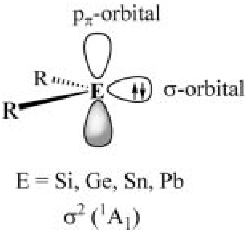
coupling of the unpaired electron with the eight ^{14}N nuclei ($I = 1$). Such an EPR spectrum pattern agrees well with the formulation of odd-electron delocalization over the Si_4 ring, which is supported by the EPR spectrum simulation.

3.2 Acyclic Ion Radicals of Heavier Group 14 Elements

Until now, no examples of stable cation radicals based on the heavier group 14 elements have been reported in the scientific literature. As for stable anion radicals, there were just a few papers devoted to this subject, published mainly in the past few years. Among them, one can recognize the following subtopics: (1) anion radicals of heavy carbene analogues, (2) anion radicals of heavy alkene analogues, (3) anion radicals of heavy alkyne analogues. Each one will be briefly considered below.

3.3 Anion Radicals of Heavy Carbene Analogues

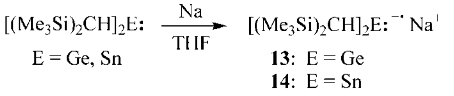
It is now well established that the heavy analogues of carbenes, that is, silylenes, germylenes, stannylenes and plumbylenes, have a singlet ground state with a σ^2 electronic configuration, implying that the two paired electrons are accommodated in the orbital of σ symmetry, corresponding to the a $^1A_1$ electronic ground state (Scheme 9).[28] However, upon either oxidation or reduction, the electronic configuration of heavy carbene analogues may be changed or may be retained depending on the substitution pattern. For example, the silylene cation radical was experimentally found to be a σ-type radical, whereas the silylene anion radical was calculated to be a π radical.[29] The anion radicals of dichlorogermylene, as well as its complexes with Lewis bases, were also calculated to be π radicals, in contrast to their cation radicals of σ type.[21]



Scheme 9. Electronic configuration of the heavy analogues of carbenes.

Although experimental data on the stable (isolable) anion radicals of heavy carbene analogues are still lacking in the scientific literature, there were several papers on the generation of such anion-radical species with lifetimes long enough to be detected and identified by EPR. The first report on the generation of anion radicals of heavy carbene analogues was published by Sita et al., who described the room-temperature EPR spectrum of the reaction mixture obtained upon the reduction of hexakis(2,6-diethylphenyl)-cyclotristannane with potassium amalgam in THF.[30] This EPR signal, exhibiting an $^{119,117}Sn$ hyperfine coupling of 15.2 mT, was reasonably assigned to the bis(2,6-diethylphenyl)stannylene anion radical; however, the assignment was not unambiguously proved. More recent developments in the field involve the direct reduction of the stable heavy carbene analogues (silylenes, germylenes, and stannylenes) with the alkali metals, providing more convincing evidence for the generation of the relatively stable anion-radical species of the heavy carbenes. The latter achievements will be briefly overviewed below.

The first paper on the generation of germylene and stannylene anion radicals was published by Egorov and Gaspar in 1995.[31] These anion radicals were prepared by the reduction of Lappert's germylene $[(Me_3Si)_2CH]_2Ge$**:** and stannylene $[(Me_3Si)_2CH]_2Sn$**:** with sodium mirror in THF (Scheme 10). Although both germylene anion radical **13** and stannylene anion radical **14** were not indefinitely stable in solution at room temperature (the lifetime for **13** was about 1.5 h, whereas for **14** it was several minutes), it was possible to characterize them by EPR spectroscopy. Germylene anion radical **13** exhibited a strong EPR resonance (g = 2.0125) as a triplet due to the coupling of the unpaired electron with the two α-protons of the alkyl substituents [a(^{1}H) = 0.26 mT]. The characteristic coupling with the ^{73}Ge nuclei was manifested in the observation of eight (of the total of ten) weak satellite signals with a(^{73}Ge) = 1.25 mT. The disappearance of the anion radical **13** in solution obeys second-order kinetics, implying that **13** dimerizes to form the diamagnetic dianion species.

