Stable Silyl, Germyl, and Stannyl Cations, Radicals, and Anions: Heavy Versions of Carbocations, Carbon Radicals, and Carbanions

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ABSTRACT
The rapidly growing chemistry of the cations, radicals, and anions based on the group 14 elements heavier than carbon (Si, Ge, Sn, and Pb) is one of the most important organometallic fields. Recent developments in this research area moved such species from the class of short-lived reactive intermediates to the class of easily accessible, isolable, and fully characterizable compounds. In this Account, we deal with the major accomplishments in the field of the stable representatives of "heavy" cations, radicals, and anions.

1. Introduction

As classes of reactive intermediates of great importance, carbocations, free radicals, and carbanions have been well recognized for more than a century, since the first generation and observation of such fundamental species as the triphenylmethyl (trityl) cation Ph_3C^+,[1] triphenylmethyl radical $Ph_3C\cdot$,[2] and Grignard reagents $RMgX$[3] at the very beginning of the 20th century. A great deal of invaluable synthetic and mechanistic information about these very important species became available in the course of their systematic investigation in the first half of the previous century. However, the modern era of reactive intermediate chemistry began in the second half of the

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20th century, associated with such milestone achievements as the synthesis of the alkyl cations in superacidic media,[4a] generation and direct EPR observation of persistent free radicals,[4b] and isolation and characterization of a variety of organometallic reagents (organolithium and organomagnesium compounds).[4c] The chemistry of the heavy congeners of the above-mentioned classes of compounds, that is Si-, Ge-, Sn-, and Pb-centered cations, radicals, and anions, is much less developed. The story of their systematic study is not long, dating back to only the early 1960s as the starting point of the most intensive and productive research. Progress in the field of such heavy cations, radicals, and anions proceeded through several evolutionary steps: the earliest observations of the short-lived species as reactive intermediates in the gas phase, then their direct identification in solution by spectroscopic means, and, finally, as the culminating step, isolation of the species as stable individual compounds and their full characterization, including determination of crystal structures.[5] We are unable to review the whole story due to the limited space of this Account; instead, we will focus on the last step concerning the chemistry of the stable, crystallographically characterizable compounds, giving particular emphasis to the synthesis and structural characterization of the representatives recently prepared in our research group.
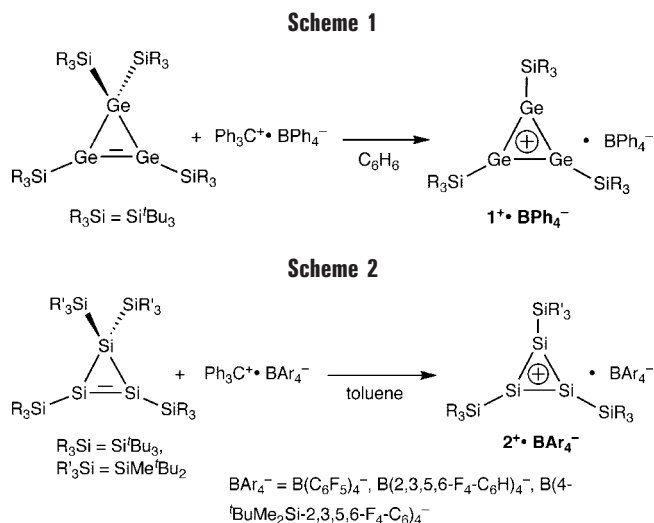
2. Cations of the Heavy Group 14 Elements

The remarkable crystal structures of the first silylium ion-like species, $[Et_3Si^+(toluene)]\cdot B(C_6F_5)_4^-$ [6] and $^iPr_3Si^{\delta+}\cdot[CB_{11}H_6Br_6]^{\delta-}$,[7] were published in 1993 by the groups of Lambert and Reed, respectively. However, their silylium ion nature, particularly that of $[Et_3Si^+(toluene)]\cdot B(C_6F_5)_4^-$, was questioned by both experimentalists and theoreticians. As a consequence of hot debates, it was finally concluded that both compounds feature a major contribution of silylium ion character with weak coordination to either toluene solvent (for Et_3Si^+)[6] or the Br atom of the counteranion (for $^iPr_3Si^+$),[7] this story being nicely covered by Reed in his recent review.[8] Thus, the goal of synthesizing true silylium, as well as germylium, stannylium, and plumbylium ions lacking any coordination to external nucleophiles, was not achieved. Resolving this problem actually required nearly a decade of very intensive research, culminating in the synthesis and structural characterization of the $RR'R''E^+$ cations, free of any detectable covalent interactions with either counterions or solvents.[5b]

Cyclic Cations. The synthesis of the first stable free cation of the heavy group 14 elements was accomplished in 1997 by Sekiguchi and co-workers. This compound, cyclotrigermenylium tetraphenylborate, $\mathbf{1^+\cdot BPh_4^-}$, was prepared by the oxidation of the cyclotrigermene $(^tBu_3Si)_4Ge_3$ with $Ph_3C^+\cdot BPh_4^-$ in benzene (Scheme 1).[9] The crystal structure analysis of $\mathbf{1^+\cdot BPh_4^-}$ revealed that

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Scheme 1

$$R_3Si = Si^tBu_3$$

Scheme 2

$$R_3Si = Si^tBu_3,$$
$$R'_3Si = SiMe^tBu_2$$

$$BAr_4^- = B(C_6F_5)_4^-, B(2,3,5,6\text{-}F_4\text{-}C_6H)_4^-, B(4\text{-}$$
$$^tBuMe_2Si\text{-}2,3,5,6\text{-}F_4\text{-}C_6)_4^-$$

the cationic portion of the molecule, 1^+, is represented by an equilateral triangle composed of the Ge–Ge bonds, whose lengths of 2.321(4)–2.356(4) Å were just intermediate between those of the typical Ge–Ge and Ge=Ge bonds. In other words, 1^+ was reliably shown to be a heavy analogue of the classical cyclopropenylium ion, in which the 2π-electron aromatic system was free from any observable interactions with either counterion or solvent molecules. Interestingly, earlier calculations by Schleyer et al.[10a] revealed the preference for the nonclassical nonplanar hydrogen-bridged C_{3v} structure over the classical cyclopropenylium-type planar D_{3h} compound for cations $E_3H_3^+$ (E = Ge, Sn, and Pb).

The silicon version of the cyclopropenylium ion, cyclotrisilenylium tetraarylborate $2^+ \cdot \textbf{BAr}_4^-$ [$BAr_4^- = B(C_6F_5)_4^-$, $B(2,3,5,6\text{-}F_4\text{-}C_6H)_4^-$, and $B(4\text{-}^tBuMe_2Si\text{-}2,3,5,6\text{-}C_6F_4)_4^-$], was also synthesized by Sekiguchi and co-workers by oxidation of cyclotrisilene with $Ph_3C^+\cdot BAr_4^-$ in toluene (Scheme 2 and Figure 1).[11] Similar to $1^+ \cdot \textbf{BAr}_4^-$,[9] $2^+ \cdot \textbf{BAr}_4^-$ also exhibited a planar 2π-electron aromatic Si_3 ring, lacking any bonding interactions in the solid state and in solution, which agreed well with the calculations that found a planar cyclopropenylium D_{3h} structure for the parent $Si_3H_3^+$ as a global minimum.[10b] Oxidation of cyclotrisilene, substituted with the less bulky $^tBu_2MeSi$

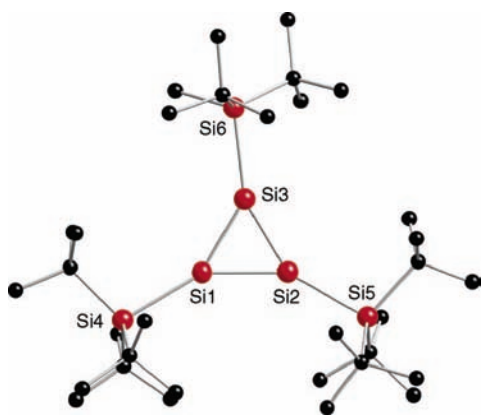**FIGURE 1.** Crystal structure of cyclotrisilenylium 2^+ [Crystal Maker view; counteranion $B(4\text{-}^tBuMe_2Si\text{-}2,3,5,6\text{-}F_4\text{-}C_6)_4^-$, crystallization solvent (toluene) molecule, and hydrogen atoms are not shown].

