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From Phantom Species to Stable Compounds

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Preface

The variety of organometallic compounds based on the group 14 elements heavier than carbon is tremendous, spanning the wide range from low(mono, di, tri)- to normal tetra- to hyper(penta, hexa)-coordinate derivatives. However, in contrast to the two last classes of compounds, the low-valent group 14 organometallics have never appeared in books. The lack of such books, which is particularly surprising given the permanently growing interest in this hot field of modern main group chemistry as reflected by the vast number of outstanding reviews and book chapters, prompted us to undertake an attempt to survey, analyse and summarize the current state of affairs in this area. The fundamental achievements in the field are associated, first of all, with the recent advances in state-of-the-art sophisticated synthetic and spectroscopic techniques, as well as rapid progress in theory and computational methods. This has enabled isolation and structural studies of unique stable low-coordinate species, which only a few decades ago were believed to exist only as fleeting intermediates, not isolable or even detectable. In our book, subtitled *From Phantom Species to Stable Compounds*, we specifically deal with the synthetic accomplishments that have been made in the field of **isolable low-coordinate derivatives of heavy group 14 elements**, giving only short comments regarding their transient congeners. Having specialized in this topic, we do not aim to compete with the previously published books on the heavy group 14 organometallics which cover a broad range of rather different topics (from theoretical insights to experimental achievements and material science applications), such as the brilliant series *The Chemistry of Organic Silicon Compounds* and The *Chemistry of Organic Germanium, Tin and Lead Compounds* (edited by Patai, Rappoport and Apeloig) and *Organosilicon Chemistry: From Molecules to Materials* (edited by Auner and Weis).

Given that the specific field of low-coordinate group 14 organometallics is flourishing with many spectacular achievements that deserve mentioning, it is not realistic to cover all of them in a single volume and we do not intend to do this. Instead, we focus on the most important and most recent (the literature coverage is up to the end of 2009 – beginning of 2010) milestone advances that are crucial for a general understanding of the peculiar structural bonding and chemical properties of the low-coordinate group 14 organometallics, which in many cases are distinctly different from those of their organic analogs. The book is organized into six chapters, each devoted to an independent class of the most fundamental low-valent species: heavy analogs of carbenium ions (Chapter 1), heavy analogs of free radicals (Chapter 2), heavy analogs of carboanions (Chapter 3), heavy analogs of carbenes (Chapter 4), heavy analogs of unsaturated hydrocarbons: alkenes, 1,3-dienes, allenes, and alkynes (Chapter 5), and heavy analogs of aromatic compounds (Chapter 6). Each chapter begins with a review of general synthetic approaches, continues with a consideration of particular structural features and synthetic applications, and concludes with a discussion of the most important recent advances in the field of stable derivatives.

We are particularly grateful to many of our highly talented and greatly motivated students, with whom we have been lucky to work with and who have made numerous outstanding experimental contributions. We would also like to thank our distinguished collaborators from many research groups from all over the world, both experimentalists and theoreticians, with whom we have been very pleased to work with throughout our research careers and whose names are listed in a number of our joint publications.

Regarding the audience of our book, we hope that it will be useful to the entire scientific community; however, first of all, we address it to advanced graduate and postgraduate students, especially to those who intend to specialize in the field of organometallic chemistry. We believe that our contributions will also be of interest and be helpful to those who have already been involved in the fascinating and challenging world of organosilicon, organogermanium, organotin, and organolead chemistry. We hope that the book will find its readers not only among specialists in the field of group 14, but also among others working in the areas of both main group and transition metal chemistry, as well as those from interdisciplinary fields such as polymer, material science, nanotechnology etc. Let us finally hope that our book will serve as a useful guide and reference source to interested specialists and even more importantly, to those inexperienced beginners who are still seeking inspiration.