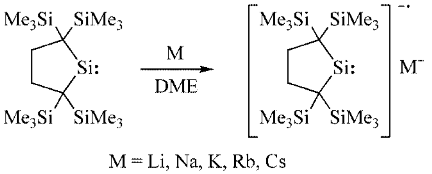


$$\underset{E = Ge, Sn}{[(Me_3Si)_2CH]_2E:} \xrightarrow[THF]{Na} [(Me_3Si)_2CH]_2E:^{-\bullet}\ Na^+ \quad \begin{array}{l}\mathbf{13}:\ E = Ge\\ \mathbf{14}:\ E = Sn\end{array}$$

Scheme 10. Generation of the germylene and stannylene anion radicals **13** and **14**.

The stannylene anion radical **14** was also identified by its EPR spectrum, which revealed a broad singlet (g = 2.0177) having a pair of unresolved satellite signals arising from the coupling of the unpaired electron with both ^{119}Sn and ^{117}Sn nuclei [a(^{119,117}Sn) = 11.6 mT].[31] The small values of the hfcc's [a(^{73}Ge) = 1.25 mT and a(^{119,117}Sn) = 11.6 mT] make possible a reliable assignment of both anion radicals **13** and **14** to a class of π radicals with the $^2B_1$ ground electronic state.

A study on the generation of the silylene anion radical was published several years later than that for germylene and stannylene anion radicals. The silylene anion radical **15** with a lifetime of about 20 minutes at room temperature was generated similarly by the direct reduction of the stable silylene **16** with potassium mirror in dimethoxyethane (Scheme 11).[32] The one-electron reduction of **16** to form anion radical **15** was also achieved by reduction with other alkali metals such as Li, Na, Rb, and Cs, to produce essentially the same EPR spectra (Scheme 11). The identification and assignment of **15** was made on the basis of its EPR spectrum, which revealed a multiplet signal (g = 2.0077) composed of more than 20 lines due to the coupling of the unpaired electron with the 36 protons of the Me_3Si groups [a(^{1}H) = 0.0189 mT] and the 4 protons of the CH_2 groups of the cyclopentane skeleton [$a(^1H)$ = 0.0378 mT]. The satellite signals due to the coupling with ^{29}Si nuclei were observed as three sets of doublets, corresponding to the coupling with the central Si atom [$a(^{29}Si)$ = 2.99 mT] and the two types of Si atoms of the Me_3Si groups [$a(^{29}Si)$ = 1.66 and 1.30 mT]. These EPR parameters of **15** are similar to those of the transient silylene anion radical $[(iPr_3Si)_2LiSi]^{-\cdot}$, generated together with other silyl-radical species by the photolysis of $[(iPr_3Si)_2Li(THF)_2Si]_2Hg$, g = 2.0073, $a(^{29}Si_\alpha)$ = 3.20 mT.[33]



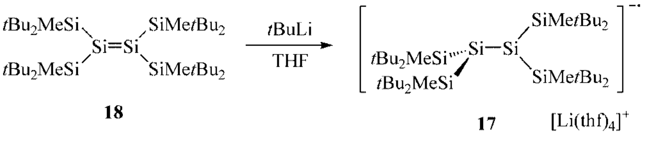
16 **15**

Scheme 11. Generation of the silylene anion radical **15**.

3.4 Anion Radicals of Heavy Alkene Analogues

The heavy analogues of alkenes of the type >E=E< (E = Si, Ge, Sn and Pb) are expected to be oxidized or reduced much more easily than the corresponding alkenes >C=C< because of the high-lying HOMOs and low-lying LUMOs of the former relative to those of the latter. There have been several reports on the formation and EPR identification of the anion radicals of heavy alkene analogues generated either by the reduction of the 1,2-dichlorodisilane precursors or by the direct reduction of disilenes with alkali metals. Weidenbruch et al. reported in 1985 the generation of the first representatives of disilene anion radicals of the type $[R_2Si{=}SiR_2]^{-\cdot}$ (R = iPr, tBu), which were generated by the reduction of the 1,2-dihalo precursors $R_2(X)Si{-}Si(X)R_2$ with alkali metals in THF.[34] The assignment of a lifetime of several minutes at room temperature to the above-mentioned anion radical species was based on its EPR spectrum, which had an hfcc, $a(^{29}Si)$, of 3.36 mT. Following this original report, Kira et al. briefly commented on the generation of disilene anion radicals by the direct reduction of stable tetrasilyldisilenes with potassium in DME; the EPR spectral parameters for these radicals were listed.[35] However, the final isolation and unambiguous structural elucidation of anion radicals of the heavy alkene analogues were achieved only in 2004.