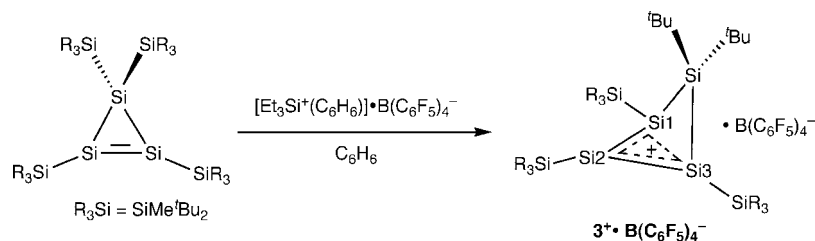groups, with $[Et_3Si^+(C_6H_6)]\cdot B(C_6F_5)_4^-$ in benzene resulted in the formation of the unexpected cationic species, cyclotetrasilenylium ion $3^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$ (Scheme 3).[12] The cation 3^+ was also free; moreover, the positive charge on it was delocalized over the three skeletal Si atoms (Si1, Si2, and Si3) accompanied by an Si1–Si3 through-space orbital interaction. This was interpreted in terms of the overall homoaromaticity of 3^+, this hypothesis being further supported by the observation of the resonance of the Si2 atom at an extraordinarily low field of 315.7 ppm.

Acyclic Cations. The stable free tricoordinate cations R_3E^+ (E = Si, Sn, and Pb) with the diagnostic trigonal-planar geometry have been a long-standing goal for many organometallic chemists. The first achievement in the synthesis of such highly desirable compounds was that of Lambert et al., who prepared the free trimesitylsilylium ion $Mes_3Si^+\cdot B(C_6F_5)_4^-$, $4^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$, by the reaction of $Mes_3Si\text{-}CH_2\text{-}CH=CH_2$ with the β-silylcarbocation $Et_3Si\text{-}CH_2CPh_2^+\cdot B(C_6F_5)_4^-$ in 1997.[13] The ^{29}Si NMR resonance of $4^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$ was observed in the low-field region at 225.5 ppm,[13] a value that agreed well with those of 230.1 (GIAO/HF) and 243.9 ppm (GIAO/DFT), calculated for the free Mes_3Si^+ cation.[14] After exchange of the counteranion from $B(C_6F_5)_4^-$ to $CB_{11}HMe_5Br_6^-$, the crystal structure of $4^+ \cdot \textbf{CB}_{11}\textbf{HMe}_5\textbf{Br}_6^-$ was determined to show the trigonal-planar geometry of 4^+, free from counterion and solvent interactions.[15] Likewise, the oxidation of allyltrimesityl-stannane $Tip_3Sn\text{-}CH_2\text{-}CH=CH_2$ with $Ph_3C^+\cdot B(C_6F_5)_4^-$ in benzene resulted in the formation of the cation $Tip_3\text{-}Sn^+\cdot B(C_6F_5)_4^-$, $5^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$, which was also characterized as a free tricoordinate planar stannylium ion.[16]
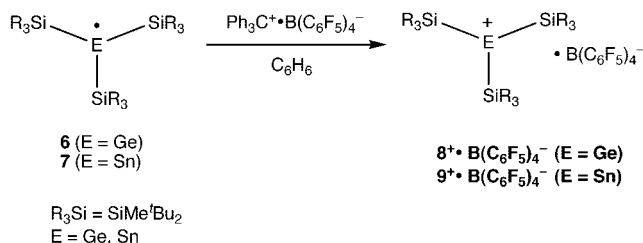
Another approach to resolving the problem of free tricoordinate silylium, germylium, and stannylium ions was recently demonstrated by Sekiguchi and co-workers.[17] As the substituents of premier choice, the electropositive $^tBu_2MeSi$ groups have been selected. The two main reasons brought about such a choice: the factor of the great steric bulkiness of this substituent (effective separation of cation from anion, nucleophilic solvent, or any other external nucleophiles) and σ-electron donating effect of the electropositive silyl substituents. A straightforward method was employed for the synthesis of such silyl-substituted heavy cations: the one-electron oxidation of the corresponding free radicals. Thus, the reaction of both germyl ($^tBu_2MeSi)_3Ge\cdot$ and stannyl ($^tBu_2MeSi)_3Sn\cdot$ radicals **6** and **7**, respectively, with $Ph_3C^+\cdot B(C_6F_5)_4^-$ in benzene cleanly produced the corresponding germylium ($^tBu_2MeSi)_3Ge^+$ and stannylium ($^tBu_2MeSi)_3Sn^+$ ions, isolated in the form of their $B(C_6F_5)_4^-$ derivatives $8^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$ [17a] and $9^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$ [17b] (Scheme 4).

In both compounds, the cations 8^+ and 9^+ displayed no interactions with either the $B(C_6F_5)_4^-$ anion or benzene solvent, implying their free status in the crystalline form and featuring perfect trigonal-planar geometries around the cationic Ge and Sn centers. This freedom was also maintained in solution, as manifested by the solvent-independent ^{29}Si NMR spectra of both $8^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$ and $9^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$.[17] In particular, the ^{119}Sn NMR resonance of $9^+ \cdot \textbf{B}(\textbf{C}_6\textbf{F}_5)_4^-$ was observed at the extremely low field
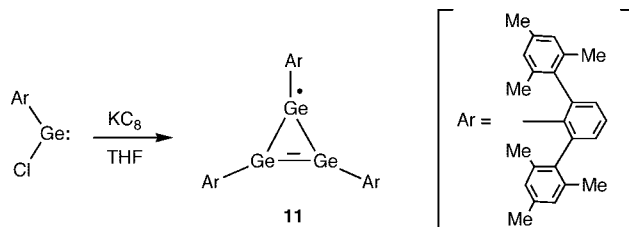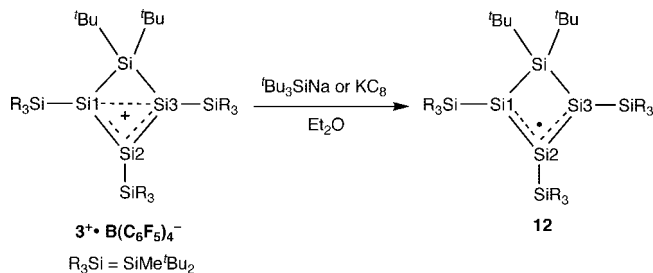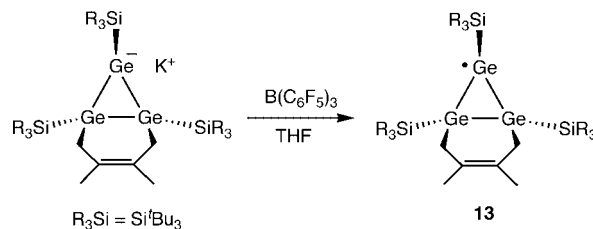
Scheme 3

$R_3Si = SiMe^tBu_2$

Scheme 4

6 (E = Ge)
7 (E = Sn)

$R_3Si = SiMe^tBu_2$
E = Ge, Sn

8[+]· $B(C_6F_5)_4^-$ (E = Ge)
9[+]· $B(C_6F_5)_4^-$ (E = Sn)

Scheme 5

11

Scheme 6

3[+]· $B(C_6F_5)_4^-$

$R_3Si = SiMe^tBu_2$

12

Scheme 7

$R_3Si = Si^tBu_3$

13

of 2653 ppm, representing a record deshielding of a Sn nucleus of all the currently known stannylium ions.[17b] This value by far exceeded the value expected from the ^{29}Si-^{119}Sn empirical correlation (1500–2000 ppm)[18] and another estimate calculated for the free trialkylstannylium ion ($\sim$1000 ppm);[19] however, it agreed reasonably with the value of 2841 ppm calculated for the model $(H_3Si)_3Sn^+$ at the B3LYP/6-311G(d) level.[17b] One should note that the extreme deshielding of the persilyl-substituted stannylium ion, in comparison to those of trialkyl-substituted species, is definitely due to the well-known effect of paramagnetic contributions, defining the total deshielding of the Sn nucleus, the magnitude of which is inversely proportional to the energy difference between the frontier orbitals HOMO (Sn–Si σ-orbital) and LUMO (Sn $5p_Z$ orbital).[20] In persilyl-substituted stannylium (as well as silylium and germylium) ions, the energy level of the Sn–Si σ-orbitals is markedly elevated, thus resulting in a decrease of the HOMO–LUMO energy gap and, consequently, in the overall strong deshielding contribution to the chemical shift of the heteroatom E cationic center. A similar oxidation of the stable silyl radical $(^tBu_2MeSi)_3Si$· **10** with Ph_3C^+·$B(C_6F_5)_4^-$ in toluene produced a transient silylium ion $[(^tBu_2MeSi)_3Si^+]$, which isomerized to $[\{Me(^tBu_2-MeSi)_2Si\}^tBu_2Si^+]$ through a 1,2-methyl migration from the peripheral silicon to the central cationic silicon atom.[21]

