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Heavy Analogs of Carbenium Ions: Si-, Ge-, Sn- and Pb-Centered Cations

1.1 Introduction

The classical textbook definition of the carbenium ions R_3C^+ (*carbenium* ions are tri-coordinate carbocations, while those with a coordination number of five and above are named *carbonium* ions) describes them as trivalent species with a positively charged central sp^2 -hybridized carbon atom, which features planar geometry and R–C–R bond angles close to ideal values of 120° . The unhybridized $2p_z$ -orbital on the central carbon is vacant and orthogonal to the R_3C plane: the geometry which has, for example, the simplest methylum ion CH_3^+ isoelectronic to BH_3 . Given the intrinsic electron deficiency of the carbenium ions, which have only six valence electrons in their valence shell, one would expect them to possess very high Lewis acidity and extreme electrophilicity. This is indeed the case, and in the early stages the carbenium ions were commonly considered only as short-lived fleeting reactive intermediates of classical electrophilic reactions, such as S_N1 solvolysis, electrophilic addition to alkenes, aromatic substitution, etc.: the pioneering contributions to this field were done by Meerwein (Germany), Ingold (UK) and Whitmore (USA). Accordingly, the existence of the transient (unobservable) carbenium ions was firmly supported by a number of experimental facts, including substituent effects, orientation in electrophilic reactions, solvent effects on the rates of solvolysis, rearrangements, etc. In a limited number of cases carbenium ions have been thermodynamically and kinetically stabilized by appropriate substituents. Thus, the first example of such persistent carbenium ions, namely the triphenylmethyl cation Ph_3C^+

(otherwise known as the trytil cation), was prepared at the very beginning of the twentieth century due to the seminal works of Norris and Wentzel in 1901 (the crystal structure of its perchlorate salt $\text{Ph}_3\text{C}^+\cdot\text{ClO}_4^-$ was reported much later, in 1965). The other milestone achievement in the chemistry of carbenium ions is related to the generation and direct NMR spectroscopic observation of the stable long-lived alkyl cations in superacidic media ($\text{SbF}_5\text{-SO}_2$, HF-SbF_5 , ‘magic’ acid $\text{HSO}_3\text{F-SbF}_5$), developed by the group of Olah and nicely covered in a series of his papers published in the 1950–1960s. The major advantage of using superacids was their extreme acidity allowing the smooth formation of carbocations through halogen abstraction from alkyl halides: $\text{Me}_3\text{CF} + \text{SbF}_5/\text{SO}_2 \rightarrow \text{Me}_3\text{C}^+\cdot\text{SbF}_6^-$. On the other hand, the very low basicity and nucleophilicity of the counteranions (SbF_6^-) prevented their reaction with carbocations, thus promoting the formation of true ion pairs.

The generation of the analogs of carbenium ions of the heavy group 14 elements, that is silylium, germylium, stannylum and plumbylium ions R_3E^+ ($\text{E} = \text{Si, Ge, Sn, Pb}$), was one of the most attractive and long-standing goals in contemporary organometallic chemistry, and is still a field of very active investigation. From the early stages of heavy carbenium ion chemistry, it quickly became apparent that there is a huge difference between the carbenium ions R_3C^+ and their heavy analogs R_3E^+ because of the sharply distinctive properties of carbon and its heavy congeners: size, polarizability and electronegativity. Consequently, the synthetic approaches, which were very successfully used for generation of stable carbenium ions in organic chemistry, proved to be rather inefficient in the synthesis of silylium ions, because of the high electrophilicity of the latter species leading to their intrinsic kinetic instability. Another important problem, hampering the generation of heavy group 14 element-centered cations, deals with the degree of ‘freedom’ of such cations from external nucleophiles, such as counter anions and solvents. It is therefore not surprising that the real nature of the bonding interaction between such cationic species and their counteranions, *ionic vs covalent*, has been one of the most important questions to solve in the problem of the true cations of the heavy group 14 elements.

Accordingly, the successful synthesis of silylium, germylium, stannylum and plumbylium ions has required the design of new synthetic strategies based upon the utilization of counterions and solvents of particularly low nucleophilicity to prevent their reaction (or coordination) to the cationic part. The first crystal structures of silylium ion derivatives were reported in the early 1990s; however, their real silylium ion nature has been severely criticized. Meanwhile, taking advantage of the particularly low nucleophilicity of borate and carborane as counteranions and using benzene and toluene as solvents finally enabled the synthesis of true R_3E^+ ($\text{E} = \text{Si, Ge, Sn, Pb}$) cations, free from any covalent interactions with either counterion or solvent. Although some of these cations were intramolecularly stabilized by cyclic π -conjugation, the acyclic tricoordinate cations were almost entirely electronically unperturbed, being genuine heavy analogs of the classical carbenium ions.

The chemistry of the heavy analogs of carbenium ions has been repeatedly reviewed during the past several decades, describing both transient and stable representatives.¹ In this chapter, we will briefly overview the whole story of the cations of heavy group 14 elements (generation of cations, their reactions and synthetic applications) with particular

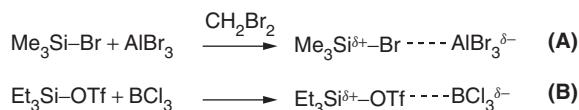
emphasis given to the latest progress in the field, which deals with the synthesis and structural characterization of stable free cations of the type R_3E^+ .²

1.2 Synthesis of $RR'R''E^+$ Cations (E = Si–Pb)

The general synthetic approaches for the preparation of the heavy group 14 element centered cationic species can be classified into several groups based on the starting material used.

1.2.1 From Halides $RR'R''EX$

Ionization of the carbon–halogen bond is a key step in the monomolecular substitution reaction $R_3C-X \rightarrow R_3C^+ + X^-$ and is the most general method for the generation of stable carbocations in organic chemistry. In a marked contrast, this synthetic approach is definitely not the best choice for the preparation of the heavy analogs of the carbenium ion $RR'R''E^+$, because of the strong E–X bonds of the precursor $RR'R''EX$ on the one hand and great reactivity of the developing cationic species $RR'R''E^+$ towards the halide leaving group X^- on the other hand (much higher halophilicity of Si–Pb compared with that of C). Therefore, cations generated by this method are to be classified as strongly polarized donor–acceptor complexes featuring only a partial positive charge on E, rather than true silylium ions (Scheme 1.1).^{3,4}



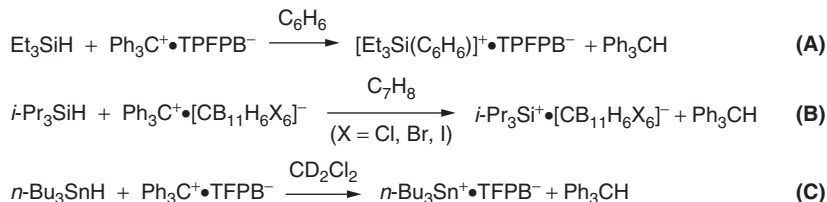
Scheme 1.1

1.2.2 From Hydrides $RR'R''EH$

This so-called ‘hydride-transfer reaction’ is the most commonly used and straightforward method for the generation of stable $RR'R''E^+$ cations. The driving force of this process, involving oxidation of the starting hydride $RR'R''EH$ with a powerful Lewis acid (typically, tritylium ion Ph_3C^+), is the relative strength of the breaking and forming bonds: stronger C–H vs weaker E–H. A variety of heavy analogs of carbenium ions, intra- or intermolecularly stabilized by coordination to n/π -donors, counteranions or nucleophilic solvents, can be readily prepared by this route (Scheme 1.2).^{5–7} As a drawback of this synthetic approach one should mention the steric bulkiness of the Ph_3C^+ reagent, which may hamper its interaction with hydrides $RR'R''EH$ bearing voluminous substituents necessary for the kinetic stabilization of the resulting cation.

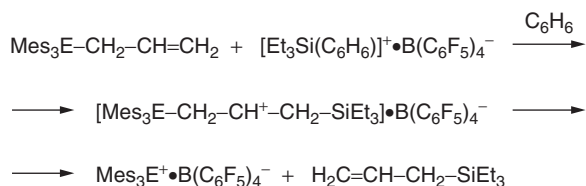
1.2.3 From $RR'R''E-R'''$ and $RR'R''E-ERR'R''$

A most impressive example of the generation of R_3E^+ cations by cleavage of R_3E^+-C bonds was reported by Lambert *et al.* They treated allylic derivatives



Scheme 1.2

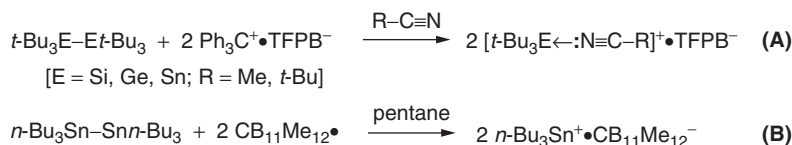
$\text{Me}_3\text{E}-\text{CH}_2-\text{CH}=\text{CH}_2$ (E = Si, Ge, Sn) with $[\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)]^+\cdot\text{B}(\text{C}_6\text{F}_5)_4^-$ to form at first intermediate β -silyl-substituted carbenium ions $\text{Me}_3\text{E}-\text{CH}_2-\text{CH}^+-\text{CH}_2-\text{SiEt}_3$, which then undergo E–C bond breaking to produce more favorable Me_3E^+ cations and allyltriethylsilane $\text{Et}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}_2$ as a side product (Scheme 1.3).⁸



Scheme 1.3

The ease of oxidation of hexamethyldistannane $\text{Me}_3\text{Sn}-\text{SnMe}_3$ by one-electron oxidizing reagents in acetonitrile, producing the solvent-coordinated trimethylstannyl cation Me_3Sn^+ , stems from the low oxidation potential of the Sn–Sn bond.⁹ Likewise, heteronuclear compounds $\text{Me}_3\text{Sn}-\text{EMe}_3$ (E = Si, Ge, Sn) can be oxidized (two-electron oxidation) forming acetonitrile-solvated cations Me_3Sn^+ and Me_3E^+ , whereas disilane $\text{Me}_3\text{Si}-\text{SiMe}_3$, digermane $\text{Me}_3\text{Ge}-\text{GeMe}_3$ and silagermane $\text{Me}_3\text{Si}-\text{GeMe}_3$ were inert under such oxidation conditions because of the markedly higher oxidation potentials of the Si–Si, Ge–Ge and Si–Ge bonds.^{9a} Hexaphenyldiplumbane $\text{Ph}_3\text{Pb}-\text{PbPh}_3$ can also be oxidized by Ag^+ ions in acetonitrile to generate the solvated cation Ph_3Pb^+ .¹⁰

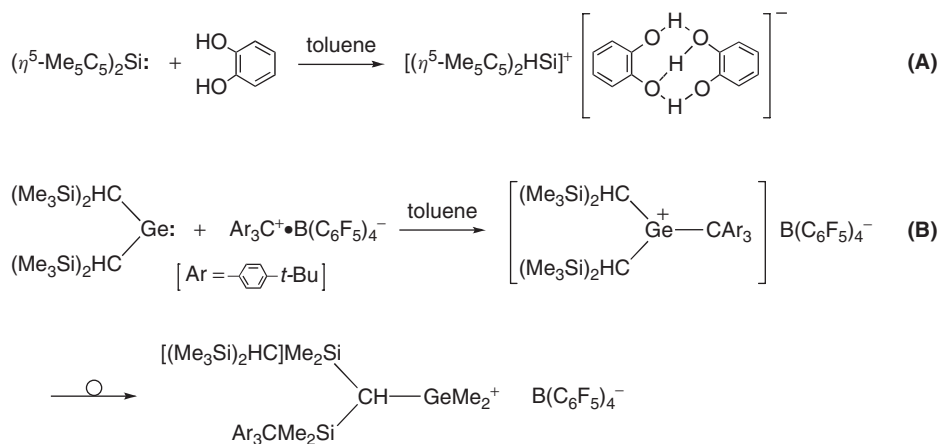
Other examples of R_3E^+ cations generated by cleavage of the E–E bonds of $\text{R}_3\text{E}-\text{ER}_3$ with a strong Lewis acid include: (1) oxidation of $t\text{-Bu}_3\text{E}-Et\text{-Bu}_3$ (E = Si, Ge, Sn) with $\text{Ph}_3\text{C}^+\cdot\text{TFPB}^-$ in the presence of nitriles $\text{R}-\text{C}\equiv\text{N}$ (R = Me, $t\text{-Bu}$) to form nitrilium complexes of $t\text{-Bu}_3\text{E}^+$ cations¹¹ (Scheme 1.4, A); (2) oxidation of $n\text{-Bu}_3\text{Sn}-\text{Snn}-\text{Bu}_3$ with the free radical $\text{CB}_{11}\text{Me}_{12}\cdot$ to produce a solvent-free $n\text{-Bu}_3\text{Sn}^+$ cation weakly coordinated to the Me groups of two $\text{CB}_{11}\text{Me}_{12}^-$ counteranions^{12a} (Scheme 1.4, B). Similarly, $\text{Me}_3\text{E}^+\cdot\text{CB}_{11}\text{Me}_{12}^-$ derivatives (E = Ge, Sn, Pb), lacking solvent coordination, were synthesized by the oxidation of $\text{Me}_3\text{Ge}-\text{GeMe}_3$, $\text{Me}_3\text{Sn}-\text{SnMe}_3$ and Me_4Pb in pentane with the free radical $\text{CB}_{11}\text{Me}_{12}\cdot$.^{12b}



Scheme 1.4

1.2.4 From Heavy Carbene Analogs RR'E:

The oxidative addition of Lewis acids to the heavy analogs of carbenes results in an increase of the central element coordination number from 2 to 3 and formation of element-centered cations, strongly stabilized by intramolecular electron donation. Such a synthetically attractive approach is still not widely developed, and one can mention only a couple of representative examples, namely the reaction of decamethylsilicocene ($\eta^5\text{-Me}_5\text{C}_5$)₂Si: with catechol producing a silyl cation in the form of protonated decamethylsilicocene¹³ (Scheme 1.5, A) and the reaction of the stable Lappert's germylene [(Me₃Si)₂CH]₂Ge: with [(4-*t*-Bu-C₆H₄)₃C⁺•TPFPB⁻ unexpectedly yielding an intramolecularly stabilized germyl cation after a series of consecutive rearrangements¹⁴ (Scheme 1.5, B).