The first virtually stable disilene anion radical **17** was synthesized by the reduction of the disilene $(tBu_2MeSi)_2Si{=}Si(SiMe tBu_2)_2$ (**18**) with tBuLi in THF (Scheme 12).[36]



18 **17**

Scheme 12. Synthesis of the disilene anion radical **17**.

The crystal structure analysis of **17** revealed a solvent-separated ion pair with a highly twisted (88°) central Si–Si bond with a bond length of 2.341(5) Å (about 4% longer than that of the neutral precursor **18**) (Figure 9). The geometry around the two central Si atoms was different, nearly planar at Si2 (sum of the bond angles 359.9°) and pyramidal at Si1 (sum of the bond angles 352.7°), implying that the odd electron and the negative charge were separated, hence the radical character of Si2 and the anionic character of Si1. The EPR spectrum of **17** exhibited a central signal with g = 2.0061 accompanied by a pair of satellites due to the coupling of the unpaired electron with the ^{29}Si nuclei, $a(^{29}Si)$ = 2.45 mT (Figure 10). However, this hfcc is less than half that of the structurally very similar tris(di-*tert*-butylmethylsilyl)silyl radical **7** (5.80 mT).[20] This variation in magnitude was explained by the delocalization of the unpaired-electron-spin density over the Si1 and Si2 atoms of **17** on the EPR time scale (Scheme 13). At low temperature (120 K), the observed coupling constant in the EPR spectrum of **17** increased to 4.50 mT, indicating that the fast spin exchange was suppressed under glass matrix conditions.

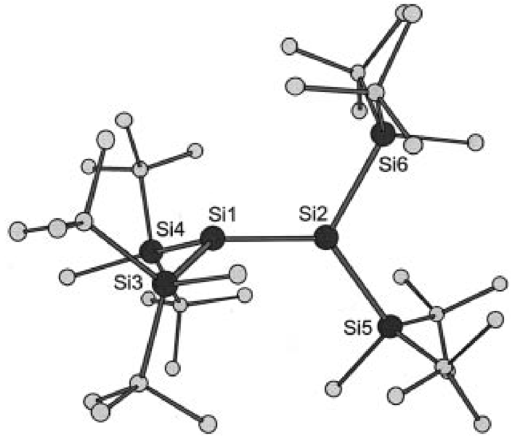


Figure 9. Crystal structure of disilene anion radical **17**.

The tin homologue of the above-mentioned compound, distannene anion radical **19**, was also synthesized by Sekiguchi et al., using the same synthetic protocol, that is, the direct reduction of the precursor distannene $(tBu_2MeSi)_2Sn{=}Sn(SiMe tBu_2)_2$ (**20**) with potassium mirror in THF in the presence of [2.2.2]cryptand (Scheme 14).[37]

The crystal structure of **19** is reminiscent of that of the silicon analogue **17**:[36] a highly twisted (74°) Sn–Sn skeleton with a bond length of 2.8978(3) Å, which is 0.2295 Å longer than that in the starting distannene **20** because of the decrease in bond order upon one-electron reduction (Figure 11). As in the case of **17** mentioned above, the geometry around the two Sn atoms is different: one of them is essentially planar (355.4°), whereas the other one is highly pyramidal (323.2°), again assuming that the negative charge and the unpaired electron are effectively separated between the two Sn atoms. However, in contrast to disilene anion radical **17**,[36] such charge–electron separation is also maintained in the solution of distannene anion radical **19**. This was demonstrated by the EPR spectrum of **19** showing a signal (g = 2.0517) with two distinct pairs of $^{119,117}Sn$-satel-

