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Tricoordinate silyl cations (silylium ions)

Vladimir Ya. Lee

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba Tsukuba 305 – 8571, Ibaraki, Japan

Being silicon analogues of carbenium ions, which are ubiquitous in organic chemistry, silylium ions play a pivotal role in organosilicon chemistry. However, unlike widespread carbenium ions, silylium ions are much less accessible and much more difficult to stabilize due to the lower electronegativity of the silicon atom, its greater polarizability and notably larger size (compared to those of carbon atom), which results in extraordinarily high electrophilicity and Lewis acidity of silylium ions. These peculiar characteristics of silylium ions require very special, sophisticated synthetic approaches for their generation, isolation and structural elucidation, on the one hand, and open the door for their use as exceptionally potent Lewis acids in a number of catalytic transformations, on the other hand. In this review, we present and discuss the latest advances in the field of stable silylium ion derivatives, particularly emphasizing the state-of-the-art procedures for their synthesis, structural studies both in solution and in the solid state, most remarkable recent representatives of the isolable silylium ions, and finally, discuss the use of silylium ions in synthetic organic chemistry.
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1. Introduction

Silylium ions, featuring tricoordinate (in ideal case, trigonal-planar) six-valence electron cationic silicon centre, are silicon analogues of the ubiquitous carbenium ions R_3C^+, and they are also isoelectronic and isolobal to neutral boranes R_3B. Because of their electronic sextet, silylium ions are electron-deficient species with a vacant p-orbital at the silicon centre, acting accordingly as extraordinarily powerful Lewis acids. As such, silylium ions manifest the chemical behaviour that is sharply distinctive from that of carbenium ions in organic chemistry. This is because silicon is not carbon, and although silicon and carbon share the same group 14 in the Periodic Table, they have very different properties. The principal distinctions between the silicon and carbon atoms are their *electronegativity*, *polarizability*, and *size*: silicon is remarkably more electropositive than carbon (1.90 *vs.* 2.55: Pauling electronegativity scale), more polarizable, and notably larger. Such intrinsic silicon features should seemingly favour easier generation and stabilization of silylium ions R_3Si^+, comparing to analogous carbenium ions R_3C^+. This comes true in the gas phase, where a vast number of silylium ion derivatives was successfully generated and identified. However, this is not the case in the condensed phase, where the situation is reversed, and carbenium ions (rather than silylium ions) are by far easier to be stabilized. The instability of the latter species, surprising at the first glance, is undoubtedly kinetic in its origin, being caused by the exceptionally high electrophilicity of silylium ions (greatly exceeding that of carbenium ions), which are able to react with virtually every available nucleophile, σ-, π- or n-donor, in solution or even in the solid state. Accordingly, even weak Lewis bases, such as typically innocent solvents and counter-anions, can and do readily coordinate to silylium ions, forming the corresponding donor – acceptor complexes in which the cationic silicon centre is not trigonal planar anymore but is instead tetrahedral. Consequently, because of stabilizing electron donation from the external Lewis base, the cationic character at the silicon atom is substantially diminished if not completely lost. This problem was finally overcome by the smart introduction of the counter-anions of exceptionally low nucleophilicity (such as borates and carboranes) and by the use of nonpolar aromatic hydrocarbons (such as benzene or toluene) as the reaction solvents. The right choice of the substituents at the cationic silicon centre was also of a

V.Ya.Lee Lecturer at the Department of Chemistry, University of Tsukuba (Ibaraki, Japan).
E-mail: leevya@chem.tsukuba.ac.jp
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crucial importance for the successful isolation of silylium ions. This was governed by two major demands: 1) sufficient bulkiness required for the steric protection of the cationic centre from the external attack by both counter-anions and solvent molecules (kinetic stabilization); 2) strong electron donation stabilizing the positive charge on silicon (thermodynamic stabilization). When all above-described requirements for stabilization of silylium ions are met (right choice of counter-anion, reaction solvent and substituents at silicon), then the genuine cationic derivatives with the positive charge centred at the silicon atom can be successfully synthesized and isolated.

In this overview, we briefly cover the whole story of silylium ions: general synthetic strategies for their generation, their structural studies by NMR spectroscopy and X-ray crystallography, isolable representatives of silylium ions, and finally application of silylium ions in the modern organic synthesis. This highly challenging topic has been previously repeatedly reviewed[1–6] (comprehensive review by Kochina *et al.*[2] can be particularly mentioned); therefore, in our paper we focused on the latest advances in this field, mostly published within a couple of the past decades. Moreover, we deal only with the low-coordinate six-valence electron silylium ions with the cationic silicon in its +4 oxidation state, whereas four-valence electron silyliumylidene derivatives RSi:$^+$,[7–16] featuring silicon centre in the +2 oxidation state, are outside the framework of this review. Likewise, numerous hypercoordinate (penta- and hexacoordinate) silicon cation derivatives,[17] as well as silicon-centred radical cations,[18,19] are also beyond the scope of our contribution. Discussing silylium ions in the condensed phase, we will not cover vast number of examples of their gas-phase generation and gas-phase reactions, referring interested readers to the original contributions and reviews on this topic.[2,20–25] We also do not touch computational aspects of the silylium ion field, which have already been comprehensively reviewed.[1,4,5]

List of abbreviations:

All — Allyl,
CP-MAS — cross polarization magic angle spinning,
DCM — dichloromethane,
DFT — density functional theory,
dr — diastereomeric ratio,
er — enantiomeric ratio,
Fc — ferrocenyl,
FLP — frustrated Lewis pair,
GIAO/DFT — gauge independent atomic orbital method for the density functional theory calculation of nuclear magnetic resonance chemical shifts,
GIAO/HF — gauge independent atomic orbital method for the Hartree–Fock calculation of nuclear magnetic resonance chemical shifts,
Mes — 2,4,6-trimethylphenyl,
MMA — methyl methacrylate,
Naph — naphthyl,
NHC — *N*-heterocyclic carbene
NHI — *N*-heterocyclic imine,
ROP — ring-opening polymerization,
Ter — 2,6-bis(2,4,6-trimethylphenyl)phenyl,
Tf — triflate,
TMS — trimetylsilyl,
Ts — tosyl
WBI — Wiberg bond index.

2. Generation of silylium ions R_3Si^+

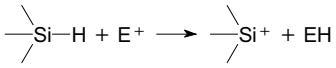
The major obstacle in the preparation and isolation of silylium ions is undoubtedly their intrinsic kinetic instability caused by their extraordinary high electrophilicity. Accordingly, silylium ions are exceptionally reactive towards practically any nucleophiles, even such solvents and counter-anions that are otherwise considered as innocent. Therefore, for the successful generation of silylium ions, the use of the least nucleophilic solvents, such as arenes (benzene, toluene) and halogenated arenes, is of crucial importance. Likewise, counter-anions should be the least coordinating ones, such as fluorinated perarylborates ($[B(C_6F_5)_4]^-$), halogenated *closo*-carboranes ($[HCB_{11}H_5Br_6]^-$) or perhalogenated *closo*-boranes ($[B_{12}Cl_{12}]^{2-}$).[1,4,26] One can also mention the recently synthesized tetrabutylammonium salts of the weakly coordinating and low-nucleophilic anions of the fluoride-encapsulated octaorganosilsesquioxanes, such as TBA($F^-@T_8R_8$), as potential counter anions for the generation of stable silylium ion derivatives.[27,28]

Depending on the starting material used, there are several approaches for the synthesis of isolable silylium ion derivatives R_3Si^+. Each method has both advantages and disadvantages, and these will be discussed below.

2.1. From silyl hydrides R_3Si-H

This approach, which is based on the favourable polarization of the $Si^{\delta+}-H^{\delta-}$ bond, is by far most popular and most frequently used for generation of silylium ions, often being referred to as Bartlett–Condon–Schneider 'hydride-transfer reaction'[29,30] (Scheme 1).

Scheme 1

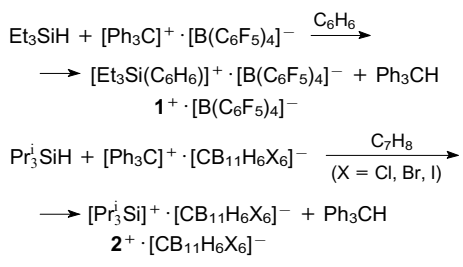


The process driven to completion by the relative strength of the breaking and forming bonds (stronger E–H *vs.* weaker Si–H bond) involves oxidation of the silyl hydride with a powerful electrophile (trityl cation Ph_3C^+ is the most commonly used Lewis acid). As the innocent counter-anions, perarylborates, halogenated *closo*-carboranes and perhalogenated *closo*-borates are most popular.

The evident advantage of such synthetic strategy is its simplicity and ready availability of the Lewis acid reagents (such as $[Ph_3C]^+[B(C_6F_5)_4]^-$, with which the reaction typically proceeds within several minutes). However, the important drawback in the use of trityl cation is its steric bulkiness, which hinders its direct approach towards silyl hydrides with sterically demanding substituents at Si atom, thus making trityl cation ineffective for generation of such silylium ions (for example, Mes_3Si^+, which was prepared by the alternative 'allyl leaving group approach' procedure, see next Section 2.2).

A vast number of silylium ions intra- or intermolecularly stabilized by coordination to n- or π-donors, counter-anions or nucleophilic solvents are readily available by this hydride transfer reaction approach, for example, triethylsilylium (**1**$^+$) and triisopropylsilylium (**2**$^+$) ions (Scheme 2).[1,3,4,31–33]

Scheme 2

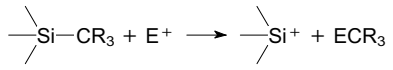


Moreover, most recent advances in the generation of stabilized silylium ions were all achieved by application of this method (see Section 4.1).

2.2. From silanes R_3Si-CR_3

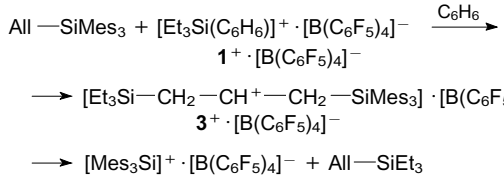
The method of generation of silylium ions from tetraorganosilanes (Scheme 3) is less common than the above-discussed hydride transfer reaction (see Scheme 1), requiring very powerful electrophiles (such as carbenium or silylarenium ions) to break rather strong Si – C bond.

Scheme 3



Nevertheless, this approach was best suited for the isolation of trimesitylsilylium Mes_3Si^+, the very first stable silylium ion, which is free from any intra- or intermolecular interactions with donors and, therefore, is least electronically perturbed. By contrast, the general hydride transfer reaction (*vide supra*) failed in this case, because of the very high steric demand of the three bulky mesityl substituents at the silicon centre. Using their trademarked 'allyl leaving group approach', Lambert *et al.*[34,35] generated Mes_3Si^+ by the reaction of allyltrimesitylsilane $All-SiMes_3$ with $[Et_3Si(C_6H_6)]^+ \cdot [B(C_6F_5)_4]^-$ ($\mathbf{1}^+ \cdot [B(C_6F_5)_4]^-$), which gave transient β-silyl-substituted carbenium ion $\mathbf{3}^+$. The latter underwent selective cleavage of the $CH_2-SiMes_3$ bond to give more favourable silylium ion Mes_3Si^+, together with allyltriethylsilane $All-SiEt_3$ as a side product (Scheme 4).

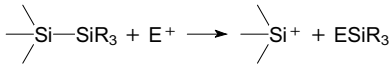
Scheme 4



2.3. From disilanes $R_3Si-SiR_3$

This method (Scheme 5) is also not universal. Oxidative cleavage of the central Si – Si bond on treatment with strong Lewis acids was observed only for the remarkably sterically overloaded disilanes, such as hexa-*tert*-butyldisilane $Bu^t_3Si-SiBu^t_3$. Oxidation of the latter with the trityl cation derivative $[Ph_3C]^+ \cdot [B(3,5\text{-}(F_3C)_2C_6H_3)_4]^-$ (2 mol.) in the presence of pivalonitrile Bu^tCN yielded the corresponding tri-*tert*-butylsilylium nitrile complex $[Bu^t_3Si \leftarrow :N\equiv C-Bu^t]^+ \cdot [B(3,5\text{-}(F_3C)_2C_6H_3)_4]^-$.[36]

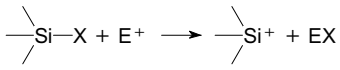
Scheme 5



2.4. From silyl halides R_3Si-X

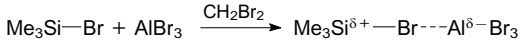
Although the method involving ionization of the C – X bonds is general for generation of the stable carbenium ions R_3C^+ in organic chemistry, it has many limitations when applied to generate silylium ion derivatives R_3Si^+, because of two major obstacles: 1) silicon – halogen bonds in the precursor R_3SiX are very strong; and 2) the generated silylium ions R_3Si^+ manifest great affinity towards the halide leaving group X^- caused by the exceptionally high halophilicity of silicon compared to that of carbon (Scheme 6). Therefore, silylium ions generated in this way feature only a partial positive charge on the silicon centre, being better classified as strongly polarized donor – acceptor complexes rather than the true silylium ions (Scheme 7).[37,38]

Scheme 6



X = Cl, Br, I

Scheme 7



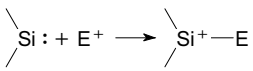
2.5. From low-coordinate organosilicon derivatives

Low-coordinate organosilicon derivatives, such as silylenes R_2Si**:** and silyl radicals $R_3Si^{\bullet}$, might serve as precursors for silylium ions by either oxidative addition of cations to silylenes or one-electron oxidation of silyl radicals. However, the scope of synthetic applicability of this seemingly attractive approach is greatly restricted by the limited availability of the stable low-coordinate species (silylenes and silyl radicals). Accordingly, there are only a few examples of silylium ions prepared by this method.