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January 2010

Abbreviations

Ad	1-Adamantyl
acac	2,4-Pentanedionate
AIBN	Azobisisobutyronitrile
ASE	Aromatic Stabilization Energy
Bbt	2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl
BLYP	Becke 1988 Exchange Functional with the Lee–Yang–Parr Correlation Functional
B3LYP	Becke Three-Parameter Hybrid Functional with the Lee–Yang–Parr Correlation Functional
BP86	Becke Exchange Functional and the Perdew Correlation Functional
CC-pVDZ	Correlation-Consistent Polarized Valence Double-Zeta Basis Set
CCSD(T)	Coupled Cluster Method Including Singles, Doubles and Optional Triples terms
CGMT	Carter–Goddard–Malrieu–Trinquier
CI	Configuration Interaction
CIDNP	Chemically Induced Dynamic Nuclear Polarization
CIP	Contact Ion Pair
CISD	Single and Double Excitations, Single Reference CI
Cp	Cyclopentadienyl η^5-C_5H_5
Cp*	Pentamethylcyclopentadienyl η^5-C_5Me_5
CPMAS	Cross Polarization Magic Angle Spinning
CSA	Chemical Shift Anisotropy
CST	Chemical Shift Tensor
CV	Cyclic Voltammetry
CW	Continuous Wave
Cy	Cyclohexyl
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DFT	Density Functional Theory
diglyme	Bis(2-methoxyethyl) ether
diox	1,4-Dioxane
Dip	2,6-Diisopropylphenyl

Dis	Bis(trimethylsilyl)methyl
Ditp	2,6-Bis(2-*iso*-propylphenyl)phenyl
DME	1,2-Dimethoxyethane
dmpe	1,2-Bis(dimethylphosphino)ethane
DMPU	N,N'-Dimethylpropyleneurea
DZD	Double-Zeta Diffuse Basis Set
DZP	Double-Zeta with Polarization Basis Set
DZVP	Double Zeta Valence Basis Set Augmented with Polarization Functions
EA	Electron Affinity
ECP	Effective Core Potential
EDA	Energy Decomposition Analysis
ENDOR	Electron Nuclear Double Resonance
EPR	Electronic Paramagnetic Resonance
eV	Electron volt
EXAFS	Extended X-Ray Absorption Fine Structure
FT	Fourier Transformation
G2	Gaussian-2
GIAO	Gauge Independent Atomic Orbital
HF	Hartree–Fock
hfcc	Hyperfine Coupling Constant
HMPA	Hexamethylphosphortriamide
HOMO	Highest Occupied Molecular Orbital
IE	Ionization Energy
IGLO	Individual Gauge for Localized Orbital
IR	Infrared
LDMAN	Lithium 1-(dimethylamino)naphthalenide
LUMO	Lowest Unoccupied Molecular Orbital
Λ	Diamagnetic Susceptibility Exaltation
MCSCF	Multiconfigurational SCF
Mes	2,4,6-Trimethylphenyl
Mes*	2,4,6-Tri-*tert*-butylphenyl
2-Me-THF	2-Methyltetrahydrofuran
MO	Molecular Orbital
3-MP	3-Methylpentane
MP2	Second-order Møller–Plesset Perturbation Theory
MP4	Fourth-order Møller–Plesset Perturbation Theory
MPW1PW91	Hybrid Density Functional Employing Modified Perdew–Wang 1991 Exchange and Perdew–Wang 1991 Correlation
NBO	Natural Bond Orbital
NHC	N-Heterocyclic Carbene
NICS	Nucleus Independent Chemical Shift
NMR	Nuclear Magnetic Resonance
NPA	Natural Population Analysis
NL–SCF	Non-Local Self-Consistent Field
OTf^-	$OSO_2CF_3{}^-$

PBE1PBE	Adiabatic Connection Method Functional Derived from Perdew–Burke–Enzerhof Functional
PES	Potential Energy Surface
PES	Photoelectron Spectroscopy
PMDTA/PMDETA	Pentamethyldiethylenetriamine
PSO	Paramagnetic Nuclear Spin–Electron Orbit
Py	Pyridine
Pz	Pyrazolyl
RE	Resonance Energy
REMPI	Resonance-Enhanced Multiphoton Ionization Spectroscopy
RHF	Restricted HF
SCF	Self-Consistent Field
SDB-cc-pVTZ	Stuttgart–Dresden–Bonn Relativistic Effective Core Potential with the Correlation-Consistent Polarized Valence Triple Zeta Basis Set
SDD	Stuttgart–Dresden Effective Core Potential with the Double Zeta Basis Set
SET	Single Electron Transfer
SINDO1	Intermediate Neglect of Differential Overlap Method Modified on the Basis of Symmetrically Orthogonalized Orbitals and Commutator Relations
S_N2	Substitution Nucleophilic Bimolecular
SOMO	Singly Occupied Molecular Orbital
SSIP	Solvent-Separated Ion Pair
STO-3G	Slater-Type Orbital Minimal Basis Set using Three Gaussians to Fit an Exponential
Tbt	2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl
TCSCF	Two-Configurational SCF
TD-DFT	Time-Dependent Density Functional Theory
TfOH	Trifluoromethanesulfonic acid
$TFPB^-$	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
Tip	2,4,6-Triisopropylphenyl
Titp	2,6-Bis(2,4-diisopropylphenyl)phenyl
TMDAP	1,3-Bis(dimethylamino)propane
TMEDA	Tetramethylethylenediamine
TPB^-	Tetraphenylborate
$TPFPB^-$	Tetrakis(pentafluorophenyl)borate
$TSFPB^-$	Tetrakis{4-[*tert*-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}borate
$TTFPB^-$	Tetrakis(2,3,5,6-tetrafluorophenyl)borate
TZ2P	Triple-Zeta Basis Set with Two Sets of Polarization Functions
TZV	Triple Zeta Valence Basis Set
TZVP	Triple Zeta Valence Basis Set Augmented with Polarization Functions
UB3LYP	Unrestricted B3LYP