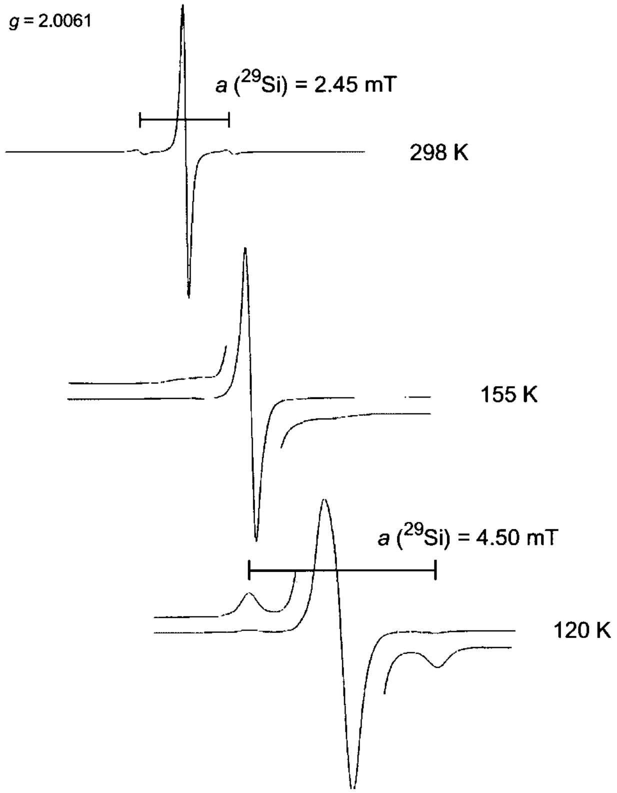
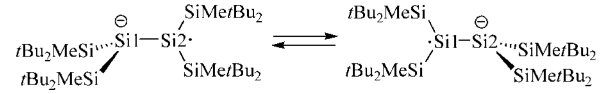


Figure 10. VT-EPR spectra of disilene anion radical **17**.



Scheme 13. Delocalization of unpaired electron over Si1 and Si2 atoms in **17**.

lite signals with hfcc values of 34.0 mT ($^{119,117}Sn_{\alpha}$) and 18.7 mT ($^{119,117}Sn_{\beta}$), respectively, implying that the odd electron localized on only one of the two Sn atoms (Figure 12).[37]

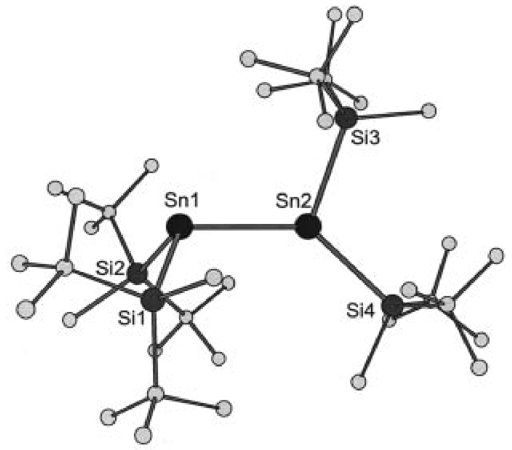


Figure 11. Crystal structure of distannene anion radical **19**.

