Highlight Review

Making Stable Radicals of Heavy Elements of Groups 14 and 13: The Might of Silyl Substitution

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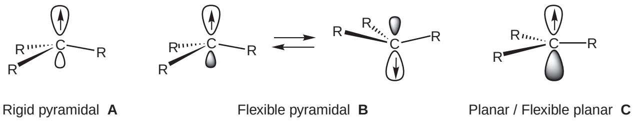
Abstract

Recent developments in the field of stable free radicals centered on the heavy elements of groups 14 and 13, neutral and charged, are covered in this review. The diagnostic geometrical characteristics and bonding features of the title species are presented. The thermodynamic and kinetic factors, affecting the stability and electronic configuration of radicals, are also discussed, with particular emphasis being given to the stabilizing influence of the bulky silyl substituents.

♦ Introduction

The classical organic chemistry textbooks typically describe free radicals as atoms with an unpaired electron, that is, as open-shell species. Given such intrinsic electron deficiency of free radicals, one should be prepared for their high electronic demand and, consequently, extreme reactivity. Indeed, organic free radicals are commonly considered as short-lived fleeting reactive intermediates, which in some cases can be stabilized with the appropriate choice of substituents to an extent allowing their direct EPR spectroscopic observation (*persistent* radicals) or even isolation and structural characterization (*stable* radicals).[1]

Apart from the stability, another fundamental feature of free radicals is their geometry, pyramidal vs. planar, which is directly related to the nature of their SOMO: whether it is of the p-type (trigonal-planar π radicals) or sp^3-type (pyramidal σ radicals). Consequently, the radicals can adopt one of three configurations: rigid pyramidal (**A**), flexible pyramidal (**B**), or planar/flexible planar (**C**) (Scheme 1). **A**-type radicals are classified as σ radicals, whereas **C**-type radicals belong to the class of π radicals, **B**-type radicals being intermediate between the **A** and **C** extremes. The geometry of radicals is affected by the influence of substituents, both electronic and steric. Thus, electronegative σ-accepting and π-donating groups (halogens, amino, etc.) markedly increase the trend for pyramidalization at the radical center. This can be reasonably explained in terms of the decrease in the SOMO–LUMO energy gap, caused by the rise of the SOMO energy level due to the substituents π donation and lowering of the LUMO energy level through the substituents σ acceptance. Accordingly, the SOMO (unpaired electron)–LUMO (central element–electronegative substituent σ^* orbital) interaction becomes progressively favored, resulting in pyramidalization at the radical center. As expected, the electropositive π-accepting (boryl) and σ-donating (silyl and germyl) groups have entirely opposite effects on the radical configuration, greatly favoring their planarization. The steric bulkiness of the substituents also has a crucial influence on the geometries. Very large groups prefer the most remote arrangement from each other, leading to a significant flattening at the radical center.



Scheme 1. Geometry of organic free radicals.

A great deal of information on the electronic structure and geometry at the radical centers can be obtained from their EPR spectra, taking into account the tendency for a marked increase in hyperfine coupling constant (hfcc) values with increase in the radical SOMO s character. Thus, the pyramidal σ radicals typically manifest large values of the hfcc, whereas those of the planar π radicals are much smaller.

The study of the free radicals centered on the heavy group 14 elements (that is, Si, Ge, Sn, and Pb radicals) started several decades ago, and to date many transient representatives have been reported.[2] The EPR spectra of some persistent radicals were recorded at room temperature, and finally, a few isolable radicals of heavy group 14 elements were structurally characterized in their crystalline form.[3] We also contributed to the field and reported the first X-ray structures of the stable silyl, germyl, and stannyl radicals, the chemistry of which we will present in this review.

♦ Stable Neutral Radicals of the Heavy Group 14 Elements: Cyclic Species

One of the best known silyl-substituted silyl radicals is tris(trimethylsilyl)silanyl $(Me_3Si)_3Si\bullet$, comprehensively studied by Chatgilialoglu and co-workers, particularly from the viewpoint of its synthetic utility.[4] However, because of the insufficient bulk of the Me_3Si ligands, this radical cannot be classified as either stable or persistent.