3. Radicals of the Heavy Group 14 Elements

Neutral Cyclic Radicals. The very first radical of this type, **11**, the germanium version of the cyclopropenyl radical, was synthesized by Power's group by the reduction of chlorogermylene :Ge(Cl)(2,6-Mes$_2$-C$_6$H$_3$) with KC$_8$ in THF in 1997 (Scheme 5).[22] The solid state structure of **11** features an odd electron on one of the Ge atoms and a double bond between the other two Ge atoms. The solution structure of **11** was deduced on the basis of its EPR spectrum [$g = 2.0069$, hfcc $a(^{73}Ge) = 1.6$ mT]: the small $a(^{73}Ge)$ value is indicative of the predominantly p
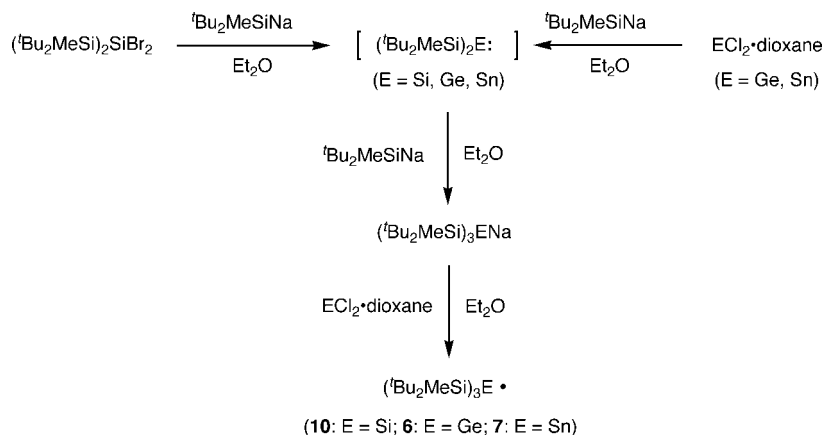
character of the SOMO, implying sp^2 hybridization of the Ge radical centers and their planarity.

The silicon version of the cyclobutenyl radical, cyclotetrasilenyl radical **12**, was prepared by Sekiguchi's group by the one-electron reduction of the cationic precursor **3**[+]·$B(C_6F_5)_4^-$ (section 2) with either $^tBu_3SiNa$ or KC$_8$ in Et$_2$O (Scheme 6).[23]

The unpaired electron in **12** was delocalized over the three Si atoms of the Si$_4$ ring (allylic-type radical), as evidenced from its crystal structure: a nearly planar four-membered ring, Si1–Si2 and Si2–Si3 bonds intermediate between the typical Si–Si and Si=Si bonds. The EPR characteristics of **12** [$g = 2.0058$, hfcc values $a(^{29}Si) = 1.55$, 3.74, and 4.07 mT], in particular the small values of $a(^{29}Si)$, are consistent with the planarity of radical **12** in solution.[23]

An interesting bicyclic Ge-centered radical, 1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl **13**, was recently synthesized by Sekiguchi and co-workers by the one-electron oxidation of the bicyclic anion with $B(C_6F_5)_3$ in THF

Scheme 8

$$(^{t}Bu_2MeSi)_2SiBr_2 \xrightarrow[Et_2O]{^{t}Bu_2MeSiNa} [\,(^{t}Bu_2MeSi)_2E:\,] \xleftarrow[Et_2O]{^{t}Bu_2MeSiNa} ECl_2\cdot dioxane$$

(E = Si, Ge, Sn)   (E = Ge, Sn)

$^{t}Bu_2MeSiNa \Big|\, Et_2O$

$(^{t}Bu_2MeSi)_3ENa$

$ECl_2\cdot dioxane \Big|\, Et_2O$

$(^{t}Bu_2MeSi)_3E\,\cdot$

(**10**: E = Si; **6**: E = Ge; **7**: E = Sn)

(Scheme 7).[24] In contrast to the delocalized radicals **11** and **12**, the unpaired electron in **13** was specifically accommodated on the Ge atom featuring trigonal-planar geometry.

Neutral Acyclic Radicals. The simple tricoordinate radicals $R_3E\cdot$ (E = Si, Ge, Sn, and Pb), lacking the stabilizing but highly perturbing effects of the cyclic π-delocalization, represent the most desired challenge among the stable radicals of group 14.

The major breakthrough in the development of such derivatives was accomplished only several years ago by Sekiguchi and co-workers, who reported the synthesis of a series of stable radicals of the type $(^{t}Bu_2MeSi)_3E\cdot$ (E = Si, Ge, and Sn).[25] All these radicals, **10** (E = Si),[25a] **6** (E = Ge),[25a] and **7** (E = Sn),[25b] kinetically and thermodynamically stabilized by the bulky electropositive silyl substituents, were uniformly prepared by very simple synthetic procedures: oxidation of the intermediary anionic derivatives $(^{t}Bu_2MeSi)_3ENa$ (E = Si, Ge, and Sn) with $GeCl_2\cdot diox$[25a] or $SnCl_2\cdot diox$[25b] in Et_2O (Scheme 8 and Figure 2).

All the radicals, **6**, **7**, and **10**, featured perfectly trigonal-planar geometries, implying sp^2 hybridization of the central element (Si, Ge, or Sn) and p character of the SOMO.[25] Such a spatial arrangement of the $^{t}Bu_2MeSi$ substituents promotes the hyperconjugative stabilization of the unpaired electron over the antibonding σ^* orbitals of the Si–C(^{t}Bu) bonds. The solution structures of radicals **6**, **7**, and **10** were deduced fro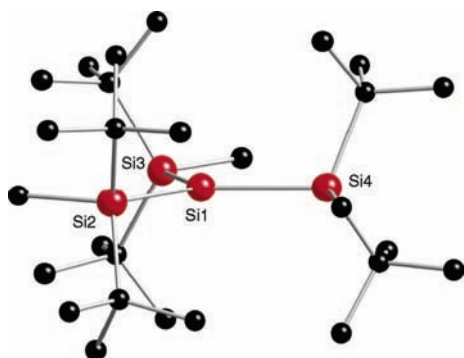m their EPR spectra: **10** [g = 2.0056, $a(^{29}Si)$ = 5.80 (α-Si) and 0.79 mT (β-Si)],[25a] **6** [g = 2.0229, $a(^{73}Ge)$ = 2.00 mT],[25a] and **7** [g = 2.0482, $a(^{119,117}Sn)$ = 32.9 mT][25b] (Figure 3). The very small values for the hfcc definitely are evidence of the p character of the SOMO of these radicals, as well as their planarity in solution; that is, **6**, **7**, and **10** truly belong to the class of π-radicals,[25] which is in marked contrast to the highly pyramidalized simple alkyl and aryl σ-radicals.[5c–e]

Charged Anion Radicals. The two classes of anion radical species will be discussed below: anion radicals of heavy alkenes $R_2E=ER_2$ and anion radicals of the heavy alkynes $RE\equiv ER$ (E = Si or Sn), the isolation and structural characterization of which were accomplished only very recently.

The first stable disilene anion radical derivative **14**$^{\bullet-}\cdot$[**Li$^+$(thf)$_4$**] was synthesized by the direct reduction of the very sterically crowded disilene $(^{t}Bu_2MeSi)_2$-Si=Si(SiMe^{t}Bu$_2$)$_2$ with $^{t}BuLi$ in THF (Scheme 9).[26] The central Si–Si bond of the starting disilene became highly

FIGURE 3. EPR spectrum of silyl radical $(^{t}Bu_2MeSi)_3Si\cdot$ **10**.

g = 2.0056

$a(\alpha^{-29}Si)$ = 5.80 mT

$a(\beta^{-29}Si)$ = 0.79 mT

FIGURE 2. Crystal structure of silyl radical $(^{t}Bu_2MeSi)_3Si\cdot$ **10** (Crystal Maker view, hydrogen atoms are not shown).