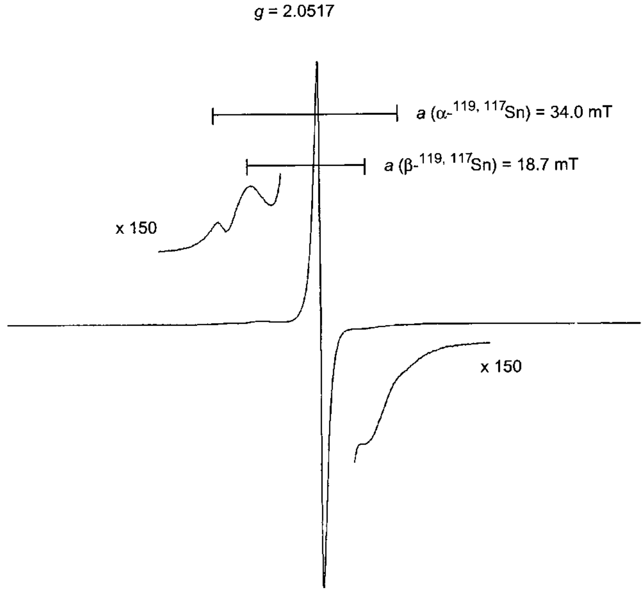
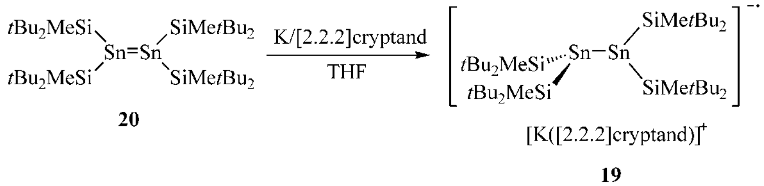


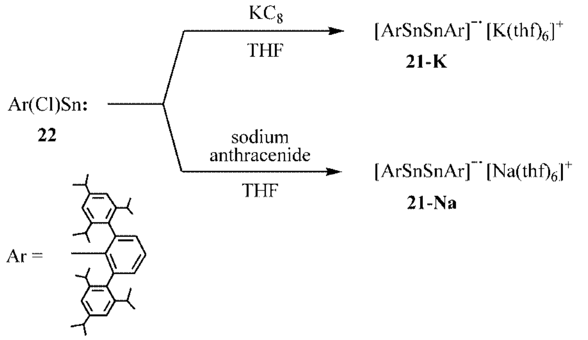
Figure 12. ERP spectrum of distannene anion radical **19** in 2-Me-THF at 310 K.

3.5 Anion Radicals of Heavy Alkyne Analogues

Further increasing the degree of unsaturation of the precursors, one can imagine the triply bonded compounds of heavier group 14 elements as possible candidates for one-electron reduction to produce their corresponding anion radicals. However, until very recently such heavy alkyne analogues were not available as stable species because of their intrinsic instability and high reactivity. Just a few years ago, the first compounds of this class containing a formal triple bond between elements heavier than carbon were synthesized, making possible the study of their reduction.[38] The synthesis of the first, and still the only, example of a singly reduced heavy alkyne analogue was recently reported by Power et al. This product, compound **21-K**, representing the anion radical of the valence isomer of distannyne, was produced by reduction of the precursor chlorostannylene **22** with potassium graphite in THF (Scheme 15).[39]



Scheme 14. Synthesis of the distannene anion radical **19**.



Scheme 15. Synthesis of the distannyne valence isomer anion radicals **21-K** and **21-Na**.

The crystal-structure analysis of **21-K** revealed a highly *trans*-bent configuration of the substituents at both Sn atoms with an Sn–Sn–C bond angle of 95.20(13)° and an Sn–Sn bond length of 2.8123(9) Å (Figure 13). The EPR spectrum of **21-K** displayed a signal with g = 2.0069 and hyperfine coupling with both ^{119}Sn and ^{117}Sn nuclei, which were simulated to produce the values $a(^{117}Sn)$ = 0.83 mT and $a(^{117}Sn)$ = 0.85 mT. The small hfcc values provide evidence for the localization of the unpaired electron in an orbital of π symmetry. Such structural and spectral properties of **21-K** are most consistent with the *trans*-bent structure **23**, in which each tin atom bears a lone pair and the unpaired electron is accommodated in a (5p-5p) π orbital of the tin atoms (Figure 14). The species **23**, with a formal Sn–Sn bond order of 1.5 and highly pronounced *trans*-bending of substituents, was suggested to have little hybridization between the tin atoms, implying poor overlap of the 5p-orbitals to form a weak π bond.