The first persistent radicals of the heavy group 14 elements were prepared by Lappert et al. in the mid-1970s [*g*-factor, hfcc(^{29}Si, ^{73}Ge, or ^{117}Sn and ^{119}Sn) in mT, half-life]: $[(Me_3Si)_2CH]_3Si\bullet$ (2.0027, 19.3, ≈10 min), $[(Me_3Si)_2CH]_3Ge\bullet$ (2.0078, 9.2, unchanged after four months), $[(Me_3Si)_2CH]_3Sn\bullet$ (2.0094, 169.8 and 177.6, ≈one year), $[(Me_3Si)_2N]_3Ge\bullet$ (1.9991, 17.1, >five months), $[(Me_3Si)_2N]_3Sn\bullet$ (1.9912, 317.6 and 342.6, ≈three months).[5] All these persistent radicals $R_3E\bullet$ ($R{=}CH(SiMe_3)_2$ or $N(SiMe_3)_2$; E=Si, Ge, and Sn) feature a

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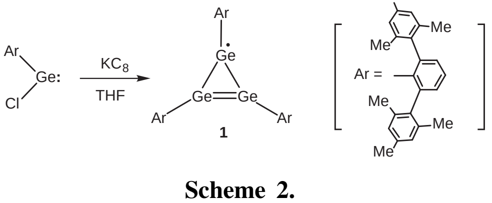
markedly pronounced pyramidal geometry, being intermediate between the planar H_3C• and nearly tetrahedral X_3E• (X=F and Cl; E=Si, Ge, and Sn) radicals, in line with the increase in electronegativity difference between the central and substituent atoms.

A family of silyl-substituted silyl radicals $(Et_nMe_{3-n}Si)_3Si$• ($n = 1$–3) highly persistent at room temperature was reported by the group of Matsumoto [g-factor, hfcc(α-^{29}Si) in mT, hfcc(β-^{29}Si) in mT, half-life]: $(EtMe_2Si)_3Si$• (2.0060, 6.28, 0.71, 3 h); $(Et_2MeSi)_3Si$• (2.0060, 6.03, 0.73, 1 day); $(Et_3Si)_3Si$• (2.0063, 5.72, 0.79, 1.5 month).[6] The increase in the steric bulk around the radical center resulted in an increase in its planarity on going from $(EtMe_2Si)_3Si$• to $(Et_3Si)_3Si$•, which was manifested in the simultaneous decrease of the hfcc(α-^{29}Si) values. Accordingly, the delocalization of the radical spin density over the σ^*(Si–C) orbitals of the silyl substituents becomes more important. Even more bulky per(silyl)silyl radicals were generated as remarkably persistent species [g-factor, hfcc(α-^{29}Si) in mT, half-life]: $(i\text{-}Pr_3Si)_3Si$• (2.0061, 5.56, 5 days),[7] $(t\text{-}BuMe_2Si)_3Si$• (2.0055, 5.71, 1 day).[8] The small values of the hfcc(α-^{29}Si) of sterically highly congested $(Et_3Si)_3Si$•, $(i\text{-}Pr_3Si)_3Si$•, and $(t\text{-}BuMe_2Si)_3Si$• radicals provided convincing evidence for the significant planarity of these Si radical centers.

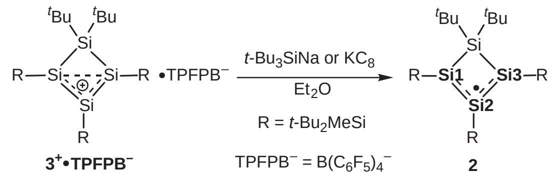
Apeloig and co-workers recently reported the persistent planar silyl-substituted silyl radical $(Me_3SiMe_2Si)_3Si$• [g-factor, hfcc(α-^{29}Si) in mT, half-life]: 2.0065, 5.99, 6 min.[9] They also generated rather interesting metal (Li, Hg)-substituted silyl radicals [g-factor, hfcc(α-^{29}Si) in mT]:[10] $(i\text{-}Pr_3Si)_2SiLi$• (2.0073, 3.2), (thf)Li$(t\text{-}Bu_2MeSi)_2Si$• (2.0067, 3.33), t-BuHg–Si$(t\text{-}Bu_2MeSi)_2$–Hg–Si$(t\text{-}Bu_2MeSi)_2$• (1.984, 5.60), HSi-$(t\text{-}Bu_2MeSi)_2$–Hg–Si$(t\text{-}Bu_2MeSi)_2$• (1.983, 5.60), and (thf)Li–Si$(t\text{-}Bu_2MeSi)_2$–Hg–Si$(t\text{-}Bu_2MeSi)_2$• (1.984, 5.60).