Scheme 1.5

1.2.5 From Free Radicals RR'R''E•

This synthetic route, involving one-electron oxidation of the free radicals RR'R''E• with powerful Lewis acids (such as Ph₃C⁺), represents one of the best methods for cleanly forming element-centered cations RR'R''E⁺ with no formation of any side products, except for the inert Ph₃CH. Although this approach requires isolable radical species as readily available starting materials, the recent discovery of the stable persilyl-substituted

radicals of the type $(t\text{-Bu}_2\text{MeSi})_3\text{E}\bullet$ (E = Si, Ge, Sn) (see Chapter 2, Section 2.4.1.2) turned this approach into a highly attractive and easily realizable synthetic route for preparation of the stable ‘free’ $(t\text{-Bu}_2\text{MeSi})_3\text{E}^+$ cations (Scheme 1.6).¹⁵



Scheme 1.6

1.3 Reactions and Synthetic Applications of $\text{RR}'\text{R}''\text{E}^+$ Cations¹⁶

Although reactivity studies and synthetic utilization of the heavy group 14 element analogs of carbenium ions are not sufficiently realized yet, even now it is evident that the major synthetic interest of silylium, germlyium, stannylum and plumbylum ion derivatives is parallel to that of the classical carbocations. Thus, among the typical reactions of carbocations in organic chemistry one should mention: (1) reaction with nucleophiles to form substitution products with a novel C–C σ -bond ($\text{S}_{\text{N}}1$ mechanism); (2) removal of a proton to form elimination products with a novel C=C π -bond (E1 mechanism); and (3) electrophilic addition to alkenes to form new cationic adducts (cationic polymerization). For the $\text{RR}'\text{R}''\text{E}^+$ cations (E = Si–Pb), whose enhanced (compared with their carbon counterparts) electrophilicity was exploited as a major synthetic advantage, reaction routes (1) and (3) were mainly realized, both resulting in the formation of novel cationic species. Thus, for example, silylium ions smoothly add to the $>\text{C}=\text{C}<$ double bond to produce stable β -silyl carbocations,¹⁷ and to the $-\text{C}\equiv\text{C}-$ triple bond to form persistent silyl-substituted vinyl cations.¹⁸ They can also react with siloxanes to give trisilyloxonium ions capable of catalysing cyclosiloxane polymerization.¹⁹ One of the most synthetically useful silylium ion reagents is $[\text{Et}_3\text{Si}(\text{arene})]^+$ cation, recently successfully employed for the generation of a variety of carbenium and silylium ions. An important contribution to this field was made by the group of Reed *et al.* They generated, for example, the strongest currently known Brønsted superacid $\text{H}^+\bullet[\text{CHB}_{11}\text{R}_5\text{X}_6]^-$ (R = H, Me, Cl; X = Cl, Br, I) by the simple treatment of $[\text{Et}_3\text{Si}(\text{arene})]^+\bullet[\text{CHB}_{11}\text{R}_5\text{X}_6]^-$ with HCl.²⁰ The Brønsted acidity of this superacid is extremely high, enabling it to protonate readily at ambient temperatures such stable aromatic systems as fullerene C_{60} and Me-substituted benzenes $\text{C}_6\text{Me}_n\text{H}_{6-n}$ ($n = 0, 1, 2, 3, 5, 6$) generating the fullerene cation $[\text{HC}_{60}]^{+20\text{b}}$ and benzenium ions $[\text{HC}_6\text{Me}_n\text{H}_{6-n}]^+$,^{20\text{a-c}}} respectively. On the other hand, the treatment of $[\text{Et}_3\text{Si}(\text{arene})]^+\bullet[\text{CHB}_{11}\text{Me}_5\text{X}_6]^-$ (X = Cl, Br) with alkyl triflates ROTf (R = Me, Et) resulted in the formation of alkylum ion derivatives $\text{R}^+\bullet[\text{CHB}_{11}\text{Me}_5\text{X}_6]^-$, which are extremely electrophilic alkylating reagents, even stronger than alkyl triflates.²¹ Thus, the high electrophilic power of $\text{Me}^+\bullet[\text{CHB}_{11}\text{Me}_5\text{Br}_6]^-$ was spectacularly demonstrated by its reactions with benzene C_6H_6 and alkanes R-H (R = C_4H_9 , C_5H_{11} , C_6H_{13}), providing access to the corresponding toluenium $[\text{Me}(\text{C}_6\text{H}_6)]^+$ and tertiary carbenium R^+ ions, respectively.²¹ Undoubtedly, the extreme reactivity of $\text{R}^+\bullet[\text{CHB}_{11}\text{Me}_5\text{X}_6]^-$ exceeds that of the conventional alkyl triflates. Reaction of $[\text{Et}_3\text{Si}(\text{arene})]^+\bullet[\text{CHB}_{11}\text{I}_{11}]^-$ with

p -F-C₆H₄-CF₃ or CH₃CF₃ results in immediate fluorine abstraction to produce intermediate p -F-C₆H₄-CF₂⁺ or CH₃CF₂⁺ difluorocations, which subsequently participate in an electrophilic aromatic substitution reaction with the fluorobenzene solvent to form the stable (p -F-C₆H₄)₂CF⁺ or (p -F-C₆H₄)CH₃CF⁺ fluorinated carbocation derivatives.²² [Et₃Si(arene)]⁺•[CHB₁₁H₅Cl₆]⁻ reagent is able to abstract a chloride ion from the [IrCl(CO)(PPh₃)₂] complex to form a new [Ir(CHB₁₁H₅Cl₆)(CO)(PPh₃)₂] system undergoing an unusually smooth oxidative addition of chlorobenzene to produce the coordinatively unsaturated [IrCl(C₆H₅)(CO)(PPh₃)₂]⁺ cation.²³ Among other examples of the practical applications of silylium ion derivatives, one can mention silanorbornyl cations, which were shown to be the key intermediates in the metal-free catalytic intramolecular hydrosilylation of C=C double bonds under mild conditions,²⁴ as well as chiral silyl cation complexes with acetonitrile, claimed to be novel Lewis acid catalysts for Diels–Alder cycloaddition reactions.²⁵ Readily available cationic complexes [Me₃Si(arene)]⁺•B(C₆F₅)₄⁻ (arene = benzene, toluene) smoothly reacted with persilylated phosphane and arsane (Me₃Si)₃E (E = P, As) to produce the corresponding phosphonium and arsonium salts [(Me₃Si)₄E]⁺•B(C₆F₅)₄⁻.²⁶

The reactivity of cations centered on the heavier than silicon group 14 elements is represented mainly by that of stannylum ions. Thus, n -Bu₃Sn⁺•[CB₁₁Me₁₂]⁻ readily reacted with PhMgBr to produce n -Bu₃SnPh almost quantitatively.^{12a} It was found that stannyl cations R₃Sn⁺ (R = Me, Bu) can serve as excellent leaving groups in electrophilic aromatic *ipso*-substitution reactions, widening the scope of the Friedel–Crafts acylation, Vilsmeier formylation, sulfinations, and sulfonations.²⁷ Stannylum ions are also able to promote the cationic polymerization of simple alkenes. For example, the stable *sec*-alkyl β -stannylcarbocation, believed to be formed through the addition of a transient Me₃Sn⁺ cation to the C=C double bond, effectively polymerized a number of simple alkenes, such as isobutene, to produce high-molecular weight polymers.²⁸ The stannylum ion [n -Bu₃Sn]⁺•TPFPB⁻, generated *in situ* from n -Bu₃SnH and [Ph₃C]⁺•TPFPB⁻, may serve as an effective catalyst for allylation of *ortho*-anisaldehyde with n -Bu₃Sn–CH₂–CH=CH₂, providing an excellent *ortho*–*para* regioselectivity.²⁹ The bis(acetonitrile) complexes of trialkylstannylum ions [R₃Sn(N≡CMe)₂]⁺•SbF₆⁻ (R = cyclohexyl, *tert*-butyl, neopentyl), prepared from the corresponding bromides R₃SnBr or hydrides R₃SnH, have been shown to be effective Lewis acid catalysts for the Diels–Alder addition of α,β -unsaturated nitriles to furan.³⁰

The reactivity of the stable ‘free’ cations of heavy group 14 elements, such as (t -Bu₂MeSi)₃E⁺ (E = Ge, Sn) (see below), is still largely unexplored. One can mention only the pronounced electrophilicity of the germylium derivative (t -Bu₂MeSi)₃Ge⁺•B(C₆F₅)₄⁻, which readily forms a complex with acetonitrile [(t -Bu₂MeSi)₃Ge ← :N≡C–CH₃]⁺•B(C₆F₅)₄⁻, can be reduced with LiAlH₄ to form the hydride (t -Bu₂MeSi)₃GeH, undergoes one-electron reduction with t -BuLi to produce the free radical (t -Bu₂MeSi)₃Ge• and causes a ring-opening polymerization of THF.^{15a}

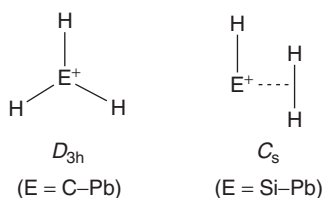
1.4 Theoretical Studies

The computational accomplishments have been thoroughly discussed in the recent reviews by Apeloig *et al.*,³¹ Schleyer *et al.*,^{11, 32} and Müller,^{1p} therefore in this section

we will just very briefly overview the most important achievements illuminating the theoretical contribution to the chemistry of heavy analogs of carbenium ions.

1.4.1 Structure of Cations

Two minima structures were located on the PES of EH_3^+ ions (E = group 14 element): a planar D_{3h} form (for E = C–Pb) and C_s side-on complex $\text{HE}^+\cdots\text{H}_2$ (for E = Si–Pb) (Scheme 1.7).³³ For silylium H_3Si^+ and germylium H_3Ge^+ ions the D_{3h} structure represents a global minimum, $D_{3h}/C_s = 0/27.1$ and $0/10.0$ kcal/mol; whereas for stannylum H_3Sn^+ and plumbylum H_3Pb^+ ions the C_s complex is most favorable, $D_{3h}/C_s = 0/-5.2$ and $0/-23.3$ kcal/mol [calculated at the B3LYP DFT level of theory with the 6-311++G(2d,2p) (for C, Si and Ge) and TZ+2P (for Sn and Pb) basis sets].^{33b}



Scheme 1.7

The remarkable preference for the C_s structure over its symmetrical D_{3h} counterpart for H_3Pb^+ can be attributed to relativistic effects, which stabilize the 6s lone pair on the H–Pb⁺ fragment.^{33b} Such side-on C_s complexes $\text{HE}^+\cdots\text{H}_2$ are best viewed as donor–acceptor aggregates, in which the HOMO (H–H σ -bond) donates its electron density to the LUMO (empty p-orbital on E of the HE^+ fragment).^{33b,c}

1.4.2 Stability of Cations

The stability of the parent cations H_3E^+ steadily increases going down from C to Pb (stabilization energies in kcal/mol calculated at the MP2/VDZ+P level are given in parentheses): $\text{H}_3\text{C}^+(0.0) < \text{H}_3\text{Si}^+(58.9) < \text{H}_3\text{Ge}^+(70.7) < \text{H}_3\text{Sn}^+(87.5) < \text{H}_3\text{Pb}^+(97.9)$.^{31,34} This trend of increasing thermodynamic stability descending group 14 is evidently due to the changes in intrinsic properties of group 14 elements: decrease of electronegativity and increase of polarizability.

Although the same type of substituents stabilize both carbenium and silylium ions, the extent of such stabilization for the latter class of cations is markedly lower, which leads to an appreciable decrease of the inherent stability of H_3Si^+ vs H_3C^+ in their substituted derivatives.^{31a} Thus, while the benefits of the stabilization of heavy group 14 element cations with electropositive silyl substituents are still rather important [$(\text{H}_3\text{Si})_3\text{Si}^+$ and $(\text{H}_3\text{Si})_3\text{Pb}^+$ are more stable than $(\text{H}_3\text{Si})_3\text{C}^+$ by 32.9 and 63.5 kcal/mol, respectively], the stabilization effect of alkyl substituents is markedly smaller (Me_3Si^+ and Me_3Pb^+ are more stable than Me_3C^+ by 12.0 and 35.2 kcal/mol, respectively).^{1p} The extent of substituents stabilization further drops in the case of the phenyl group: Ph_3Pb^+ is more

stable than Ph_3C^+ by only 10.5 kcal/mol, whereas Ph_3Si^+ is destabilized compared with Ph_3C^+ by 2.7 kcal/mol.^{1p}

Moreover, whereas the effect of stabilization of carbenium ions by alkyl substituents is highly pronounced, it is markedly smaller for the heavy analogs. Thus, if Me_3C^+ is more stable than H_3C^+ by 74.8 kcal/mol, the analogous stabilization of Me_3Si^+ and Me_3Pb^+ ions (vs their unsubstituted analogs H_3Si^+ and H_3Pb^+) amounts to only 40.6 and 29.7 kcal/mol, respectively. Even phenyl groups, traditionally commonly used for stabilization of carbenium ions in organic chemistry (Ph_3C^+ is more stable than H_3C^+ by 111.3 kcal/mol), are much less effective in stabilization of the heavier cations (stabilization energies of Ph_3Si^+ and Ph_3Pb^+ ions (vs H_3Si^+ and H_3Pb^+) are only 64.5 and 42.2 kcal/mol, respectively).^{1p} On the other hand, the silylium ions were predicted to be stabilized by electropositive substituents such as Li and BeH.^{31a,35} Thus, the D_3 tris(dimethylboryl)silylium ion $(\text{Me}_2\text{B})_3\text{Si}^+$ was stabilized by 61.9 kcal/mol compared with the parent H_3Si^+ (B3LYP/6-31G* level), whereas the Me_3Si^+ ion was more stable than H_3Si^+ by only 43.2 kcal/mol.³⁶

In contrast to carbenium ions, which are stabilized by any halogen substituents (this effect increases from F to I), such stabilization is much less pronounced in the case of the cations of the heavy group 14 elements. Thus, although Br and I stabilize the silylium ion R_3Si^+ , the more electronegative F and Cl destabilize it. Only the most electropositive I stabilizes germylium R_3Ge^+ and stannylum R_3Sn^+ ions, whereas all other halogens destabilize them. For the most electropositive Pb atom, all halogens destabilize its cation R_3Pb^+ .^{31b,34}

Amino groups are also capable of stabilizing the silylium ions, although the degree of such stabilization is smaller than that of carbon analogs. Thus, the D_3 tris(amino)silylium ion $(\text{H}_2\text{N})_3\text{Si}^+$ can benefit from ca. 40% of the stabilization energy of the corresponding carbenium ion $(\text{H}_2\text{N})_3\text{C}^+$.³⁷ It was therefore concluded that amino groups are significantly more effective than methyl groups in the stabilization of silylium ions.

Overall, it can be concluded that the substituent effects for the heavy analogs of carbenium ions do not play such a decisive role in their thermodynamic stabilization as they play in the chemistry of organic carbocations.

1.4.3 Calculation of the NMR Chemical Shift of Cations

The central element E of the cationic tricoordinate derivatives of group 14 elements R_3E^+ is diagnostically strongly deshielded with respect to neutral tetracoordinate counterparts R_4E . It is therefore evident that NMR chemical shift calculations (for E = C, Si, Sn, Pb) represent a very powerful tool for straightforward identification of cationic species in the condensed phase and estimation of their degree of ionicity. Below, the major conclusions drawn from the ²⁹Si and ¹¹⁹Sn NMR chemical shift calculations of R_3Si^+ and R_3Sn^+ cations will be discussed. Neither good empirical estimates nor reliable ²⁰⁷Pb NMR chemical shift calculations are available for plumbylum ion derivatives. Because ¹³C NMR chemical shift calculations of the heavy group 14 element centered cations are only of very limited value, they will not be discussed in the present chapter. Sometimes the ¹³C NMR computational data are useful in identification of the germylium ions R_3Ge^+ , because the direct NMR spectroscopic observation of germanium centers is precluded by the lack of a convenient and sensitive Ge nuclide.