Scheme 9

$R_3Si = SiMe^{t}Bu_2$

14$^{\bullet-}\cdot$ [**Li$^+$(thf)$_4$**]

Scheme 10

$R_3Si = SiMe^tBu_2$

15 $^{\bullet-}$ [K$^+$(2.2.2)cryptand)]

Scheme 11

16 $^{\bullet-}$ [K$^+$(thf)$_6$]

twisted (88°) and elongated [2.341(5) Å] upon reduction due to the decrease in bond order. One of the core Si atoms in **14**$^{\bullet-}$ (Si2) features a planar geometry, being a radical center, whereas the other core Si atom (Si1) is pyramidal, representing an anionic center. In contrast, the solution EPR characteristics of **14**$^{\bullet-}$·[Li$^+$(thf)$_4$] [g = 2.0061, a(^{29}Si) = 2.45 mT] provide evidence of delocalization of the unpaired electron over both core Si atoms (Si1 and Si2): the hfcc value of 2.45 mT of **14**$^{\bullet-}$[26] is less than half that of the structurally similar silyl radical **10** (5.80 mT).[25a]

The distannene anion radical derivative **15**$^{\bullet-}$·[K$^+$-(2.2.2)cryptand] was also synthesized by Sekiguchi and co-workers by the reduction of the distannene ($^tBu_2$MeSi)$_2$Sn=Sn(SiMe$^tBu_2$)$_2$ with potassium mirror in THF in the presence of (2.2.2)cryptand (Scheme 10).[27] Distannene anion radical **15**$^{\bullet-}$ also has a highly twisted (74°) and stretched [2.8978(3) Å] Sn–Sn bond, in which one of the Sn atoms (Sn2) is essentially planar and the other Sn atom (Sn1) is distinctly pyramidal, indicating separation of the unpaired electron and the negative charge. Such a separation was also preserved in solution, as manifested by the EPR spectrum of **15**$^{\bullet-}$·[K$^+$(2.2.2)-cryptand], showing a resonance with a g value of 2.0517 accompanied by two pairs of satellite signals with hfcc a(^{119,117}Sn) values of 34.0 (α-Sn) and 18.7 mT (β-Sn).[27] At low temperatures, **15**$^{\bullet-}$·[K$^+$(2.2.2)cryptand] forms paramagnetic triplet biradical dimers, as confirmed by the observation of the diagnostic *half-field* EPR resonance at 163.1 mT corresponding to a forbidden ΔM_S = 2 electronic transition.[27b]

The anion radical of the valence isomer of distannyne **16**$^{\bullet-}$·[K$^+$(thf)$_6$] was synthesized by Power et al.[28] by the reduction of chlorostannylene :Sn(Cl)Ar (Ar = 2,6-Tip$_2$-C$_6$H$_3$) with potassium graphite in THF (Scheme 11). The two substituents at the Sn atoms are strongly *trans*-bent, and the length of the Sn–Sn bond of 2.8123(9) Å is normal for the Sn–Sn single bond. **16**$^{\bullet-}$·[K$^+$(thf)$_6$] revealed an EPR signal (g = 2.0069), the hfcc values of which were simulated as follows: a(^{117}Sn) = 0.83 mT and a(^{119}Sn) = 0.85 mT. The small values of the hfcc were indicative of the p character of the SOMO and, hence, the π-character of **16**$^{\bullet-}$. These experimental data point to the formulation

of a resonance structure of **16**$^{\bullet-}$ in which both tin atoms bear a lone pair and the unpaired electron is accommodated over their 5p$_\pi$ orbitals.

Sekiguchi and co-workers performed a reduction of the stable disilyne [(Me$_3$Si)$_2$CH]$_2$^{i}PrSi–Si≡Si–Si^{i}Pr[CH-(SiMe$_3$)$_2$]$_2$[29] with an equivalent amount of potassium graphite in THF, which provided straightforward access to a disilyne anion radical derivative **17**$^{\bullet-}$·[K$^+$(dme)$_4$] (Scheme 12).[30] The anionic portion **17**$^{\bullet-}$, free from counter-cation interaction, revealed a *trans*-bent geometry around the central Si–Si bond, whose length of 2.1728(14) Å was indicative of its double bond character. This distance was ~5% longer than that of the disilyne precursor [2.0622(9) Å],[29] due to the evident decrease in the bond order taking place upon reduction. The EPR resonance of **17**$^{\bullet-}$·[K$^+$(dme)$_4$] was measured as a triplet [coupling with the two δ-H atoms of the ^{i}Pr group, a(^{1}H) = 0.23 mT] centered at a g of 1.99962, which is among the smallest g values known for silyl radicals. Similar to the case of the disilene anion radical **14**$^{\bullet-}$,[26] the unpaired electron in **17**$^{\bullet-}$ was also delocalized over both central Si atoms, as manifested in the hfcc a(^{29}Si) values being equal to 3.92 (α-Si) and 2.24 mT (β-Si), of which the former was smaller than that of silyl radical **10** (5.80 mT).[30]
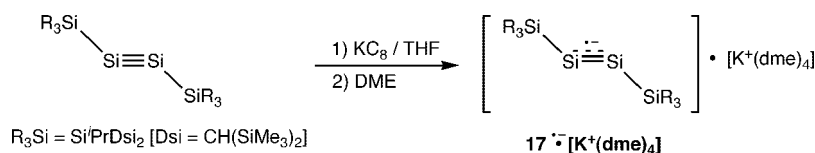
4. Anions of the Heavy Group 14 Elements

There have been many important accomplishments in this field; in this Account, we will deal only with the most recent of them, published mainly since 2000.
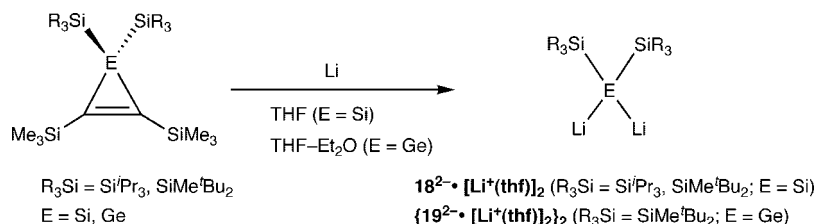
Acyclic sp³ Anions. The preparation of 1,1-dianionic compounds of the type R$_2$EM$_2$ (E = heavy group 14 element, M = alkali metal), the heavy congeners of the synthetically very useful dilithiomethane derivatives R$_2$CLi$_2$,[31] was one of the very attractive targets for organometallic chemists. However, the experimental realization of this problem was achieved only several years ago, when Sekiguchi and co-workers published the synthesis of the first stable 1,1-dilithiosilane and 1,1-dilithiogermane derivatives (R$_3$Si)$_2$ELi$_2$ **18**$^{2-}$·[Li$^+$(thf)]$_2$[32a] (R$_3$Si = $^tBu_2$MeSi or ^{i}Pr$_3$Si; E = Si) and {**19**$^{2-}$·[Li$^+$(thf)]$_2$}$_2$ (R$_3$Si = $^tBu_2$MeSi; E = Ge),[32b] prepared by the reduction of silirene and germirene derivatives, respectively, with metallic lithium in THF (Scheme 13).

The central anionic Si atom in **18**$^{2-}$·[Li$^+$(thf)]$_2$ (R$_3$Si = ^{i}Pr$_3$Si) is sp³ hybridized, being directly bonded to the two Li atoms in the crystalline state. The Si–Li bonding was also maintained in the solution of **18**$^{2-}$·[Li$^+$(thf)]$_2$, as manifested in its ^{29}Si NMR spectrum displaying the resonance of the anionic Si atom at −292 ppm as a quintet due to coupling with the two ^{6}Li nuclei (I = 1) with a
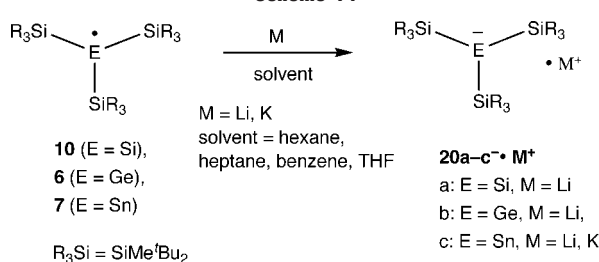
Scheme 12

R_3Si—Si≡Si—SiR_3 $\xrightarrow[\text{2) DME}]{\text{1) KC}_8\text{ / THF}}$ [R_3Si—Si≡Si—SiR_3]·− [K+(dme)_4]

R_3Si = Si^iPrDsi_2 [Dsi = CH(SiMe_3)_2]

17·− [K+(dme)_4]

Scheme 13

(cyclic structure with R_3Si, SiR_3, E, Me_3Si, SiMe_3) $\xrightarrow[\text{THF–Et}_2\text{O (E = Ge)}]{\text{Li, THF (E = Si)}}$ (structure with R_3Si, SiR_3, E, Li, Li)

R_3Si = Si^iPr_3, SiMe^tBu_2
E = Si, Ge

18^{2−}·[Li+(thf)]_2 (R_3Si = Si^iPr_3, SiMe^tBu_2; E = Si)
{**19**^{2−}·[Li+(thf)]_2}_2 (R_3Si = SiMe^tBu_2; E = Ge)

to that in **21**^−·[Li+(dme)_2]: 2.2092(7) and 2.192(1) Å, respectively. The anionic sp^2 silicon atom in **22**^−·[Li+(thf)_3] was much more deshielded (277.6 ppm) than the other doubly bonded silicon atom (63.1 ppm).