UHF	Unrestricted Hartree–Fock
UHF–NO CI	Unrestricted Hartree–Fock Natural Orbitals Configuration Interaction
UMP2	Unrestricted Second-order Møller–Plesset Perturbation Theory
UV	Ultraviolet
UV–PES	Ultraviolet Photoelectron Spectroscopy
VDZ+P	Valence Double Zeta Plus Polarization Functions Basis Set
WBI	Wiberg Bond Index
Xyl	2,6-Dimethylphenyl
6-31G(d)	Valence Double Zeta Basis Set with d-Type Polarization Functions for Heavy Atoms
6-311G(d)	Valence Triple Zeta Basis Set with d-Type Polarization Functions for Heavy Atoms
6-311+G(2d,p)	Valence Triple Zeta Basis Set with s- and p-Type Diffuse Functions for Heavy Atoms, Two d-Type Polarization Functions for Heavy Atoms, and One p-Type Polarization Function for Hydrogen
6-311+G(2df,p)	Valence Triple Zeta Basis Set with s- and p-Type Diffuse Functions for Heavy Atoms, Two d-Type and One f-Type Polarization Functions for Heavy atoms, and One p-Type Polarization Function for Hydrogen

1

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 methylium 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 triphenylmethylium ion Ph_3C^+

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(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 $Ph_3C^+•ClO_4^-$ 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 (SbF_5–SO_2, HF–SbF_5, 'magic' acid HSO_3F–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: $Me_3CF + SbF_5/SO_2 \rightarrow Me_3C^+•SbF_6^-$. 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, stannylium and plumbylium ions R_3E^+ (E = 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, stannylium 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^+ (E = 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 $R_3C\text{–}X \rightarrow R_3C^+ + X^-$ 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]

$$Me_3Si\text{–}Br + AlBr_3 \xrightarrow{CH_2Br_2} Me_3Si^{\delta+}\text{–}Br\text{----}AlBr_3{}^{\delta-} \qquad \textbf{(A)}$$

$$Et_3Si\text{–}OTf + BCl_3 \longrightarrow Et_3Si^{\delta+}\text{–}OTf\text{----}BCl_3{}^{\delta-} \qquad \textbf{(B)}$$

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, trityluim 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

$$\mathrm{Et_3SiH + Ph_3C^+{\bullet}TPFPB^- \xrightarrow{C_6H_6} [Et_3Si(C_6H_6)]^+{\bullet}TPFPB^- + Ph_3CH} \qquad \textbf{(A)}$$

$$i\text{-}\mathrm{Pr_3SiH + Ph_3C^+{\bullet}[CB_{11}H_6X_6]^- \xrightarrow[(X\,=\,Cl,\ Br,\ I)]{C_7H_8}} i\text{-}\mathrm{Pr_3Si^+{\bullet}[CB_{11}H_6X_6]^- + Ph_3CH} \qquad \textbf{(B)}$$

$$n\text{-}\mathrm{Bu_3SnH + Ph_3C^+{\bullet}TFPB^- \xrightarrow{CD_2Cl_2}} n\text{-}\mathrm{Bu_3Sn^+{\bullet}TFPB^- + Ph_3CH} \qquad \textbf{(C)}$$