1.4.3.1 ^{29}Si NMR Chemical Shift Calculations

Reliable NMR chemical shift calculations for organosilicon compounds became available at the beginning of the 1990s. Since then, such computations have been widely used as a major tool for proof (or disproof) of claims on the synthesis of genuine silylium ions.

Similar to their carbon analogs, silylium ion derivatives exhibit characteristic highly deshielded ^{29}Si NMR chemical shifts, a tendency that was nicely supported by theoretical calculations. Thus, the deshielding of R_3Si^+ ions (R = alkyl group) compared with their R_3SiH precursors amounts to ca. 400 ppm.^{1p} The chemical shifts of H_3Si^+ and Me_3Si^+ ions in the gas phase were calculated to be 264.7 and 346.7 ppm, respectively.³² One should note that in solution the extent of NMR deshielding of the silylium ion species strongly correlates with the degree of solvent nucleophilicity, sharply dropping with an increase in the solvent coordinating ability. This tendency was computationally studied in the elaborate work by Cremer *et al.*³⁸ (see Section 1.5). The predicted region for the tricoordinate silylium ions is very wide, ranging from the rather high-field resonance of $(\text{Me}_2\text{N})_3\text{Si}^+$ (42 ppm)³⁷ to the extremely low-field signals of $(\text{Me}_2\text{B})_3\text{Si}^+$ (572 ppm)³⁶ and particularly $(\text{Me}_3\text{Si})_3\text{Si}^+$ (920 ppm).³⁹ Clearly, the magnitude of the ^{29}Si NMR chemical shifts of the above-mentioned silylium ion derivatives is totally governed by the influence of substituents: strongly π -donating Me_2N groups vs electropositive Me_3Si substituents. This phenomenon is now well-recognized and was realized on the basis of the following considerations.^{1p,39} The paramagnetic contribution, which is dominant in the overall NMR chemical shifts of heteronuclei, is directly related to the energy gap between occupied and vacant frontier orbitals. When this gap tends to decrease, the paramagnetic contribution becomes larger and consequently, the nucleus is more deshielded. In tricoordinate cations R_3E^+ such occupied and vacant orbitals are typically represented by the $\sigma(\text{E}-\text{R})$ - and $n\text{p}(\text{E})$ -orbitals, respectively. When R is electropositive silyl group, the $\sigma(\text{E}-\text{R})$ -orbitals level is raised resulting in a decrease of $\sigma(\text{E}-\text{R})-n\text{p}(\text{E})$ energy separation and consequently in a strongly deshielding contribution for E. By contrast, electronegative substituents lead to an increase in the energy gap and decrease in the deshielding contribution. The same is true for the π -donating groups R (such as amino groups), which destabilize the vacant $n\text{p}(\text{E})$ -orbitals through their interaction, resulting in an increase of the energy separation.

The cationic Si centers of the H_3Si^+ and Me_3Si^+ ions were markedly shielded upon the approach of such typically inert molecules as CH_4 , He, Ne and Ar. On the basis of this computational result, Schleyer *et al.* concluded that the silylium ions can be coordinated by even such non-nucleophilic media as aliphatic hydrocarbons and noble gases.^{11,32} This led them to a rather pessimistic statement: "Thus, it seems unlikely that free silyl cations can exist in solution, not even in the most non-nucleophilic solvents, unless, perhaps, very bulky substituents hinder coordination. . . . One major conclusion can be drawn: the prospects for obtaining and observing truly "free" silyl cations in condensed phases are very poor."³² However, this discouraging conclusion proved to be somewhat exaggerated, at least from the viewpoint of experimental organometallic chemists. Actually, the highly desirable synthetic challenge of the preparation and isolation of tricoordinate silylium, gerylium and stannylum ions, truly 'free' in both solid state and in solution, was realized by the groups of Lambert and Sekiguchi in the early 2000s (see Section 1.6.2.2).

1.4.3.2 ^{119}Sn NMR Chemical Shift Calculations

Accurate calculations of the ^{119}Sn chemical shifts, which cover a very broad range from ca. -2500 to $+4000$ ppm using Me_4Sn as a reference, turned out to be an important computational tool only recently.^{1p,40} Before that, estimation of the ^{119}Sn resonances of stannylum ions was made based on the empirical correlation between the ^{29}Si and ^{119}Sn NMR chemical shifts, which was successfully applied for the evaluation of the chemical shifts of isostructural tetracoordinate organosilicon and organotin compounds.⁴¹ Accordingly, the ^{119}Sn chemical shifts of stannylum ion derivatives R_3Sn^+ were predicted to be ca. 1770 ppm (for $\text{R} = \text{alkyl}$) and ca. 1250 ppm (for $\text{R} = \text{aryl}$).^{1p} However, such expectations, based on the empirical ^{29}Si - ^{119}Sn chemical shift correlation, overestimated the degree of deshielding of the cationic Sn centers in stannylum ions, as was demonstrated by IGLO calculations giving the Me_3Sn^+ chemical shift estimation as ca. 1075 ppm.⁴² Subsequent computations revealed that the ^{119}Sn chemical shifts of the ‘free’ stannylum ions spread over a wide region, ranging from 596 ppm for H_3Sn^+ [GIAO/HF level with the 6-31G(d) and tzv basis sets] to 3450 ppm for $(\text{Me}_3\text{Si})_3\text{Sn}^+$ [GIAO/MPW1PW91 level with the 6-31G(d) and tzv basis sets].^{1p} The chemical shifts of the Me_3Sn^+ ion were calculated to be in the range of 1075 – 1466 ppm depending on the theoretical method used, whereas those of the Me_3Sn^+ and Tip_3Sn^+ ions were estimated as 856 and 763 ppm, respectively.^{1p} The extreme deshielding of the persilyl-substituted stannylum ions [3450 ppm for $(\text{Me}_3\text{Si})_3\text{Sn}^+$ and 2880 ppm for $(\text{H}_3\text{Si})_3\text{Sn}^+$ vs 1466 ppm for H_3Sn^+ at the same computational level]^{1p} is explained by the same reasons as those responsible for the deshielding of structurally related tris(silyl)silylium ions (see above); namely, by the very large paramagnetic contribution to the overall NMR chemical shift because of the small energy gap between the occupied $\sigma(\text{Sn-Si})$ - and vacant $5p(\text{Sn})$ -orbitals. This agrees well with a recent experimental finding: the resonance of the $(t\text{-Bu}_2\text{MeSi})_3\text{Sn}^+$ ion was observed at a record low-field shift of 2653 ppm^{15b} (see Section 1.6.2.2).

1.5 Early Studies of $\text{RR}'\text{R}''\text{E}^+$ Cations: Free or Coordinated?

The early belief in the ease of preparation of silylium ions $\text{RR}'\text{R}''\text{Si}^+$ (and other cations of heavier group 14 elements) was based on the higher polarizability and lower electronegativity of silicon (as well as germanium, tin and lead) compared with that of carbon (1.90 for Si vs 2.55 for C, Pauling electronegativity scale).⁴³ It was, for example, expected that the heterolysis of the $\text{R}_3\text{Si-X}$ bond would be facilitated by the thermodynamic stabilization of silylium ions R_3Si^+ compared with their carbon analogs R_3C^+ . This was indeed the case in the gas phase, where a number of tricoordinate silylium ions have been detected and their reactivity studied by both classical mass spectrometry and special methods, such as ion cyclotron resonance spectroscopy and tandem mass spectrometry techniques.^{16a-e} Thus, the recent investigation of the relative hydride affinities for silylium and carbenium ions and equilibrium constants of hydride transfer reactions by FT ion cyclotron resonance spectroscopy clearly demonstrated that the silylium ions in the gas phase are significantly thermodynamically stabilized compared with the corresponding carbenium ions, and the positive charge of the silylium ions is mostly localized on the Si atom.⁴⁴ The existence of silylium ions in the gas phase was reliably supported

by theoretical calculations, which also confirmed that the planar D_{3h} silylium ion H_3Si^+ is substantially more stable than its carbon analog, methyl cation H_3C^+ , at all computational levels.^{11,31} However, the generation of silylium ions in condensed media, mostly desired by synthetic organometallic chemists, was a long-standing problem whose solution has required several decades of very intensive research. Given the above-discussed intrinsic thermodynamic stabilization of silylium ions, one should definitely acknowledge the kinetic origin of their overall instability. The extreme electrophilicity of silylium ions, greatly exceeding that of their carbon counterparts, results in the interaction of the former species with a variety of π - and σ -donors, including even such weakly nucleophilic and typically inert solvents as toluene and benzene. This prevented the use of traditional leaving groups (such as tosylates and halides), that have been widely and very efficiently used for the generation of carbenium ions in organic chemistry, due to the extraordinarily high oxo- and halophilicity of the silylium ions. Thus, whereas the *tert*-butylium ion derivative $Me_3C^+ \cdot Sb_2F_{11}^-$ can be smoothly generated and isolated under superacidic conditions,⁴⁵ the corresponding silylium ion derivative did not exist as an ion pair, forming instead a neutral compound with a covalent bond between silicon and oxygen or fluorine atoms.⁴⁶ The other problem, greatly contributing to the overall instability of silylium ions, is the significant difference in the size of the silicon and carbon atoms: atomic radii are 117 and 77 pm, respectively.⁴³ For this reason, the bonds from substituents to silicon are longer than those to carbon, which results in an appreciable decrease in the degree of hyperconjugative stabilization of the cationic center on going from carbon to silicon. On the other hand, the bigger size of silicon is associated with its increased coordination sphere, which is manifested in the general tendency of the silicon compounds (unlike their carbon counterparts) to form hypercoordinate derivatives with the coordination numbers 5 or 6 because of the intra- or intermolecular stabilizing coordination of Lewis bases, which results in a partial or complete loss of the silylium ion character. It is, therefore, not surprising that the story of generation, identification and, at last, isolation of truly ionic silylium ions was neither straightforward nor simple, being full of controversial reports and hot debates concerning the real nature of the 'silylium ion' species, the synthesis of which has been declared from time to time.^{1,31,32} It is therefore particularly instructive to follow the progress in the search for tricoordinate silylium ion derivatives.

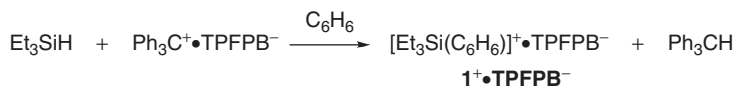
As the first step towards the synthesis of cations of heavy group 14 elements, several groups in the 1970s tried to prove the existence of silylium ion derivatives by physicochemical methods previously successfully used for the study of carbenium ions (cryoscopic, conductivity, UV and NMR measurements), however, all of these attempts failed to observe silicon centered cationic species.^{1a} A number of attempts were made to detect the presence of silylium ions as reactive intermediates in solvolysis reactions (hydrolysis of Ph_3SiF), halogen abstraction from a carbon next to a silicon in R_3Si-CH_2-X by Lewis acids ($AlCl_3$, SbF_5 , BF_3), reaction of β -functional silicon compounds $R_3Si-CH_2-CH_2-X$, hydride transfer reactions from the hydrosilane Ph_3SiH to the carbenium ion derivatives $Ph_3C^+ \cdot X^-$, and reactions accompanied by racemization at the silicon center.^{1a} However, in no cases has clear evidence for the formation of silylium ion intermediates been obtained.

In the following decade an important contribution to the problem of silylium ions was made by the group of Lambert, whose work, however, has led sometimes to controversial conclusions.^{1d,47} Thus, they presented experimental data on the attempted ionization of simple silyl perchlorates [such as (*i*-PrS)₃SiOCIO₃, Ph₃SiOCIO₃, Me₃SiOCIO₃] in CH₂Cl₂ and sulfolane, the results of which were interpreted in terms of the formation of stable R₃Si⁺ (R = *i*-PrS, Ph, Me) cations in the form of their perchlorate salts as a silicon analog of the trityl cation, Ph₃C⁺.^{1c,48} However, the subsequent detailed investigation by Olah *et al.* disproved such claims based on a careful investigation of the NMR spectral and X-ray crystal data along with theoretical calculations, clearly demonstrating the covalent, rather than ionic, nature of the bonding between the R₃Si and OCIO₃ parts and, consequently, absence of the free silylium ion species in solution.⁴⁹

Thus, at the beginning of the 1990s the synthesis of real silylium ions, featuring a positive charge on the Si atom, had not been achieved. It became clear that their successful synthesis required nonclassical approaches greatly distinctive from traditional organic chemistry methods. The numerous unsuccessful attempts described above led to a definite conclusion that the three important factors most responsible for either success or failure in the synthesis of silylium ion derivatives are: the counteranion, solvent and substituents. The first problem to be solved was the right choice of the counteranion and solvent, which was finally overcome at the beginning of the 1990s. The major requirement for counteranions was their minimal nucleophilicity to prevent their close contact with the target silylium ions to form tight ion pairs or, in the extreme case, formation of covalently bonded compounds (such as triphenylsilyl perchlorate).^{48b,49b} The requirements for the solvents were the same: as low as possible nucleophilicity to avoid possible coordination to the highly electrophilic silylium ion. In the case of such coordination of either counteranion or solvent, one should expect an appreciable transfer of the positive charge onto the nucleophilic counterpart (counteranion, solvent) and, consequently, significant electronic perturbation around the cationic center. Overall, this will result in a great (or complete) loss of the silylium ion character. The major breakthrough in resolving the silylium ion problem was achieved following the successful introduction of borate and carborane counteranions of particularly low nucleophilicity B(C₆F₅)₄⁻ and CB₁₁H₆Br₆⁻, and utilization of nonpolar aromatic hydrocarbons (benzene, toluene) as the solvents of choice. The critical choice of the substituents was determined by two major demands: (1) steric bulkiness necessary for kinetic stabilization of the cationic center to avoid coordination of both anions and solvents; (2) electron donating properties essential for the thermodynamic stabilization of the positive charge.