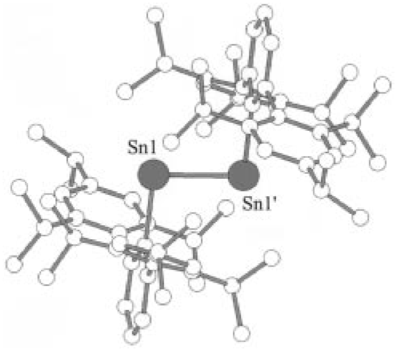


Figure 13. Crystal structure of the distannyne valence isomer anion radical **21-K** (only the anionic part of the molecule is shown).

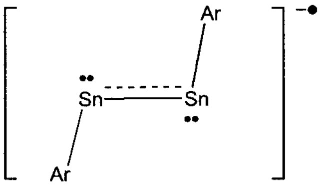


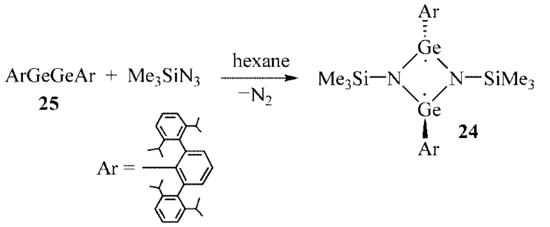
Figure 14. Bonding model of $[ArSnSnAr]^{-\cdot}$ anion radical **23** (Ar = 2,6-$Tip_2C_6H_3$).

The anion radical **21-Na**, having a sodium counterion, was also prepared by the reduction of chlorostannylene **22** with sodium anthracenide in THF (Scheme 15).[40] Although **21-Na** was isolated as a contact ion pair, in contrast to the potassium salt **21-K** obtained as a solvent-separated ion pair,[39] the EPR spectral and X-ray structural parameters of the two salts were almost completely identical, not being notably affected by the difference in their counterions. Thus, although the Sn–Sn–C bond angles in **21-Na**[40] were just a little bit wider than those in **21-K**:[39] 98.0(4) vs. 95.20(13)°, the Sn–Sn bond lengths in **21-Na** and **21-K** were practically the same, 2.8107(13) vs. 2.8123(9) Å, respectively. That is, the bonding model description **23** is fully applicable to the sodium derivative **21-Na**.

4. Heavier Group 14 Elements Centered Biradicals

The last class of free radicals based on the heavier group 14 elements has just very recently become synthetically accessible and is represented by compounds featuring the singlet biradical character. Such biradicals (or, more precisely speaking, biradicaloids, that is, the closed-shell derivatives of singlet biradicals exhibiting a weak partial coupling between the radical centers) were expected to be more stable than their carbon analogues.[41] Although several papers devoted to the stable carbon- and boron-centered biradicaloids incorporated in four-membered rings have been reported in the scientific literature since 1995,[42] there are very few examples of the stable compounds of heavier group 14 elements with some degree of biradical character. The two latest examples of stable biradicaloids, representing very attractive heteroatom analogues of the classical organic cyclobutane-1,3-diyl, were simultaneously reported in 2004 by research groups of Power and Lappert.[43,44] Both compounds have similar four-membered-ring skeletons composed of the two 1,3-nitrogen atoms and the 2,4-heavier group 14 elements (Ge in Power's paper and Sn in Lappert's paper) with the two radical centers localized on the group 14 elements. In this review, we will highlight the properties of only these two latter compounds.

The first biradicaloid, 1,3-diaza-2,4-digermacyclobutane-1,3-diyl **24**, was synthesized by the reduction of the digermyne **25** with trimethylsilyl azide in hexane (Scheme 16).[43] The crystal structure of **24** revealed a perfectly planar Ge_2N_2 four-membered ring, in which both nitrogen atoms are trigonal-planar [359.97(8)°], whereas the two germanium atoms are pyramidal [322.10(7)°] and the two aryl substituents at the germanium atoms are *trans* to each other (Figure 15). The Ge–Ge separation of 2.755 Å is nearly 0.3 Å longer than the typical Ge–Ge single bond (av. 2.44 Å),[45] indicating no Ge–Ge bonding in the Ge_2N_2 skeleton of **24**. Such tricoordination of both Ge atoms is consistent with the localization of the unpaired electrons on them, that is, with the formulation of **24** as a singlet biradicaloid. Accordingly, no signals were detected in the EPR spectrum of **24** in the temperature range 77–300 K, whereas the usual NMR spectra were observed. The biradical structure of **24** was supported by theoretical calculations, which revealed the absence of the Ge–Ge bonding, showing that the HOMO of the molecule consisted mainly of a nonbonding combination of the two lone-pair p-orbitals centered on the two Ge atoms.