2.5.1. From silylenes R_2Si**:**

The oxidative addition of a strongly Lewis acidic electrophile E^+ to silylene $>Si$**:** is accompanied by the increase in the coordination number of silicon from 2 (in the starting silylene) to 3 (in the resulting silylium ion) (Scheme 8).

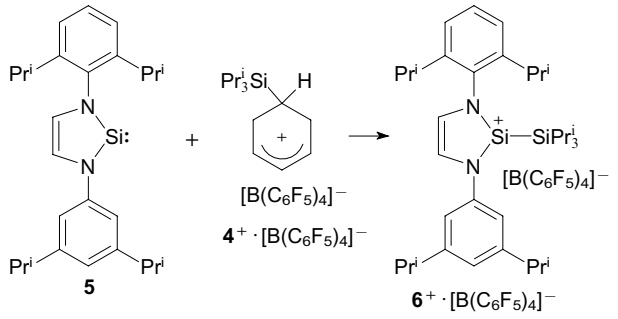
Scheme 8



As a representative example of such synthetic approach one can mention the oxidative addition of the electrophilic silylarenium ion **4** (as a synthetic equivalent of silylium ion) to nucleophilic *N*-heterocyclic silylene **5** to give silaimidazolium ion $\mathbf{6}^+ \cdot [B(C_6F_5)_4]^-$ (Scheme 9).[39]

The reaction of decamethylsilicocene $(\eta^5\text{-}Me_5C_5)_2Si$**:** with catechol gives rise to a silyl cation in the form of protonated decamethylsilicocene $[(\eta^5\text{-}Me_5C_5)_2HSi]^+$.[40,41]

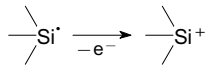
Scheme 9



2.5.2. From silyl radicals $R_3Si^{\bullet}$

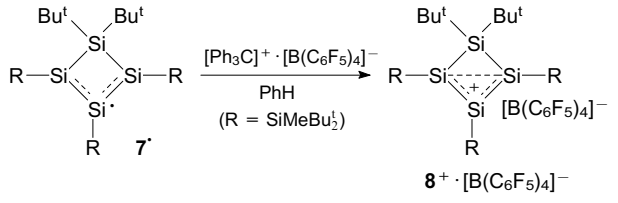
Selective oxidation of the stable silyl radicals $R_3Si^{\bullet}$ with strong Lewis acids (typically, Ph_3C^+, as 'one-electron transfer' reagent) is one of the latest developments in the generation of stable silylium ions (Scheme 10). The evident advantages of this method are the remarkable ease of the experimental procedure and lack of the side products (except for readily separable Ph_3CH), whereas drawback of this approach is the very limited availability of the stable silyl radicals with only few examples of them being currently reported.[3,42–45]

Scheme 10



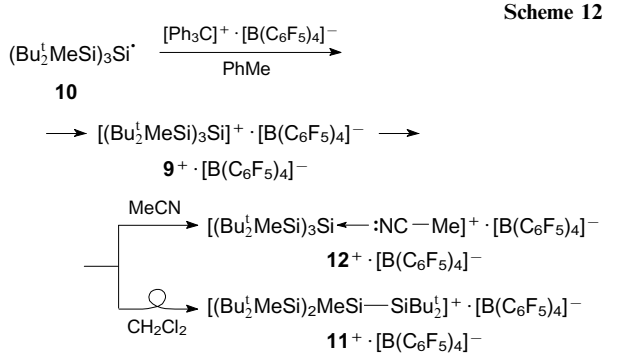
A representative example of such silyl radical to silylium ion transformation is the one-electron oxidation of the isolable cyclotetrasilenyl radical **7** (Ref. 46) to the homoaromatic cyclotetrasilenylium ion $\mathbf{8}^+$ (Scheme 11).[47]

Scheme 11



However, a similar attempt to generate the silylium ion $(Bu^t_2MeSi)_3Si^+$ ($\mathbf{9}^+$) by one-electron oxidation of the stable silyl radical **10** (Ref. 48) with $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$ was unsuccessful, resulting in the formation of a rearranged product, namely, (dialkylsilyl)silylium ion $\mathbf{11}^+ \cdot [B(C_6F_5)_4]^-$ (Scheme 12).[49] The latter was formed upon unavoidable 1,2-Me-migration from the substituent Si to the cationic Si centre (as a silicon variation of the Wagner–Meerwein rearrangement) in the initially formed transient silylium ion derivative $\mathbf{9}^+ \cdot [B(C_6F_5)_4]^-$.[49] Desired [tris(silyl)]silylium ion $\mathbf{9}^+$ can be stabilized and isolated in the form of its nitrile complex $\mathbf{12}^+ \cdot [B(C_6F_5)_4]^-$ by the reaction of cation $\mathbf{9}^+$ with acetonitrile (Scheme 12).[49]

Scheme 12



In a sharp contrast, heavier analogues of the above-mentioned transient silylium ion derivative $\mathbf{9}^+ \cdot [B(C_6F_5)_4]^-$, namely, germylium and stannylium ion derivatives $[(Bu^t_2MeSi)_3Ge]^+ \cdot [B(C_6F_5)_4]^-$ (Ref. 50) and $[(Bu^t_2MeSi)_3Sn]^+ \cdot [B(C_6F_5)_4]^-$ (Ref. 51), similarly generated by the one-electron oxidation of the corresponding free radicals $(Bu^t_2MeSi)_3Ge^{\bullet}$ (Ref. 48) and $(Bu^t_2MeSi)_3Sn^{\bullet}$ (Ref. 51) with trityl cation $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$, were quite stable and were isolated and structurally characterized.

3. Structural assessment of silylium ions

There are two major instrumental tools in the toolbox of organosilicon chemist to get the structural information on silylium ions, namely, ^{29}Si NMR spectroscopy and X-ray crystallography. Of these two, the former method, ^{29}Si NMR spectroscopy, is of paramount importance for the identification and characterization of silylium ions in solution, whereas the latter one, X-ray diffraction analysis, is indispensable for structural assessment of silylium ion derivatives in their crystalline state. The ^{29}Si NMR chemical shift of the silylium ion centre and planarity of the latter extracted from these two methods are commonly recognized as measures of the degree of cationic character of R_3Si^+ species.

3.1. ^{29}Si NMR spectroscopy

In tricoordinate silylium ions R_3Si^+, the cationic silicon centre is diagnostically remarkably deshielded (compared to their neutral tetracoordinate counterparts R_3SiX), appearing in unusually low fields. Such enormous deshielding is caused by the very small energy gap between the interacting orbitals that are mixed in the applied magnetic field, typically occupied $\sigma(Si-C)$ and low-energy lying vacant 3p(Si) orbitals,[1,3,4] which results in the increase in paramagnetic contribution and, consequently, in the overall deshielding of the cationic silicon nucleus.[52]

Thus, in the trimesitylsilylium Mes_3Si^+, which is the first representative of a free tricoordinate silylium ion derivatives (see also Section 2.2, Scheme 4), the cationic silicon resonated at $\delta_{Si} = +225.5$ ppm.[34,35] Likewise, in other triarylsilyluim ions Ar_3Si^+, the chemical shifts of the cationic silicon centres were found in similar low-field positions, at +216 to +230 ppm (in aromatic hydrocarbons).[4]

When the substituents at the cationic silicon are electropositive silyl groups, as in the tri(silyl)silylium ions $(R_3Si)_3Si^+$, the deshielding of the cationic centre is even more pronounced. This is because in such cations the energy level of the $Si_{central}-Si_{substituent}$ σ-orbital is notably elevated [compared with that of the Si–C bond in the tri(alkyl)silylium ions R_3Si^+], which gives rise to the further decrease in the $\sigma-3p$ orbitals energy separation and finally extreme deshielding of the cationic silicon centre. Theoretical calculations predicted exceptional low-field resonance for the

central silicon atom in the tricoordinate tri(silyl)silylium ions $(R_3Si)_3Si^+$, reaching unprecedented $\delta_{Si} = +920$ ppm for $(Me_3Si)_3Si^+$ (Ref. 53). However, given their extreme electrophilicity and reactivity, stable tri(silyl)silylium ion derivatives and, accordingly, such low-field extremes for their chemical shifts have never been confirmed experimentally. At present, homoaromatic cyclotetrasilenylium ion $\mathbf{8}^+ \cdot [B(C_6F_5)_4]^-$ with $\delta_{Si} = +315.7$ ppm for its central silicon atom (see also Section 2.5.2, Scheme 11) represents a record low-field shift for isolable cationic silicon species.[47]

Surprisingly, structurally similar cyclotetrasilenylium ion derivative cyclo-$Bu^t_2MeSi[Si(SiBu^t)_2SiBu^t_2]^+ \cdot [B(C_6F_5)_4]^-$, $\mathbf{13}^+ \cdot [B(C_6F_5)_4]^-$, differing from the above-described homoaromatic $\mathbf{8}^+ \cdot [B(C_6F_5)_4]^-$ analogue only by substituents at the bridgehead silicons (Bu^t *vs.* Bu^t_2MeSi), manifested sharply distinct structural features, namely, those of the allylic group lacking 1,3-orbital interaction characteristic of a homoaromatic system.[54] Accordingly, as is diagnostic for the allylic system, the most deshielded atoms in $\mathbf{13}^+$ were the terminal silicons ($\delta_{Si} = +286.8$ ppm) whereas the central silicon of the allylic system resonated at much higher field ($\delta_{Si} = +183.8$ ppm).

'Free' tri(alkyl)silylium ions R_3Si^+ (also unknown experimentally) were theoretically predicted to resonate at much higher fields than the tri(silyl)silylium ions $(R_3Si)_3Si^+$, for example, $\delta_{Si} = +404$ ppm for Me_3Si^+. By contrast, the experimental values for their coordinated analogues were found at remarkably lower frequencies, for example, $\delta_{Si} = +138$ ppm for $[Me_3Si^+][C_2H_5CB_{11}F_{11}]^-$, in which cationic silicon is stabilized by coordination to one of the F atoms of the *closo*-carborane anion.[55]

Intrinsically unstable silylium ions can be stabilized by coordination to electron donors (n-, σ- or π-donors), which can be either intramolecular (to substituents) or intermolecular (to solvents or counter-anions). However, this happens at the expense of the amount of positive charge at the silicon centre and, hence, the degree of its cationic nature, which remarkably decreases upon donor coordination, finally resulting in the notable shielding of the cationic centre. Thus, the calculated chemical shifts of the tricoordinate silylium ions span over a very broad range depending on the effect of substituents: from high-field [$\delta_{Si} = +40$ ppm for $(Me_2N)_3Si^+$][56] to exceptionally low-field [$\delta_{Si} = +572$ ppm for $(Me_2B)_3Si^+$ (Ref. 57) and $\delta_{Si} = +920$ ppm for $(Me_3Si)_3Si^+$ (Ref. 53)].

3.2. X-Ray crystallography

Although X-ray crystallographic data are currently available for a vast number of silylium ion derivatives, in the overwhelming majority of them, the cationic silicon centre is not 'free' being either intra- or intermolecularly coordinated to nucleophiles. Such stabilizing coordination results in the substantial transfer of the positive charge from silicon to the nucleophile, thus altering the true cationic nature of the silicon centre.