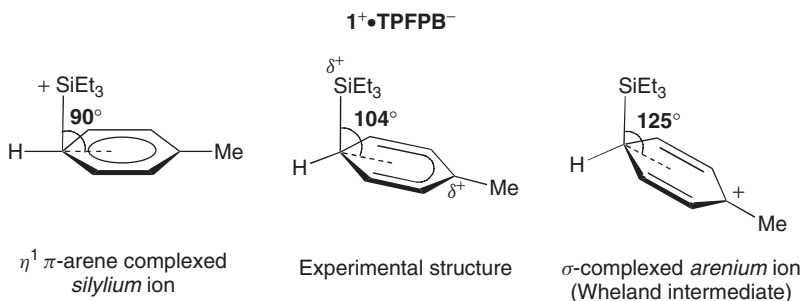
The first milestone discoveries were accomplished in 1993, when the groups of Lambert⁵⁰ and Reed⁵¹ published the crystal structures of their Et₃Si⁺ and *i*-Pr₃Si⁺ derivatives. Thus, [Et₃Si(toluene)]⁺•TPFPB⁻ (**1**⁺•TPFPB⁻) was prepared by Lambert *et al.* by the hydride transfer reaction between Et₃SiH and Ph₃C⁺•TPFPB⁻ in benzene (Scheme 1.8).⁵⁰

The crystal structure analysis of **1**⁺•TPFPB⁻ revealed no direct cation–anion interaction, however, there was a ‘distant’ coordination of the Si cationic center to the solvent (toluene) with a long Si–C interatomic distance of 2.18 Å. The geometry of the toluene molecule was almost undistorted and essentially planar, which was realized as an



Scheme 1.8

indication of its very weak bonding interaction with the Si cation, resulting in extraordinary little (if at all) charge transfer from the Si to the C atom. Thus, the authors concluded that **1⁺** represents a stable silylium ion lacking coordination to the counteranions and only very weakly coordinated to the toluene solvent. However, two experimental observations were in sharp conflict with such a conclusion: (1) the Si cationic center was pronouncedly pyramidal (the sum of the bond angles around the Si atom was 342°), whereas trigonal-planar geometry (360°) was expected for the real silylium ion; (2) the resonance of the cationic Si atom of **1⁺** was observed at 92.3 ppm, a value that was by far high-field shifted compared with the several hundred ppm calculated for the planar non-coordinated silylium ion. These problematic issues provoked very hot debates around the real nature of **1⁺**, in the course of which Lambert's original claim of the nearly 'free' silylium ion was severely criticized by both experimentalists and theoreticians (Scheme 1.9).

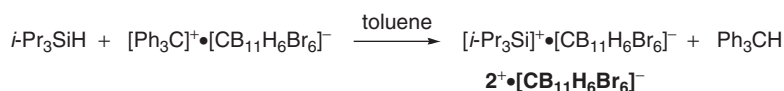


Scheme 1.9

Thus, Pauling pointed out that the calculated bond order between the Si and *para*-C of a coordinated toluene molecule in **1⁺•TPFPB⁻** is 0.35, a value that cannot be neglected.⁵² Olah *et al.* calculated that the ²⁹Si NMR resonance of the planar free Et₃Si⁺ cation should be expected at a very low field, 354.6 ppm^{53a} or even at 371.3 ppm,^{53b} whereas the experimentally observed value of 92.3 ppm⁵⁰ in **1⁺•TPFPB⁻** was rather attributed to the covalently bonded compound that can be best described as a Wheland σ -complex (Scheme 1.9).⁵³ In independent experimental studies, the formation of such a σ -complex in the gas phase was confirmed by radiolytic experiments and FT ion cyclotron resonance mass spectrometry.⁵⁴ The comprehensive theoretical insight by Cremer *et al.*³⁸ agreed well with Olah's conclusions⁵³ regarding the degree of deshielding of the cationic Si atom: ²⁹Si NMR resonances of R₃Si⁺ (R = Me, Et) were calculated to be ca. 400 ppm (in the gas phase, free silylium ions), 370–400 ppm (in noncoordinating solvents), or 200–370 ppm (in weakly coordinating solvents). Such a shift to higher field

clearly reflects the progressive decrease in cationic character in line with the increasing coordinating power of the solvents. In the limiting case of nucleophilic solvents, the silylium ion character is totally lost because of the covalent bonding between the cationic center and solvent molecules. Schleyer *et al.* also concluded that the pyramidalization at the silyl cation center and relatively high-field ^{29}Si NMR resonance of $1^+ \cdot \text{TPFPB}^-$ testify to its σ -complex structure.⁵⁵ To reach a consensus, Reed *et al.* suggested⁵⁶ (and Lambert finally concurred)^{1n,5b} that the real structure of $[\text{Et}_3\text{Si}(\text{toluene})]^+$ represents a hybrid of an $\eta^1 \pi$ -complex and σ -complex (Scheme 1.9) with a predominant contribution from the former.

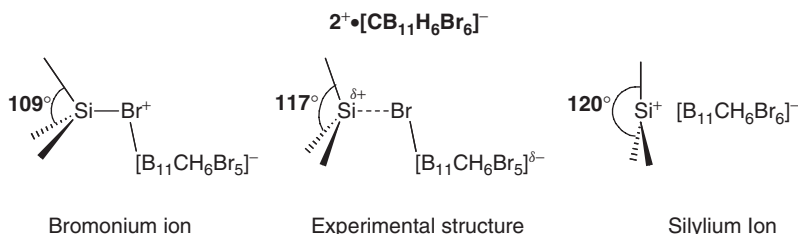
The next milestone contribution to the silylium ions issue was achieved by Reed *et al.*, who synthesized $i\text{-Pr}_3\text{Si}^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, ($2^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$), by the hydride transfer reaction of $i\text{-Pr}_3\text{SiH}$ and $\text{Ph}_3\text{C}^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ in toluene,^{51a} taking advantage of the very low nucleophilicity of the carborane anion⁵⁷ (Scheme 1.10).



Scheme 1.10

Although exhibiting no interaction with toluene solvent, the $i\text{-Pr}_3\text{Si}^+$ cation 2^+ was not totally 'free', being weakly bound to a carborane ion through its Br atoms with a long Si–Br distance of 2.479(9) Å. However, $i\text{-Pr}_3\text{Si}^+$ 2^{+51a} was more planar than Et_3Si^+ 1^{+50} (351° vs 342°) and more deshielded (109.8 ppm vs 92.3 ppm), observations that led to the conclusion that $2^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ more closely approached the 'free' silyl cation, possessing the highest degree of silylium ion character yet observed. This claim, however, was doubted by Olah *et al.*,⁵³ who assigned the structure of $2^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ to a polarized silylbromonium zwitterion rather than the true silylium ion. Again, similar to the above case of $[\text{Et}_3\text{Si}(\text{toluene})]^+ \cdot \text{TPFPB}^-$, Reed has concluded that $2^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ can be best viewed as '... lying on a continuum between a bromonium ion and a silylium ion' with the major contribution from the latter (Scheme 1.11).⁵⁶

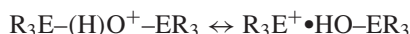
In due course, Reed *et al.* prepared several other trialkylsilylium ion derivatives $\text{R}_3\text{Si}^+ \cdot [\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ ($\text{R}_3\text{Si}^+ = \text{Et}_3\text{Si}^+$, $t\text{-Bu}_2\text{MeSi}^+$, and $t\text{-Bu}_3\text{Si}^+$) employing the same synthetic protocol; namely, hydride abstraction from R_3SiH by



Scheme 1.11

$\text{Ph}_3\text{C}^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$.⁵⁸ All of these compounds featured structural and spectral characteristics very similar to those of $2^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$: a long Si–Br interatomic distance (2.43–2.48 Å), tendency to planarization around the Si-cationic center (345–351°), and low-field ²⁹Si NMR resonances (105–115 ppm). The high degree of silylium ion character of these compounds was proved by their smooth reactions with organic halides to form silyl halides R_3SiX and with water to give protonated silanols $\text{R}_3\text{Si}(\text{OH}_2)^+$.⁵⁸ In subsequent studies, Reed *et al.* expanded the range of their least-coordinating weakly nucleophilic anions by adding newly synthesized hexachloro- and hexaiodocarboranes $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ (X = Cl, I) to the original hexabromocarborane (X = Br).⁶ Consequently, the novel salts of the *i*-Pr₃Si⁺ cation, *i*-Pr₃Si⁺• $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ (X = Cl, I), were successfully prepared, of which the hexachloro derivative developed the highest degree of silylium ion character, whereas the hexaiodo derivative manifested the strongest halonium ion character and the most covalent Si–X bond.⁶ Thus, the *i*-Pr₃Si⁺• $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ derivative represented the closest approach to a trialkylsilylium ion known at that time.^{1k}

The search for stable heavier congeners of silylium ions, namely, germylium and stannylum ions, met with little success in the 1990s. Lambert *et al.* reported the synthesis of the protonated digermyl and distannyl ethers $(\text{R}_3\text{E})_2\text{OH}^+\cdot\text{TPFPB}^-$ (R = Me, Et; E = Ge, Sn), which were claimed to possess considerable amounts of germylium and stannylum ions character.⁵⁹



The same authors also prepared the cationic derivative *n*-Bu₃Sn⁺• $\text{B}(\text{C}_6\text{F}_5)_3\text{H}^-$ by the oxidation of the stannyl hydride *n*-Bu₃SnH with $\text{B}(\text{C}_6\text{F}_5)_3$ and characterized it as a tricoordinate stannylum ion because of its low-field ¹¹⁹Sn NMR resonance of 360 ppm.⁶⁰ The identical *n*-Bu₃Sn⁺ cation with a TFPBP[−] counterion revealed a less deshielded value of +263 ppm (room temperature),^{17a} which was, however, corrected in subsequent studies to +434 ppm (−60 °C).^{29,61} Kira *et al.* also prepared the *n*-Bu₃Sn⁺ derivative as its TFPBP[−] salt, using the traditional hydride transfer method (Section 1.2.2, Scheme 1.2, C) and reported the low-field resonance of the cationic Sn atom to be 356 ppm.⁷ This conclusion was, however, later questioned by Edlund *et al.*,⁴¹ who pointed out that the values of 360⁶⁰ and 356⁷ ppm assigned to the cationic Sn atom are better attributed to the covalently bound arene complexes, quite similar to the case discussed above of the silylium ions vs Wheland σ -complexes problem. On the basis of an empirical correlation between the ²⁹Si and ¹¹⁹Sn NMR chemical shifts, the resonance of the truly free trigonal-planar Me₃Sn⁺ cation was expected to be observed at a much lower field of 1500–2000 ppm, a conclusion that also gained support from theoretical calculations.⁴¹

1.6 Stable RR'R''E⁺ Cations

1.6.1 Intramolecularly Stabilized (Coordinated) Cations

Stabilization of the highly electrophilic cations of the heavy group 14 elements can be achieved either intermolecularly (by coordinating solvents, see previous section) or intramolecularly (by *n*- or π -donating atoms or groups, such as N, O, C=C, C≡C, etc.).

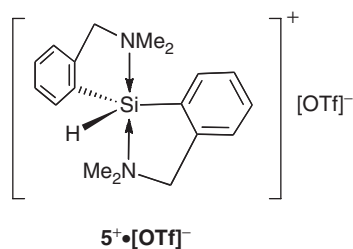
However, such stabilization occurs at the expense of the degree of cationic character at the central atom, thus leading to an increase in its coordination number and formation of cationic species which are not tricoordinate but tetra-, penta- or hexacoordinate instead. Because such species cannot be classified as real low-coordinate derivatives, we will just briefly overview the most important achievements in this field describing the crystal structures of these compounds. Some of them, in which the positive charge is incorporated into the bis- or trishomoaromatic 2π -electron cyclic system, will be discussed in the last chapter devoted to the aromaticity of group 14 organometallics (see Chapter 6, Section 6.3.3).

The first compound of this type, a 1:1 adduct of $\text{Me}_3\text{SiBr}/\text{Me}_3\text{SiI}$ and pyridine (Py) $[\text{Me}_3\text{Si}\leftarrow:\text{Py}]^+\cdot\text{X}^-$ ($\text{X} = \text{Br}, \text{I}$), $3^+\cdot\text{X}^-$, was described in 1983.⁶² In the solid state the $[\text{Me}_3\text{Si}(\text{py})]^+$ cation of $3^+\cdot\text{X}^-$ revealed no interaction with the X^- counteranions, featuring a distorted trigonal-pyramidal geometry of the tetracoordinate Si atom and a long Si–N bond distance of 1.858(9) Å.

Reed *et al.* reported a remarkable protonated silanol $[t\text{-Bu}_3\text{Si}\leftarrow:(\text{OH}_2)]^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, $4^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, that according to NMR (strongly low-field shifted resonance of the coordinated water protons at 8.04 ppm) and X-ray [trigonal flattening around the tetracoordinate Si center, long Si–O bond of 1.779(9) Å] data, contains a predominantly silylium ion $t\text{-Bu}_3\text{Si}^+\leftarrow:(\text{OH}_2)$ rather than oxonium ion $t\text{-Bu}_3\text{Si}-(\text{OH}_2)^+$.⁶³ In the crystalline form the $[t\text{-Bu}_3\text{Si}\leftarrow:(\text{OH}_2)]^+$ cation of $4^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ was weakly coordinated to the carborane anion through the hydrogen bonding of its acidic O–H bonds to the carborane Br atoms.

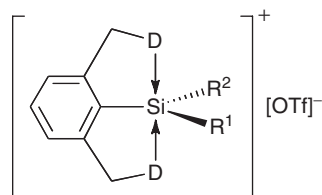
Several silylnitrilium and silyloxonium ion derivatives, $[\text{R}_3\text{Si}^+\text{N}\equiv\text{C}-\text{CH}_3]\cdot\text{TFPB}^-$ [$\text{R}_3\text{Si} = \text{Me}_3\text{Si}, \text{Ph}_2\text{MeSi}, (2\text{-thienyl})_2\text{MeSi}, (3,5\text{-}t\text{-Bu}_2\text{-C}_6\text{H}_3)_3\text{Si}$] and $[\text{R}_3\text{Si}^+\text{OEt}_2]\cdot\text{TFPB}^-$ [$\text{R}_3\text{Si} = \text{Me}_3\text{Si}, \text{Ph}_2\text{MeSi}, (2\text{-thienyl})_2\text{MeSi}$], were prepared by standard hydride transfer reactions of the corresponding hydrides R_3SiH with $\text{Ph}_3\text{C}^+\cdot\text{TFPB}^-$ and were detected by low temperature NMR spectroscopy.⁶⁴

Stabilization of silyl cations by the intramolecular coordination of two n-donating ligands (N, O, S) results in the trigonal-bipyramidal geometry of the pentacoordinate Si atom. Thus, bis{2-[(dimethylamino)methyl]phenyl}silyl triflate $5^+\cdot[\text{OTf}]^-$, featuring no interaction between the cationic and anionic parts, revealed a perfectly planar Si center having both dimethylamino groups at the apical positions with considerably longer Si–N bond distances (Scheme 1.12).⁶⁵



Scheme 1.12

Similarly, silyl triflates $6^+ \cdot [\text{OTf}]^-$ were prepared by reaction of the corresponding chlorosilane precursors with trimethylsilyl triflate (Scheme 1.13).⁶⁶



$6^+ \cdot [\text{OTf}]^-$

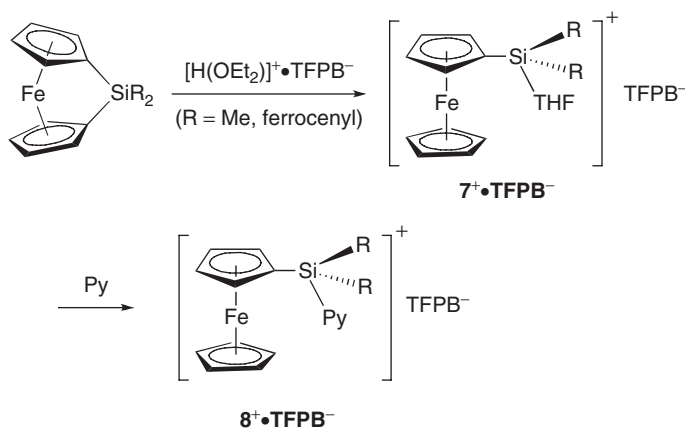
[D = OMe, SMe; R¹ = Me, Ph; R² = H, Me]

Scheme 1.13

The cationic portions of $6^+ \cdot [\text{OTf}]^-$ were well separated from their anionic parts in the solid state, featuring a slightly distorted trigonal-bipyramidal configuration at the Si center with the n-donating ligands at the apical positions.