The first stable radical of the heavy group 14 elements, cyclotrigermenyl radical **1** with bulky 2,6-Mes_2-C_6H_3 substituents (Mes = 2,4,6-trimethylphenyl), was synthesized in 1996 by Power et al. by the reduction of the chlorogermylene (2,6-Mes_2-C_6H_3)(Cl)Ge: with KC_8 in THF (Scheme 2).[11] Radical **1**, featuring an unpaired electron on one Ge atom and a double bond between the other two Ge atoms, represents an all-Ge version of the organic cyclopropenyl radical. The planar structure of **1** in solution was deduced from its EPR spectrum, which showed a single resonance ($g = 2.0069$) with the hfcc $a(^{73}\text{Ge}) = 1.6$ mT.



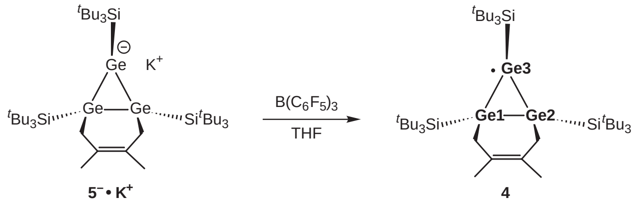
Scheme 2.

The first crystal structure of a stable silicon-centered free radical was reported for the cyclotetrasilenyl radical **2** bearing large protecting t-Bu_2MeSi groups (a silicon variation of the cyclobutenyl radical), prepared in 2001 by Sekiguchi et al. by the reduction of cyclotetrasilenylium ion $\mathbf{3^+ \cdot TPFPB^-}$ [$TPFPB^-$ = tetrakis(pentafluorophenyl)borate] with either t-Bu_3SiNa or KC_8 in Et_2O (Scheme 3).[12]



Scheme 3.

The four-membered Si_4 ring of **2** is nearly planar with the Si1–Si2 and Si2–Si3 bonds being intermediate between the typical Si–Si and Si=Si bonds, thus providing evidence for the allylic-type structure of radical **2**. The planarity of the Si_4 ring was also retained in solution, as manifested in the small values of the hfcc(^{29}Si), resulting from the coupling of an unpaired electron ($g = 2.0058$) with the two terminal (Si1 and Si3) and one central (Si2) nuclei of the delocalized allylic Si1–Si2–Si3 unit: 4.07, 3.74, and 1.55 mT.



Scheme 4.

A notable bicyclic Ge-centered radical, 1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl **4**, was recently prepared by Sekiguchi and co-workers by the one-electron oxidation of the bicyclic anion $\mathbf{5^- \cdot K^+}$ with $B(C_6F_5)_3$ in THF (Scheme 4).[13]

The diagnostic endo conformation of **4** favors the intramolecular through-space SOMO(Ge3)–π(C=C) orbitals interaction facilitated by their spatial proximity: 3.63 Å between the Ge3 and C=C bond, which is in the range of van der Waals interactions. In solution, however, such an endo conformer is unable to gain the same level of stability as in its crystalline form, and consequently the inversion at the Ge3 radical center resulted in the smooth endo–exo isomerization on the EPR time scale, and overall formation of the mixture of both stereoisomers of **4** observed as a pair of distinct EPR resonances: $g = 2.0210$ and 2.0223. The Ge3 center in both stereoisomers clearly represents a planar π radical, which was manifested in the diagnostically small values of its hfcc(α-^{73}Ge) (3.4 and 2.6 mT). Interestingly, in contrast to the above-described allylic-type delocalized cyclotetrasilenyl radical **2**,[12] bicyclic radical **4** possesses a localized structure. This can be understood by taking into account the absence of π bonds adjacent to the Ge3 radical center in **4**, resulting in the lack of effective through-bond delocalization of its unpaired electron, whereas the through-space Ge3•–C=C interaction is not strong enough for the notable radical delocalization.

◆ Stable Neutral Radicals of the Heavy Group 14 Elements: Acyclic Species

The above-discussed examples of cyclotrigermenyl **1** and cyclotetrasilenyl **2** radicals have rather special cyclic structures. Tricoordinate acyclic radicals of the type R_3E• (E=Si, Ge, Sn, and Pb), lacking the stabilizing but strongly electronically perturbing effects of the cyclic π-delocalization, represent a greatly challenging and highly desirable class of stable organometallic radicals.[3] However, until our investigations, isolable radicals of such a type were unknown.