In the field of the most fundamental tricoordinate trigonal-planar silylium ions, which are least electronically perturbed by nucleophilic coordination, the major breakthroughs were achieved in 1993 when Lambert's and Reed's research groups independently reported the crystal structures of tri(alkyl)silylium ion derivatives, $[Et_3Si(C_6H_5Me)]^+ \cdot [B(C_6F_5)_4]^-$ (Ref. 58) and $[Pr^i_3Si]^+ \cdot [CB_{11}H_6Br_6]^-$ (Ref. 59), respectively. Both compounds were prepared by the classical 'hydride transfer reaction' (see Section 2.1) of the corresponding hydrosilanes Et_3SiH or Pr^i_3SiH with the strongly Lewis acidic tritylium ion Ph_3C^+ employing counter-anions of exceptionally low nucleophilicity (borate $[B(C_6F_5)_4]^-$ or carborane $[CB_{11}H_6Br_6]^-$) (see, for example, Scheme 2). However, original claims of both Lambert and Reed on their closest approach to the 'free' silylium ions were severely criticized and disproved by both experimentalists and theoreticians. Thus, based on the structural and spectroscopic evidences supported by the theoretical calculations, both $[Et_3Si(C_6H_5Me)]^+ \cdot [B(C_6F_5)_4]^-$ and $[Pr^i_3Si]^+ \cdot [CB_{11}H_6Br_6]^-$ were found to be not entirely 'free', clearly manifesting remarkable coordination of the cationic silicon centre to either toluene solvent (in the case of Et_3Si^+ ion) or carborane counter-anion $[CB_{11}H_6Br_6]^-$ (in the case of $Pr^i_3Si^+$), resulting in a substantial positive charge transfer from the Si to the C (or Br) atoms. Accordingly, the cationic silicon centres in both Et_3Si^+ and $Pr^i_3Si^+$ were notably pyramidalized (the sums of the bond angles around Si were 342° and 351°, respectively), and their resonances were found at relatively high fields (δ_{Si} of +92.3 ppm and +109.8 ppm, respectively). Conversely, for the truly 'free' electronically unperturbed silylium ions, one can expect the diagnostic trigonal-planar configuration and sp^2-hybridized Si centre, with the sum of the bond angles around the Si atom being 360°, and several hundred ppm in the low-field region for the chemical shift of the cationic silicon atom. Finally, it was concurred that the Lambert's Et_3Si^+ is best described as arenium ion (Wheland σ-complex) rather than the genuine silylium ion, whereas $Pr^i_3Si^+$ is better viewed as something in-between two resonance extremes, bromonium and silylium ions.[1, 3, 60, 61]

As was briefly mentioned in Section 2.2 (see Scheme 4), the very first truly 'free' silylium ion derivative $[Mes_3Si]^+ \cdot [B(C_6F_5)_4]^-$, free from any observable interactions with nucleophiles, was synthesized in 1997 by Lambert *et al.*[34, 35] The cationic silicon centre in $[Mes_3Si]^+ [B(C_6F_5)_4]^-$ was observed at a very low field, $\delta_{Si} = +225.5$ ppm[34, 35] (see also Section 3.1), which perfectly matched the values calculated for the 'free' $[Mes_3Si]^+$ in the gas phase: $\delta_{Si} = +230.1$ ppm (GIAO/HF) and $\delta_{Si} = +243.9$ ppm (GIAO/DFT).[62]

The replacement of the borate $[B(C_6F_5)_4]^-$ counter-anion by the *closo*-carborane counter-ion $[CB_{11}HMe_5Br_6]^-$ enabled isolation of the $[Mes_3Si]^+ \cdot [CB_{11}HMe_5Br_6]^-$ salt and its subsequent unequivocal structural characterization (Fig. 1).[63] In this ionic derivative, $[Mes_3Si]^+$ possesses truly 'free' silylium ion structure, lacking any observable interactions with either carborane counter-ion or solvent molecules, and thus featuring ideal trigonal-planar geometry (359.9° for the sum of the bond angles around Si) and remarkable low-field ^{29}Si NMR resonance for the cationic silicon centre ($\delta_{Si} = +225.5$ ppm in solution and $\delta_{Si} = +226.7$ ppm in the solid state).

In their recent follow-up report, Müller and co-workers[52] described the solid-state structure of the second representative of the 'free' tri(aryl)silylium ions family, namely tris(pentamethylphenyl)silylium dodecachloro-*closo*-dodecaborane $[(Me_5C_6)_3Si^+]_2 \cdot [B_{12}Cl_{12}]^{2-}$ [$(\mathbf{14}^+)_2 \cdot [B_{12}Cl_{12}]^{2-}$], prepared by the hydride transfer reaction involving also exchange of substituents (Scheme 13).

Like in the case of $[Mes_3Si]^+$, the cationic silicon centre in $\mathbf{14}^+$ manifested trigonal-planar configuration (360.0°)

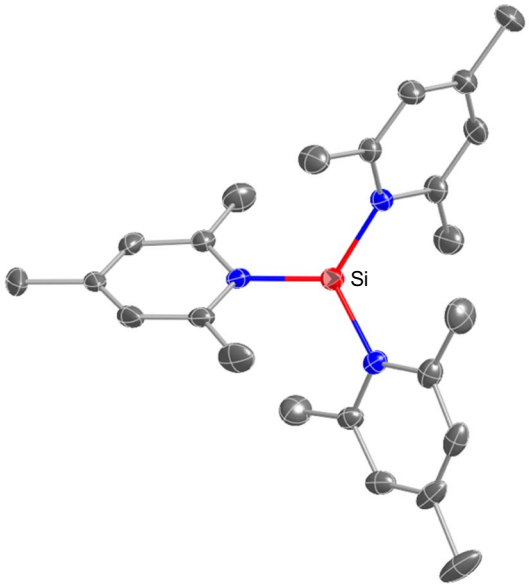


Figure 1. Crystal structure of the trimesitylsilylium ion salt $[Mes_3Si]^+ \cdot [CB_{11}HMe_5Br_6]^-$ (hydrogen atoms and $[CB_{11}HMe_5Br_6]^-$ counter-anion are not shown). [This crystal structure was generated with the CrystalMaker 8.6 program using cif-file available in the Cambridge Structural Database (CSD) System 2012 Release, v5.33, from the Cambridge Crystallographic Data Centre (CCDC)].

Scheme 13

$$3\,Ar_2(Me)Si-H + Ph_3C^+ \xrightarrow[-Ph_3CH]{} 2\,Ar_3Si^+ + Me_3Si-H$$

Ar = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,3,5,6-Me_4C_6H, Me_5C_6

and characteristic low-field ^{29}Si NMR chemical shift (δ_{Si} = +216.2 ppm in solution and δ_{Si} = +223.5 ppm in the solid state).

4. Stable and isolable silylium ions

4.1. Synthesis of intra- and intermolecularly stabilized silylium ions

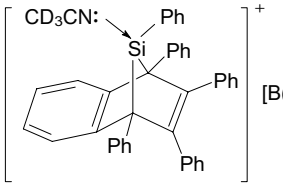
A vast number of intra- or intermolecularly stabilized silylium ions, in which the coordination number of the cationic silicon is expanded from the ideal 3 ('free' non-coordinated cations) to 4, 5 or even 6 (stabilized coordinated cations) because of the coordination of internal or external nucleophiles, was reported within the past two decades. Many of them were comprehensively and repeatedly covered in the recent reviews;[1–6] therefore, in our chapter, we deal only with the latest advances in the field, representing most spectacular examples of the donor-stabilized silylium ion derivatives and published mostly after 2000.

4.1.1. Oxidation of the Si – H bond

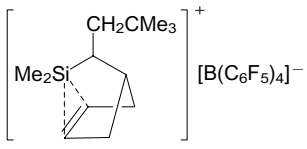
This synthetic approach, the so-called hydride transfer reaction, is by far the most popular and most frequently employed method for generation of silylium ions, which takes advantage of its straightforward experimental procedure and ready availability of the starting silyl hydride reagents. The vast majority of the recently reported stabilized silylium ion derivatives were prepared by this hydride transfer reaction (see Section 2.1 and Scheme 1); several most remarkable examples will be briefly described below.

Müller and co-workers[64–74] reported a series of intramolecularly stabilized silylium ions, along with silyl-substituted vinyl cations and arenium ions, uniformly prepared by the hydride transfer reaction using $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$ as a Lewis acid, including: (a) nitrilium complex of the intermediate 7-silanorbornadien-7-ylium ion $[\mathbf{15} \leftarrow :NCCD_3)]^+ \cdot [B(C_6F_5)_4]^-$,[64,71] (b) 2-silanorbornyl cation $\mathbf{16}^+ \cdot [B(C_6F_5)_4]^-$,[65,70,71] (c) silyl cation $\mathbf{17}^+ \cdot [B(C_6F_5)_4]^-$ featuring a three-centre two-electron

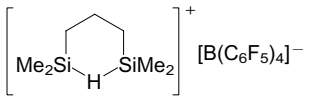
Structures 15 – 22



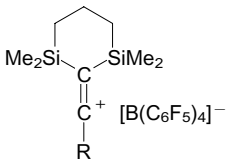
$[\mathbf{15} \leftarrow :NCCD_3]^+ \cdot [B(C_6F_5)_4]^-$



$\mathbf{16}^+ \cdot [B(C_6F_5)_4]^-$

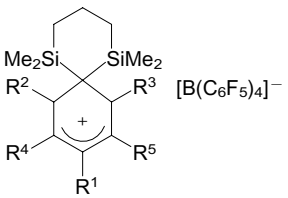


$\mathbf{17}^+ \cdot [B(C_6F_5)_4]^-$



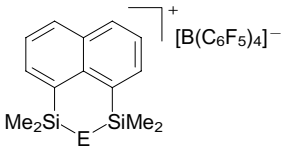
$\mathbf{18}^+ \cdot [B(C_6F_5)_4]^-$

R = Me, Ph, Bu^t



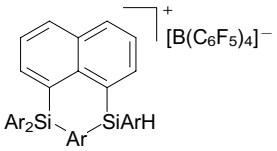
$\mathbf{19}^+ \cdot [B(C_6F_5)_4]^-$

R^1, R^2, R^3, R^4, R^5 = H, Me



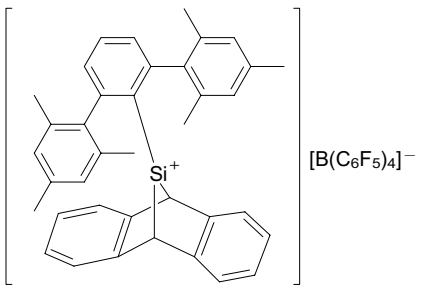
$\mathbf{20}^+ \cdot [B(C_6F_5)_4]^-$

E = H, F



$\mathbf{21}^+ \cdot [B(C_6F_5)_4]^-$

Ar = Ph, C_6H_4Me-4



$\mathbf{22}^+ \cdot [B(C_6F_5)_4]^-$

Si – H – Si bond,[67,68] (d) β-disilacyclohexenylidene-substituted vinyl cations **18**$^+ \cdot [B(C_6F_5)_4]^-$,[66,68,74] (e) bis-silylated arenium ions **19**$^+ \cdot [B(C_6F_5)_4]^-$,[68,69] (f) hydrogen-bridged bis(silyl)cations **20**$^+ \cdot [B(C_6F_5)_4]^-$,[72] and (g) aryl-bridged bis(silyl)cations **21**$^+ \cdot [B(C_6F_5)_4]^-$ (Ref. 73) (structures **15** – **21**).

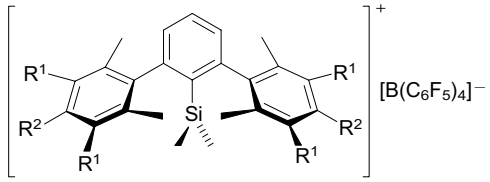
Müller and co-workers[11] were also able to stabilize the cationic dibenzosilanorbornadienylium isolated in the form of its tetraarylborate salt **22**$^+ \cdot [B(C_6F_5)_4]^-$ by employing very demanding 2,6-bis(2,4,6-trimethylphenyl)phenyl (Ter) group to further increase the steric bulk of substituent at the Si atom. However in **22**$^+ \cdot [B(C_6F_5)_4]^-$, the NMR resonance of the cationic silicon centre was found at rather high field (as compared to other triarylsilylium ions: $\delta_{Si} = +216$ to $+230$ ppm, see Section 3.1), being virtually independent of the NMR solvent used: $\delta_{Si} = +1.3$ ppm (in C_6D_6), $+1.2$ ppm (in $C_6D_5CD_3$) and $\delta_{Si} = +2.2$ ppm (in C_6D_5Cl).

This remarkable shielding of the cationic silicon is caused by the intramolecular π-donation from the flanking aryl groups, further enhanced by the homoconjugation of the π-system of the dibenzonorbornadiene part and the cationic silicon centre.

As is typical of the silylium ion derivatives, addition of acetonitrile to **22**$^+ \cdot [B(C_6F_5)_4]^-$ resulted in the formation of the corresponding stable nitrilium complex [**22**← :NCMe]$^+ \cdot [B(C_6F_5)_4]^-$, the structure of which was undoubtedly confirmed by X-ray crystallography.

Combination of electronic [3*p*(Si) – π(aryl) interaction] and steric (extraordinarily bulky aryl substituents) stabilizing factors enabled successful isolation of **23**$^+ \cdot [B(C_6F_5)_4]^-$, stable at room temperature.[75] The cationic silicon centre in **23**$^+ \cdot [B(C_6F_5)_4]^-$ also enjoyed a stabilization through the intramolecular π-donation from the flanking aryl groups. However, such stabilization occurred at the expense of the degree of silylium ion character in **23**$^+$, which was remarkably diminished. This can be seen in the relatively high-field ^{29}Si NMR resonances of **23**$^+$ ($+58.6$ to $+80.1$ ppm) and in a notable pyramidalization of the cationic silicon centre (the sum of the bond angles around Si is 346.1°). Nevertheless, due to its highly effective steric protection, cation **23**$^+$ does not reveal any observable interactions with either solvent molecules or counter-ions.