Reduction of the disilene (^tBu_2MeSi)_2Si=Si(SiMe^tBu_2)_2 with alkali metal naphthalenides also produced disilenide derivatives of the type (^tBu_2MeSi)_2Si=Si(SiMe^tBu_2)M **23a–c**^−·M+ (M = Li for **23a**, M = Na for **23b**, and M = K for **23c**).[36] Both sp^2 silicon atoms in **23a**^−·[Li+(thf)_2] revealed planar geometries around them with the length of the Si=Si bond being 2.1983(18) Å. As in the case described above, the anionic sp^2 silicon atoms resonate
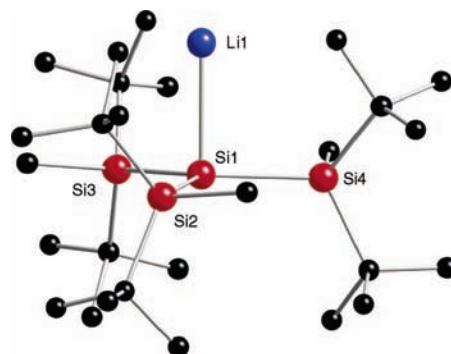
Scheme 14

(structure with R_3Si, SiR_3, E, SiR_3, radical) $\xrightarrow[\text{solvent}]{\text{M}}$ (structure with R_3Si, SiR_3, E, SiR_3, anion) ·M+

10 (E = Si),
6 (E = Ge),
7 (E = Sn)

R_3Si = SiMe^tBu_2

M = Li, K
solvent = hexane,
heptane, benzene, THF

20a–c^−·M+
a: E = Si, M = Li
b: E = Ge, M = Li,
c: E = Sn, M = Li, K

coupling constant of 15 Hz.[32a] In contrast to monomeric 1,1-dilithiosilane **18**^{2−}·[Li+(thf)]_2, 1,1-dilithiogermane derivative {**19**^{2−}·[Li+(thf)]_2}_2 was represented by a dimeric structure in the crystalline form.[32b]

A family of tricoordinate persilyl anions (^tBu_2-MeSi)_3E^−·M+ (E = Si, Ge, or Sn; M = Li or K), **20a–c**^−·M+, was recently synthesized by Sekiguchi and co-workers by a straightforward one-electron reduction of the stable radicals (^tBu_2MeSi)_3E· **6**, **7**, and **10** (section 3) with alkali metals (Scheme 14).[33] The structural diversity of **20a–c**^−·M+ depends on the polarity of the solvent, resulting in a variety of structural modifications: monomeric or dimeric, solvated or nonsolvated, covalently bonded or ionic. Thus, in hexane silyl- and germyllithium derivatives **20a,b**^−·Li+ (E = Si for **20a** and E = Ge for **20b**) adopt nonsolvated monomeric structures, in which the geometry around the central anionic atom E is almost planar due to the great steric bulk of the ^tBu_2MeSi substituents and an intramolecular Li–CH_3 (^tBu groups) agostic inter-action[33a] (Figure 4 and Figure 5).

Acyclic sp^2 Anions. The first representative of such species, Tip_2Si=Si(Tip)Li (Tip = 2,4,6-triisopropylphenyl) **21**^−·[Li+(dme)_2], was prepared by Scheschkewitz by the reduction of Tip_2SiCl_2 with metallic Li.[34] In the solid state, **21**^−·[Li+(dme)_2] exhibited a 2.192(1) Å Si=Si bond, which was longer than that in neutral Tip_2Si=SiTip_2 (2.144 Å). The doubly bonded Si atoms in **21**^−·[Li+(dme)_2] are deshielded compared with those of Tip_2Si=SiTip_2: 94.5 and 100.5 ppm versus 53.4 ppm.

In the same year, Sekiguchi's group synthesized an-other disilenyllithium derivative (^tBu_2MeSi)_2Si=Si(Mes)Li **22**^−·[Li+(thf)_3] by the reduction of tetrasila-1,3-butadiene (^tBu_2MeSi)_2Si=Si(Mes)–Si(Mes)=Si(SiMe^tBu_2)_2 with ^tBu-Li.[35] The Si=Si bond length in **22**^−·[Li+(thf)_3] was close

FIGURE 4. Crystal structure of silyl anion derivative (^tBu_2MeSi)_3SiLi **20a**^−·Li+ (Crystal Maker view, hydrogen atoms are not shown).
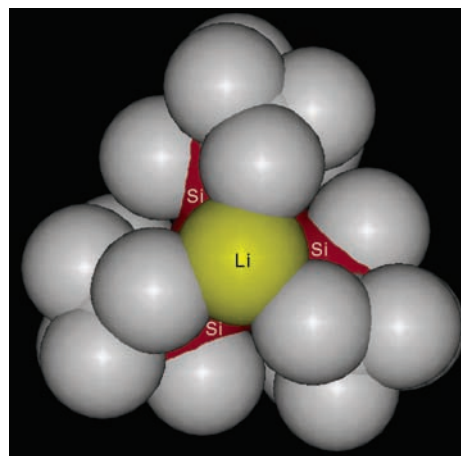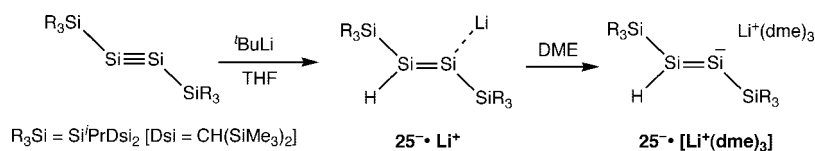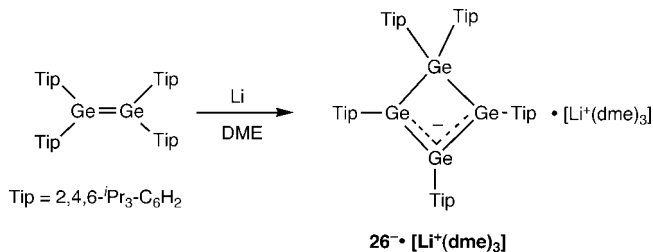

FIGURE 5. Space filling model of (^tBu_2MeSi)_3SiLi **20a**^−·Li+ (hydrogen atoms are not shown; gray for C, yellow for Li, and red for Si).
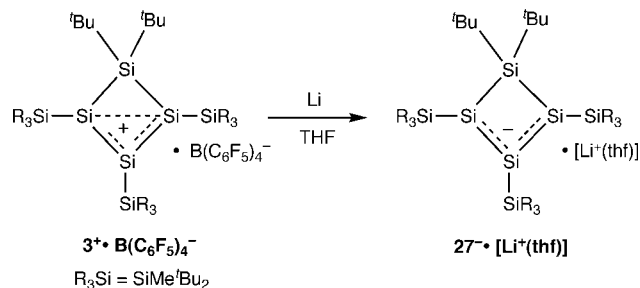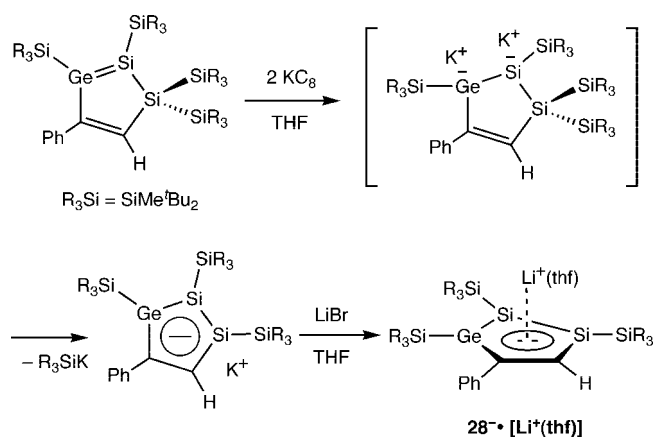
Scheme 15

$R_3Si = Si^iPrDsi_2$ [Dsi = CH(SiMe_3)_2]

Scheme 16

Tip = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$

26⁻·[Li⁺(dme)₃]

Scheme 17

3⁺·B(C₆F₅)₄⁻

R₃Si = SiMe^{t}Bu₂

27⁻·[Li⁺(thf)]

Scheme 18

R₃Si = SiMe^{t}Bu₂

28⁻·[Li⁺(thf)]

at a diagnostic very low field: 328.4 (**23a⁻**), 325.6 (**23b⁻**), and 323.1 ppm (**23c⁻**).

