

# “Tamed” Silylium Ions: Versatile in Catalysis\*\*

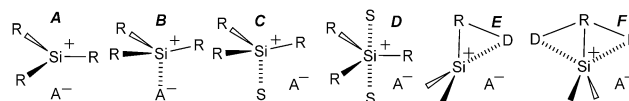
Axel Schulz\* and Alexander Vllinger

bond activation · homogeneous catalysis ·  
Lewis acids · silylium ions · triarylsilylium ions

Whoever coined the name for the element silicon assuredly did not have in mind the highly reactive silylium ions when it was named after the omnipresent pebble (Latin *silex* or *silicis*).<sup>[1]</sup> Silylium ions are increasingly finding their way into practice, because of their high reactivity (Lewis acidity) and the possibility of reactivity design. It is, therefore, certainly correct to say that silylium ions have long shed their status as laboratory curiosities, and in practice have justifiably arrived at the interface of classical inorganic and organic chemistry.<sup>[2]</sup> Starting from a contribution from the Müller research group,<sup>[3]</sup> in which a new, elegant synthetic route to triarylsilylium ions and their use in hydrogen activation is described, we will discuss in this Highlight the potential of silylium ions.

Silylium ions (also known as silylenium or silicenium ions)<sup>[4]</sup> are in many respects remarkable: the electron sextet and an empty 3p valence orbital on the silicon atom makes them electron-deficient compounds, and for this reason very strong Lewis acids, which in the condensed phase are significantly more difficult to generate than the analogous carbenium ions  $R_3C^+$ . The lower tendency for stabilization by hyperconjugation or  $\pi$  conjugation (caused by a lower effective overlap because of the diffuse Si valence orbitals) can be put forward as the cause of this, and results in greater Lewis acidity. This permits, for example, the activation of small molecules.<sup>[3]</sup> Moreover, the  $Me_3Si^+$  ion can, for example, also be considered to be a large proton, which, in analogy to superacid media (e.g.  $aHF + SbF_5$ ,  $aHF$  = anhydrous hydrogen fluoride),<sup>[5]</sup> can be used for the generation of super-Lewis acid media (e.g.  $Me_3Si-F + [Me_3Si_{(solv.)}]^+[WCA]^-$ ; WCA = weakly coordinated anion, solv. =  $Me_3Si-F$ ; Scheme 1 species C).<sup>[6]</sup>

Whereas the search for a stable trivalent Si cation stood at the origin of silylium ion chemistry, and in this context the question of how strong the interaction with the environment is in the condensed phase was investigated extensively (Scheme 1), the design of silylium ions and their use in synthesis are at the forefront of today's targeted syntheses.<sup>[2]</sup> The only known examples of triorganosilylium salts in which



**Scheme 1.** Stabilization of silylium ions by interaction with the anion (B), with solvent molecules (C, D), and with intramolecular donor atoms (E, F). Species A represents the free silylium ion without significant interaction with the anion.

no interactions (species A) with solvent molecules (C and D), anions (B), or intramolecular coordination (E and F) are involved are the borates or carboranates of trimesitylsilylium (mesityl = 2,4,6-trimethylphenyl) and tridurylsilylium (duryl = 2,3,5,6-tetramethylphenyl), which can be prepared by allyl fragmentation reactions.<sup>[7]</sup> Since this fragmentation reaction is problematical with regard to the synthesis of triaryl(allyl)silane  $Ar_3Si(C_3H_5)$ , the Müller synthesis,<sup>[3]</sup> based on the reaction of diaryl(methyl)silane  $Ar_2(Me)SiH$  with  $[Ph_3C][B(C_6F_5)_4]$  leading to triarylsilylium ions (Scheme 2),



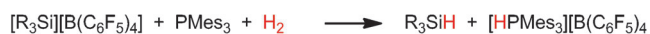
**Scheme 2.** Synthesis of triarylsilylium ions.

represents an important step in silylium ion chemistry, since triarylsilylium ions are now more readily accessible. This is actually the classical Bartlett–Condon–Schneider hydride transfer reaction, which by using diaryl(methyl)silanes is superimposed by a substituent exchange so that  $Ar_3Si^+$  and  $Me_3SiH$  are formed in addition to  $Ph_3CH$ . However, the substitution exchange is restricted to bulky alkyl residues which are no smaller than the xylene group. The substituent exchange is not limited to methyl groups, but is also observed with ethyldimesitylsilane, but not with ethylbis(triisopropylphenyl)silane. This leads to the conclusion that both steric effects on the arene ring and the ability of the alkyl group to migrate is of pivotal importance for the substitution. The rate-determining step is the hydride transfer, which is accompanied by a rapid alkyl–aryl exchange with neutral silane.