Structure 23

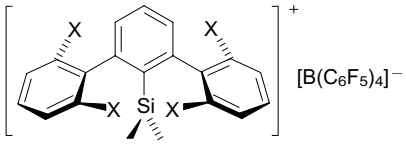


23$^+ \cdot [B(C_6F_5)_4]^-$

R^1, R^2 = H, Me

In the silylium ion **24**$^+ \cdot [B(C_6F_5)_4]^-$, representing a modification of **23**$^+ \cdot [B(C_6F_5)_4]^-$ with halogen substituents in the *ortho*-positions of the flanking aryl groups, the cationic silicon centres were more deshielded [$\delta_{Si} = +89$ ppm (for X = F) and $\delta_{Si} = +91$ ppm (for X = Cl)], although such values were still far from those expected for the free silylium ions.[76] X-Ray crystallography of **24**$^+ \cdot [B(C_6F_5)_4]^-$ (X = F) revealed efficient stabilization of the cationic silicon centre by the electron

Structure 24



24$^+ \cdot [B(C_6F_5)_4]^-$ X = F, Cl

donation from the two F substituents at the apical positions of the silicon trigonal bipyramidal structure.

Recently, the same authors also reported a series of structurally similar silylium ion derivatives **25**$^+$ featuring flanking aryl groups with different *ortho*-substituents: *ortho*-Me (like in **23**$^+$) and *ortho*-F (like in **24**$^+$).[77,78] Two stabilization modes of the cationic silicon centre through the coordination of either *ortho*-F or π-electron-rich aromatic ring were found in the crystal structure of **25**$^+$, and the delicate balance between these coordination modes was discussed.

Müller and co-workers[52,79] proposed recently a novel, synthetically rather attractive, strategy to triarylsilylium ions as a reasonable alternative to the classical allyl leaving group approach. This method is based on the common hydride transfer reaction synthetic protocol involving oxidation of diaryl(methyl)silanes $Ar_2(Me)SiH$ with $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$, unexpectedly forming triarylsilylium ions Ar_3Si^+ as a result of substituent scrambling. Like in the first reported isolable silylium ion Mes_3Si^+,[34,35] in the Ar_3Si^+ ions, the resonances of the cationic silicon atoms were observed in a characteristic low field region, with δ_{Si} being $+216$ to $+230$ ppm, irrespective of the NMR solvent used, thus manifesting the lack of notable interactions between the silylium ion and solvent molecules.

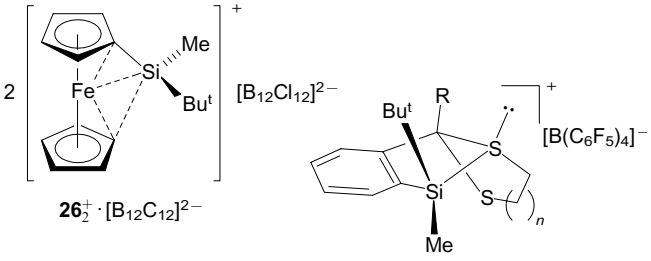
Likewise, in several examples of the Wagner – Meerwein type rearrangements of germapolysilanes, the isomerization of intermediate germylium ions to intermediate silylium ions was proposed [for example, in the $Al(Fe)Cl_3$-catalyzed isomerization of $(Me_3Si)_3SiGeMe_3$ into $(Me_3Si)_4Ge$, see Scheme 14].[80–83]

Scheme 14

$$(Me_3Si)_3Si-\overset{+}{G}eMe_2 \longrightarrow (Me_3Si)_2\overset{+}{S}i-GeMe_2(SiMe_3) \longrightarrow$$
$$\longrightarrow (Me_3Si)_2MeSi-\overset{+}{G}eMe(SiMe_3) \longrightarrow$$
$$\longrightarrow (Me_3Si)Me\overset{+}{S}i-GeMe(SiMe_3)_2 \longrightarrow$$
$$\longrightarrow (Me_3Si)Me_2Si-\overset{+}{G}e(SiMe_3)_2 \longrightarrow Me_2\overset{+}{S}i-Ge(SiMe_3)_3$$

The ferrocenyl substituent can also effectively stabilize silylium ion, as was shown in relation to recently prepared [Fc(Bu^t)MeSi]$^+ \cdot [B(C_6F_5)_4]^-$ (Fc is ferrocenyl), **26**$^+ \cdot [B(C_6F_5)_4]^-$.[84–87] After the replacement of the $[B(C_6F_5)_4]^-$ counter-anion by $[B_{12}Cl_{12}]^{2-}$, X-ray diffraction study of the crystal structure of $2[Fc(Bu^t)MeSi]^+ \cdot [B_{12}Cl_{12}]^{2-}$ showed that neither the solvent molecules nor the counter-ion notably coordinate to the cationic silicon centre. The positive charge in **26**$^+$ is still largely maintained on the silicon atom, as can be seen in its nearly planar geometry and remarkable deshielding of the silicon nucleus (^{29}Si NMR resonance: $+114.5$ ppm).

Structures of cations 26 and 27



$\mathbf{26}_2^+ \cdot [B_{12}C_{12}]^{2-}$

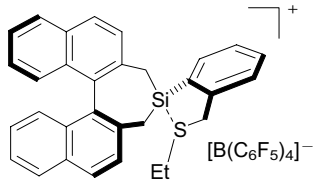
$\mathbf{27}^+ \cdot [B(C_6F_5)_4]^-$

R = H, Me; n = 1, 2

While further extending the range of intramolecularly stabilized silylium ion derivatives, the same authors[88] reported spectroscopic characterization of several 1,3-dithiolane-/1,3-dithiane-stabilized silylium ions $\mathbf{27}^+$, featuring cationic silicon centres reversibly coordinated by a sulfur n-donor.

Sulfur-stabilized silylium ion $\mathbf{28}^+$ with chiral binaphthyl backbones was also readily available by the standard hydride transfer reaction of the corresponding silyl hydride and $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$.[89]

Structure 28



$\mathbf{28}^+ \cdot [B(C_6F_5)_4]^-$

The simplest trialkylsilylium ion derivative, namely, the remarkable trimethylsilylium ion, was isolated in the form of its *closo*-carborane salt $[Me_3Si]^+ \cdot [RCB_{11}F_{11}]^-$ (R = H, Et) by the standard hydride transfer reaction between $[Ph_3C]^+ \cdot [RCB_{11}F_{11}]^-$ and Me_3SiH.[55] In the crystal structure of $[Me_3Si]^+ \cdot [RCB_{11}F_{11}]^-$, the cationic silicon centre was coordinated to one of the fluorine atoms of the carborane counter-anion, which caused its slight pyramidalization (354.4°) and stretching of the B – F bonds of the carborane cage. In the solution, $[Me_3Si]^+ \cdot [RCB_{11}F_{11}]^-$ also maintained anion coordination, as was seen in its ^{29}Si NMR resonance of the cationic silicon observed at + 138 ppm. This value, even being shifted downfield compared with that of the trimethylsilylium borate salt $[Me_3Si]^+ \cdot [B(C_6F_5)_4]^-$ (δ_{Si} = + 84.8 ppm),[32] was still far smaller than δ_{Si} = + 400 ppm calculated for the 'free' Me_3Si^+ cation.

The crystal structure of the closely related salt $[Me_3Si(arene)]^+ \cdot [B(C_6F_5)_4]^-$ (arene = $R_nC_6H_{6-n}$; R = H, Me, Et, Pr, Bu; n = 0 – 6) was reported several years later, revealing significant cation – anion interactions.[90] For example, in $[Me_3Si(C_6H_6)]^+ \cdot [B(C_6F_5)_4]^-$, silicon was notably pyramidalized (the sum of the bond angles around Si was 341.7 – 343.1°, for different sets of single crystals).

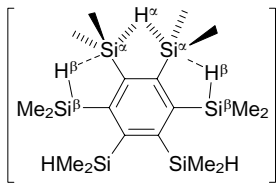
The reaction of $[Me_3Si]^+ \cdot [B(C_6F_5)_4]^-$ with Me_3Si-X (X = F, Cl, Br, I) produced a series of bis-silylated halonium ion salts $[Me_3Si-X-SiMe_3]^+ \cdot [B(C_6F_5)_4]^-$, in which the $[Me_3Si]^+$ unit almost completely lost its silylium ion character featuring covalently bound tetarcoordinate silicon centre (like in $Me_3Si-O-SiMe_3$).[91]

Homologous trialkylsilylium ions $[R_3Si^+]_2 \cdot [B_{12}Cl_{12}]^{2-}$ (R = Me, Et, Pr^i) were also readily available by the hydride transfer reaction of $[Ph_3C^+]_2 \cdot [B_{12}Cl_{12}]^{2-}$ and 2 equivalents R_3SiH in 1,2-difluorobenzene.[92] Remarkable coordination of silylium ions to the $[B_{12}Cl_{12}]^{2-}$ anion (*via* Si – Cl contacts) was confirmed by X-ray crystallography (349 – 350° around the silicon centre) and CP-MAS ^{29}Si NMR spectroscopy (δ_{Si} = + 117 to 126 ppm).

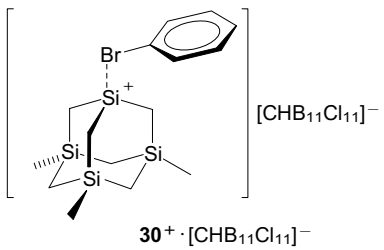
Unusual silylium zwitter-ion $[Me_2Si^+ - CH_2 - (CB_{11}Cl_{11})^-]$ was prepared by the treatment of the precursor $[Bu_4N]^+ \cdot [HMe_2Si-CH_2-CB_{11}Cl_{11}]^-$ with $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$.[93] The cationic silicon centre in $[Me_2Si^+ - CH_2 - (CB_{11}Cl_{11})^-]$, although stabilized by the weak coordination of a chlorine atom [Si···Cl = 2.304(8) Å], still maintained notable silylium ion character, as was evidenced by its only modest pyramidalization (351°) and relatively low-field resonance observed at δ_{Si} = + 137.4 ppm (solid-state ^{29}Si NMR).

In the silylium ion $\mathbf{29}^+ \cdot [B(C_6F_5)_4]^-$ stabilized by the polyagostic Si – H···Si interactions, a hydride transfer takes place between the two Si$^\alpha$-centres assisted by the agostic bonding to the Si$^\alpha$ – H bonds, which can be observed in its ^{1}H and ^{29}Si NMR spectra.[94] Such H-bridged silylium ion, featuring two Si$^\alpha \leftarrow$H – Si$^\beta$ agostic interactions, was later confirmed by the DFT calculations.[95] According to these theoretical studies, the cationic Si$^\alpha$-centres were nearly planar (358.9), and the Wiberg bond order (WBI) for the three-centre two-electron Si$^\alpha$ – H$^\alpha$ – Si$^\alpha$ bonding was substantially larger than that for the Si$^\alpha \leftarrow$H – Si$^\beta$ agostic interaction (0.426 *vs.* 0.182). Accordingly, the electron population of the Si$^\beta$ – H bond was reduced to 1.806, as a result of the electron transfer to the adjacent cationic Si$^\alpha$-centres.

Structures of cations 29 and 30



$\mathbf{29}^+ \cdot [B(C_6F_5)_4]^-$



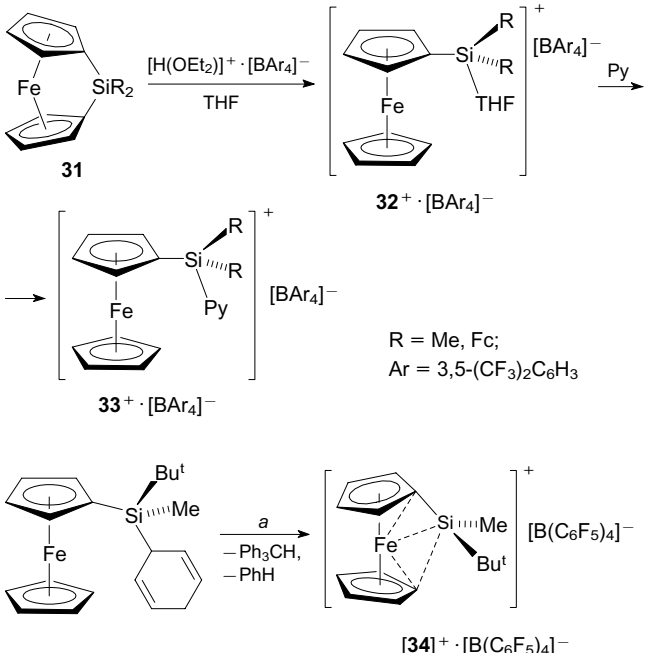
$\mathbf{30}^+ \cdot [CHB_{11}Cl_{11}]^-$

Highly constrained bridgehead silylium ion salt $\mathbf{30}^+ \cdot [CHB_{11}Cl_{11}]^-$ was also available under the conditions of the hydride transfer reaction.[96] X-ray diffraction analysis of $\mathbf{30}^+ \cdot [CHB_{11}Cl_{11}]^-$ revealed coordination of the silylium ion to the aromatic solvent (benzene, toluene, bromobenzene) with no direct contacts to the anionic part of the molecule. Such formulation was further supported by the ^{29}Si NMR spectroscopy observations: the chemical shift of the silylium ion was found to be + 105 ppm (in C_6D_5Br).