An interesting method for the generation of transient THF solvated silylium ion species by the treatment of [1]silaferrocenophanes with $[\text{H}(\text{OEt}_2)]^+ \cdot \text{TFPB}^-$ was recently described by Manners *et al.* Being fleeting under ambient conditions, such ferrocenyl-substituted silylium ions $7^+ \cdot \text{TFPB}^-$ can be stabilized by coordination with Lewis bases, such as pyridine, to form room temperature stable pyridinium ion derivatives $8^+ \cdot \text{TFPB}^-$ (Scheme 1.14).⁶⁷ The Si–N bond order in the cation 8^+ of 0.61, estimated from its bond length of 1.858(5) Å, is characteristic of a predominantly covalent interaction, which agrees well with the marked pyramidalization about the Si atom (337.7°).

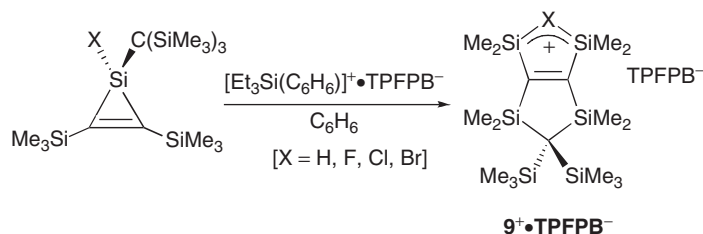
A series of organosilicon compounds featuring pentacoordinate cationic Si centers, stabilized by the intramolecular coordination of the two O-ligands at the apical positions of the trigonal bipyramid, was reported by Baukov *et al.*⁶⁸



Scheme 1.14

Nitrilium complexes $[t\text{-Bu}_3\text{E}^+ \leftarrow \text{N}\equiv\text{C-R}]^+ \cdot \text{TFPB}^-$ (E = Si, Ge, Sn; R = Me, *t*-Bu) were synthesized by the oxidative cleavage of E–E bonds with the Ph_3C^+ ion in the presence of either acetonitrile or pivalonitrile, as depicted in Scheme 1.4, A (Section 1.2.3). All of these complexes uniformly displayed a tetracoordinate central atom E featuring a greatly distorted tetrahedral geometry as a result of the interaction with the nucleophilic nitrile molecule occupying the fourth coordination site around the E center.¹¹

The delocalized halogen-bridged cation $\mathbf{9}^+ \cdot \text{TPFPB}^-$ was prepared by the unusual reaction of bromosilirene with $[\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)]^+ \cdot \text{TPFPB}^-$ (Scheme 1.15).⁶⁹ The ^{29}Si NMR resonance of $\mathbf{9}^+ \cdot \text{TPFPB}^-$ (X = Br) was observed at 90.8 ppm, that is, far upfield of the free silyl cations range, which testified to the minor extent of its silylium ion character and the major contribution of the bromonium ion character.

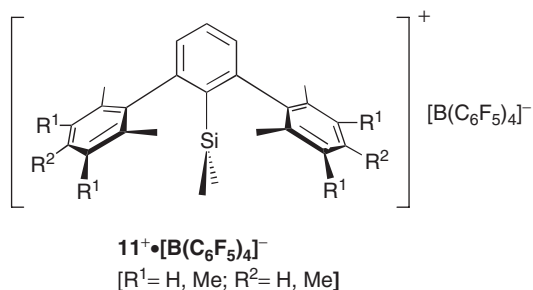


Scheme 1.15

Several important intramolecularly stabilized silyl cation derivatives have been published very recently. Among them one should mention the remarkable trimethylsilylium ion salt $\text{Me}_3\text{Si}^+ \cdot [\text{RCB}_{11}\text{F}_{11}]^-$ (R = H, Et) $\mathbf{10}^+ \cdot [\text{RCB}_{11}\text{F}_{11}]^-$ prepared by the hydride transfer reaction between $\text{Ph}_3\text{C}^+ \cdot [\text{RCB}_{11}\text{F}_{11}]^-$ and Me_3SiH .⁷⁰ $\mathbf{10}^+ \cdot [\text{RCB}_{11}\text{F}_{11}]^-$ revealed a conductivity that is typical of ionic liquids; however, in contrast to most of them it was highly reactive. In the crystalline form $\mathbf{10}^+ \cdot [\text{RCB}_{11}\text{F}_{11}]^-$ revealed coordination of the cationic Me_3Si^+ units to one of the fluorine atoms of the carborane counteranion, which caused a slight pyramidalization (354.4°) at the Si centers and stretching of the coordinating B–F bonds of the carborane cage (compared with the noncoordinating B–F bonds). In the liquid phase without solvent, $\mathbf{10}^+ \cdot [\text{RCB}_{11}\text{F}_{11}]^-$ was also not entirely ‘free’ from anion coordination as was manifested by its ^{29}Si NMR resonance observed at 138 ppm. Despite this value being low-field shifted compared with that of $\text{Me}_3\text{Si}^+ \cdot [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (84.8 ppm),^{5b} it was still by far smaller than the value of 400 ppm calculated for the ‘free’ Me_3Si^+ cation.

The stabilization of silyl cations can also be achieved through intramolecular coordination of π -donors. Thus, the cationic derivatives $\mathbf{11}^+ \cdot [\text{B}(\text{C}_6\text{F}_5)_4]^-$, possessing some degree of silylium ion character, were synthesized by the classical hydride transfer between $\text{Ph}_3\text{C}^+ \cdot [\text{B}(\text{C}_6\text{F}_5)_4]^-$ and dimethylarylsilyl hydrides (Scheme 1.16).⁷¹ The very bulky aryl substituent, featuring flanking rings at the 2- and 6-positions, provided sufficient kinetic (steric protection) and thermodynamic (p - π interaction) stabilization, thus enabling the isolation of $\mathbf{11}^+ \cdot [\text{B}(\text{C}_6\text{F}_5)_4]^-$ as a room temperature stable derivative.

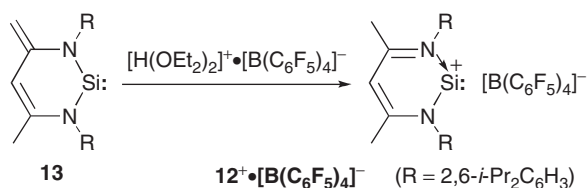
From the NMR spectral data it was concluded that the interaction of the $\mathbf{11}^+$ cation with either the aromatic solvents (C_6D_6 or C_7D_8) or the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counteranion was



Scheme 1.16

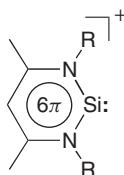
very small. However, the importance of the stabilizing intramolecular π -coordination of the flanking aryl rings to the vacant $3p_z$ -orbital of the cationic Si center was clearly manifested in the ^{29}Si NMR resonances of $11^+ \cdot [B(C_6F_5)_4]^-$ observed in the range 58.6–80.1 ppm, rather far from the region expected for ‘free’ (noncoordinated) silylium ions. The ^{13}C NMR spectral data of $11^+ \cdot [B(C_6F_5)_4]^-$ suggest that such $\text{Si}^+ \leftarrow \text{Ar}$ interaction involves the C_β atoms of the flanking rings. This was indeed confirmed by the crystal structure analysis of $11^+ \cdot [B(C_6F_5)_4]^-$, which shows no interaction of the 11^+ cation with solvent molecules or counteranions. The $\text{Si}^+ - C_\beta(\text{aryl})$ coordinating bond distance of 2.126(1) Å was ca. 16% longer than the average Si–C covalent bond (bond order approximately 0.66). The intramolecular π -coordination resulted in a significant departure of the geometry of the Si center from planarity: the sum of the bond angles around the Si atom was 346.1° , reflecting its marked pyramidity. Overall, the structure of the cationic portion 11^+ of the molecule was described on the basis of an η^1 π -coordination of the flanking tetramethylphenyl ring to the cationic Si center.

An interesting silyl cation derivative $12^+ \cdot [B(C_6F_5)_4]^-$ featuring a two-coordinate Si center was synthesized by Driess *et al.* by the protonation of N-heterocyclic silylene **13** with the Brønsted acid $[H(\text{OEt}_2)_2]^+ \cdot [B(C_6F_5)_4]^-$ (Scheme 1.17).⁷²



Scheme 1.17

$12^+ \cdot [B(C_6F_5)_4]^-$ exists as a separated ion pair with no cation–anion contacts in the solid state. The ^1H NMR chemical shift of the $\text{C}=\text{CH}$ proton of the SiC_3N_2 ring was observed at 6.92 ppm, thus suggesting the presence of aromatic 6π -electron stabilization (the resonance of the Si atom was observed at 69.3 ppm). The cyclic π -delocalization was manifested also by the shortening of the cyclic N–C bonds and stretching of the

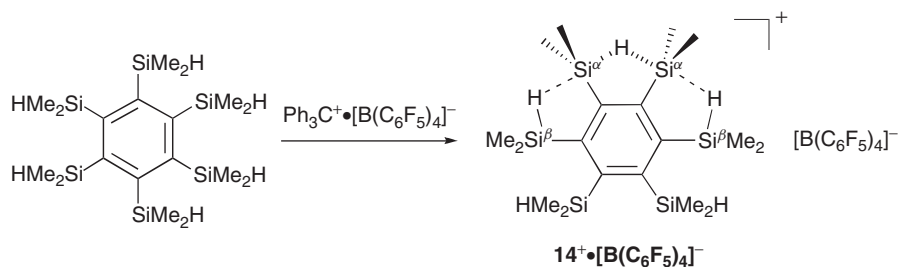


Scheme 1.18

Si–N bonds, taking place upon the protonation of **13** to form $\mathbf{12}^+ \cdot [\mathbf{B}(\text{C}_6\text{F}_5)_4]^-$. This points to an important contribution of the resonance structure with a delocalized system of the cyclic 6π -electrons (Scheme 1.18), which was corroborated also with the magnetic properties calculation on the appropriate model compound: $\text{NICS}(1) = -3.9$.

The germanium version of $\mathbf{12}^+$ with the $[\text{HO}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ counteranion was reported earlier by Power *et al.*⁷³ The cationic part of the molecule was well separated from its anion (closest approach from Ge to the nearest F atom was 3.01 Å), exhibiting structural properties similar to those of its silicon homolog $\mathbf{12}^+ \cdot [\mathbf{B}(\text{C}_6\text{F}_5)_4]^-$ (an essentially planar GeC_3N_2 ring with the two-coordinate Ge atom, cyclic Ge–N, N–C and C–C bond distances diagnostic of a cyclically delocalized system of 6π -electrons). The structural characteristics of this germyl cation are reminiscent of those of other structurally comparable Ge-centered cations intramolecularly stabilized by adjacent nitrogen ligands. They include an aminotroponimate salt with a two-coordinate cationic Ge(II) unit featuring weak interactions to two Cl atoms from counteranions,⁷⁴ and a poly(pyrazolyl)borate complex in which the cationic Ge(II) center is pyramidally coordinated by the three neighboring nitrogen ligands with the germanium lone pair occupying the fourth tetrahedral site.⁷⁵

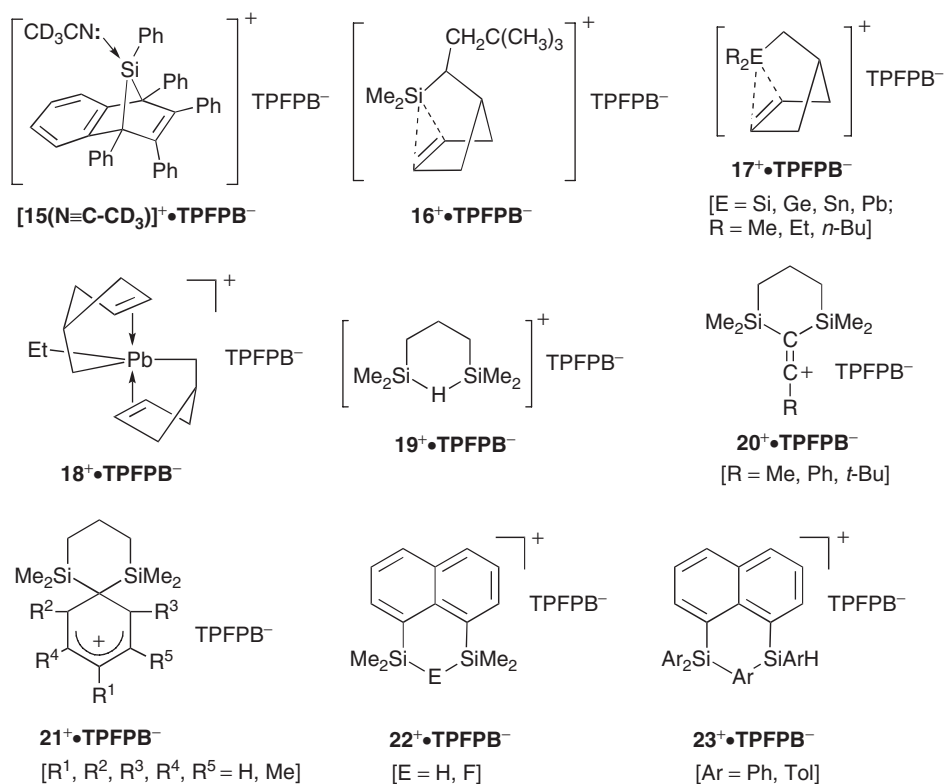
A silylium ion $\mathbf{14}^+ \cdot [\mathbf{B}(\text{C}_6\text{F}_5)_4]^-$, stabilized by polyagostic Si–H···Si interactions, was prepared by the hydride transfer reaction between hexakis(dimethylsilyl)benzene and $\text{Ph}_3\text{C}^+ \cdot [\mathbf{B}(\text{C}_6\text{F}_5)_4]^-$ (Scheme 1.19).⁷⁶ The manifestation of the hydride transfer between the Si^α centers, assisted by the agostic bonding with the $\text{Si}^\beta\text{–H}$ bonds, was seen in the ^1H - and ^{29}Si NMR spectra of $\mathbf{14}^+ \cdot [\mathbf{B}(\text{C}_6\text{F}_5)_4]^-$ measured at -80°C and at room temperature. The existence of such a H-bridged silylium ion structure, featuring two $\text{Si}^\alpha \leftarrow \text{H} \text{--} \text{Si}^\beta$ agostic interactions, was further supported by DFT calculations. The



Scheme 1.19

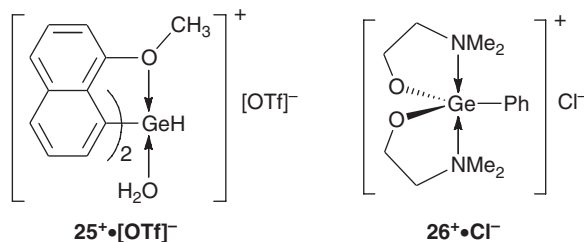
α -silylium center was found to be essentially planar (358.9°), and the three-center two-electron $\text{Si}^\alpha\text{-H}^\alpha\text{-Si}^\alpha$ bond was characterized by the markedly larger Wiberg bond order (0.426) than the $\text{Si}^\alpha\text{-H-Si}^\beta$ agostic bonding (0.182). Accordingly, the NBO electron occupancy of the $\text{H}^\beta\text{-Si}^\beta$ bond was reduced to 1.806 because of the electron density transfer to the adjacent cationic Si^α centers.

