Silylium Ions

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A New Synthesis of Triarylsilylium Ions and Their Application in Dihydrogen Activation**

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One decade after the first reports on the synthesis and NMR spectroscopic characterization of silylium ions,[1,2] the ingenious use of their enormous electrophilicity for applications in synthesis or catalysis has attracted attention.[3] In view of the impressive success of the concept of frustrated Lewis pairs (FLPs) developed and popularized by the groups of Stephan and Erker,[4] we were intrigued by the idea to utilize the enormous Lewis acidity of silylium ions, R_3Si^+, to activate small molecules. The use of silylium ions in FLP chemistry will lead to an increase of the reactivity of the FLP, and a shift of the reactivity spectrum to stronger Lewis acids and weaker Lewis bases can be expected.[5]

The only examples for triorganosubstituted silylium salts in which the cation lacks coordination to solvent or counteranion are borates or carboranates of trimesitylsilylium (**1a**; mesityl = 2,4,6-trimethylphenyl) and tridurylsilylium (**1b**; duryl = 2,3,5,6-tetramethylphenyl). These sterically crowded silylium ions were synthesized by applying the allyl leaving-group method.[1] In an attempt to circumvent the severe synthetic problems that arise from the high steric demands made in this approach on the precursor silane $Ar_3SiC_3H_5$, we used diaryl (methyl)silanes $Ar_2(Me)SiH$, **2**, as starting materials for the classical Bartlett–Condon–Schneider hydride transfer reaction to prepare diaryl(methyl) silylium ions or their complexes with solvent molecules.[6] Quite unexpectedly, a substituent exchange reaction took place under these conditions, and triarylsilylium ions Ar_3Si^+ and trimethylsilane, Me_3SiH, were formed (Scheme 1). This finding opens a new, feasible synthetic route to triarylsilylium ions. Furthermore, the successful application of these triarylsilylium ions in dihydrogen activation was demonstrated.

$$3\,\underset{\mathbf{2}}{Ar_2(Me)SiH} + 2\,Ph_3C^+ \longrightarrow 2\,\underset{\mathbf{1}}{Ar_3Si^+} + Me_3SiH + 2\,Ph_3CH$$

Scheme 1. Synthesis of triarylsilylium ions **1** from diaryl(methyl) silanes **2**. [**a**: Ar = 2,4,6-trimethylphenyl (Mes); **c**: Ar = 2,6-dimethylphenyl (Xylyl); **d**: Ar = 2,4,6-tri-*iso*-propylphenyl (Tipp); **e**: Ar = 2,3,4,5,6-pentamethylphenyl (Pemp)].

The reaction of dimesityl(methyl)silane (**2a**) with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ in benzene at room temperature gave a two-phase reaction mixture, which is typical for solutions of salts of the $[B(C_6F_5)_4]^-$ anion in aromatic hydrocarbon solvents. NMR spectroscopic investigation of the upper nonpolar phase revealed the complete consumption of the starting silane **2a** and the formation of triphenylmethane, Ph_3CH. Inspection of the lower ionic phase by ^{29}Si NMR spectroscopy indicated the formation of a single silicon-containing species, which was characterized by a ^{29}Si NMR signal at very low field ($\delta(^{29}Si) = 225.3$ ppm). This ^{29}Si NMR chemical shift is practically identical to the value reported previously for Mes_3Si^+ (**1a**; $\delta(^{29}Si) = 225.5$ ppm).[1] Further comparison of the ^1H and ^{13}C NMR data with that reported for **1a**[1] confirmed that exclusively Mes_3Si^+ was formed in the reaction.[7] Interestingly, the ^1H and the ^{13}C NMR data of the ionic phase clearly showed the presence of excess trityl cation. The formation of trimesitylsilylium (**1a**) was further substantiated by its derivatization applying $(nBu)_3SnH$ and the subsequent detection of trimesitylsilane, Mes_3SiH. The only silicon-containing by-product of the reaction, trimethylsilane, Me_3SiH, was detected in the nonpolar phase. The presence of excess trityl cation resulted in the ionization of trimethylsilane and the isolation of $[Me_3Si(C_7H_8)][B(C_6F_5)_4]$ in the form of colorless crystals from toluene.[7]