4.1.2. Oxidation of the Si–C bond

A novel approach to the generation of silylium ions was developed by Manners *et al.*[97–99] They took advantage of the high strain of sila[1]ferrocenophanes **31** and cleaved their strained Si–C bond with $[H(OEt_2)]^+ \cdot \{B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4\}^-$, smoothly generating the intermediate THF-solvated ferrocenyl-substituted silylium ion derivative $\mathbf{32}^+ \cdot \{B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4\}^-$, which can be further stabilized by coordination of a stronger Lewis base (such as pyridine) forming isolable pyridinium salt $\mathbf{33}^+ \cdot \{B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4\}^-$ (see Scheme 15, top).[97–99] Upon coordination of the fourth ligand (pyridine), the silicon centre in $\mathbf{33}^+ \cdot \{B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4\}^-$ was strongly pyramidalized, with the sum of the bond angles around Si being 337.7°.

Scheme 15

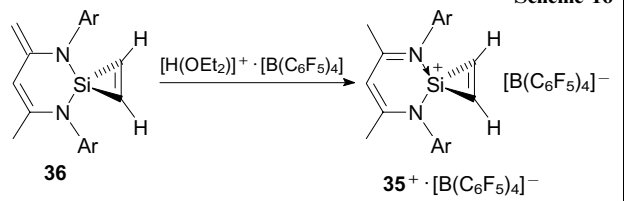


In an alternative method coined as the 'cyclohexadienyl leaving group approach' (in analogy with the original Lambert's 'allyl leaving group approach'[34,35]), intramolecularly stabilized ferrocenyl-substituted silylium ion $[Fc(Bu^t)MeSi]^+ \cdot [B(C_6F_5)_4]^-$ ($\mathbf{34}^+ \cdot [B(C_6F_5)_4]^-$) was prepared taking advantage of the ready elimination of the cyclohexa-2,5-dien-1-yl group from the corresponding silane precursor upon its treatment with $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$ (see Scheme 15, bottom).[100] Silylium ion $\mathbf{34}^+$ can also be stabilized intermolecularly by coordination of the appropriate external Lewis base, for example, Ph_2S.

4.1.3. Miscellaneous methods

An unusual cyclic silylium ion, silacyclopropenylium ion $\mathbf{35}^+ \cdot [B(C_6F_5)_4]^-$, featuring cationic spiro-Si centre shared by the six-membered ring *N*-heterocyclic unit and the three-membered ring cyclopropene moiety, was generated by protonation of the *N*-heterocyclic silacyclopropene precursor **36** with $[H(OEt_2)]^+ \cdot [B(C_6F_5)_4]^-$ (Scheme 16).[101] The highly electrophilic silylium centre in $\mathbf{35}^+$ was efficiently stabilized by the intramolecular n-electron donation from the adjacent N atom.

Scheme 16

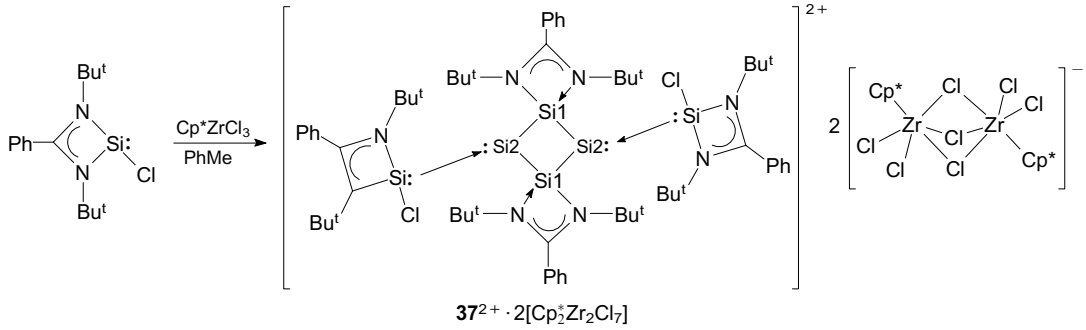


N-Heterocyclic carbenes (NHC) are also capable of efficient stabilization of intermediate silylium ions. Thus, the parent silylium ion H_3Si^+ was successfully stabilized and isolated as its NHC adducts $[NHC \rightarrow SiH_3]^+ \cdot OTf^-$ and $[NHC \rightarrow SiH_3 \leftarrow NHC]^+ \cdot OTf^-$ [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene].[102] According to X-ray crystallography data, the geometry of the cationic silicon centre in mono- and bis-NHC adducts of H_3Si^+ was a distorted tetrahedron and a distorted trigonal bipyramid, respectively.

Likewise, *N*-heterocyclic imines (NHI) can also stabilize intermediate silylium ions. For example, $[Me_2Si^+ - N{=}C(NBu^t - CH{=}CH - NBu^t)]$ intermolecularly coordinated by $Me_3SiNIBu^t$ [$NIBu^t$ = bis(*tert*-butyl)-imidazolin-2-imino] was isolated as its $[MeB(C_6F_5)_3]^-$ salt.[103]

Among other recently reported notable examples of the donor-stabilized silylium ion derivatives, one can mention tetrasilacyclobutadiene dication $\mathbf{37}^{2+} \cdot 2[Cp^*_2Zr_2Cl_7]^-$ (Refs 104 and 105) and disilenyl cation $\mathbf{38}^+ \cdot [OTf]^-$.[106] The former compound was unexpectedly generated upon the reaction of *N*-heterocyclic chlorosilylene with Cp^*ZrCl_3 in a 3 : 2 molar ratio (Scheme 17).[104] In cation $\mathbf{37}^{2+}$, the planar rhombic Si_4-core is composed of two *N*-donor-

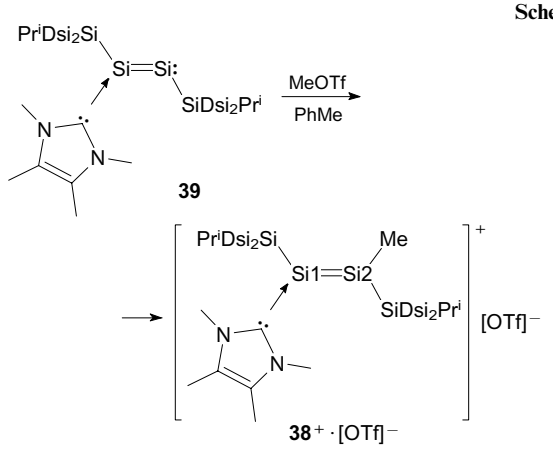
Scheme 17



stabilized silylium units (tetracoordinate Si1) and two silylene-like moieties (tricoordinate Si2). The cationic silicon centres Si1 in **[37]**$^{2+}$ resonated at relatively high field ($\delta_{Si} = +53.4$ ppm) because of the electron donation from the amidinato ligand. The major resonance contributor to the overall structure of **[37]**$^{2+}$ is the charge-localized form in which both positive charges are situated on the Si1 atoms, as was confirmed by both experimental and computational studies. According to the theoretical treatment, such tetrasilacyclobutadiene dication is best classified as a non-aromatic compound lacking a conjugated π-ring system required by the Hückel's rule.[105]

The reaction of the NHC complex of stable disilyne **39**[107] with MeOTf resulted in the formation of the disilenyl cation **38**$^{+}\cdot$[OTf]$^{-}$.[106] In **38**$^{+}$, the cationic NHC-substituted Si1 atom resonated at +54.0 ppm, the Si1 – Si2 bond length of 2.192(2) Å was characteristic of the Si=Si double bond, and the geometry around both sp^2-Si atoms (Si1 and Si2) was nearly planar (Scheme 18). On the basis of the combined experimental and computational data, the structure of **38**$^{+}$ was described as a hybrid between the two resonance extremes: (a) NHC-stabilized disilenyl cation with a positive charge at the Si1 atom and (b) imidazolium-substituted disilene with a positive charge delocalized over the whole NHC moiety.

Scheme 18



Dsi = $CH(SiMe_3)_2$

4.2. Coordination-free silylium ions

The quest for the genuine 'free' silylium ions, featuring tricoordinate cationic silicon centres with ideal trigonal-planar geometry, was one of the long-standing goals for experimental silicon chemists for several decades. To achieve this goal, it was first of all necessary to solve the problem of exceptional electrophilicity of silylium ions, which can coordinate to practically any electron donor (n, π or σ type), including even typically innocent solvents and inert counter-ions (such as the perchlorate ion). Finally, the silylium ion problem was resolved by the use of solvents and counter-anions of particularly low nucleophilicity, namely: (a) nonpolar aromatic hydrocarbons (benzene, toluene) as the reaction solvents and (b) borate and carborane anions (such as $[B(C_6F_5)_4]^-$, $[CB_{11}H_6Br_6]^-$ and $[B_{12}Cl_{12}]^{2-}$) as the counter-ions.[60] Moreover, the right choice of substituents in the silylium ion was also crucial, in particular, bulky (for the kinetic stabilization of the cationic centre) and electron-donating (for its thermodynamic stabilization) substituents are required.

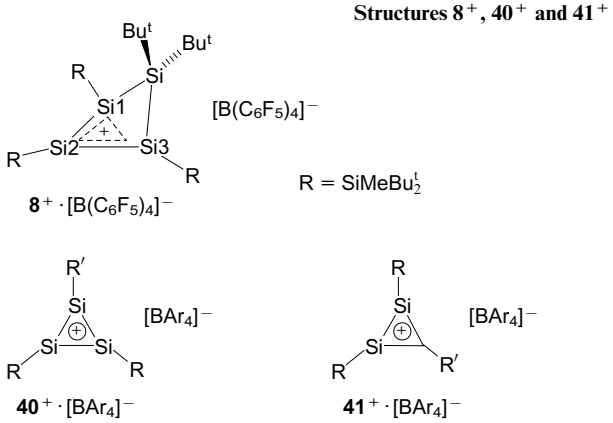
4.2.1. Acyclic trigonal-planar silylium ions

The 'free' tricoordinate trigonal-planar silylium ions R_3Si^+ (R = alkyl, aryl, silyl) are the most challenging synthetic targets, as they represent the least electronically perturbed silicon-centred cations, lacking coordination of either counter-ions or solvents. However, as for the 'free' tri(alkyl)- or tris(organosilyl)silylium ions, no examples of their stable representatives were reported to date. For the isolable tri(aryl)silylium ion derivatives, only two examples are currently known: $[Mes_3Si]^+\cdot[CB_{11}HMe_5Br_6]^-$ (Ref. 63) (see also Sections 2.2, 3.1, and 3.2) and $[Ar_3Si^+]_2\cdot[B_{12}Cl_{12}]^{2-}$ (Ar = Me_5C_6)[52] (see also Section 3.2).

4.2.2. Cyclic delocalized silylium ions

Several cyclic organosilicon compounds in which the positive charge is delocalized over the whole ring (or part of it) leading to the overall aromatic stabilization of the cationic system were reported within the past two decades (structures **8**$^+$, **40**$^+$ and **41**$^+$).[47,108,109] In these cyclic compounds, the tricoordinate silicon atoms were not truly trigonal-planar (as the silylium ions described-above in the Section 4.2.1); however, such cationic species were still 'free' from any sort of coordination with either solvents or counter-ions, as was evidenced by X-ray crystallography.

Structures 8$^+$, 40$^+$ and 41$^+$



R = $SiBu^t_3$; R′ = $SiMeBu^t_2$; Ar = C_6F_5, 2,3,5,6-F_4C_6H, 4-(Bu^tMe_2Si)C_6F_4

R = $SiBu^t_3$; R′ = 1-adamantyl; Ar = C_6F_5, 4-(Bu^tMe_2Si)C_6F_4

The first representative of these cyclic cationic derivatives, homoaromatic cyclotetrasilenylium ion **8**$^+\cdot[B(C_6F_5)_4]^-$, was prepared by Me-group abstraction from the corresponding cyclotrisilene precursor *cyclo*-[$R_2Si-Si(R)=Si(R)$] (R = $SiMeBu^t_2$) on treatment with $[Et_3Si(C_6H_6)]^+\cdot[B(C_6F_5)_4]^-$ (Ref. 47) (for alternative preparation of **8**$^+\cdot[B(C_6F_5)_4]^-$ by one-electron oxidation of the stable radical **7**$^\bullet$ with $[Ph_3C]^+\cdot[B(C_6F_5)_4]^-$, see Section 2.5.2, Scheme 11).