Power et al.[37] recently reported the reduction of the (aryl)chlorogermylene and (aryl)chlorostannylene (2,6-Tip₂-C₆H₃)(Cl)E**:** (E = Ge and Sn) with alkali metals (Na and K), resulting in the formation of the doubly reduced species (2,6-Tip₂-C₆H₃)E=E(2,6-Tip₂-C₆H₃)²⁻·2M⁺ **24a,b²⁻·2M⁺** (E = Ge and M = Na for **24a**, and E = Sn and M = K for **24b**), in which the two elements E are formally doubly bonded. Accordingly, the Ge–Ge distance of 2.3943(13) Å in **24a²⁻·2Na⁺** is comparable to those of typical Ge=Ge bonds, whereas the Sn–Sn distance of 2.7663(9) Å in **24b²⁻·2K⁺** is in the range of those of normal Sn=Sn bonds.

The reduction of the above-mentioned disilyne [(Me₃Si)₂CH]₂^{i}PrSi–Si≡Si–Si^{i}Pr[CH(SiMe₃)₂]₂[29] with ^{t}BuLi in THF resulted in the formation of disilenyllithium **25⁻·Li⁺** as a result of the formal addition of LiH across the Si≡Si bond through the initial single-electron transfer step (Scheme 15).[30] The Si=Si bond in **25⁻·[Li⁺(dme)₃]** of 2.2034(9) Å was longer than those of the starting disilyne [2.0622(9) Å] and even that of the disilyne anion radical **17•⁻·[K⁺(dme)₄]** [2.1728(14) Å]. Both sp² Si atoms in **25⁻·Li⁺** were observed as expected in the low-field region: 165.0 (Si-Li) and 124.7 ppm (Si-H).

Cyclic and Polycyclic Anions. The remarkable cyclotetragermanide ion **26⁻·[Li⁺(dme)₃]** was prepared by Weidenbruch et al.[38] by the reduction of the tetraaryldigermene Tip₂Ge=GeTip₂ (Tip = 2,4,6-triisopropylphenyl) with metallic lithium (Scheme 16). The negative charge in **26⁻** is delocalized over the allylic Ge₃ fragment of the planar four-membered ring with two sharply different Ge–Ge bonds of 2.5116(6) and 2.3679(6) Å.

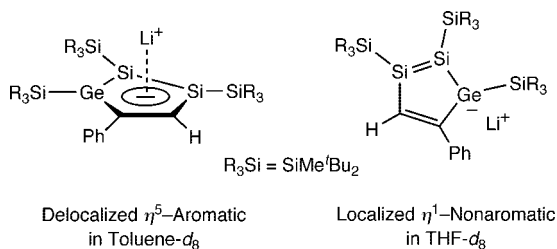A silicon version of the above compound, cyclotetrasilenide ion **27⁻·[Li⁺(thf)]**, was synthesized by Sekiguchi and co-workers by the two-electron reduction of cyclotetrasilenylium ion **3⁺·B(C₆F₅)₄⁻** (section 2) with Li (Scheme 17).[39] **27⁻·[Li⁺(thf)]** also exhibited an allylic ion-type structure both in the solid state and in solution: tricoordination of the Li⁺ ion to the three skeletal Si atoms with an extremely deshielded central Si atom of the Si₃ unit (273.0 ppm).

The heavy analogue of the cyclopentadienide ion, lithium 1,2-disila-3-germacyclopenta-2,4-dienide **28⁻·[Li⁺(thf)]** was prepared by the reduction of disilagermacyclopentadiene with potassium graphite followed by exchange of the countercation from K⁺ to Li⁺ by treatment with LiBr (Scheme 18).[40]
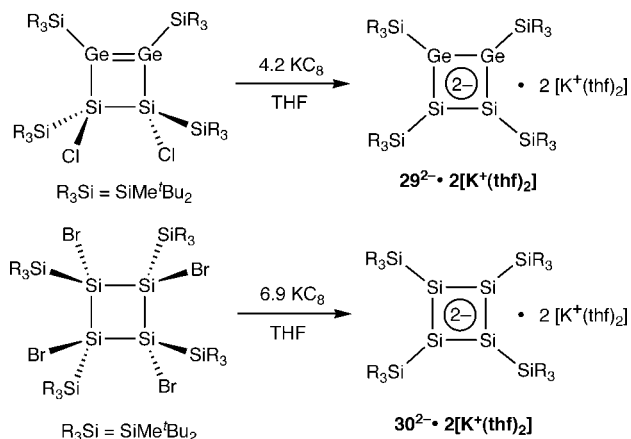
Despite the incorporation of three heavy group 14 elements into the cyclopentadiene ring, **28⁻·[Li⁺(thf)]** still features a stabilizing aromatic delocalization, as evidenced by its crystal structure characteristics. The nucleus-independent chemical shift [NICS(1)] value for the model of **28⁻·[Li⁺(thf)]**, computed at 1 Å above the ring center, was negative (−12.0), indicating the aromatic ring current effects. The aromaticity of **28⁻·[Li⁺(thf)]** is preserved in nonpolar solvents (toluene and benzene), as manifested by the diagnostic high-field shift of the ⁷Li NMR resonance of −5.4 ppm.[40] However, in polar THF **28⁻·[Li⁺(thf)]** is unable to benefit from the aromatic delocalization any further; instead, NMR spectral data point to the preferential localization of the negative charge on the Ge atom. That is, in THF, the coordination mode was dramatically changed from the delocalized η^5 to a localized η^1 coordination (Scheme 19).

Other examples of charged 6π-electron ring systems, the heavy analogues of the cyclobutadiene dianion, disiladigermacyclobutadiene dianion **29²⁻·2[K⁺(thf)₂]**, and

Scheme 19

Delocalized η^5–Aromatic
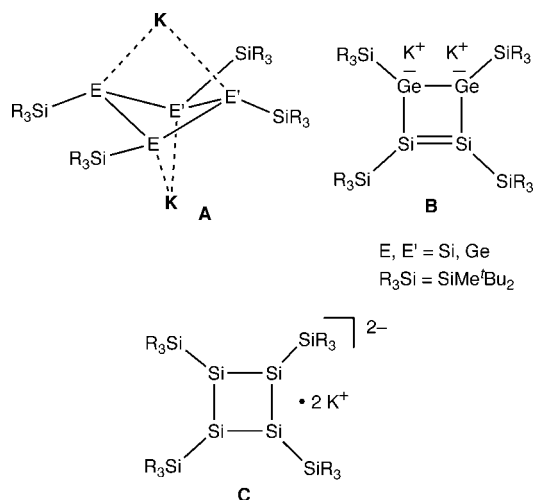in Toluene-d_8

Localized η^1–Nonaromatic
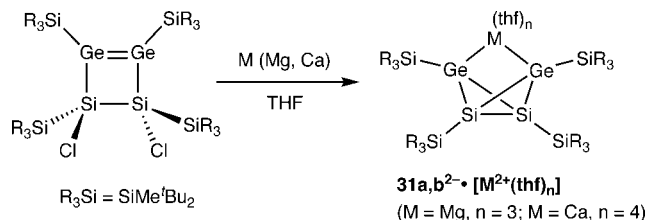in THF-d_8

Scheme 20

Scheme 21

tetrasilacyclobutadiene dianion $30^{2-} \cdot 2[K^+(thf)_2]$, were synthesized by the reductive dehalogenation of the dichlorodisiladigermetene and tetrabromotetrasiletane precursors with KC_8 in THF (Scheme 20).[41] In contrast to the aromatic heavy cyclopentadienide $28^- \cdot [Li^+(thf)]$, both $29^{2-} \cdot 2[K^+(thf)_2]$ and $30^{2-} \cdot 2[K^+(thf)_2]$ were classified as nonaromatic compounds on the basis of their spectral and crystal structure characteristics. Thus, the four-membered rings of these compounds were puckered with both potassium cations being alternatively dihaptocoordinated above and below the ring at the 1,3- and 2,4-positions (Scheme 21, **A**). Moreover, the skeletal Si–Si bonds in $30^{2-} \cdot 2[K^+(thf)_2]$ were not equivalent to each other. The magnetic criterion of aromaticity is also not satisfied for $29^{2-} \cdot 2[K^+(thf)_2]$ and $30^{2-} \cdot 2[K^+(thf)_2]$: NICS(1) values for the model compounds were calculated as 4.3 and 6.1,

Scheme 22

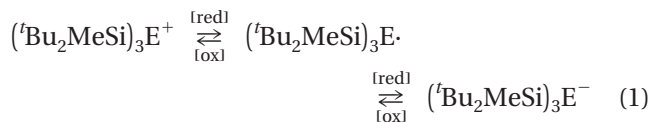**31a,b^{2-}• [M^{2+}(thf)$_n$]**
(M = Mg, n = 3; M = Ca, n = 4)

respectively. In solution, $29^{2-} \cdot 2[K^+(thf)_2]$ acquires the properties of the localized cyclobutene-1,2-diide, featuring the Si=Si bond and both negative charges, localized on the more electronegative Ge atoms (Scheme 21, **B**).[41] In contrast, the degree of delocalization of the two negative charges in $30^{2-} \cdot 2[K^+(thf)_2]$ is more important than that in $29^{2-} \cdot 2[K^+(thf)_2]$, because the electronegativity difference (Si vs Ge) favors electron localization[41] (Scheme 21, **C**).