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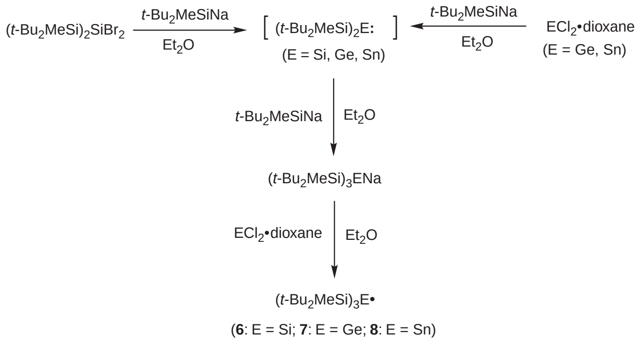


Scheme 5.

The first breakthrough was achieved several years ago by the synthesis of a homologous series of (t-Bu$_2$MeSi)$_3$E$\cdot$ (E=Si, Ge, and Sn) radicals lacking conjugation to the π bond.[3b–3d] All of these radicals, efficiently stabilized by the bulky electropositive silyl groups both kinetically and thermodynamically, were synthesized by a very simple and straightforward method, allowing their preparation in gram-order scales. Thus, the preparation of the lightest member in this series, silyl radical (t-Bu$_2$MeSi)$_3$Si$\cdot$ (**6**), was smoothly achieved by oxidation of the silylsodium derivative (t-Bu$_2$MeSi)$_3$SiNa with dichlorogermylene–dioxane complex GeCl$_2\cdot$diox in Et$_2$O (Scheme 5).[14]

In the solid state, silyl radical **6** features a perfectly trigonal-planar geometry around the sp^2-Si radical center, implying that **6** is a true π radical with the SOMO represented by the central silicon 3p$_z$ orbital (Figure 1).[14] The hyperconjugative delocalization of the unpaired electron over the antibonding σ^*(Si–C$_{t\text{-Bu}}$) orbitals notably contributes to the overall stabilization of **6**. As expected, three σ-donating silyl substituents in **6** greatly promote flattening at the Si radical center, resulting in the lowering of its inversion barrier. Moreover, such a planar geometry makes it possible to move the very bulky t-Bu$_2$MeSi groups away from each other as far as possible to avoid their mutual steric repulsion.

The EPR resonance of **6** was observed in a region typical for silyl-substituted silyl radicals ($g = 2.0056$), whereas the diagnostically small value of the hfcc(α-^{29}Si) of 5.80 mT was indicative of the high p character of its SOMO (Figure 2).[14] Accordingly, one should recognize that the per(silyl)silyl radical **6** retains its planarity in solution, and should be definitely classified as the planar/flexible planar type **C** shown in Scheme 1.

The Ge and Sn versions of **6**, per(silyl)germyl radical (t-Bu$_2$MeSi)$_3$Ge$\cdot$ (**7**)[14] and per(silyl)stannyl radical (t-Bu$_2$MeSi)$_3$Sn$\cdot$ (**8**)[15] (the first structurally characterized stannyl radical) were prepared by a similar, albeit still simpler, procedure (Scheme 5). The direct reduction of either GeCl$_2\cdot$diox or SnCl$_2\cdot$diox with t-Bu$_2$MeSiNa in Et$_2$O resulted in the intermediate formation of germylsodium (t-Bu$_2$MeSi)$_3$GeNa or stannylsodium (t-Bu$_2$MeSi)$_3$SnNa, which were subsequently oxidized with another equivalent of ECl$_2\cdot$diox to produce the final radicals **7** and **8**.[14,15] It should be noted that in this reaction, GeCl$_2\cdot$diox and SnCl$_2\cdot$diox complexes play two roles: at first, as a substrate for generation of germyl and stannyl anions, and then as a mild electron-transfer reagent, whose oxidizing ability was well documented in the previous electrochemical studies.[16] The right choice of the oxidizing reagent was quite crucial for synthetic success: thus, using SnCl$_2$ itself [$E_{1/2}$(red) $= -0.21$ and -1.20 V] resulted in the unavoidable direct oxidation of t-Bu$_2$MeSiNa with SnCl$_2$ to form t-Bu$_2$MeSi–SiMet-Bu$_2$ and metallic tin instead of tin radical **8**.[15] In contrast, utilization of the SnCl$_2\cdot$diox complex [$E_{1/2}$(red) $= -0.78$ V], in which the oxidizing ability of SnCl$_2$ is markedly decreased by its complexation to dioxane, allows the achievement of the best matching of the redox properties of the t-Bu$_2$MeSiNa and SnCl$_2\cdot$diox pair to prevent the undesirable direct oxidation of silylsodium.