As was already briefly mentioned in Section 3.1, the central atom Si2 in cation **8**$^+$ is extraordinarily deshielded (+315.7 ppm), which is diagnostic for the homoaromatic systems, whereas the signals of terminal atoms Si1 and Si3 are observed at much higher fields (+77.3 ppm). Also in

accord with its homoaromatic composition, the geometry at the cationic silicon atoms (Si1, Si2, and Si3) in $\mathbf{8}^+$ was perfectly planar with Si1 – Si2 and Si2 – Si3 bond lengths of 2.240(2) Å and 2.244(2) Å, respectively, which were just in-between the values for typical single and double bond lengths. The interatomic Si1···Si3 distance of 2.692(2) Å was rather short, being just 15% longer than the typical Si – Si single bond, which was indicative of the homoaromatic Si1 – Si3 interaction.

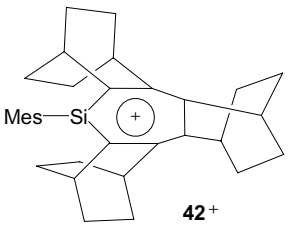
As the silicon analogues of cyclopropenylium ion, the 2π-electron aromatic cyclotrisilenylium $\mathbf{40}^+ \cdot [BAr_4]^-$ (Ref. 108) and disilacyclopropenylium $\mathbf{41}^+ \cdot [BAr_4]^-$ (Ref. 109) were prepared by the oxidative elimination of one of the silyl substituents from the corresponding precursors on treatment with $[Ph_3C]^+ \cdot [BAr_4]^-$ (see Section 2.3). Both cations $\mathbf{40}^+$ and $\mathbf{41}^+$ were 'free' without any notable interactions with either solvents or counter-ions, both in the solid state and in solution, and their 2π-electron aromatic delocalization was confirmed by X-ray diffraction and NMR data. Thus, in the solid state, cation $\mathbf{40}^+$ revealed an almost perfect equilateral triangle structure with internal Si – Si – Si bond angles of nearly 60° (in average) and endocyclic Si – Si bond lengths of 2.217(3) Å (in average), the latter value being intermediate between the standard Si – Si single and Si = Si double bond lengths. In solution, $\mathbf{40}^+ \cdot [BAr_4]^-$ and $\mathbf{41}^+ \cdot [BAr_4]^-$ exhibited diagnostic exceptional deshielding of the cationic silicon and carbon atoms: δ_{Si} of +284.6 and +288.1 ppm (for $\mathbf{40}^+ \cdot [BAr_4]^-$) and $\delta_{Si} = +208.2$ ppm and $\delta_C = +253.7$ ppm (for $\mathbf{41}^+ \cdot [BAr_4]^-$).

A couple of other closely related cationic 'free' silaaromatic compounds were also reported, although their structural data were not disclosed. These are:

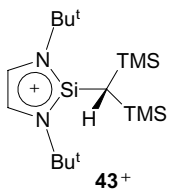
1) 6π-electron silatropylium ion $\mathbf{42}^+$ (stable below −50 °C) generated by the hydride transfer reaction and featuring characteristic low-field resonance of the cationic silicon atom ($\delta_{Si} = +142.9$ ppm);[110, 111]

2) 2-silaimidazolium ion $\mathbf{43}^+$ generated from the corresponding chlorosilane precursor by chlorine abstraction on treatment with $[Et_3Si(C_6H_6)]^+ \cdot [B(C_6F_5)_4]^-$ (this species was stable below −10 °C)[112] (see Section 2.4) or by the reaction of *N*-heterocyclic silylenes with $[Et_3Si(C_6H_6)]^+ \cdot [B(C_6F_5)_4]^-/[Pr^i_3Si(C_6H_6)]^+ \cdot [B(C_6F_5)_4]^-$ (Ref. 39) (see Section 2.5.1, Scheme 9, $\mathbf{6}^+ \cdot [B(C_6F_5)_4]^-$).

Structures 42^+ and 43^+



$\mathbf{42}^+$



$\mathbf{43}^+$

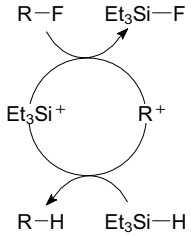
5. Synthetic application of silylium ions in organic chemistry

The practical importance of the silylium ion derivatives was acknowledged only very recently. The reactivity and thus applicability of silylium ions is dominated by their exceptionally high Lewis acidity,[113] making them very useful in organic synthesis, particularly in catalytic processes.[114, 115] The use of silylium ions as novel advanced catalysts for a broad range of organic chemistry transformations is currently their most important practical application. Some most representative examples of such catalytic reactions are described below.

5.1. Hydrodefluorination reactions

The first catalytic reaction of silylium ions that attracted a great deal of attention was hydrodefluoriniation reaction, that is, the catalytic transformation of C – F bonds in fluoroalkanes to C – H bonds. The very first example of the room temperature catalytic hydrodefluoriniation of aliphatic C – F bonds was reported by Ozerov and co-workers in 2005.[116] The authors allowed $[Et_3Si]^+ [B(C_6F_5)_4]^-$ to react with trifluorotoluenes and 1-fluoropentane, which resulted in generation of Et_3SiF and carbenium ion species R^+ at the first step, being followed by the reaction of the latter with Et_3SiH (as the hydride source) regenerating silylium ion catalyst Et_3Si^+ and thus completing the catalytic cycle (Scheme 19).

Scheme 19



RF = $PhCF_3$, 4-$XC_6H_4CF_3$ (X = F, Cl, Br), 3-$FC_6H_4CF_3$, 2,4-$Cl_2C_6H_4CF_3$, $C_5H_{11}F$

Carboranes can also be used as the counter-ions, and a novel catalytic system $Et_3SiH/[Ph_3C]^+ \cdot [CHB_{11}H_5Cl_6]^-$ (as precursor for $[Et_3Si]^+ \cdot [CHB_{11}H_5Cl_6]^-$) was developed for hydrodefluorination of $C_6F_5CF_3$, $C_6H_5(CH_2)_2CF_3$, and $CF_3(CF_2)_3CH_2CH_3$.[117] With an excess of Et_3SiH, $C(sp^3) - F$ bonds are catalytically transformed into C – H bonds at room temperature with very high turnover numbers (up to 2700).

Subsequently, the same authors extended the hydrodefluorination process to more general hydrodehalogenation of C – Hal bonds (Hal = F, Cl, Br) (Scheme 20).[118]

Scheme 20

$$R^1_3C-Hal + R^2_3Si-H \xrightarrow{Cat} R^1_3C-H + R^2_3Si-Hal \quad (42-97\%)$$

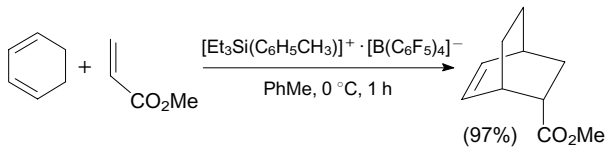
R^1_3CHal = $C_6H_5CF_3$, 4-$FC_6H_4CF_3$, $C_6F_5CF_3$, n-$C_{10}H_{21}F$, $C_6H_5(CH_2)_2CF_3$, $Br(CH_2)_5CF_3$, $C_6F_5CCl_3$, 4-$FC_6H_4CCl_3$, CyCl, *etc.*; R^2 = Et, n-C_6H_{13}; Hal = F, Cl, Br; Cat = $[Ph_3C]^+ \cdot X^-$ (X^- = $[CHB_{11}Cl_{11}]^-$, $[CHB_{11}H_5Cl_6]^-$, $[CHB_{11}H_5Br_6]^-$)

In a similar vein, Müller and co-workers[72,119–121] demonstrated that the reaction of fluorodecane or benzyl trifluoride (in the presence of equimolar amount of Et_3SiH) with a catalytic amount of their hydrogen- (or fluorine)-bridged silylium ion derivatives $\mathbf{20}^+ \cdot [B(C_6F_5)_4]^-$ (see Section 4.1.1) gives the corresponding alkanes as the hydrodefluorination products.

5.2. Diels – Alder reactions

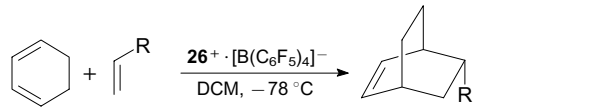
The very first development in this challenging area of catalytic applications of silylium ions in the carbon – carbon bond formation was published in 2005 by Sawamura and co-workers.[122] Thus, they reported an excellent catalytic performance in Diels – Alder reactions of the silylium ion derivative $[Et_3Si(C_6H_5CH_3)]^+ \cdot [B(C_6F_5)_4]^-$ [superior to the commonly used Me_3SiOTf and Me_3SiNTf_2 (or Et_3SiNTf_2)]: for example, in the reaction of 1,3-cyclohexadiene and methyl acrylate, the corresponding cycloadduct was formed in an almost quantitative yield (Scheme 21).

Scheme 21

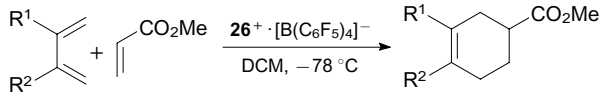


Oeistreich and co-workers[84, 123 – 125] successfully employed their ferrocene-stabilized silylium ion $[Fc(Bu^t)MeSi]^+ \cdot [B(C_6F_5)_4]^-$, $\mathbf{26}^+ \cdot [B(C_6F_5)_4]^-$ (see Section 4.1) as [4 + 2] cycloaddition catalyst for a variety of deactivated 1,3-dienes (cyclohexadiene, butadienes) and dienophiles (α,β-unsaturated carbonyl compounds), which reacted with excellent *endo*-selectivity even at low temperatures (Scheme 22).

Scheme 22



R = CHO, C(O)Me, CO_2Me, *etc.*



$R^1 = R^2 = Me$ (97%); $R^1 = H$, $R^2 = Cl$ (68%); DCM = CH_2Cl_2

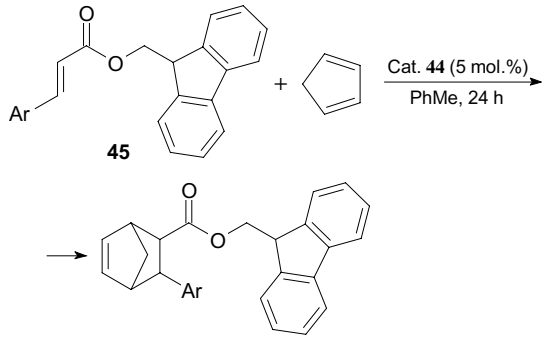
Sulfur-stabilized silylium ions $\mathbf{27}^+$ (Ref. 88) can also catalyze the Diels – Alder reactions in a similar way at temperatures as low as 0 °C. Sulfur-stabilized silylium ions $\mathbf{28}^+$ with chiral binaphthyl backbones[89] also catalyzed Diels – Alder reactions, involving cyclohexadiene and pentadiene as a diene, but the reaction enantioselectivity did not exceed 24%.

Silylium ion – carbanion pair **44** generated *in situ* was proved to catalyze the enantioselective Diels – Alder reaction of cinnamates **45** and cyclopentadiene with excellent enantiomeric and diastereomeric ratios (Scheme 23).[126]

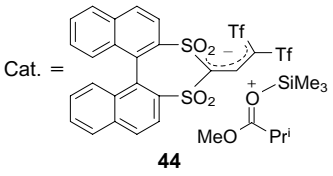
5.3. Friedel – Crafts reactions

Omann and Oestreich[127] reported recently a general procedure for the Friedel – Crafts type catalytic transformation of the readily available *ortho*-silylated biphenyls **46** into mono- and difunctionalized dibenzosiloles **47**. This intramolecular electrophilic aromatic substitution involves catalytically

Scheme 23



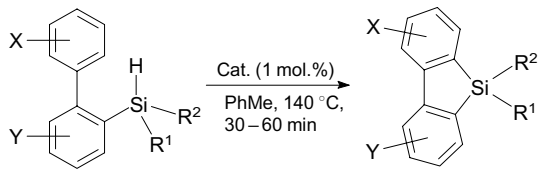
(88% – 97%, *er* = 93 : 7 – 97 : 3, *dr* > 25 : 1)



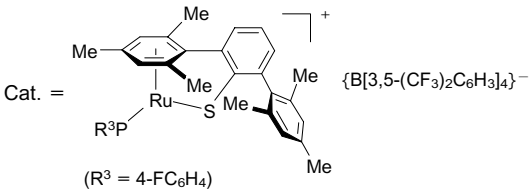
Ar = Ph, 4-XC_6H_4 (X = MeO, O_2N, F, Cl, Br, I, Me); 3-XC_6H_4 (X = Me, O_2N), *etc.*

generated silylium ions and results in the silylation of the C – H bond and formation of the target products in up to 99% yields (Scheme 24).