Surprisingly, when the same dichlorodisiladigermetene was reduced with alkaline earth metals (Mg and Ca) instead of alkali metals, totally different products were isolated: Mg or Ca derivatives of 1,3-disila-2,4-digermabicyclo[1.1.0]butane-2,4-diide $31a,b^{2-} \cdot [M^{2+}(thf)_n]$ (M = Mg and n = 3 for **31a**, and M = Ca and n = 4 for **31b**) (Scheme 22).[42]

5. Conclusion and Outlook

Being considered just a few decades ago only as fleeting reactive intermediates, silyl, germyl, and stannyl cations, radicals, and anions now constitute an important class of real, observable, and in many cases isolable and fully characterizable compounds. The interplay and interconversion among the heavy cations, radicals, and anions is very important for the future development of synthetic organometallic chemistry. A clear example of such an interplay is represented by the reversible oxidation–reduction transformations between the persilyl germyl and stannyl cations, radicals, and anions:

$$({}^tBu_2MeSi)_3E^+ \underset{[ox]}{\overset{[red]}{\rightleftarrows}} ({}^tBu_2MeSi)_3E\cdot$$
$$\underset{[ox]}{\overset{[red]}{\rightleftarrows}} ({}^tBu_2MeSi)_3E^- \quad (1)$$

(see section 2 for cations,[17] section 3 for radicals,[25] and section 4 for anions[33]).

However, despite the recent important progress in this field, the chemistry of the stable cations, radicals, and anions of heavy group 14 elements is far from complete, and there is much that remains to be done. Looking to the future, one should first of all expect further developments in the synthesis of such compounds, based on sophisticated experimental techniques and advanced theory of bonding and reactivity of organometallic compounds. Apart from the synthesis itself, the widespread utilization of such derivatives in organometallic chemistry, just like that of the extremely synthetically useful carbocations, free radicals, and carbanions in organic chemistry, is highly desirable.

References

(1) Olah, G. A. 100 Years of Carbocations and Their Significance in Chemistry. *J. Org. Chem.* **2001**, *66*, 5493–5501, and references therein.

(2) Gomberg, M. An Instance of Trivalent Carbon: Triphenylmethyl. *J. Am. Chem. Soc.* **1900**, *22*, 757–771.

(3) Grignard, V. Mixed Organomagnesium Combinations and Their Application in Acid, Alcohol, and Hydrocarbon Synthesis. *Ann. Chim.* **1901**, *24*, 433–490.

(4) (a) McClelland, R. A. Carbocations. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: Hoboken, 2004; Chapter 1, pp 3–40. (b) Newcomb, M. Radicals. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: New York, 2004; Chapter 4, pp 121–163. (c) Gronert, S. Carbanions. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: Hoboken, 2004; Chapter 3, pp 69–119.

(5) Recent reviews. Heavy group 14 cations: (a) Müller, T. Cations of Group 14 Organometallics. *Adv. Organomet. Chem.* **2005**, *53*, 155–215. (b) Lee, V. Ya.; Sekiguchi, A. Silicon-, Germanium-, and Tin-Centered Cations, Radicals, and Anions. In Reviews of Reactive Intermediate Chemistry; Platz, M. S., Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 2007; Chapter 2, pp 47–120. Heavy group 14 radicals: (c) Power, P. P. Persistent and Stable Radicals of the Heavier Main Group Elements and Related Species. *Chem. Rev.* **2003**, *103*, 789–809. (d) Lee, V. Ya.; Sekiguchi, A. Si-, Ge-, and Sn-Centered Free Radicals: From Phantom Species to Grams-Order-Scale Materials. *Eur. J. Inorg. Chem.* **2005**, 1209–1222. (e) See ref 5b. Heavy group 14 anions: (f) Tamao, K.; Kawachi, A. Silyl Anions. *Adv. Organomet. Chem.* **1995**, *38*, 1–58. (g) Lickiss, P. D.; Smith, C. M. Silicon Derivatives of the Metals of Groups 1 and 2. *Coord. Chem. Rev.* **1995**, *145*, 75–124. (h) Belzner, J.; Dehnert, U. Alkaline and Alkaline Earth Silyl Compounds: Preparation and Structure. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 14, pp 779–825. (i) Sekiguchi, A.; Lee, V. Ya.; Nanjo, M. Lithiosilanes and Their Application to the Synthesis of Polysilane Dendrimers. *Coord. Chem. Rev.* **2000**, *210*, 11–45. (j) See ref 5b.

(6) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. Crystal Structure of a Silyl Cation with No Coordination to Anion and Distant Coordination to Solvent. *Science* **1993**, *260*, 1917–1918. (b) Lambert, J. B.; Zhang, S. Triethylsilyl Cations (Response). *Science* **1994**, *263*, 984–985.

(7) (a) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. Closely Approaching the Silylium Ion (R_3Si^+). *Science* **1993**, *262*, 402–404. (b) Reed, C. A.; Xie, Z. Triethylsilyl Cations (Response). *Science* **1994**, *263*, 985–986. See also: (c) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. The Silylium Ion (R_3Si^+) Problem: Effect of Alkyl Substituents R. *Organometallics* **1995**, *14*, 3933–3941. (d) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. Approaching the Silylium (R_3Si^+) Ion: Trends with Hexahalo (Cl, Br, I) Carboranes as Counterions. *J. Am. Chem. Soc.* **1996**, *118*, 2922–2928.

(8) Reed, C. A. The Silylium Ion Problem, R_3Si^+. Bridging Organic and Inorganic Chemistry. *Acc. Chem. Res.* **1998**, *31*, 325–332.

(9) (a) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. A Free Cyclotrigermenium Cation with a 2π-Electron System. *Science* **1997**, *275*, 60–61. See also: (b) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. Synthesis and Structure of Cyclotrigermenium Salt of the Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate Anion. A Stable Free Germyl Cation in the Condensed Phase. *Chem. Lett.* **1998**, 1045–1046. (c) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Ishida, Y. Synthesis and Structure of Cyclotrigermenium Salts of Tetrakis{3,5-bis-(trifluoromethyl)phenyl}borate, Tetrakis(pentafluorophenyl)borate and Tetrakis{4-[tert-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}-borate: A Stable Free Germyl Cation in the Condensed Phase. *Eur. J. Inorg. Chem.* **2000**, 1155–1159.

(10) (a) Jemmis, E. D.; Srinivas, G. N.; Leszczynski, J.; Kapp, J.; Korkin, A. A.; Schleyer, P. v. R. Group 14 Analogs of the Cyclopropenium Ion: Do They Favor Classical Aromatic Structures? *J. Am. Chem. Soc.* **1995**, *117*, 11361–11362. (b) Srinivas, G. N.; Jemmis, E. D.; Korkin, A. A.; Schleyer, P. v. R. Ab Initio MO Study of Diverse $Si_3H_3^+$ Isomers. *J. Phys. Chem. A* **1999**, *103*, 11034–11039.

(11) Ichinohe, M.; Igarashi, M.; Sanuki, K.; Sekiguchi, A. Cyclotrisilenylium Ion: The Persilaaromatic Compound. *J. Am. Chem. Soc.* **2005**, *127*, 9978–9979.

(12) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. The Homocyclotrisilenylium Ion: A Free Silyl Cation in the Condensed Phase. *J. Am. Chem. Soc.* **2000**, *122*, 11250–11251.

(13) Lambert, J. B.; Zhao, Y. The Trimesitylsilylium Ion. *Angew. Chem., Int. Ed.* **1997**, *36*, 400–401.

(14) Müller, T.; Zhao, Y.; Lambert, J. B. Computational Evidence for a Free Silylium Ion. *Organometallics* **1998**, *17*, 278–280.

(15) Kim, K.-C.; Reed, C. A.; Elliott, D. W.; Mueller, L. J.; Tham, F.; Lin, L.; Lambert, J. B. Crystallographic Evidence for a Free Silylium Ion. *Science* **2002**, *297*, 825–827.

(16) Lambert, J. B.; Lin, L.; Keinan, S.; Müller, T. A Free, Tricoordinate Stannylium Cation. *J. Am. Chem. Soc.* **2003**, *125*, 6022–6023.