In light of the impressive success in the use of frustrated Lewis pairs (FLPs) in synthesis and catalysis, it seems logical to form FLPs with the extremely Lewis acidic silylium ions and use them for molecule activation. Indeed, triarylsilylium ions form FLPs with sterically demanding phosphanes (e.g.  $P(C_6F_5)_3$ ), which can be used, for example, for irreversible hydrogen activation (Scheme 3).<sup>[3]</sup>

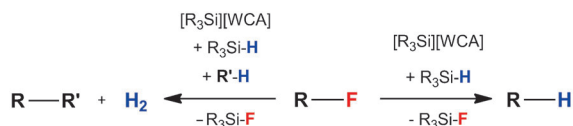
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**Scheme 3.** H<sub>2</sub> activation by a silylium-phosphane Lewis pair (R = pentamethylphenyl).

The best investigated use of silylium ions is the hydrodefluorination of fluoro- and perfluoroalkyl groups which was published in 2005 by Douvris and Ozerov (Scheme 4, right).<sup>[8]</sup>

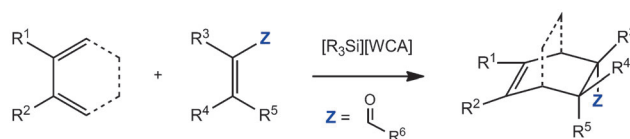


**Scheme 4.** Hydrodefluorination versus a C–C coupling reaction.

Here, C(sp<sup>3</sup>)–F bonds can be transformed catalytically into C–H bonds selectively relative to C(sp<sup>2</sup>)–F bonds under mild conditions. Salts of the weakly coordinating chlorocboranates such as [HCB<sub>11</sub>H<sub>3</sub>Cl<sub>6</sub>]<sup>–</sup> have proved especially useful as the R<sub>3</sub>Si<sup>+</sup> source because of the high stability. The electrophilic silylium cation initiates the formation of an intermediate carbenium ion R<sub>3</sub>C<sup>+</sup> by fluoride abstraction. This ion reacts with a stoichiometric triorganosilane R<sub>3</sub>Si–H added as the hydride source with formation of a C–H bond; the silylium cation is regenerated at the same time.

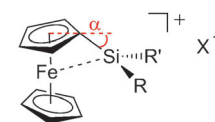
Another class of reactions catalyzed by silylium ions is the coupling of carbon atoms, with the coupling of C<sub>aryl</sub>–C<sub>aryl</sub> and C<sub>aryl</sub>–C<sub>alkyl</sub> bonds having previously been observed (Scheme 4 left).<sup>[8–10]</sup> Multiple C–C coupling reactions to a substrate molecule are also possible, depending on the degree of substitution on the arene ring (R'–H). As with hydrodefluorination, the strong bonding tendency of the Si–F bond (*D*(Me<sub>3</sub>Si–H) = 94.6 kcal mol<sup>–1</sup> versus *D*(Me<sub>3</sub>Si–F) = 158.0 kcal mol<sup>–1</sup>) is exploited to defluorinate the substrate R–F in the first step. The resulting carbocation R<sup>+</sup> is now in position to attack the C atom of a further molecule through a Friedel–Crafts alkylation. The cationic σ complex thus formed can then be deprotonated by reaction with a hydride source R<sub>3</sub>Si–H, which leads to the formation of the cross-coupling product, the release of hydrogen, and the regeneration of the silylium ion. However, what becomes clear from this is that, depending on the electronic situation of the substrate and the steric demands of the coupling partner, the C–C bond coupling (Scheme 4, left) is in competition with hydrodefluorination (Scheme 4, right), as Douvris and Ozerov as well as Müller and co-workers were able to demonstrate.<sup>[8,10]</sup> Consequently, the highest selectivities and yields are observed in intramolecular reactions, as demonstrated impressively by Siegel and co-workers in their synthesis of a series of polyaromatic hydrocarbons.<sup>[9]</sup>

Likewise, the Diels–Alder reactions described by the research groups of Sawamura and Oestreich can be ranked as C–C coupling reactions catalyzed by a silylium ion Lewis acid (Scheme 5).<sup>[11]</sup> While the reactions carried out by Sawamura and co-workers with Lambert's salt [Et<sub>3</sub>Si–toluene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with the same substrates and a similar catalyst loading required “high” temperatures between 0 °C and room tem-



**Scheme 5.** A Diels–Alder reaction catalyzed by a silylium ion Lewis acid.

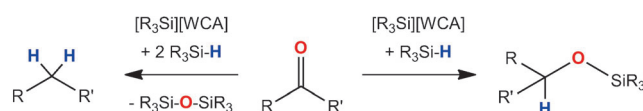
perature, the [tBuFcMeSi][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] salt (Fc = ferrocenyl; Scheme 6 and species **E** in Scheme 1) first described by Oestreich and co-workers is highly reactive even at low temperatures of down to –78 °C. Both systems lead selectively to the *endo* diastereoisomers in almost quantitative yields. Moreover, the chiral ferrocenyl-silylium derivative leads to a high regioselectivity and high yields even with deactivated butadienes (e.g. R<sup>2</sup> = Cl in Scheme 5).