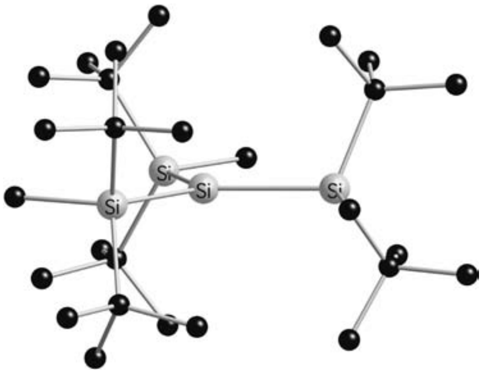


Figure 1. Crystal structure of silyl radical (t-Bu$_2$MeSi)$_3$Si$\cdot$ (**6**) (hydrogen atoms are not shown).

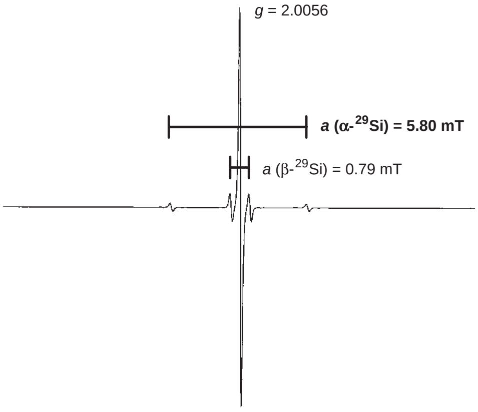


Figure 2. EPR spectrum of silyl radical (t-Bu$_2$MeSi)$_3$Si$\cdot$ (**6**).

Both germyl radical **7** (Figure 3) and stannyl radical **8** are totally isostructural to the above-described silyl radical **6**, being

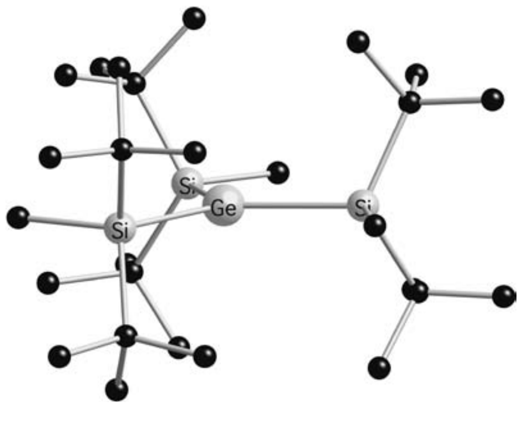


Figure 3. Crystal structure of germyl radical (t-Bu$_2$MeSi)$_3$Ge$\cdot$ (**7**) (hydrogen atoms are not shown).

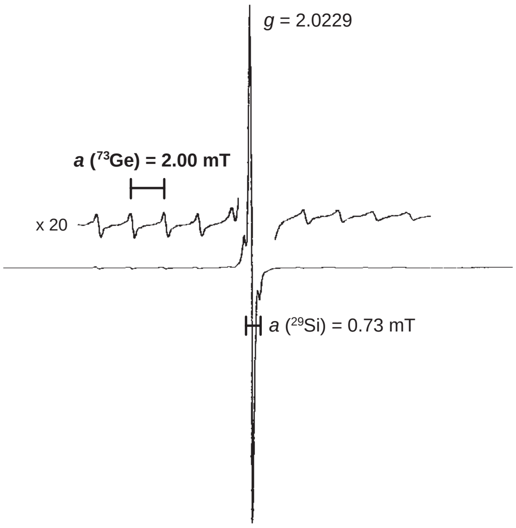


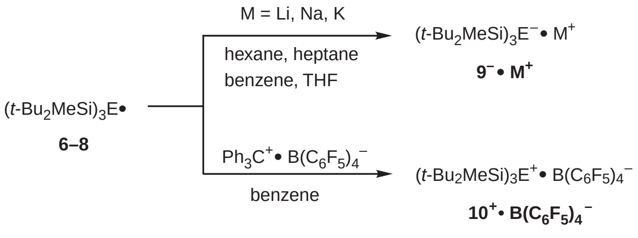
Figure 4. EPR spectrum of germyl radical $(t\text{-Bu}_2\text{MeSi})_3\text{Ge}\cdot$ (**7**).