Scheme 16. Synthesis of 1,3-diaza-2,4-digermacyclobutane-2,4-diyl **24**.

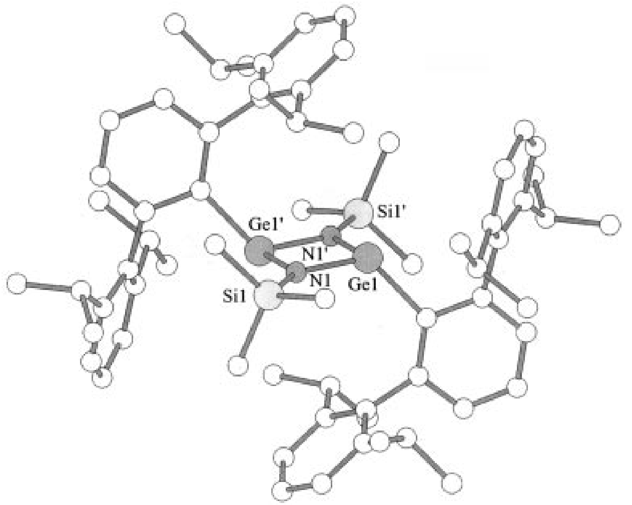


Figure 15. Crystal structure of 1,3-diaza-2,4-digermacyclobutane-2,4-diyl **24**.

The second biradicaloid, 1,3-diaza-2,4-distannacyclobutane-1,3-diyl **26**, was prepared by the rather unusual reaction of the chloro(amino)stannylene dimer $[Sn\{N(SiMe_3)_2\}(\mu\text{-}Cl)]_2$ **(27)** and AgOCN in diethyl ether (Scheme 17).[44] This compound featured an unusual solvent-dependent behavior of its ^{119}Sn NMR chemical shift: δ = –87 (C_6D_6), –83 (toluene/C_6D_6), –102 (CD_2Cl_2), –140 (THF/C_6D_6), –285 (HMPA/toluene/C_6D_6). This was explained by the increasing electron-donating ability of the solvents to the Sn centers in the order C_6D_6 < toluene < CD_2Cl_2 < THF < HMPA, which progressively shifted the ^{119}Sn NMR resonance to higher field. Similar to the above-mentioned Ge_2N_2 biradicaloid **24**, the four-membered ring of **26** is planar, the two *trans*-silyl substituents are nearly in the same plane, and the two Cl atoms are positioned perpendicular to this Sn_2N_2 plane (Figure 16). The central Sn–Sn separation of 3.398 Å is well outside the range of covalent interaction, which indicates the absence of transannular 2,4-bonding. Such pyramidalization and tricoordination of both Sn atoms implies that each Sn atom represents a radical center, therefore simple electron counting provides the overall value of six electrons for the Sn_2N_2 ring: each N atom contributes two electrons (lone pair) to the ring and each Sn atom one (odd) electron. Thus, the most appropriate bonding description of **26** is a six-π-electron-four-center system. The biradicaloid **26** is diamagnetic, being EPR-silent both in the solid state and in solution, which is typical for singlet biradicaloids. Indeed, the theoretical calculations have demonstrated that the singlet state of **26** is more stable than its triplet state with a singlet–triplet energy separation [Δ(S–T)] of 13.6 kcal/mol. This is in agreement with the recent calculations on 2,4-diphosphacyclobutane-1,3-diyl, which revealed that the σ-donating substituents at the phosphorus atoms increase the Δ(S–T) value in favor of the singlet ground state.[46] As one can see, the structural and bonding peculiarities of both 1,3-diaza-2,4-digermacyclobutane-1,3-diyl **24** and 1,3-diaza-2,4-distannacyclobutane-1,3-diyl **26** are very similar to each other, and both of them can be reliably included in the new class of singlet biradicaloids of heavier group 14 elements.