Scheme 24



R^1, R^2 = Me, Ph



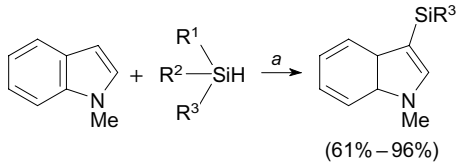
X = Y = H, 4-Cl; Y = H: X = 4-CF_3, 4-Me, 3-Me, 3-pyrrolyl, 3-Cl, *etc.*

Similarly, catalytic S_EAr C – H silylation of 2- and 3-substituted pyridines with hydrosilanes in the presence of a transition metal catalyst involves breaking of the Si – H bond with generation of a silylium ion, thus forming the corresponding 5-silylated pyridines in 24% – 86% yields.[128]

Stabilized silylium ions formed *in situ* upon the reaction of hydrosilanes with strong Brønsted acids (for example, $[H(OEt_2)_2]^+ \cdot [BAr^F_4]^-$) promote S_EAr C – H silylation of electron-rich heteroarenes such as indoles (Scheme 25).[129, 130]

Friedel – Crafts variation of the intramolecular aryl coupling can also be initiated by silylium ion catalyst, being enabled by the formation of Si – F bonds (which are stronger than C – F bonds), thus resulting in the formation of a number of polycyclic arenes and graphene fragments in up to 93% yields.[131, 132] As a representative example of the above reaction, one can mention the reaction of

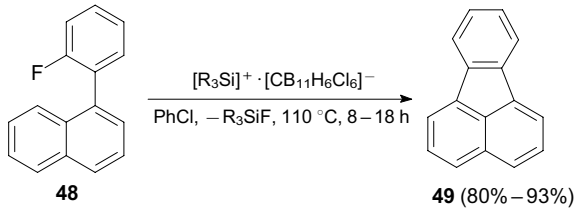
Scheme 25



(*a*) $[H(OEt_2)_2]^+ \cdot [BAr^F_4]^-$ (1.0 equiv.), norbornene (1.0 equiv.), PhMe, 80 °C or rt, 18 h; $R^1 = R^2 = Me$, $R^3 = Ph$; $R^1 = R^2 = Ph$, $R^3 = Me$; $R^1 = R^2 = Ph$, Et; $R^3 = H$

$[Pr^i_3Si]^+ \cdot [CB_{11}H_6Cl_6]^-$ with 1-(2-fluorophenyl)naphthalene **48** causing the activation of the C – F bond and formation of a new arene – arene bond, finally leading to the fluoranthene derivative **49** (Scheme 26).

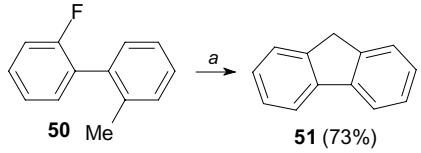
Scheme 26



R = Pr^i, Mes

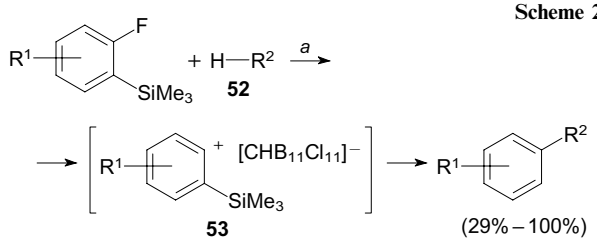
In a similar vein, the same authors [133] reacted 2-fluoro-2′-methylbiphenyl **50** with a catalytic amount (5 mol.%) of $[Pr^i_3Si]^+ \cdot [CB_{11}H_6Cl_6]^-$ and stoichiometric amount of Me_2SiMes_2 forming C – F/C – H activation couple, in which silylium ion was a catalytic initiator and dimethyldimesitylsilane was a Brønsted base and pro-Lewis acid catalyst. In this case, silylium ion-promoted C – F activation of the substrate results in the formal C – H activation and the formation of new $C_{aryl} - C_{alkyl}$ bond in the final fluorene product **51** (Scheme 27). Such synthetically very attractive direct catalytic cross-coupling [134] culminated in the very recently reported C – H arylation of simple arenes and alkanes **52** (including even methane) catalyzed by *in situ* generated silylium ions (Scheme 28).[135] This synthetic strategy is initiated by silylium ion-mediated fluoride abstraction from β-silylfluoroarene, followed by the Friedel – Crafts or C – H insertion reactions of the resulting β-silyl-stabilized aryl cation equivalents. The insertion of the latter species into sp^3 and sp^2 C – H bonds provides a ready access to a wide range of important aromatic products.

Scheme 27

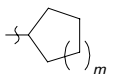


(*a*) $[Pr^i_3Cl]^+ \cdot [CHB_{11}H_5Cl_6]^-$ (5 mol.%), Me_2SiMes_2, PhCl, 90 °C, 70 min

Scheme 28

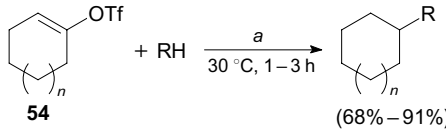


(*a*) $[Ph_3C]^+ \cdot [CHB_{11}C_{11}]^-$ (5 mol.%), Pr^i_3SiH (10 mol.%), C_6H_5Cl; R^1 = Ar, Alk, Hal, silyl; $R^2 = CH_3$, $CH_2(CH_2)_nCH_3$ (n = 3, 4)

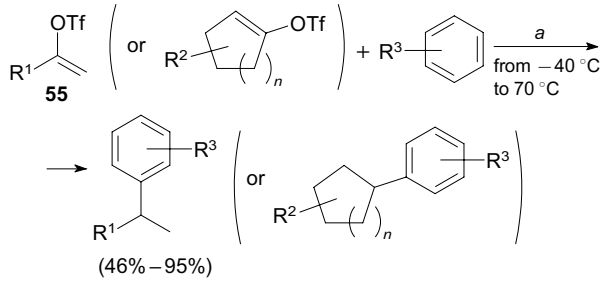


(m = 1 – 3), C_6H_5

Scheme 29



(*a*) $[Ph_3C]^+ \cdot [CHB_{11}Cl_{11}]^-$ (2 mol.%), Et_3SiH (1.5 equiv.); n = 1, 3; R = cyclo-C_6H_{11}, cyclo-C_7H_{13}, n-C_5H_{11}



R^1 = Et, R^3 = H, 2,4,6-Me_3, 2,5-F_2; R^1 = Ph, R^3 = 4-Me; n = 2: R^2 = H, R^3 = 2-F, 5-Bn, 2,4,6-Me_3; n = 2: R^2 = 4,4-Me_2, 3,3-Me_2, 4-Bu^t, *etc.*; n = 0 – 3: $R^2 = R^2 = R^3$ = H

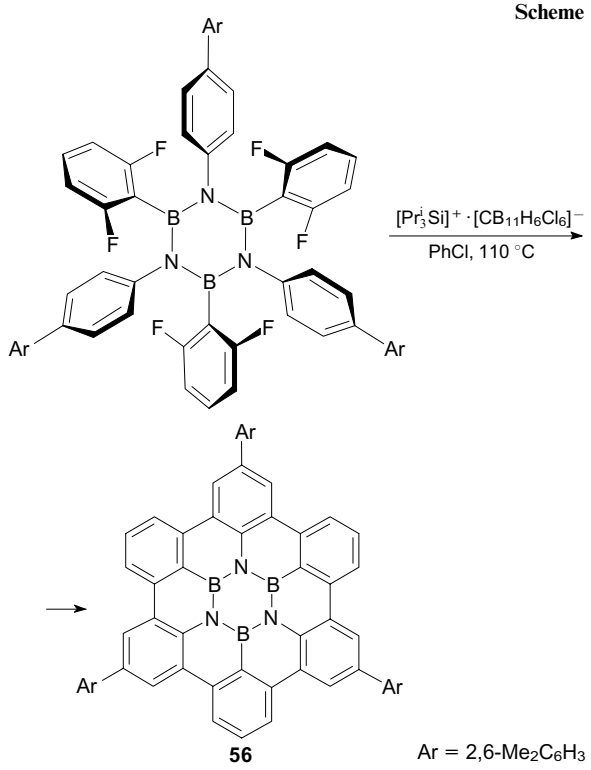
The tremendous synthetic potential of the above-discussed catalytic cross-coupling approach was very convincingly demonstrated in the straightforward synthesis of the borazino-doped coronene derivative **56**, involving six simultaneous $C(sp^2) - C(sp^2)$ Friedel-Crafts ring-closure steps (Scheme 30).[137]

Schulz and co-workers [90] recently reported that arene solvent-coordinated silylium ion $[Me_3Si(arene)]^+[B(C_6F_5)_4]^-$ they obtained is able to promote catalytic Friedel – Crafts disproportionation of *tert*-butylbenzene to give a mixture of 1,3- (8.4%) and 1,4-di-*tert*-butylbenzene (64.4%) and 1,3,5-tri-*tert*-butylbenzene (27.2%).

5.4 Small molecule activation

Silanes R_3SiH (R = Et, Pr^t) can reduce CO_2 in the presence of stoichiometric amounts of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in chlorobenzene to afford (after hydrolysis) formic acid

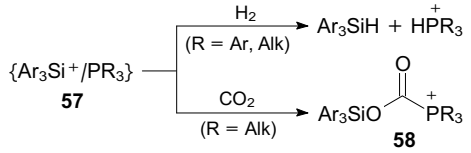
Scheme 30



HCOOH and methanol MeOH. The reaction of CO_2 with the pre-synthesized $[Et_3Si(C_6H_6)]^+[B(C_6F_5)_4]^-$ in benzene yields (after hydrolysis) benzoic acid PhCOOH (Scheme 31).[138]

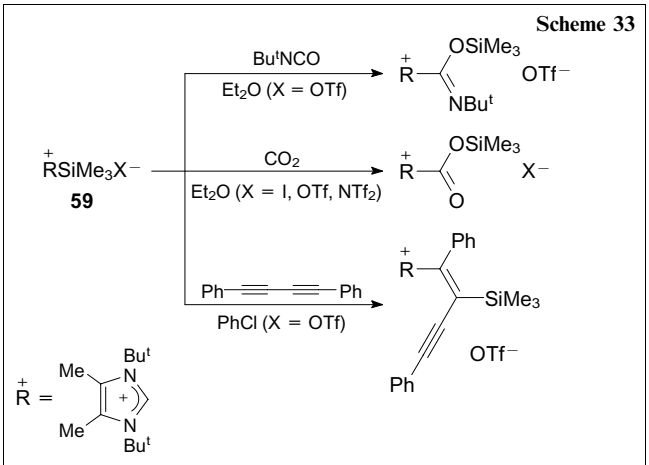
With the sterically congested phosphines, triarylsilylium borates $[Ar_3Si]^+[B(C_6F_5)_4]^-$ can form frustrated Lewis pairs (FLPs, **57**), which can irreversibly cleave dihydrogen at ambient conditions, thus forming Ar_3SiH.[79, 80, 139, 140] Moreover, silylium ion/phosphine FLPs, $(Me_5C_6)_3Si^+/PR_3$ (R = Bu^t, Cy), can bind CO_2 to give silylacylphosphonium salt **58** (Scheme 32).[139]

Scheme 32



Ar = C_6Me_5, 2,4,6-$Me_3C_6H_2$, 2,3,5,6-Me_4C_6H; R = Bu^t, Cy, Ph, 2-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, 2,4,6-$Pr^i_3C_6H_2$, *etc*.