trigonal-planar in their crystalline form and keeping their planarity in solution judging from their small hfcc values (g-factor, hfcc(^{73}Ge or ^{119,117}Sn) in mT): **7** (2.0229, 2.00) (Figure 4) and **8** (2.0482, 32.9).[14,15]

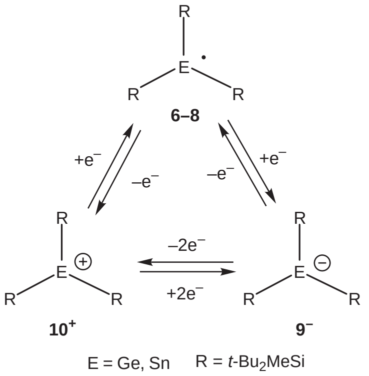
Undoubtedly, the uniformity of the structural and spectral peculiarities of π radicals $(t\text{-Bu}_2\text{MeSi})_3\text{E}\cdot$ (E=Si, Ge, and Sn) **6**–**8** both in the solid state and in solution should be ascribed to the immediate influence of their voluminous electropositive silyl substituents t-Bu$_2$MeSi.[3b–3d,17] In marked contrast, it is well known that using simple alkyl and aryl substituents leads to a highly pronounced pyramidalization at the radical centers, in which the unpaired electron typically occupies the orbital with a high s contribution (σ radicals).[2b,4]

Taking into account the inherent electron deficiency and high electronic demand of free radicals, it is not surprising that all heavy group 14 element-centered radicals **6**–**8** readily undergo one-electron reduction to form the corresponding silyl, germyl, and stannyl anions $(t\text{-Bu}_2\text{MeSi})_3\text{E}^-$ (E=Si, Ge, and Sn) **9**$^-$ (Scheme 6).[18] However, still more exciting was their very smooth one-electron oxidation to produce even more electron-deficient cationic species, namely, silylium, germylium, and stannylium ions $(t\text{-Bu}_2\text{MeSi})_3\text{E}^+$ (E=Si, Ge, and Sn) **10**$^+$, of which the last two species were isolated and structurally characterized as the first examples of the stable trigonal-planar germylium and stannylium ions (Scheme 6).[15,19]

Such readiness of radicals **6**–**8** to undergo oxidation could be reasonably explained in terms of their rather low first ionization potentials, corresponding to the removal of an unpaired electron from their SOMOs. It is particularly interesting that the cations **10**$^+$ and anions **9**$^-$, generated from the free radicals **6**–**8** by their oxidation and reduction, could be quantitatively converted back to the starting **6**–**8** by reduction and oxidation processes, respectively, thus making a fully reversible redox system (Scheme 7).[3b–3d]



Scheme 6.



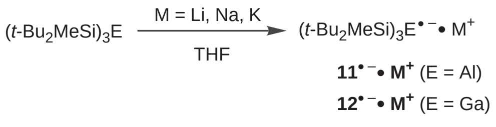
Scheme 7.

◆ Stable Anion-Radicals of the Heavy Group 13 Elements

The stable silyl-substituted anion-radicals of the heavy group 13 elements, isoelectronic to the above-discussed heavy group 14 element-centered radicals **6**–**8**, have also recently been synthesized. Utilizing the highly efficient protecting advantage of the t-Bu$_2$MeSi group, we succeeded in the preparation of the aluminum- and gallium-centered anion-radicals $(t\text{-Bu}_2\text{MeSi})_3\text{E}^{\cdot-}$ (E=Al and Ga) **11**$^{\cdot-}$ (E=Al) and **12**$^{\cdot-}$ (E=Ga). Both compounds were isolated as alkali metal salts by the direct reduction of the neutral precursors $(t\text{-Bu}_2\text{MeSi})_3\text{E}$ with alkali metals (Li, Na, and K) in THF (Scheme 8).[20]

The aluminum anion-radical derivative **11**$^{\cdot-}\cdot$**K**$^+$ was isolated as a solvent-separated ion pair after complexation of the potassium cation with the [2.2.2]cryptand. Similarly to the above case of heavy group 14 element-centered radicals **6**–**8**, **11**$^{\cdot-}$ showed a nearly planar geometry around the Al atom (the sum of the bond angles being 358.4°) as a consequence of the influence of three electropositive and bulky t-Bu$_2$MeSi substituents (Figure 5).[20] The stabilizing hyperconjugative SOMO[3p$_z$(Al)–σ^*(Si–C$_{t\text{-Bu}}$)] orbitals interaction is also operative in this case, the manifestation of which was the shortening of the Al–Si bond lengths in **11**$^{\cdot-}$ (compared with its neutral precursor) by ca. 0.04 Å upon the reduction. Thus, the crystal structure data provide evidence that the aluminum anion-radical **11**$^{\cdot-}$ also represents a π radical with its unpaired electron occupying the aluminum 3p$_z$ orbital.