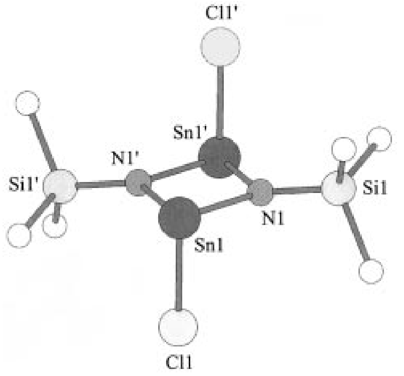
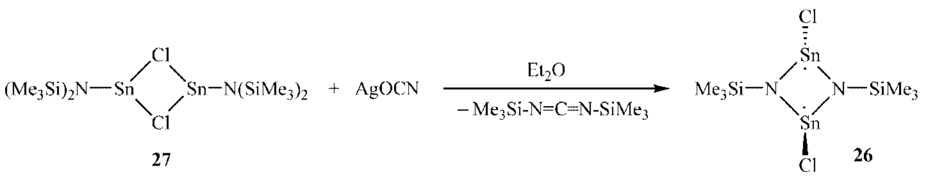


Figure 16. Crystal structure of 1,3-diaza-2,4-distannacyclobutane-2,4-diyl **26**.

5. Summary and Outlook

The evolution of our knowledge of free radicals centered on group 14 elements heavier than carbon is rather spectacular: those molecules which were originally treated several decades ago as very short-lived elusive transient species



Scheme 17. Synthesis of 1,3-diaza-2,4-distannacyclobutane-2,4-diyl **26**.

only, were later stabilized as "persistent" radicals with a *relatively* long lifetime, and were finally synthesized as absolutely stable crystalline individual compounds, whose identity was unambiguously verified by X-ray structural determination. The latest developments in the field of stable free radicals of heavier group 14 elements enable the relatively easy synthesis, isolation, and investigation of compounds of this type in the preparative (sometimes in the order of grams) scale. The most prominent achievements in this area, offering deep insight into the electronic and crystal structure of the stable radical species (primarily by means of X-ray crystallography and EPR spectroscopy accompanied by theoretical calculations), should stimulate further interest in this field of organometallic chemistry. Despite the evident and important progress that has been made in this area in just the past few years, there are still many "white spots" to be uncovered on the spacious "map" of free radical chemistry. This concerns, first of all, the synthetic availability of the stable radicals of heavier group 14 elements: these compounds are still not widespread in organometallic chemistry. More general and sophisticated synthetic methods for the preparation of stable Si-, Ge-, Sn-, and Pb-centered radicals are definitely required; for the Pb radicals such experimental procedures should be discovered for the first time, since no stable examples of such compounds have been reported to date. Another great challenge is the synthesis of the charged radical compounds: cationic and anionic. Both stable cation radicals and anion radicals of low-coordinated species, such as heavy carbene analogues or heavy alkene analogues, are among the research goals of primary importance. Deeper and more fundamental theoretical elucidation of the structural peculiarities, bonding nature, multiplicity, and hybridization of free radical species of group 14 elements, both already synthesized and theoretically predicted, is certainly necessary to verify and clarify the recent experimental findings. In the very young and promising field of stable biradicals of group 14 elements (or their combinations with group 13 or 15 elements), new synthetic breakthroughs are also expected in the near future, which could even be extended to the chemistry of stable polyradicals. As one of the most logical and very important developments in the field, the possible applications of stable radicals and polyradicals in the design of new advanced materials with a variety of prospective (for example, magnetic) properties can also be anticipated as an impressive example of the real interplay between fundamental and applied organometallic chemistry.

Acknowledgments

We wish to thank all our coworkers, whose names are listed in the references, for their important experimental contribution to this work. We are also grateful for the permanent financial support of the Ministry of Education, Science, and Culture of Japan (Nos. 147078204, 16205008), and COE (Center of Excellence) program funds.

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Received: December 2, 2004