An important contribution to the field was made by Müller and his group, who published a series of papers describing the synthesis of intramolecularly stabilized cations of the heavy group 14 elements as well as silyl-substituted vinyl cations and arenium ions, prepared by classical hydride transfer reactions with $\text{Ph}_3\text{C}^+\cdot\text{TPFPB}^-$.⁷⁷ Thus, the transient 7-silanorbornadien-7-ylum ion **15**⁺ was stabilized by coordination to nitrile and isolated as the nitrilium complex $[\mathbf{15}\leftarrow:\text{N}\equiv\text{C-CD}_3]\text{TPFPB}^-$ (Scheme 1.20), whereas the free **15**⁺ was unstable at room temperature and rearranged possibly into the highly reactive $[\text{PhSi}^+/\text{tetraphenyl-naphthalene}]$ complex.^{77a,i} In contrast, 2-silanorbornyl cation **16**⁺ $\cdot\text{TPFPB}^-$ (Scheme 1.20) was stable because of the effective internal coordination of its silylium ion center to the C=C double bond and revealed no interaction with either counterion or solvent.^{77b,h,i} The intramolecular π -complexation was manifested in the ²⁹Si NMR chemical shift of **16**⁺ $\cdot\text{TPFPB}^-$ observed at 87.4 ppm, in the range diagnostic for silyl cation- π arene complexes, as well as by the appreciable



Scheme 1.20

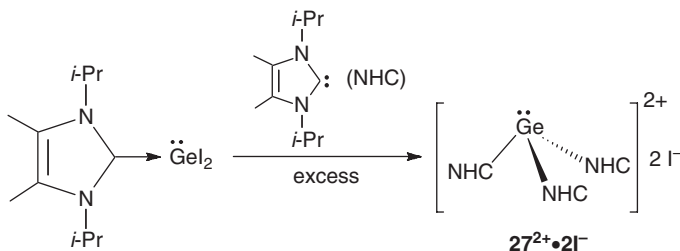
deshielding of the olefinic C atoms (ca. 20 ppm compared with the starting hydrosilane) indicating substantial charge transfer from the Si to the C=C bond. Like the transient 15^+ , 16^+ can be readily stabilized by coordination of the highly nucleophilic acetonitrile forming the corresponding silylated nitrilium ion. Certainly, 16^+ possesses some degree of silylium ion character, although it can be alternatively viewed as a bridged β -silyl carbocation. The scope of this synthetic approach was then expanded to produce novel stable norbornyl cations free from aromatic solvent interaction $17^+\cdot\text{TPFPB}^-$, based on the heavier group 14 elements (Ge, Sn, Pb) (Scheme 1.20).^{77c,i} These cations $17^+\cdot\text{TPFPB}^-$ revealed the characteristic low-field resonance of their central nuclei at 80.2–87.2 ppm (E = Si), 334.0 ppm (E = Sn) and 1049 ppm (E = Pb); values that, however, were markedly smaller than those expected for the free tricoordinate ions. Cations of this type can be stabilized by the intramolecular π -coordination of the two C=C double bonds from a pair of cyclopentenyl ligands (Scheme 1.20).^{77d} The plumbylum ion $18^+\cdot\text{TPFPB}^-$ was stable at room temperature for several weeks, exhibiting a low-field ^{207}Pb NMR resonance at 807 ppm. Its crystal structure analysis revealed well-separated cationic and anionic parts, and a trigonal-bipyramidal coordination geometry around the Pb atom.^{77d} The silyl cation $19^+\cdot\text{TPFPB}^-$, featuring a three-center two-electron Si–H–Si bond with hydrogen as a bridging atom, exhibited a low-field resonance of the cationic Si atom at 76.7 ppm, was observed as a doublet with a $^1J(^{29}\text{Si}-^1\text{H})$ coupling constant of 39 Hz (Scheme 1.20).^{77e,f} Stable β -disilacyclohexenylidene-substituted vinyl cations $20^+\cdot\text{TPFPB}^-$, formed upon the intramolecular addition of the transient silylium ion to a C \equiv C triple bond, were also free from solvent interaction (Scheme 1.20).^{18a,77f} Their high stability was reasonably attributed to the hyperconjugative interaction of the vinyl cationic center with the two β -silyl substituents, as well as to electron donation from the α -phenyl group. The crystal structure of 20^+ (R = *t*-Bu) with the hexabromocarborene counterion, $20^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, disclosed a free vinyl cation with a markedly short C=C double bond length of 1.221 Å, closely approaching the length of a usual C \equiv C triple bond.^{18b,77f} Moreover, the =C–Si bonds were rather long (1.984 and 1.946 Å), thus providing solid support for the existence of β -silyl hyperconjugation, giving the 20^+ cation some extent of silylium ion character. A series of bisilylated arenium ions $21^+\cdot\text{TPFPB}^-$ was prepared by the intramolecular complexation of the transient silylium ions with aromatic rings (Scheme 1.20).^{77f,g} Similar to the above case of 20^+ , the surprising thermodynamic stability of $21^+\cdot\text{TPFPB}^-$ was ascribed to the important hyperconjugative effects of the two β -silyl substituents. The hydrogen-bridged bis(silyl)cation $22^+\cdot\text{TPFPB}^-$ (E = H) revealed the deshielded resonance of its Si atoms at 54.4 ppm ($^1J_{\text{Si-H}} = 46$ Hz).^{77j} In the solid state cation 22^+ , both tetracoordinated Si atoms of which revealed a pyramidal geometry (345.5° and 346.7°), showed no covalent contacts to the TPFPB $^-$ counteranion. Interestingly, a fluoronium ion $22^+\cdot\text{TPFPB}^-$ (E = F) was formed upon the reaction of $22^+\cdot\text{TPFPB}^-$ (E = H) with alkyl fluorides (C $_{10}$ H $_{21}$ F, PhCF $_3$). The ^{29}Si NMR chemical shift of $22^+\cdot\text{TPFPB}^-$ (E = F) was observed at 77.2 ppm ($^1J_{\text{Si-F}} = 243$ Hz). Similar to the case of 22^+ (E = H), 22^+ (E = F) also exists as a ‘free’ cation, lacking any bonding interaction to either counteranion or solvent, and featuring a tetrahedral coordination of the Si atoms (345.9° and 347.7°). The bonding in the two cations $22^+\cdot\text{TPFPB}^-$ (E = H) and $22^+\cdot\text{TPFPB}^-$ (E = F) is different: electron-deficient two-electron, three-center Si–H–Si bonding in $22^+\cdot\text{TPFPB}^-$ (E = H) and Lewis acid–base interaction in $22^+\cdot\text{TPFPB}^-$ (E = F). The aryl-bridged



Scheme 1.22

Such a classification was based on the crystal structure peculiarities of these ionic species, namely, lack of cation–anion interactions, considerably stretched Ge–O [1.90 Å (av.)] and Sn–O [2.12 Å (av.)] bonds and observable flattening about the Ge [348° (av.)] and Sn (352.8°) centers.

An interesting Ge-containing dication $27^{2+} \cdot 2I^-$ was prepared by the reaction of the N-heterocyclic carbene (NHC)–GeI₂ complex with an excess of carbene (Scheme 1.23).⁸¹ The Ge center in 27^{2+} revealed no bonding contacts to the iodide ions (closest Ge–I distance of 5.96 Å), however, the iodides were weakly interacting with the methyl H atoms (3.11 Å). The geometry about the Ge atom was pyramidal with Ge–C bond distances of 2.070(6) Å (slightly longer than the average Ge–C bond lengths of 1.90–2.05 Å).⁸¹ Given the strong Lewis basicity of NHC ligands and the presence of nucleophilic THF solvent and iodide counteranions, it is hard to imagine both positive charges being situated exclusively on the Ge center, which corresponds to [Ge²⁺ ← (NHC)₃] contribution **A**. Another resonance form **B** [Ge[−]–(NHC⁺)₃], in which a negatively charged Ge atom is bound to the three positively charged NHC ligands as the result of intramolecular charge transfer, may also significantly contribute to the overall Ge–NHC ligand bonding situation. Apparently, the real nature of this dication $27^{2+} \cdot 2I^-$ is somewhere between these two resonance extremes **A** and **B**, in which the Ge center possesses some, but by no means full, gerymyl dication character.

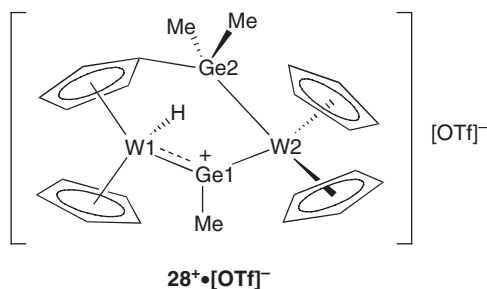


Scheme 1.23

Several remarkable Si- and Ge-containing cationic transition metal complexes were sometimes viewed as derivatives of trivalent silylium or gerymylium ions of the type R₂E⁺–M (E = Si, Ge; M = transition metal fragment).^{1h} However,

such a classification is questionable, taking into account the importance of another resonance contributor $R_2E=M^+$, ascribing to the compound the properties of silylene (or germylene) transition metal complexes featuring a double bond between the group 14 element and transition metal. Thus, the cationic derivatives $[(\eta^5-C_5Me_5)(PMe_3)_2Ru=Si(SR)_2]^+ \cdot BPh_4^-$ ($R = Et, p-MeC_6H_4$),^{82a} $[(\eta^5-C_5Me_5)(PMe_3)_2Ru=SiR_2]^+ \cdot [B(C_6F_5)_4]^-$ ($R = Me, Ph$),^{82b} $[trans-(Cy_3P)_2(H)Pt=Si(SET)_2]^+ \cdot [BPh_4]^-$,^{82c} and neutral $(\eta^5-C_5Me_5)(PMe_3)_2RuSi[S(p-MeC_6H_4)]Os(CO)_4$,^{82d} were described by Tilley *et al.* as the base-free silylene complexes, in which sp^2 -hybridized Si centers manifested short bonds to transition metals, planar geometry and very low-field ^{29}Si NMR resonances (259.4–311.0 ppm).

Similarly, the cationic Ge complex 28^+ , which had no bonding contacts to its triflate counteranion, revealed a planar geometry about the cationic Ge1 center (360°) and short Ge1–W1 bond distance [2.487(2) Å] (Scheme 1.24).⁸³ Based on such structural peculiarities, the most important resonance structure of 28^+ was described as $Me(W_2)Ge1=W1^+$, with the significant Ge1=W1 double bond character due to the π back-donation from tungsten to electron-deficient germanium, rather than the $Me(W_2)Ge1^+-W1$ contributor, featuring a full cationic charge situated on the germanium center.⁸³ The marked shortening of the Si–Fe and Ge–Fe bonds in the related base-stabilized μ -silylyne and μ -germylyne diiron complexes was realized in terms of the partial double bond character of Si=Fe and Ge=Fe.⁸⁴

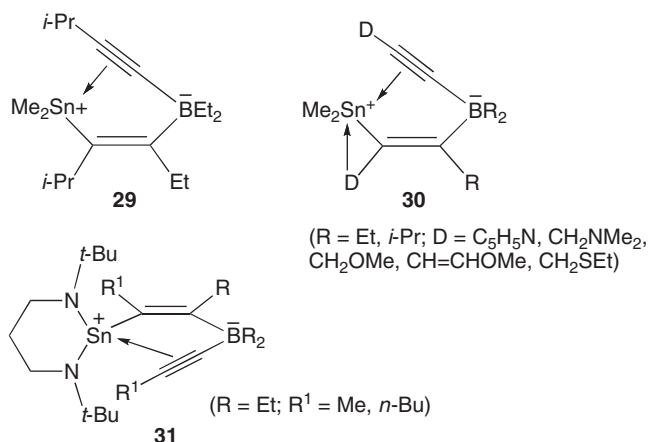


Scheme 1.24

Many intramolecularly stabilized stannyl cations have been synthesized, and some of them will be described below. In the early stages, several cationic derivatives with no bonding interaction to the low-coordinating anions were reported as featuring diagnostically pentacoordinate cationic Sn centers stabilized by the intra- or intermolecular coordination of n -donating ligands ($:NR_2$, $:N \equiv C-R$, $:OH_2$, etc.) at the apical positions of a trigonal bipyramid.⁸⁵

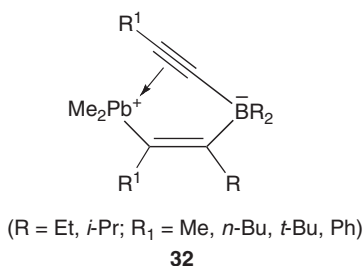
The perstannylated ammonium and phosphonium salts $[(Me_3Sn)_4E]^+ \cdot [OTf]^-$ and $[(Me_3Sn)_4E]^+ \cdot [BPh_4]^-$ ($E = N, P$), dissociating in solution and thus being a masked source of the Me_3Sn^+ ions, can be alternatively viewed as the Lewis-base-stabilized trimethylstannylium ions $[Me_3Sn^+ \leftarrow :E(SnMe_3)_3]$.^{26a} In contrast to $[(Me_3Sn)_4E]^+$ ions, the persilylated phosphonium and arsonium derivatives $[(Me_3Si)_4E]^+ \cdot [B(C_6F_5)_4]^-$ ($E = P, As$) do not dissociate to form Me_3Si^+ ions, which is explained by the stronger Si–E bonds and higher Lewis acidity of the Me_3Si^+ ions.^{26b}

A family of stannyl cations **29–31**, stabilized by intramolecular side-on π -coordination to the $\text{C}\equiv\text{C}$ bond of an alkynylborate fragment, was synthesized by Wrackmeyer *et al.* (Scheme 1.25).⁸⁶ The X-ray diffraction analysis of **29** revealed a somewhat pyramidal geometry about the cationic Sn atom (351.1°), which was oriented towards the $\text{C}\equiv\text{C}$ bond, thus allowing their effective through-space interaction.^{86a} The π -coordination of the cationic fragment to a carbon–carbon triple bond was also clearly manifested in the appreciable shielding of the Sn atoms observed in the ^{119}Sn NMR spectra of these derivatives.