Scheme 1.2

$Mes_3E–CH_2–CH{=}CH_2$ (E = Si, Ge, Sn) with $[Et_3Si(C_6H_6)]^+{\bullet}B(C_6F_5)_4^-$ to form at first intermediate β-silyl-substituted carbenium ions $Mes_3E–CH_2–CH^+–CH_2SiEt_3$, which then undergo E–C bond breaking to produce more favorable Mes_3E^+ cations and allyltriethylsilane $Et_3Si–CH_2–CH{=}CH_2$ as a side product (Scheme 1.3).[8]

$$\mathrm{Mes_3E{-}CH_2{-}CH{=}CH_2 + [Et_3Si(C_6H_6)]^+{\bullet}B(C_6F_5)_4^- \xrightarrow{C_6H_6}}$$

$$\mathrm{\longrightarrow [Mes_3E{-}CH_2{-}CH^+{-}CH_2{-}SiEt_3]{\bullet}B(C_6F_5)_4^- \longrightarrow}$$

$$\mathrm{\longrightarrow Mes_3E^+{\bullet}B(C_6F_5)_4^- + H_2C{=}CH{-}CH_2{-}SiEt_3}$$

Scheme 1.3

The ease of oxidation of hexamethyldistannane $Me_3Sn–SnMe_3$ 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 $Me_3Sn–EMe_3$ (E = Si, Ge, Sn) can be oxidized (two-electron oxidation) forming acetonitrile-solvated cations Me_3Sn^+ and Me_3E^+, whereas disilane $Me_3Si–SiMe_3$, digermane $Me_3Ge–GeMe_3$ and silagermane $Me_3Si–GeMe_3$ 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 $Ph_3Pb–PbPh_3$ 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 $R_3E–ER_3$ with a strong Lewis acid include: (1) oxidation of t-$Bu_3E–Et$-Bu_3 (E = Si, Ge, Sn) with $Ph_3C^+{\bullet}TFPB^-$ in the presence of nitriles R–C≡N (R = Me, t-Bu) to form nitrilium complexes of t-Bu_3E^+ cations[11] (Scheme 1.4, A); (2) oxidation of n-$Bu_3Sn–Snn$-Bu_3 with the free radical $CB_{11}Me_{12}{\bullet}$ to produce a solvent-free n-Bu_3Sn^+ cation weakly coordinated to the Me groups of two $CB_{11}Me_{12}^-$ counteranions[12a] (Scheme 1.4, B). Similarly, $Me_3E^+{\bullet}CB_{11}Me_{12}^-$ derivatives (E = Ge, Sn, Pb), lacking solvent coordination, were synthesized by the oxidation of $Me_3Ge–GeMe_3$, $Me_3Sn–SnMe_3$ and Me_4Pb in pentane with the free radical $CB_{11}Me_{12}{\bullet}$.[12b]

$$t\text{-Bu}_3\text{E–E}t\text{-Bu}_3 + 2\,\text{Ph}_3\text{C}^+\bullet\text{TFPB}^- \xrightarrow{\text{R–C≡N}} 2\,[t\text{-Bu}_3\text{E}\leftarrow\text{:N≡C–R}]^+\bullet\text{TFPB}^- \quad \textbf{(A)}$$

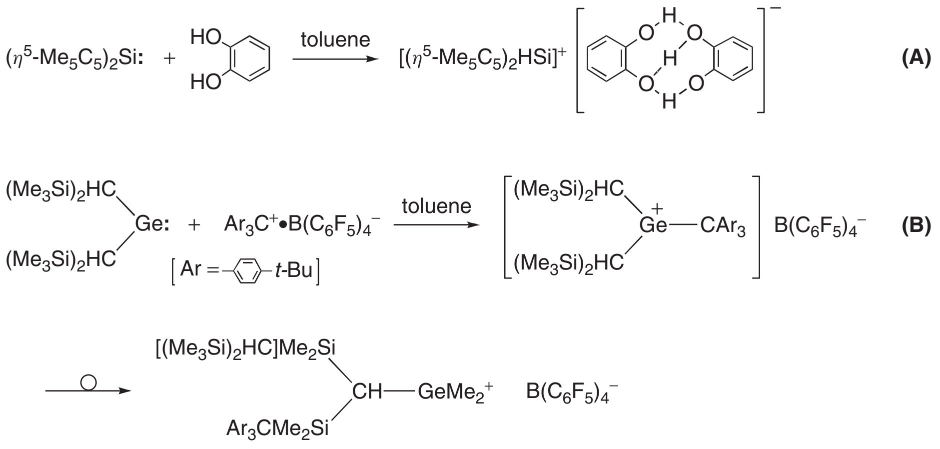
[E = Si, Ge, Sn; R = Me, *t*-Bu]

$$n\text{-Bu}_3\text{Sn–Sn}n\text{-Bu}_3 + 2\,\text{CB}_{11}\text{Me}_{12}\bullet \xrightarrow{\text{pentane}} 2\,n\text{-Bu}_3\text{Sn}^+\bullet\text{CB}_{11}\text{Me}_{12}^- \quad \textbf{(B)}$$