The structures of both **11**$^{\cdot-}$ and **12**$^{\cdot-}$ in THF solution, in which they exist as the solvent-separated ion pairs, were elucidated from their EPR spectra [g-factor, hfcc(^{27}Al or ^{69}Ga and ^{71}Ga) in mT]: **11**$^{\cdot-}$ (2.005, 6.2) (Figure 6) and **12**$^{\cdot-}$ (2.015, 12.3 and 15.7).[20] The hfcc values of both **11**$^{\cdot-}$ and **12**$^{\cdot-}$ are di-



Scheme 8.

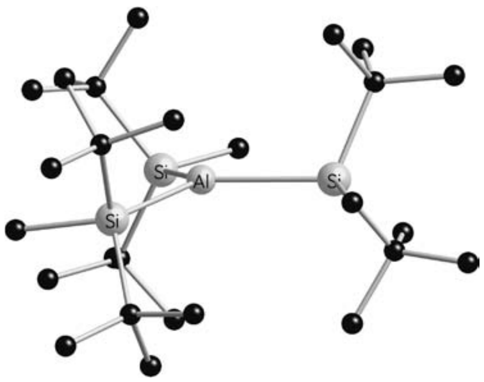


Figure 5. Crystal structure of aluminum anion-radical (t-$Bu_2MeSi)_3Al^{\bullet-}$ **11**$^{\bullet-}$ (counter cation K^+, hydrogen atoms, [2.2.2]cryptand and benzene molecules are not shown).

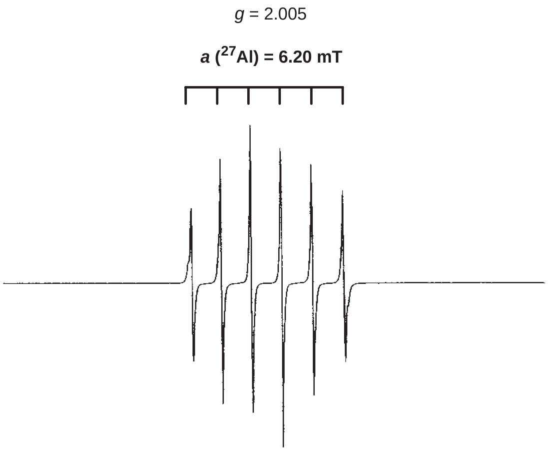
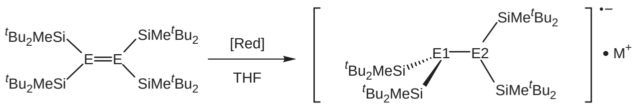


Figure 6. EPR spectrum of aluminum anion-radical (t-$Bu_2MeSi)_3Al^{\bullet-}$ (**11**$^{\bullet-}$).

agnostically small, compared with those of the parent $H_3Al^{\bullet-}$ (15.4 mT)[21] and $H_3Ga^{\bullet-}$ (42.0 mT for ^{69}Ga and 53.4 mT for ^{71}Ga),[22] thus pointing to the planarity of both **11**$^{\bullet-}$ and **12**$^{\bullet-}$ in solution. Overall, the aluminum and gallium anion-radicals **11**$^{\bullet-}$ and **12**$^{\bullet-}$ should be definitely assigned to the class of planar/flexible planar radicals of type **C**, as depicted in Scheme 1. This is in sharp contrast to anion-radicals $H_3Al^{\bullet-}$ and $H_3Ga^{\bullet-}$, both of which feature ca. 16% of unpaired electron spin density on the 3s(Al) and 4s(Ga) orbitals, being markedly pyramidal.[21,22]