Scheme 1.25

Likewise, the isostructural plumbyl cations **32**, intramolecularly π -coordinated to the $\text{C}\equiv\text{C}$ bond of an alkynylborate moiety, were prepared by the same research group (Scheme 1.26).⁸⁷

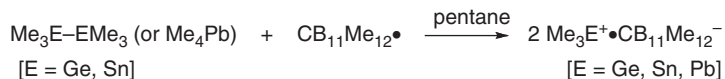


Scheme 1.26

The intramolecular stabilization of the cationic Pb center occurs at the expense of its departure from the idealized trigonal-planar geometry, leading to a slight pyramidalization about the Pb atom [355.7° for **32** (R = *i*-Pr, R¹ = Me)]. The low-coordination of the

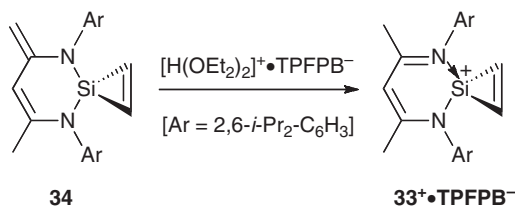
metallic center in **32** was manifested in its ^{207}Pb NMR resonances observed in the range 630–750 ppm, shifted low-field by 600–800 ppm with respect to tetraorganoplumbanes.

Michl *et al.* reported the crystal structure of the cationic derivative $n\text{-Bu}_3\text{Sn}^+\cdot[\text{CB}_{11}\text{Me}_{12}]^-$, prepared according to Scheme 1.4, B (Section 1.2.3).^{12a} Lacking bonding interaction to the solvent, $n\text{-Bu}_3\text{Sn}^+$ was weakly coordinated to the Me groups of the carborane anion $[\text{CB}_{11}\text{Me}_{12}]^-$ featuring a long Sn–C(Me) bond distance (av. 2.81 Å) and not quite perfectly planar geometry around the Sn atom (353.1°). The resonance of the Sn atom in $n\text{-Bu}_3\text{Sn}^+\cdot[\text{CB}_{11}\text{Me}_{12}]^-$ was observed at 454.3 ppm,^{12a} far upfield from the 1500–2000 ppm range estimated for the trimethylstannylum ion,⁴¹ indicating that the same cation aggregation through Me coordination exists also in solution. Employing the same synthetic approach, Michl *et al.* prepared a series of novel germylium, stannylum and plumbylum ion derivatives $\text{Me}_3\text{E}^+\cdot[\text{CB}_{11}\text{Me}_{12}]^-$ (E = Ge, Sn, Pb) (Scheme 1.27).^{12b} Similar to the above case of $n\text{-Bu}_3\text{Sn}^+\cdot[\text{CB}_{11}\text{Me}_{12}]^-$, all Me_3E^+ cations revealed a remarkable interaction with the Me groups of the $\text{CB}_{11}\text{Me}_{12}^-$ counterion featuring long E–C(Me) bond distances of 2.5–3.0 Å (EXAFS). This was manifested in the appearance of NMR chemical shifts of the central nuclei of $\text{Me}_3\text{E}^+\cdot[\text{CB}_{11}\text{Me}_{12}]^-$ in the relatively high field: 335.9 ppm in CD_2Cl_2 at -60°C (E = Sn) and 1007.4 ppm in CD_2Cl_2 at room temperature (E = Pb).^{12b} The cation–anion interaction was estimated to be predominantly ionic with some contribution (from 1/4 to 1/3) from covalent bonding, and the strength of this interaction was found to increase in the order: $\text{Me}_3\text{Pb}^+ < \text{Me}_3\text{Sn}^+ \ll \text{Me}_3\text{Ge}^+$.



Scheme 1.27

An interesting example of the *n*-donor-supported silacyclopropenylium ion is the derivative $\mathbf{33}^+\cdot\text{TPFPB}^-$, in which the cationic spiro-Si center is shared by the six-membered ring N-heterocyclic unit and three-membered ring cyclopropene moiety. This was recently prepared by Driess *et al.* by the protonation of N-heterocyclic silacyclopropene **34** with $[\text{H}(\text{OE}t_2)_2]^+\cdot\text{TPFPB}^-$ (Scheme 1.28).⁸⁸ The highly electrophilic silylium center in $\mathbf{33}^+$ is effectively stabilized by the intramolecular electron donation from the adjacent N atom.



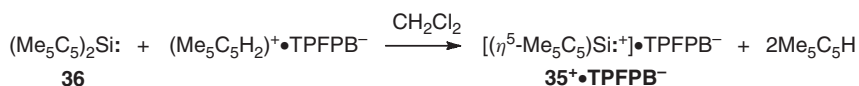
Scheme 1.28

1.6.2 Free (Noncoordinated) Cations

1.6.2.1 Cyclic π -Conjugated Cations

The heavy group 14 element centered cations stabilized by cyclic π -conjugation were the first isolable representatives of the family of cationic species free from observable interactions with either external (counteranions, nucleophilic solvents) or internal (intramolecular n- or π -donors) coordination. The most important of these, stable 2π -electron aromatic cyclotrigermylium, cyclotrisilylium and disilacyclopropenylium derivatives, 6π -electron aromatic silatropylium derivative, homoaromatic cyclotetrasilenylium, bishomoaromatic germacyclopropenylium, and trishomoaromatic cationic Ge-cluster derivatives, as well as transient aromatic 2-silaimidazolium and bishomoaromatic 7-silanorbornadienylium salts, will be discussed in detail in the Chapter 6, devoted to the issue of aromaticity among the group 14 organometallics.

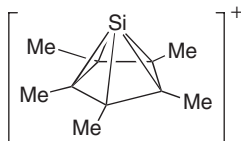
Among other important examples of the cyclic π -conjugated cations, one should mention the very remarkably stable $(\eta^5\text{-Me}_5\text{C}_5)\text{Si}^+$ cation derivative $\mathbf{35}^+\cdot\text{TPFPB}^-$, which was prepared by the oxidation of decamethylsilicocene $\mathbf{36}$ with $(\text{Me}_5\text{C}_5\text{H}_2)^+\text{Si}^+\cdot\text{TPFPB}^-$ in CH_2Cl_2 (Scheme 1.29).⁸⁹



Scheme 1.29

In the crystalline form, the cation $\mathbf{33}^+$ exhibited only a weak interaction with the TPFPB^- anion, featuring a nearly ideal pentagonal-pyramidal geometry (Scheme 1.30).

Such a pentagonal-pyramidal configuration of $\mathbf{35}^+\cdot\text{TPFPB}^-$ was maintained also in solution, as shown by the observation of only a single resonance at 2.23 ppm for all five Me groups of the Me_5C_5 unit even at low temperature. Moreover, a resonance of the Si atom of $\mathbf{35}^+\cdot\text{TPFPB}^-$ was observed at very high field (-400.2 ppm), diagnostic of the π -complexes of a divalent Si atom. Overall, both X-ray diffraction and NMR spectroscopy studies confirmed the structure of $\mathbf{33}^+$ as a cationic π -complex featuring the $\eta^5\text{-Me}_5\text{C}_5$ ligand bound to a 'naked' Si center. Alternatively, the $(\eta^5\text{-Me}_5\text{C}_5)\text{Si}^+$ cation $\mathbf{35}^+$ can be viewed as a *pentacoordinated* analog of the highly challenging *mono-haptocoordinated* silyliumylidene ion $(\eta^1\text{-Me}_5\text{C}_5)\text{Si}^+$. Reactivity of $\mathbf{35}^+\cdot\text{TPFPB}^-$ has proved to be very attractive. Thus, it reacts with $(\text{Me}_3\text{Si})_2\text{NLi}$ to produce transient



Scheme 1.30

silylene $[(\text{Me}_3\text{Si})_2\text{N}](\text{Me}_5\text{C}_5)\text{Si}$, undergoing subsequent dimerization finally to form the rather unusual *trans*-1,2-diaminodisilene $(\eta^1\text{-Me}_5\text{C}_5)[(\text{Me}_3\text{Si})_2\text{N}]\text{Si}=\text{Si}[\text{N}(\text{SiMe}_3)_2](\eta^1\text{-Me}_5\text{C}_5)$, in which both Me_5C_5 groups are σ -bonded to the Si atoms.⁸⁹

1.6.2.2 *Acyclic Cations Lacking π -Conjugation*⁹⁰

The most challenging tricoordinate cations R_3E^+ (R = alkyl, aryl, silyl; E = Si–Pb) featuring an ideal trigonal-planar geometry and ‘freedom’ from both counteranions and solvents, thus being the least electronically perturbed by coordination to either external or internal nucleophiles, are very attractive targets for long-standing experimental and theoretical pursuits.

The first experimental breakthrough was achieved by Lambert and his group, who reported preparation of the free trimesitylsilylium ion $\text{Mes}_3\text{Si}^+\cdot\text{TPFPB}^-$ (**37⁺•TPFPB⁻**) in 1997.⁹¹ Because the classical hydride transfer reaction between Mes_3SiH and $\text{Ph}_3\text{C}^+\cdot\text{TPFPB}^-$ was unsuccessful due to the large steric bulk of the Mes groups, a novel synthetic approach involving allyl substituents as leaving groups (the so-called ‘allyl leaving group approach’)⁸ was developed. Thus, allyltrimesitylsilane $\text{Mes}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}_2$ was reacted with $[\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)]^+\cdot\text{TPFPB}^-$ to form a transient β -silylcarbenium ion $\text{Mes}_3\text{Si}-\text{CH}_2-\text{CH}^+-\text{CH}_2\text{SiEt}_3$, which underwent subsequent fragmentation to produce the more stable trimesitylsilylium ion derivative **37⁺•TPFPB⁻** accompanied by the elimination of $\text{Et}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}_2$ (Section 1.2.3, Scheme 1.3).⁸ **37⁺•TPFPB⁻** was stable in solution for several weeks and exhibited an identical ²⁹Si NMR resonance at 225.5 ppm in different aromatic solvents^{8,91} and with different counteranions,^{1n,8} thus reliably suggesting the ‘free’ state of its **37⁺** cation in solution. However, in the presence of nucleophilic reagents (CD_3CN , Et_3N) this resonance was greatly shifted to the high-field region, pointing to the highly electrophilic nature of silylium ion **37⁺**. Subsequent computations confirmed the status of Mes_3Si^+ as a free cation lacking observable coordination to solvent, in which the calculated ²⁹Si NMR chemical shift value was very close to the experimental value: 230.1 (GIAO/HF) and 243.9 (GIAO/DFT) ppm vs 225.5 ppm.⁹²

However, because TPFPB^- derivatives often form oils or clathrates precluding their crystallization, **37⁺•TPFPB⁻** has failed to crystallize. To obtain crystals suitable for X-ray crystallography, the TPFPB^- counteranion was replaced with Reed’s carborane $\text{CB}_{11}\text{HMe}_5\text{Br}_6^-$ anion. Accordingly, **37⁺•[CB₁₁HMe₅Br₆]⁻** was synthesized by the reaction of $\text{Mes}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}_2$ with $\text{Et}_3\text{Si}^+\cdot[\text{CB}_{11}\text{HMe}_5\text{Br}_6]^-$ in benzene.^{93,94} The X-ray diffraction analysis of **37⁺•[CB₁₁HMe₅Br₆]⁻** revealed that this is indeed a trigonal-planar sp^2 -silylium ion truly free from covalent interaction with either counteranion or solvent (Figure 1.1).⁹³ The solid state ²⁹Si NMR resonance of **37⁺•[CB₁₁HMe₅Br₆]⁻** was practically the same as that in solution: 226.7 ppm vs 225.5 ppm.

The range of the heavy group 14 element centered cations prepared by the ‘allyl leaving group approach’ was later expanded to those of germanium and tin. Thus, the trimesitylstannylium ion $\text{Mes}_3\text{Sn}^+\cdot\text{TPFPB}^-$ (**38⁺•TPFPB⁻**) was successfully formed by the treatment of $\text{Mes}_3\text{Sn}-\text{CH}_2-\text{CH}=\text{CH}_2$ with $[\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)]^+\cdot\text{TPFPB}^-$ or $[\text{Et}_3\text{SiCH}_2\text{CPh}_2]^+\cdot\text{TPFPB}^-$ in benzene (Scheme 1.3).⁸ The cationic Sn atom in **38⁺•TPFPB⁻** resonated at a low field of 806 ppm, a signal that was independent of the solvent used, thus testifying to the noncoordinated nature of the stannylium ion

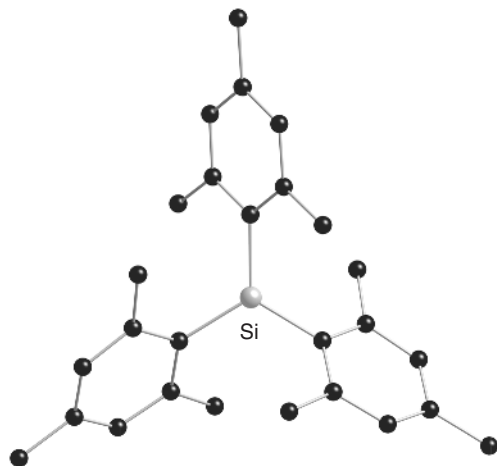


Figure 1.1 Crystal structure of the silylium ion derivative $\text{Mes}_3\text{Si}^+\cdot\text{TPFPB}^-$ ($37^+\cdot\text{TPFPB}^-$) (hydrogen atoms and TPFPB^- counterion are not shown)

38^+ . The trimesitylgermylium ion derivative $\text{Mes}_3\text{Ge}^+\cdot\text{TPFPB}^-$ ($39^+\cdot\text{TPFPB}^-$) was also synthesized by the ‘allyl leaving group approach’, and the degree of its cationic character was estimated to be comparable with those of the analogous trimesitylsilylium 37^+ and trimesitylstannylium 38^+ ions.⁸ The tridurylsilylium ion Dur_3Si^+ prepared by the same experimental procedure featured a ^{29}Si NMR resonance at 226.8 ppm, a value that was very close to that of the Mes_3Si^+ cation of 225.5 ppm.⁹⁵ This was reasonably interpreted as the manifestation of the ‘free’ status of the Dur_3Si^+ cation. However, the heavier tridurylstannylium ion Dur_3Sn^+ exhibited a ^{119}Sn NMR chemical shift at 720 ppm, which was shifted to lower frequency compared with that of the Mes_3Sn^+ cation (806 ppm), on which basis the degree of Dur_3Sn^+ true stannylium ion character was estimated as ca. 70%.⁹⁵

Utilizing the same synthetic strategy, Lambert *et al.* prepared the remarkable $\text{Tip}_3\text{Sn}^+\cdot\text{TPFPB}^-$, $40^+\cdot\text{TPFPB}^-$, by the reaction of $\text{Tip}_3\text{Sn}-\text{CH}_2-\text{CH}=\text{CH}_2$ with $\text{Ph}_3\text{C}^+\cdot\text{TPFPB}^-$.⁹⁶ In the crystalline form, 40^+ revealed no bonding interaction with either TPFPB^- counteranion or solvent, or with the methine hydrogens of the *i*-Pr groups, implying that 40^+ is indeed a ‘free’ trigonal-planar stannylium ion. The resonance of the cationic Sn atom of 40^+ was observed at 714 ppm, which was taken as evidence for its stannylium ion nature in solution (GIAO calculation at the MPW1PW91 level provided a similar value of 763 ppm).