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 (η^5-$Me_5C_5)_2Si$**:** with catechol producing a silyl cation in the form of protonated decamethylsilicocene[13] (Scheme 1.5, A) and the reaction of the stable Lappert's germylene $[(Me_3Si)_2CH]_2Ge$**:** with $[(4\text{-}t\text{-Bu–}C_6H_4)]_3C^+$•TPFPB$^-$ unexpectedly yielding an intramolecularly stabilized germyl cation after a series of consecutive rearrangements[14] (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 Ph_3C^+), 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 Ph_3CH. 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-$Bu_2MeSi)_3E$• (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-$Bu_2MeSi)_3E^+$ cations (Scheme 1.6).[15]

$$(t\text{-}Bu_2MeSi)_3E\bullet \;+\; Ph_3C^+\bullet B(C_6F_5)_4^- \xrightarrow[\text{[E = Ge, Sn]}]{C_6H_6} (t\text{-}Bu_2MeSi)_3E^+\bullet B(C_6F_5)_4^-$$

Scheme 1.6

1.3 Reactions and Synthetic Applications of RR′R″E$^+$ Cations[16]

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, germylium, stannylium and plumbylium 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 (S_N1 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 RR′R″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 >C=C< double bond to produce stable β-silyl carbocations,[17] and to the –C≡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 $[Et_3Si(arene)]^+$ 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 $H^+\bullet[CHB_{11}R_5X_6]^-$ (R = H, Me, Cl; X = Cl, Br, I) by the simple treatment of $[Et_3Si(arene)]^+\bullet[CHB_{11}R_5X_6]^-$ 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 $C_6Me_nH_{6-n}$ ($n = 0, 1, 2, 3, 5, 6$) generating the fullerene cation $[HC_{60}]^{+20b}$ and benzenium ions $[HC_6Me_nH_{6-n}]^+$,[20a–c] respectively. On the other hand, the treatment of $[Et_3Si(arene)]^+\bullet[CHB_{11}Me_5X_6]^-$ (X = Cl, Br) with alkyl triflates ROTf (R = Me, Et) resulted in the formation of alkylium ion derivatives $R^+\bullet[CHB_{11}Me_5X_6]^-$, which are extremely electrophilic alkylating reagents, even stronger than alkyl triflates.[21] Thus, the high electrophilic power of $Me^+\bullet[CHB_{11}Me_5Br_6]^-$ 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 $[Me(C_6H_6)]^+$ and tertiary carbenium R^+ ions, respectively.[21] Undoubtedly, the extreme reactivity of $R^+\bullet[CHB_{11}Me_5X_6]^-$ exceeds that of the conventional alkyl triflates. Reaction of $[Et_3Si(arene)]^+\bullet[CHB_{11}I_{11}]^-$ with *p*-F-C_6H_4-CF_3 or CH_3CF_3 results in immediate fluorine abstraction to produce intermediate *p*-F-C_6H_4-CF_2^+ or $CH_3CF_2^+$ difluorocations, which subsequently participate in an electrophilic aromatic substitution reaction with the fluorobenzene solvent to form the stable (*p*-F-$C_6H_4)_2CF^+$ or (*p*-F-C_6H_4)CH_3CF^+ fluorinated carbocation derivatives.[22] $[Et_3Si(arene)]^+\bullet[CHB_{11}H_5Cl_6]^-$ reagent is able to abstract a chloride ion from the $[IrCl(CO)(PPh_3)_2]$ complex to form a new $[Ir(CHB_{11}H_5Cl_6)(CO)(PPh_3)_2]$ system undergoing an unusually smooth oxidative addition of chlorobenzene to produce the coordinatively unsaturated $[IrCl(C_6H_5)(CO)(PPh_3)_2]^+$ 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 hydrosylilation 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 $[Me_3Si(arene)]^+\bullet B(C_6F_5)_4^-$ (arene = benzene, toluene) smoothly reacted with persilylated phosphane and arsane $(Me_3Si)_3E$ (E = P, As) to produce the corresponding phosphonium and arsonium salts $[(Me_3Si)_4E]^+\bullet B(C_6F_5)_4^-$.[26]