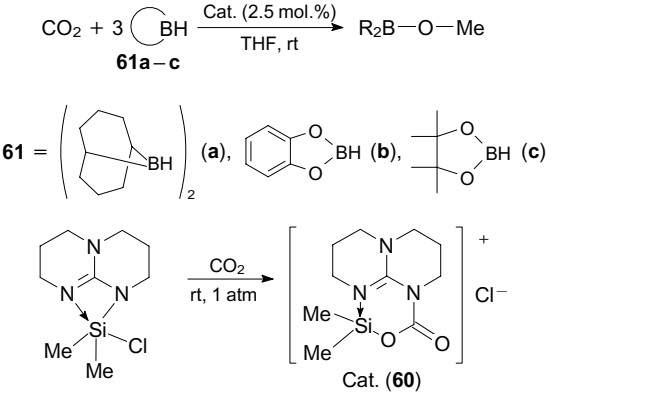
Scheme 33



Silylium ions can also form FLPs with NHC, thus giving silylium ion/NHC pairs **59**, which are capable of fixation of CO_2, Bu^{t}NCO, and Ph—C≡C—C≡C—Ph (Scheme 33).[141]

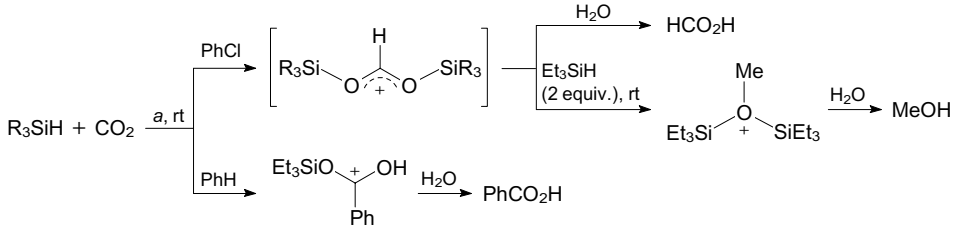
N-Stabilized silylium ions $\mathbf{60}^+$, representing novel intramolecular N/Si$^+$ FLPs, manifest excellent catalytic activity in the high-yield hydroboration of CO_2 to the methoxide level with 9-borabicyclo[3.3.1]nonane **61a**, catecholborane **61b** and pinacolborane **61c** (Scheme 34).[142]

Scheme 34



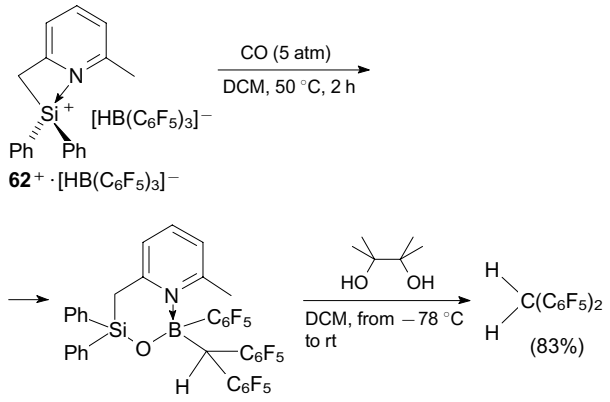
Intramolecularly pyridine-stabilized silylium ion $\mathbf{62}^+$, generated by the reaction of 2-[(diphenylsilyl)methyl]-6-methylpyridine with $B(C_6F_5)_3$, promoted complete transition-metal-free cleavage of the C≡O bond in carbon monoxide with formation of one new C—H and two new C—C bonds (Scheme 35).[143]

Scheme 31



(*a*) $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$; R = Et, Pr^i

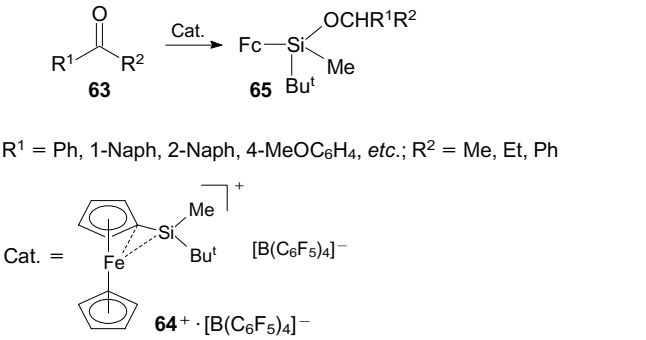
Scheme 35



5.5. Hydrosilylation

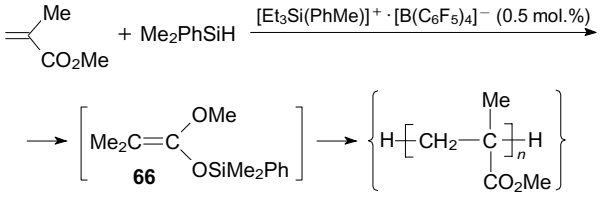
Silylium ions can also catalyze hydrosilylation reactions. Thus, Müther and Oestreich [144] reported the reduction of carbonyl compounds **63** with Fc(Bu^t)MeSiH catalyzed by the silylium ion **64**$^+$ {generated *in situ* from Fc(Bu^t)MeSiH and $[Ph_3C]^+[B(C_6F_5)_4]^-$} to afford hydrosilylation product **65** (Scheme 36).

Scheme 36



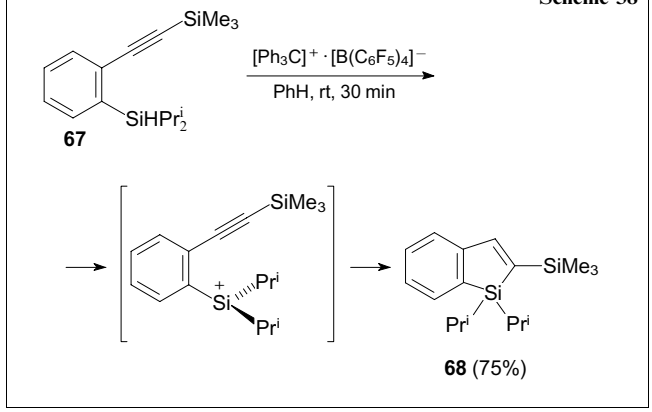
Silylium ions can also catalyze 1,4-hydrosilylation of methyl methacrylate (MMA) with R_3SiH to generate *in situ* the silyl ketene acetal initiator **66** and promote subsequent living polymerization of MMA (Scheme 37).[145]

Scheme 37



A catalytic amount of $[Ph_3C]^+[B(C_6F_5)_4]^-$ initiates intramolecular chain hydrosilylation of diorganyl[2-(trimethylsilylethynyl)phenyl]silane **67** affording the corresponding benzosilole **68** (Scheme 38).[146] *In situ* generated silylium ions play an important role of the chain carriers in this reaction.

Scheme 38

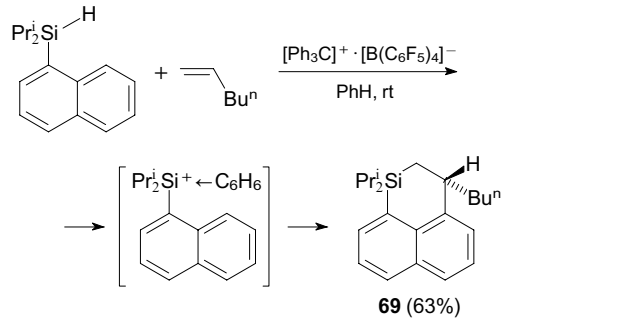


5.6. Miscellaneous reactions of silylium ions [147]

In addition to their well-documented catalytic performance, silylium ions can also:

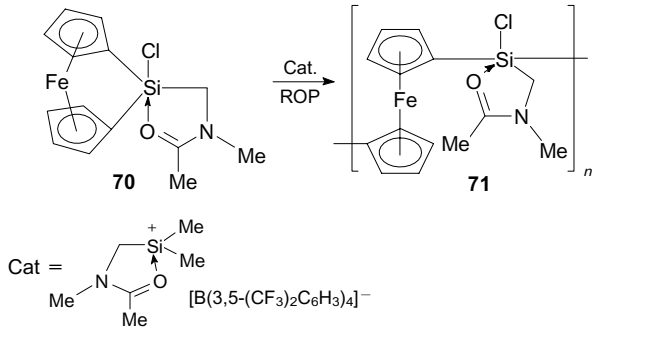
1) react with alkenes to give 2-silanaphthalenes **69** as the dehydrogenative annulation products (Scheme 39);[148, 149]

Scheme 39



2) initiate ring-opening polymerization (ROP) of cyclic pentacoordinate sila[1]ferrocenophanes **70** yielding poly(ferrocenylsilanes) **71** with pentacoordinate silicon moiety in the polymer backbone (Scheme 40);[150]

Scheme 40

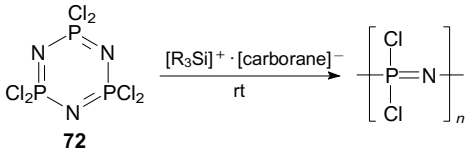


3) promote room temperature ROP of the cyclic chlorophosphazene trimer **72** (Scheme 41);[151]

4) promote reduction of aldimines **73** to the corresponding amines **74** with hydrosilanes (Scheme 42).[152]

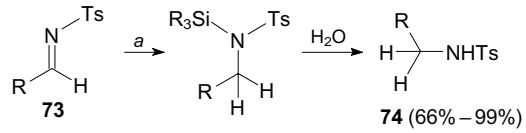
A catalytic amount of $[Me_3Si]^+$ ions induces isomerization of bis(trimethylsilyl)diazomethane **75** to bis(trimethylsilyl)aminoisonitrile **76**, followed by the unusual

Scheme 41



72

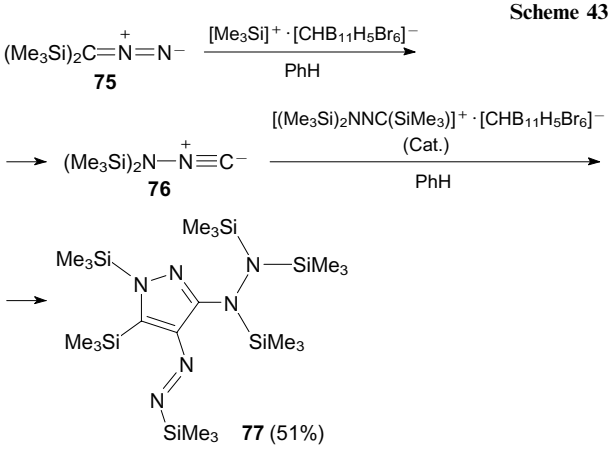
Scheme 42



73 **74** (66% – 99%)

(*a*) $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-$, $Bu^t(Fc)MeSiH$, 1,2-$Cl_2C_6H_4$, rt;
R = Bu^t, Cy, Ph, 4-BrC_6H_4, 4-MeC_6H_4, 1-Naph, 2-Naph, *etc.*

Scheme 43



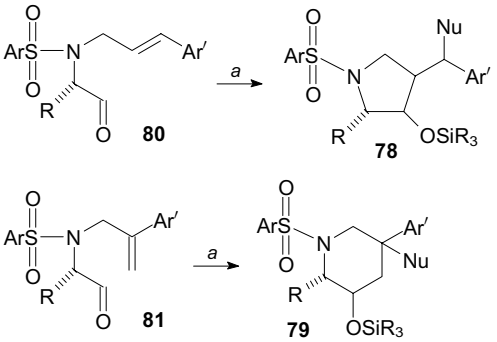
75 **76** **77** (51%)

trimerization of the latter to form exclusively 4-diazenyl-3-hydrazinylpyrazol **77** (Scheme 43).[153]

The intermediate silylium ion derivatives $[R_3Si]^+[HB(C_6F_5)_3]^-$, generated upon the oxidation of hydrosilanes R_3SiH with $B(C_6F_5)_3$, enabled the chemoselective reduction of multiple functional groups of bioactive natural products.[154]

In situ generated $[Et_3Si]^+[B(C_6F_5)_4]^-$ catalyzed stereoselective synthesis of various substituted pyrrolidine **78** and piperidine **79** derivatives from acylic aldehydes **80** and **81** under the Prins cyclization conditions and trapping of the resulting carbocation by a silyl-protected nucleophile R_3Si-Nu (Scheme 44).[155] These novel nitrogen-containing polycyclic compounds may have potential medicinal chemistry applications.

Scheme 44



80 **78** **81** **79**

(*a*) $[Ph_3C]^+ \cdot [B(C_6F_5)_4]^-/Et_3SiH$, Et_3Si-Nu, DCM, −78 °C, 1 h;
Ar = 4-BrC_6H_4, Ar′ = Ph, 2-IC_6H_4, *etc.*; R = Me, Bn;
Nu = H, All, N_3, enol ether

6. Conclusion

In contrast to the well-developed chemistry of carbenium ions, the field of their silicon congeners, silylium ions, is still far from being mature. However, the progress in this field, made particularly within a couple of last decades, is spectacular with many striking advances in the synthesis and synthetic applications of the silylium ion derivatives. Whereas early experimental efforts primarily involved generation and spectroscopic observation of otherwise transient silicon-centred species, later the research interest focus turned to isolation of the stable 'free' silylium ions lacking any observable coordination to either internal or external nucleophiles. This was achieved by the smart combination of the right substituents at the cationic silicon centre, reaction solvents and counter-ions, and was finally culminated in 2002 when the crystal structure of the first 'free' silylium ion salt, $[Mes_3Si]^+ \cdot [CB_{11}HMe_5Br_6]^-$, was reported. After such milestone synthetic advance resolving 'free' silylium ion problem, the research interest of organosilicon community moved towards the practical use of silylium ion derivatives in materials science, and in synthetic organic chemistry. Given exceptional electrophilicity of silylium ions greatly exceeding that of carbenium ions, one can expect the most prospective utilization of the former derivatives as very strong and highly potent Lewis acidic catalysts in organic syntheses. This was later experimentally proved successful, and as is discussed in Section 5, silylium ions (both pre-synthesized and *in situ* generated) are able to efficiently catalyze a number of organic transformations, including such very important ones as Diels – Alder and Friedel – Crafts reactions, as well as hydrosilylation and small molecule activation.

Looking to the future, we can expect further advances in the preparation of stable silylium ions, for example, isolation of the still elusive and highly challenging tri(silyl)silylium ion derivatives $(R_3Si)_3Si^+$. The practical use of silylium ions in organic synthesis as powerful Lewis acidic catalysts also needs its further developments, first of all, involving expansion of the scope of its synthetic applicability. Given very high research activity in this field to solve the above-mentioned problems, one can anticipate fast progress and major breakthroughs to be achieved in the near future.

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