As was mentioned in Section 1.2.5, the one-electron oxidation of the isolable free radicals represents one of the most attractive and straightforward methods for the synthesis of stable cations of the heavy group 14 elements. Thus, oxidation of the stable silyl radical $(t\text{-Bu}_2\text{MeSi})_3\text{Si}\cdot$ with $\text{Ph}_3\text{C}^+\cdot\text{TPFPB}^-$ in toluene resulted in the formation of a transient silylium ion salt $(t\text{-Bu}_2\text{MeSi})_3\text{Si}^+\cdot\text{TPFPB}^-$ ($41^+\cdot\text{TPFPB}^-$), stabilized in the form of its nitrilium complex $[41\leftarrow:\text{N}\equiv\text{C}-\text{CH}_3]^+\cdot\text{TPFPB}^-$ (Scheme 1.31).⁹⁷ Without complexation, $41^+\cdot\text{TPFPB}^-$ underwent unavoidable isomerization through the fast 1,2-Me shift from the peripheral Si to the central cationic Si atom yielding a new silyl

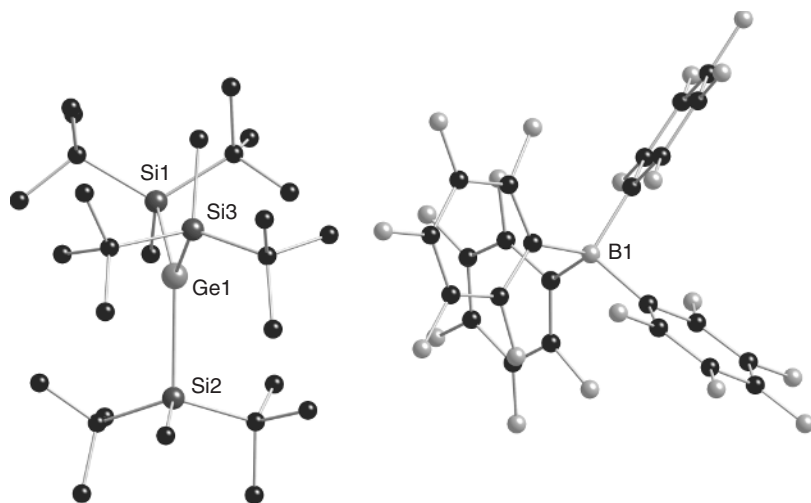
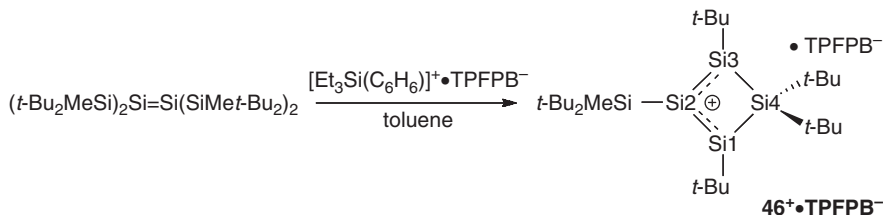


Figure 1.2 Crystal structure of germylium ion derivative $(t\text{-Bu}_2\text{MeSi})_3\text{Ge}^+\cdot\text{TPFPB}^-$ $43^+\cdot\text{TPFPB}^-$ (hydrogen atoms are not shown)

in the radical $(t\text{-Bu}_2\text{MeSi})_3\text{Sn}\cdot$. Particularly noteworthy was the exceedingly low-field ^{119}Sn NMR resonance of 44^+ , undoubtedly pointing to its ‘free’ status in solution and representing the most deshielded Sn nucleus of all low-coordinate stannyl cations ever reported. This value of 2653 ppm by far exceeded the value expected on the basis of the ^{29}Si – ^{119}Sn chemical shift empirical correlation (1500–2000 ppm) and the value (ca. 1000 ppm) calculated for a ‘free’ triorganostannylium ion,⁴² being in reasonable agreement with the value of 2841 ppm calculated for the model $(\text{H}_3\text{Si})_3\text{Sn}^+$ cation at the GIAO-B3LYP/6-311G(d) level.^{15b}

Several other remarkable representatives of the stable cations based on the heavy group 14 elements were reported quite recently. Among them is the triarylgemyl derivative $[2,6\text{-}(t\text{-BuO})_2\text{-C}_6\text{H}_3]_3\text{Ge}^+\cdot[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ $45^+\cdot[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ prepared by the dehalogenation of bromogermane $[2,6\text{-}(t\text{-BuO})_2\text{-C}_6\text{H}_3]_3\text{GeBr}$ with the silver salt of the weakly coordinating anion $\text{Ag}^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$.⁹⁸ Although stable in its crystalline form, $45^+\cdot[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ decomposed in solution at temperatures above -20°C . Similar to the previously described $43^+\cdot\text{TPFPB}^-$,^{15a} triarylgemyl derivative $45^+\cdot[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ manifested a cationic part 45^+ ‘free’ from any observable interactions with its counteranion $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$, with trigonal-planar geometry about the tricoordinate Ge center.⁹⁸

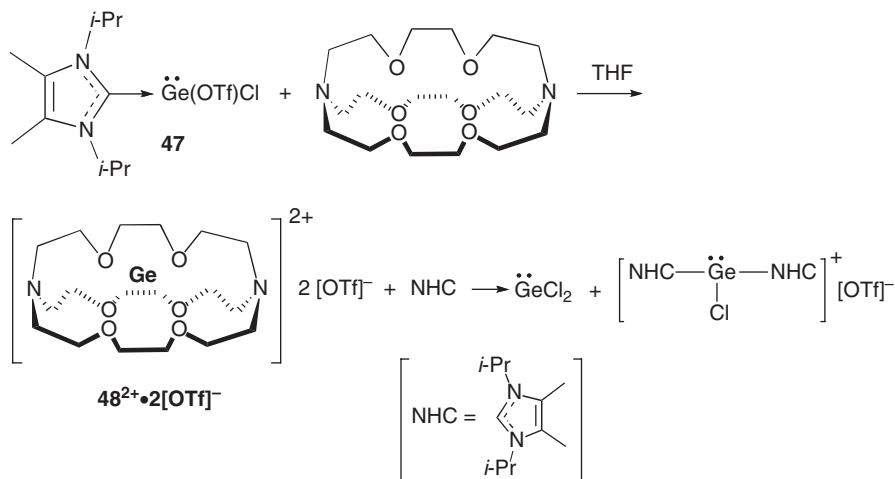
A cyclotetrasilenylium ion derivative $46^+\cdot\text{TPFPB}^-$, prepared by the oxidation of the tetrasilylidisilene $(t\text{-Bu}_2\text{MeSi})_2\text{Si}=\text{Si}(\text{SiMe}t\text{-Bu}_2)_2$ with $[\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)]^+\cdot\text{TPFPB}^-$, was also ‘free’ in the solid state (Scheme 1.32).⁹⁹ The positive charge in the cationic portion 46^+ was delocalized over the three Si atoms (Si1, Si2 and Si3), which was seen in the essentially planar geometry around them and Si1–Si2/Si2–Si3 bond lengths intermediate between those of typical single and double bonds. The allylic nature of cation 46^+ was further supported by the observation of low-field ^{29}Si NMR resonances diagnostic of



Scheme 1.32

the allylic systems: 183.8 ppm (central Si2 atom) and 286.8 ppm (terminal Si1 and Si3 atoms).

Employing a simple addition of macrocyclic [2.2.2]cryptand to the NHC complex of $\text{Cl}(\text{TfO})\text{Ge}$: **47**, Baines *et al.* were able to isolate an interesting dicationic species $48^{2+}\bullet 2[\text{OTf}]^-$ in which a doubly positively charged germanium atom, lacking any substituents, was encapsulated within a cryptand cavity (Scheme 1.33, Figure 1.3).^{100a} The remote OTf^- counterions showed no any signs of bonding interaction with the Ge dication, which was at the first glance surprising giving the non-negligible nucleophilicity of the triflate anions. Such amazing chemical stability of the Ge^{2+} ion in $48^{2+}\bullet 2[\text{OTf}]^-$ was attributed to an effective steric shielding of the cationic center by the three-dimensional network of [2.2.2]cryptand. Moreover, dicationic species $48^{2+}\bullet 2[\text{OTf}]^-$ can even survive crystallization from the Lewis basic acetonitrile, which again pointed to an important steric protection role of the macrocycle. The Ge^{2+} of the cationic portion of the molecule 48^{2+} was found to be only very weakly interacting with the oxygen and nitrogen *n*-donors of the [2.2.2]cryptand moiety, with the Ge–N [2.524(3) Å] and Ge–O [2.4856(16) Å] interatomic distances markedly exceeding those of the standard Ge–N and Ge–O single covalent bonds. The lack of observable



Scheme 1.33

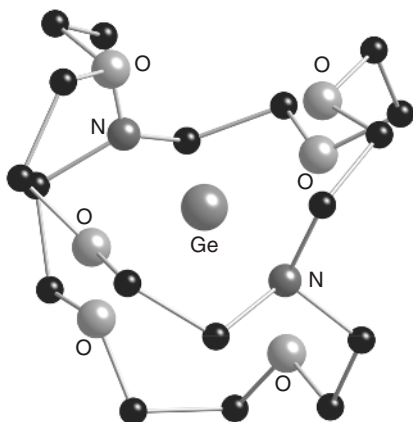


Figure 1.3 Crystal structure of [2.2.2]cryptand-encapsulated Ge(II) dicationic derivative $48^{2+} \cdot 2[\text{OTf}]^-$ (hydrogen atoms and TfO^- counteranions are not shown)

bonding interactions between the germanium dicationic guest and [2.2.2]cryptand host was further supported by NBO computations at the PBE1PBE/6-311+G(2d,p) level, which revealed the pure 4s lone pair as the Ge valence orbital.^{100a} Moreover, NPA analysis disclosed a high portion (+1.38) of the overall positive charge to be accommodated on the Ge center, even despite its donor–acceptor interactions with the cryptand *n*-donating heteroatoms. Indeed, the bond orders (WBI) for such Ge–N and Ge–O interactions were found to be exceedingly small: 0.11 and 0.10, respectively.

The high efficiency of macrocyclic structures in stabilizing Ge(II) dicationic species was further demonstrated by the complexation of Ge centers (with or without substituents) by crown ethers and azamacrocycles.^{100b,c} In the resulting host–guest complexes, the cationic germanium atoms manifested highly variable coordination numbers depending on the size of the macrocyclic host and type of the counteranion used. Accordingly, the variety of isolated Ge(II)–macrocycle complexes is represented by a range of structural modifications: from complexes where a Ge(II) dication is sandwiched between two crown ether molecules to complexes in which a Ge center is encapsulated within the cavity of a crown ether/azamacrocycle.^{100b,c}

1.7 Summary and Outlook

Carbenium ions constitute one of the most fundamental classes of organic chemistry species and have been studied for more than a hundred years. Their existence and important role as key reactive intermediates in a number of organic reactions (see Section 1.1) are now well established. The isolation and X-ray characterization of the stable carbocationic derivatives provided a great deal of invaluable information about their bonding and structure, largely supported by the conclusions drawn from state-of-the-art computational methods. The field of the heavy congeners of carbenium ions, in which the positive charge is centered on tricoordinate Si, Ge, Sn and Pb atoms, is not so mature.

Having started in the 1960–1970s, research in the field of cations of the heavy group 14 elements (first of all, silylium ions) was initially focused on the detection of such species as short-lived reactive intermediates. In the 1980s the first claims for the synthesis of stable silylium ion derivatives appeared in the literature (silyl perchlorates), which however were disproved by subsequent elaborate experimental and computational studies showing the covalent rather than ionic nature of these compounds. In contrast to the well-developed gas-phase chemistry of silyl cations, that in the condensed phase was greatly complicated by the effects of solvation and interaction with counteranions. At that time it became more or less clear that three factors are mainly responsible for the success or failure in the synthesis of truly ionic tricoordinate silyl cations: solvent, counteranion and substituents. Consequently, the right choice of the most appropriate solvents and counteranions was the first major problem to be solved. This was finally achieved by the utilization of extremely weakly coordinating anions (borates, carboranes) and solvents of particularly low nucleophilicity (benzene, toluene). Such experimental findings brought about the first milestone achievements in the synthesis of the stable silylium ion derivatives, $[\text{Et}_3\text{Si}(\text{toluene})]^+\cdot\text{TPFPB}^-$ by Lambert and $i\text{-Pr}_3\text{Si}^+\cdot[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ by Reed, in the early 1990s. These silyl cations were not completely ‘free’, being coordinated to either solvent or counteranion, for which their true silylium ion nature and degree of their ionicity were heavily criticized. Despite this, one should undoubtedly recognize the crucial importance of their discoveries to the resolution of the ‘free’ silylium ion problem. This was finally achieved in the 2000s by a combination of the previous findings, weakly coordinating anions and low nucleophilic solvents, with the right choice of bulky substituents and culminated in the synthesis of the truly ‘free’ trigonal-planar silylium ($\text{Mes}_3\text{Si}^+\cdot[\text{CB}_{11}\text{HMe}_5\text{Br}_6]^-$), germylium ($(t\text{-Bu}_2\text{MeSi})_3\text{Ge}^+\cdot\text{TPFPB}^-$) and stannylum ($(t\text{-Bu}_2\text{MeSi})_3\text{Sn}^+\cdot\text{TPFPB}^-$ and $\text{Tip}_3\text{Sn}^+\cdot\text{TPFPB}^-$) ion derivatives. However, even after such discoveries the story of the heavy analogs of carbenium ions is not complete: there are still plenty of goals to achieve and problems to solve. Looking to the future, one should expect further developments of the general synthetic approaches to the stable silylium, germylium, stannylum and plumbylum ion derivatives. Systematic studies of the specific reactivity of such compounds, representing a novel class of powerful organometallic Lewis acids, are also highly desirable. As examples of such reactivity, one can mention the coupling of the ‘heavy’ cations R_3E^+ ($\text{E} = \text{Si}–\text{Pb}$) with a variety of nucleophiles forming E–C and E–E bonds or alkene polymerization initiated by the electrophilic addition of R_3E^+ to C=C bonds. Based on the effective interplay between sophisticated experimental techniques and modern computational methods, one can anticipate major breakthroughs in the above-mentioned fields in the near future.

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