The reactivity of cations centered on the heavier than silicon group 14 elements is represented mainly by that of stannylium ions. Thus, *n*-$Bu_3Sn^+\bullet[CB_{11}Me_{12}]^-$ readily reacted with PhMgBr to produce *n*-Bu_3SnPh almost quantitatively.[12a] It was found that stannyl cations R_3Sn^+ (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] Stannylium 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 Me_3Sn^+ 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 stannylium ion $[n\text{-}Bu_3Sn]^+\bullet TPFPB^-$, generated *in situ* from *n*-Bu_3SnH and $[Ph_3C]^+\bullet TPFPB^-$, may serve as an effective catalyst for allylation of *ortho*-anisaldehyde with *n*-Bu_3Sn–CH_2–CH=CH_2, providing an excellent *ortho–para* regioselectivity.[29] The bis(acetonitrile) complexes of trialkylstannylium ions $[R_3Sn(N\equiv CMe)_2]^+\bullet SbF_6^-$ (R = cyclohexyl, *tert*-butyl, neopentyl), prepared from the corresponding bromides R_3SnBr or hydrides R_3SnH, have been shown to be effective Lewis acid catalysts for the Diels–Alder addition of α,β-unsaturated nitriles to furan.[30]

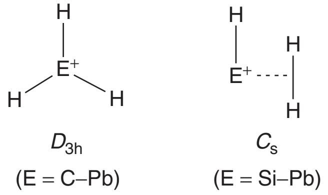
The reactivity of the stable 'free' cations of heavy group 14 elements, such as $(t\text{-}Bu_2MeSi)_3E^+$ (E = Ge, Sn) (see below), is still largely unexplored. One can mention only the pronounced electrophilicity of the germylium derivative $(t\text{-}Bu_2MeSi)_3Ge^+\bullet B(C_6F_5)_4^-$, which readily forms a complex with acetonitrile $[(t\text{-}Bu_2MeSi)_3Ge \leftarrow :N\equiv C\text{–}CH_3]^+\bullet B(C_6F_5)_4^-$, can be reduced with $LiAlH_4$ to form the hydride $(t\text{-}Bu_2MeSi)_3GeH$, undergoes one-electron reduction with *t*-BuLi to produce the free radical $(t\text{-}Bu_2MeSi)_3Ge\bullet$ 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 $HE^+\cdots H_2$ (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 stannylium H_3Sn^+ and plumbylium 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 $HE^+\cdots H_2$ 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): $H_3C^+(0.0) < H_3Si^+(58.9) < H_3Ge^+(70.7) < H_3Sn^+(87.5) < H_3Pb^+(97.9)$.[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 [$(H_3Si)_3Si^+$ and $(H_3Si)_3Pb^+$ are more stable than $(H_3Si)_3C^+$ 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 $(Me_2B)_3Si^+$ 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 stannylium 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 $(H_2N)_3Si^+$ can benefit from ca. 40% of the stabilization energy of the corresponding carbenium ion $(H_2N)_3C^+$.[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 ^{29}Si and ^{119}Sn NMR chemical shift calculations of R_3Si^+ and R_3Sn^+ cations will be discussed. Neither good empirical estimates nor reliable ^{207}Pb NMR chemical shift calculations are available for plumbylium ion derivatives. Because ^{13}C 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 ^{13}C 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 $(Me_2N)_3Si^+$ (42 ppm)[37] to the extremely low-field signals of $(Me_2B)_3Si^+$ (572 ppm)[36] and particularly $(Me_3Si)_3Si^+$ (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 σ(E–R)- and np(E)-orbitals, respectively. When R is electropositive silyl group, the σ(E–R)-orbitals level is raised resulting in a decrease of σ(E–R)–np(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 np(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, germylium and stannylium 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 stannylium 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 stannylium ion derivatives R_3Sn^+ were predicted to be ca. 1770 ppm (for R = alkyl) and ca. 1250 ppm (for R = 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 stannylium 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' stannylium 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 $(Me_3Si)_3Sn^+$ [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 Mes_3Sn^+ and Tip_3Sn^+ ions were estimated as 856 and 763 ppm, respectively.[1p] The extreme deshielding of the persilyl-substituted stannylium ions [3450 ppm for $(Me_3Si)_3Sn^+$ and 2880 ppm for $(H_3Si)_3Sn^+$ 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 σ(Sn–Si)- and vacant 5p(Sn)-orbitals. This agrees well with a recent experimental finding: the resonance of the $(t\text{-}Bu_2MeSi)_3Sn^+$ ion was observed at a record low-field shift of 2653 ppm[15b] (see Section 1.6.2.2).