♦ Stable Anion-Radicals of the Alkenes of Heavy Group 14 Elements

Employment of the same t-Bu_2MeSi substituents allowed us to synthesize the first stable anion-radicals of heavy alkenes. Thus, disilene anion-radical **13**$^{\bullet-}$ was prepared as its lithium salt by the reduction of precursor (t-$Bu_2MeSi)_2Si{=}Si(t$-$Bu_2MeSi)_2$ with t-BuLi in THF (Scheme 9: E=Si, $M^+ = [Li(thf)_4]^+$, [Red] = t-BuLi),[23] whereas distannene anion-radical **14**$^{\bullet-}$ was obtained in the form of its potassium salt by the reduction of (t-$Bu_2MeSi)_2Sn{=}Sn(t$-$Bu_2MeSi)_2$ with potassium mirror in THF in the presence of [2.2.2]cryptand (Scheme 9: E=Sn, M^+ = [K([2.2.2]cryptand)]$^+$, [Red] = K/[2.2.2]cryptand).[24] Both anion-radical derivatives were isolated as solvent-separated ion pairs with no anion–cation interactions.



13$^{\bullet-}$**• M$^+$:** E = Si, $M^+ = [Li(thf)_4]^+$, [Red] = t-BuLi
14$^{\bullet-}$**• M$^+$:** E = Sn, M^+ = [K([2.2.2]cryptand)]$^+$,
[Red] = K mirrior / [2.2.2]cryptand

Scheme 9.

One of the most peculiar structural features of both **13**$^{\bullet-23}$ and **14**$^{\bullet-24}$ is their central E1–E2 bond. Thus, upon reduction, this bond became highly twisted and stretched (twisting angle in °, E1–E2 bond length in Å, stretching of E1–E2 bond compared to that of the starting disilene and distannene in %): Si1–Si2 in **13**$^{\bullet-}$ [88, 2.341(5), 3.6] and Sn1–Sn2 in **14**$^{\bullet-}$ [74, 2.8978(3), 8.6]. This phenomenon should certainly be ascribed to a decrease in the bond order on going from the neutral heavy alkene to a resulting heavy alkene anion-radical. The unpaired electron and negative charge are well separated in the solid state structures of both anion-radicals **13**$^{\bullet-}$ and **14**$^{\bullet-}$, which was manifested in the diagnostically planar geometry of one of the central atoms E2 (radical center) and distinct pyramidality of the other central atom E1 (anionic center). Interestingly, while the distannene anion-anion **14**$^{\bullet-}$ preserved such single electron–negative charge separation in solution,[24] its silicon analogue **13**$^{\bullet-}$ showed a sharply distinct structure in which the unpaired electron is delocalized over the two central Si1 and Si2 atoms.[23] Such a difference was clearly seen in the EPR spectra of these two species. Thus, distannene anion-radical **14**$^{\bullet-}$ displayed a resonance at $g = 2.0517$ accompanied with two pairs of satellites originating from the coupling of the unpaired electron with the two nonequivalent ^{117,119}Sn nuclei: hfcc(α-^{117,119}Sn) = 34.0 mT and hfcc(β-^{117,119}Sn) = 18.7 mT. In contrast, the EPR resonance of the disilene anion-radical **13**$^{\bullet-}$ ($g = 2.0061$) was accompanied with only one pair of satellites [hfcc(^{29}Si) = 2.45 mT], whose value was less than half of that of the similar per(silyl)silyl radical (t-$Bu_2MeSi)_3Si\bullet$ (**6**) (5.80 mT),[14] thus implying the delocalization of the unpaired electron over both Si1 and Si2 atoms in **13**$^{\bullet-}$.

♦ Summary and Outlook

The free radicals, quite recently considered only as elusive short-lived reactive intermediates, have now turned into a very important class of observable, spectroscopically detectable and in many cases isolable and fully characterizable chemical reagents. The heavy congeners of organic free radicals, centered on Si, Ge, Sn, and Pb atoms, have received particular attention during the several past decades. A great deal of experimental and theoretical interest is associated with the peculiar structures and specific chemical properties of such "heavy" radical species, in many aspects distinctly different from those of their carbon analogues. Remarkable recent progress in the field of silyl, germyl, stannyl, and plumbyl radicals has resulted in a continuously growing number of stable derivatives of this class. As one of the great synthetic advantages, one should mention the utilization of the bulky silyl substituents, which allowed the efficient stabilization and isolation of a variety of novel radical species, this topic being the subject of our review.

Looking to the future, one should expect further developments in the synthesis of stable radicals of heavy elements of groups 14 and 13, based on state-of-the-art experimental techniques and advanced theory of the bonding and reactivity of organometallic compounds. Apart from their synthesis, the wide utilization of such radical species as novel and useful reagents in synthetic organometallic chemistry is highly desirable.

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