(17) (a) Sekiguchi, A.; Fukawa, T.; Lee, V. Ya.; Nakamoto, M.; Ichinohe, M. [($^tBu_2MeSi)_3Ge^+$: An Isolable Free Germyl Cation Lacking Conjugation to π Bonds. *Angew. Chem., Int. Ed.* **2003**, *42*, 1143–1145. (b) Sekiguchi, A.; Fukawa, T.; Lee, V. Ya.; Nakamoto, M. Tin-Centered Radical and Cation: Stable and Free. *J. Am. Chem. Soc.* **2003**, *125*, 9250–9251.

(18) Arshadi, M.; Johnels, D.; Edlund, U. On the Existence of Trivalent Stannyl Cations in Solution. *Chem. Commun.* **1996**, 1279–1280.

(19) Cremer, D.; Olsson, L.; Reichel, F.; Kraka, E. Calculation of NMR Chemical Shifts: The Third Dimension of Quantum Chemistry. *Isr. J. Chem.* **1994**, *33*, 369–385.

(20) Ottosson, C.-H.; Cremer, D. Nature of the $Si(SiMe_3)_3^+$ Cation in Aromatic Solvents. *Organometallics* **1996**, *15*, 5495–5501.

(21) Nakamoto, M.; Fukawa, T.; Sekiguchi, A. Silylium Ion to Silylium Ion Rearrangement Caused by 1,3-Methyl Migration. *Chem. Lett.* **2004**, *33*, 38–39.

(22) Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. Reduction of $Ge(Cl)C_6H_3Mes_2$-2,6 to Give the Cyclotrigermenyl Radical (Ge-$C_6H_3Mes_2$-2,6)$^{\bullet}$ and the Trigermenyl Anion Salt K(Ge$C_6H_3Mes_2$-2,6)$_3$. *Chem. Commun.* **1997**, 1595–1596.

(23) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. Cyclotetrasilenyl: The First Isolable Silyl Radical. *J. Am. Chem. Soc.* **2001**, *123*, 12436–12437.

(24) Ishida, Y.; Sekiguchi, A.; Kobayashi, K.; Nagase, S. 1,6,7-Trigermabicyclo[4.1.0]hept-3-en-7-yl: The Isolable Bicyclic Germyl Radical. *Organometallics* **2004**, *23*, 4891–4896.

(25) (a) Sekiguchi, A.; Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Ichinohe, M. Isolable Silyl and Germyl Radicals Lacking Conjugation with π-Bonds: Synthesis, Characterization, and Reactivity. *J. Am. Chem. Soc.* **2002**, *124*, 9865–9869. (b) See ref 17b.

(26) Sekiguchi, A.; Inoue, S.; Ichinohe, M.; Arai, Y. Isolable Anion Radical of Blue Disilene ($^tBu_2MeSi)_2Si=Si(SiMe^tBu_2)_2$ Formed upon One-Electron Reduction: Synthesis and Characterization. *J. Am. Chem. Soc.* **2004**, *126*, 9626–9629.

(27) (a) Fukawa, T.; Lee, V. Ya.; Nakamoto, M.; Sekiguchi, A. Tetrakis(di-tert-butylmethylsilyl)distannene and Its Anion Radical. *J. Am. Chem. Soc.* **2004**, *126*, 11758–11759. (b) Lee, V. Ya.; Fukawa, T.; Nakamoto, M.; Sekiguchi, A.; Tumanskii, B. L.; Karni, M.; Apeloig, Y. ($^tBu_2MeSi)_2Sn=Sn(SiMe^tBu_2)_2$: A Distannene with a $>Sn=Sn<$ Double Bond That Is Stable Both in the Solid State and in Solution. *J. Am. Chem. Soc.* **2006**, *128*, 11643–11651.

(28) (a) Olmstead, M. M.; Simons, R. S.; Power, P. P. Synthesis and Characterization of [$Sn_2\{C_6H_3$-2,6(2,4,6-i-$Pr_3C_6H_2)_2\}_2]^{\bullet-}$: A Singly Reduced Valence Isomer of a "Distannyne". *J. Am. Chem. Soc.* **1997**, *119*, 11705–11706. (b) Pu, L.; Haubrich, S. T.; Power, P. P. Synthesis and Structural Characterization of (THF)$_3$Na{(SnC_6H_3-2,6-Trip$_2)_2$} (Trip = C_6H_2-2,4,6-i-Pr_3): Effects of Cation–Anion Association on Sn-Sn Multiple Bonding. *J. Organomet. Chem.* **1999**, *582*, 100–102.

(29) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. A Stable Compound Containing a Silicon-Silicon Triple Bond. *Science* **2004**, *305*, 1755–1757.

(30) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. An Isolable Disilyne Anion Radical and a New Route to the Disilenide Ion upon Reduction of a Disilyne. *J. Am. Chem. Soc.* **2007**, *129*, 26–27.

(31) Latest review: Müller, J. F. K. Chiral Dilithiomethane Derivatives: Structure Determination and Application in Stereoselective Reactions. *Eur. J. Inorg. Chem.* **2000**, 789–799.

(32) (a) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. An Unexpected Reaction of Silacyclopropene To Form an Organodilithiosilane: Isolation and Characterization of a 1,1-Dilithiosilane Derivative. *J. Am. Chem. Soc.* **1999**, *121*, 10231–10232. (b) Sekiguchi, A.; Izumi, R.; Ihara, S.; Ichinohe, M.; Lee, V. Ya. The First Isolable 1,1-Dilithiogermane and Its Unusual Dimeric Structure: An Effective Reagent for the Preparation of Double-Bonded Derivatives of Group 14 Elements. *Angew. Chem., Int. Ed.* **2002**, *41*, 1598–1600.

(33) (a) Nakamoto, M.; Fukawa, T.; Lee, V. Ya.; Sekiguchi, A. A Nearly Planar Nonsolvated Monomeric Silyl- and Germyllithiums as a Result of an Intramolecular CH-Li Agostic Interaction. *J. Am. Chem.*

Soc. **2002**, *124*, 15160–15161. (b) Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Sekiguchi, A. Structural Diversity of the Tris(di-tert-butyl-methylsilyl)stannyl Anion: Monomeric vs Dimeric, Lithium Coordinated vs Lithium Free. *Organometallics* **2004**, *23*, 2376–2381.

(34) Scheschkewitz, D. A Silicon Analogue of Vinyllithium: Structural Characterization of a Disilenide. *Angew. Chem., Int. Ed.* **2004**, *43*, 2965–2967.

(35) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. Disilenyllithium from Tetrasila-1,3-butadiene: A Silicon Analogue of a Vinyllithium. *Organometallics* **2004**, *23*, 3088–3090.

(36) Inoue, S.; Ichinohe, M.; Sekiguchi, A. Disilenyl Anions Derived from Reduction of Tetrakis(di-tert-butylmethylsilyl)disilene with Metal Naphthalenide through a Disilene Dianion Intermediate: Synthesis and Characterization. *Chem. Lett.* **2005**, *34*, 1564–1565.

(37) Pu, L.; Senge, M. O.; Olmstead, M. M.; Power, P. P. Synthesis and Characterization of $Na_2\{Ge(C_6H_3\text{-}2,6\text{-}Trip_2)\}_2$ and $K_2\{Sn(C_6H_3\text{-}2,6\text{-}Trip_2)\}_2$ (Trip $= \text{-}C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3$): A New Class of Multiply Bonded Main Group Compounds. *J. Am. Chem. Soc.* **1998**, *120*, 12682–12683.

(38) Schäfer, H.; Saak, W.; Weidenbruch, M. Hexaaryltetragermabuta-1,3-diene: A Molecule with Conjugated Ge-Ge Double Bonds. *Angew. Chem., Int. Ed.* **2000**, *39*, 3703–3705.

(39) Matsuno, T.; Ichinohe, M.; Sekiguchi, A. Cyclotetrasilenide Ion: A Reversible Redox System of Cyclotetrasilenyl Cation, Radical, and Anion. *Angew. Chem., Int. Ed.* **2002**, *41*, 1575–1577.

(40) Lee, V. Ya.; Kato, R.; Ichinohe, M.; Sekiguchi, A. The Heavy Analogue of CpLi: Lithium 1,2-Disila-3-germacyclopentadienide, a 6π-Electron Aromatic System. *J. Am. Chem. Soc.* **2005**, *127*, 13142–13143.

(41) Lee, V. Ya.; Takanashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. Cyclobutadiene Dianions Consisting of Heavier Group 14 Elements: Synthesis and Characterization. *J. Am. Chem. Soc.* **2004**, *126*, 4758–4759.

(42) Lee, V. Ya.; Takanashi, K.; Ichinohe, M.; Sekiguchi, A. The First Bicyclo[1.1.0]butane Dianion of Heavier Group 14 Elements. *Angew. Chem., Int. Ed.* **2004**, *43*, 6703–6705.