1.5 Early Studies of RR′R″E$^+$ Cations: Free or Coordinated?

The early belief in the ease of preparation of silylium ions RR′R″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 R_3Si–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 that its carbon analog, methylium ion 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 nucleophlic 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 $Me_3C^+{\bullet}Sb_2F_{11}^-$ 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.

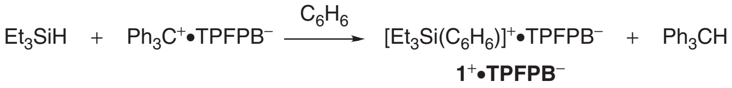
As the first step towards the synthesis of cations of heavy group 14 elements, several groups in the 1970s tried to prove the existence of silylium ion derivatives by physicochemical methods previously successfully used for the study of carbenium ions (cryoscopic, conductivity, UV and NMR measurements), 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 $Ph_3C^+{\bullet}X^-$, 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 $(i\text{-PrS})_3SiOClO_3$, $Ph_3SiOClO_3$, $Me_3SiOClO_3$] in CH_2Cl_2 and sulfolane, the results of which were interpreted in terms of the formation of stable R_3Si^+ ($R = i$-PrS, Ph, Me) cations in the form of their perchlorate salts as a silicon analog of the trityl cation, Ph_3C^+.[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 R_3Si and $OClO_3$ 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 $B(C_6F_5)_4^-$ and $CB_{11}H_6Br_6^-$, 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 Lambert[50] and Reed[51] published the crystal structures of their Et_3Si^+ and i-Pr_3Si^+ derivatives. Thus, $[Et_3Si(toluene)]^+$•$TPFPB^-$ (**1^+•$TPFPB^-$**) was prepared by Lambert *et al.* by the hydride transfer reaction between Et_3SiH and Ph_3C^+•$TPFPB^-$ in benzene (Scheme 1.8).[50]

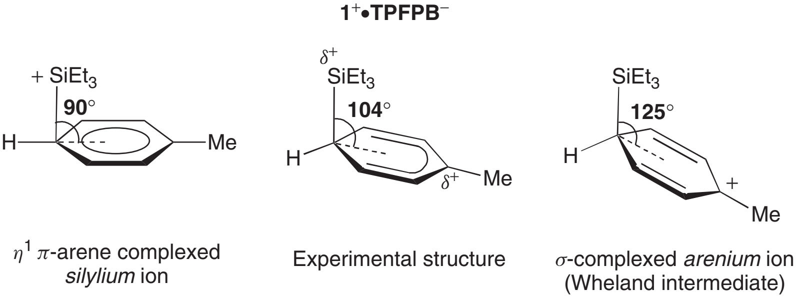
The crystal structure analysis of **1^+•$TPFPB^-$** revealed no direct cation–anion interaction, however, there was a ‘distant’ coordination of the Si cationic center to the solvent (toluene) with a long Si–C interatomic distance of 2.18 Å. The geometry of the toluene molecule was almost undistorted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



$$Et_3SiH + Ph_3C^+\bullet TPFPB^- \xrightarrow{C_6H_6} \underset{\mathbf{1^+\bullet TPFPB^-}}{[Et_3Si(C_6H_6)]^+\bullet TPFPB^-} + Ph_3CH$$

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 noncoordinated 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).



η^1 π-arene complexed *silylium* ion

Experimental structure

σ-complexed *arenium* ion (Wheland intermediate)

Scheme 1.9

Thus, Pauling pointed out that the calculated bond order between the Si and *para*-C of a coordinated toluene molecule in **$1^+\bullet$TPFPB$^-$** is 0.35, a value that cannot be neglected.[52] Olah *et al.* calculated that the ^{29}Si NMR resonance of the planar free Et_3Si^+ 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 ppm[50] in **$1^+\bullet$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 conclusions[53] regarding the degree of deshielding of the cationic Si atom: ^{29}Si NMR resonances of R_3Si^+ (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