**Scheme 6.** Structure of the [tBuFcMeSi]<sup>+</sup> ion (R = tBu, R' = Me).

That trivalent silylium ions are extraordinarily strong electron-pair acceptors which interact with almost all σ- and π-electron donors, and thus often leads to unusual bonding situations, is demonstrated by the recently published experimental and theoretical study on the [tBuFcMeSi]<sup>+</sup> ion.<sup>[12]</sup> The single-crystal X-ray structural analysis of the [tBuFcMeSi]<sub>2</sub>–[B<sub>12</sub>Cl<sub>12</sub>]<sup>–</sup> salt revealed an extreme angle of inclination (α) of the Si atom to the Fe atom in the cation (Scheme 6), which according to quantum-chemical calculations is caused by two 3c-2e bonds with involvement of the two aromatic rings of the ferrocene fragment. The positive charge remains, however, localized on the Si atom, at which, in addition, a quasiplanar configuration is maintained.

Following a similar principle as C–F activation, the reductive deoxygenation of ketones takes place on using a silane R<sub>3</sub>Si–H in the presence of a silylium cation as the catalyst (Scheme 7). As Kira et al. and Piers and co-workers

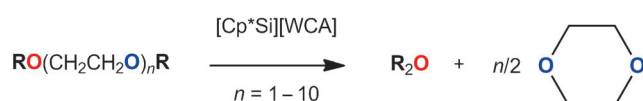


**Scheme 7.** Deoxygenation of ketones catalyzed by a silylium ion Lewis acid.

were able to demonstrate, aryl-/aryl-, aryl-/alkyl-, and alkyl-/alkyl-substituted ketones R(CO)R' are reduced to the corresponding alkane R–CH<sub>2</sub>–R' by the trialkylsilylium catalysts [R<sub>3</sub>Si][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (R = Me, Et) and the corresponding silane as the hydride source, with formation of an equivalent of the silyl ether R<sub>3</sub>Si–O–SiR<sub>3</sub> (Scheme 7, left).<sup>[13]</sup> In contrast, Oestreich and co-workers were able to demonstrate that the reaction is moderated by the use of the [tBuFcMeSi]–[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] salt as the active catalyst and tBuFcMeSiH as the reducing agent, so that the alkyl/silyl ether RR'CH–O–SiR<sub>3</sub> can be obtained as the product (Scheme 7, right).<sup>[14]</sup> Thus, the

ferrocenyl-silylium catalyst shows a similar reactivity as the FLP system  $\text{Et}_3\text{Si}-\text{H}/\text{B}(\text{C}_6\text{F}_5)_3$  of Piers and co-workers, which also leads to mixed ethers and allows the reaction to be terminated even at the oxidation stage of the alcohol instead of complete reduction to the alkane.

Although the pentamethylcyclopentadienyl-silylium(II) salt  $[\text{Cp}^*\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$  recently revealed by Jutzi and co-workers is not a silylium catalyst in the classical sense, its excellent catalytic activity in the degradation of oligo(ethylene glycol) diethers is nevertheless of note.<sup>[15]</sup> Poly(ethylene glycol) dimethyl ethers with up to ten ethylene glycol units are cleaved at room temperature to 1,4-dioxane and dimethyl-ether (Scheme 8). Although the reaction requires several days, the degradation is quantitative even with low concentrations of catalyst, and even cyclic polyethers such as [12]crown-4 are transformed totally selectively into 1,4-dioxane.



**Scheme 8.** Catalytic degradation of oligo(ethylene glycol) diethers by a pentamethylcyclopentadienylsilylium(II) salt.

In summary, it can be stated that, because of their high Lewis acidity, silylium cations are suitable for catalysis like perhaps no other class of reactive cations. As a result, it may be expected that  $\text{R}_3\text{Si}^+$  salts may also be used in most Lewis acid catalyzed reactions. Depending on the weak coordination character of the anion, the steric and electronic influence of the substituents at the silylium center, and the variation of the solvent and temperatures used, diverse reactions may be expected of silylium ions, particularly in regard to targeted design of the reaction conditions. Oligo-/polymerizations, further C-heteroatom and heteroatom-heteroatom bond activations, as well as Diels-Alder, FLP, and aldol reactions are conceivable, just to mention a few exemplary areas.

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