Three other diaryl(methyl) silanes **2c–e** were found to yield triarylsilylium ions **1c–e** upon reaction with trityl cation at room temperature (Scheme 1). In the case of the precursor silanes **2c** and **2e**, the reaction was accomplished in 60 min, while in the case of the sterically more hindered 2,4,6-triisopropylphenyl (Tipp)-substituted silane **2d**, the reaction required 5 h for the complete consumption of silane **2d**. The identity of each cation, **1c–e**, was confirmed by ^{29}Si, ^{13}C, and ^1H NMR spectroscopy.[7] Most characteristic for the formation of silylium ions **1** is the ^{29}Si resonance of the positively charged silicon atom, which is shifted downfield significantly ($\delta(^{29}Si) = 216$–230 ppm; Table 1). The ^{29}Si NMR chemical shifts measured for silylium ions **1c–e** are independent of the arene solvent used (Table 1), indicating no significant interaction between the silylium ion and the solvent molecules. In the case of silylated arenium ions $[R_3SiArH]^+$, chemical shift differences $\Delta\delta(^{29}Si)$ between the benzenium and the toluenium species of more than $\Delta\delta(^{29}Si) = 10$ ppm have been reported.[8] The substituent exchange is not restricted to methyl groups; that is, ethyldimesitylsilane **3**(Ar=Mes) cleanly undergoes the transformation to give

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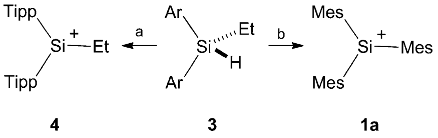
Table 1: ^{29}Si NMR chemical shifts of silylium ions $Ar_2Ar'Si^+$ (**1**) and Ar_2EtSi^+ (**4**).[a]

Ion	Ar/Ar'	$\delta(^{29}Si)$	Ion	Ar/Ar'	$\delta(^{29}Si)$
1a[b]	Mes/Mes	225.3	**1d**[b]	Tipp/Tipp	229.8
1a[c]	Mes/Mes	223.8	**1e**[b]	Pemp/Pemp	216.2
1a[d]	Mes/Mes	225.5	**1f**[b]	Mes/Tipp	217.0
1c[b]	Xylyl/Xylyl	229.9	**4**[b]	Tipp	244.7

[a] Spectra recorded at 305 K. [b] In [D$_6$]benzene. [c] In [D$_8$]toluene. [d] In [D$_5$]chlorobenzene.

trimesitylsilylium **1a**. However, when ethylbis(triisopropylphenyl)silane **3**(Ar=Tipp) was used as starting material no substituent exchange took place and the ethylbis(triisopropylphenyl) silylium ion **4** was obtained (Scheme 2). Silylium ion **4** is characterized by an even stronger deshielded silicon atom ($\delta(^{29}Si)=244.7$ ppm), and in this case the $^1H/^{29}Si$ HMQC spectrum clearly indicated the presence of the aryl and the ethyl substituent at the central silicon atom (Figure 1). This result suggests that the formation of triarylsilylium ions according to Scheme 1 is significantly influenced by steric effects. On the other hand, aryl substituents smaller than xylyl groups did not initiate the reaction. For instance, methyldiphenylsilane formed the corresponding arenium ion $[Ph_2MeSi(C_6H_6)]^+$ upon reaction with trityl cation. This was indicated by a ^{29}Si NMR resonance at a frequency typical for silylarenium ions ($\delta(^{29}Si)=74.0$ ppm).[8]



Scheme 2. Hydride transfer reaction with diaryl (ethyl)silanes **3**. a) Ph_3C^+, room temperature, benzene, Ar=Tipp; b) Ph_3C^+, room temperature, benzene, Ar=Mes.

Triarylsilylium borate $\mathbf{1}[B(C_6F_5)_4]$ and diaryl(ethyl) silylium borate $\mathbf{4}[B(C_6F_5)_4]$ are stable at room temperature in the solid state for several weeks. In arene solution, however, slow decomposition occurs even at −10 °C. This severely hampered all attempts for crystallization, because only decomposition products such as perfluorinated tetraaryl borates of protonated arenes were isolated. For example, mesitylenium tetrakispentafluorophenylborate was isolated from a benzene solution of $\mathbf{1a}[B(C_6F_5)_4]$ after several days at room temperature.[7]

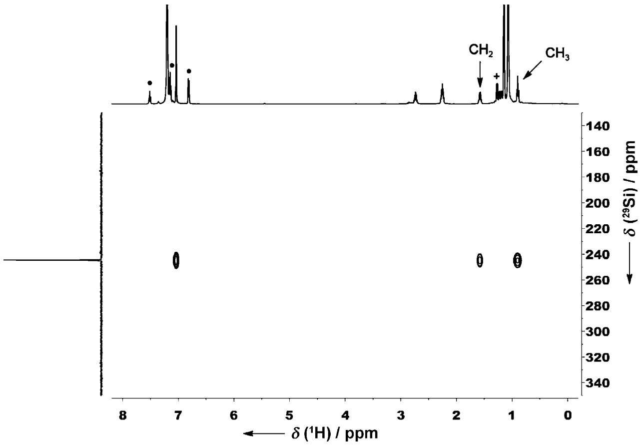
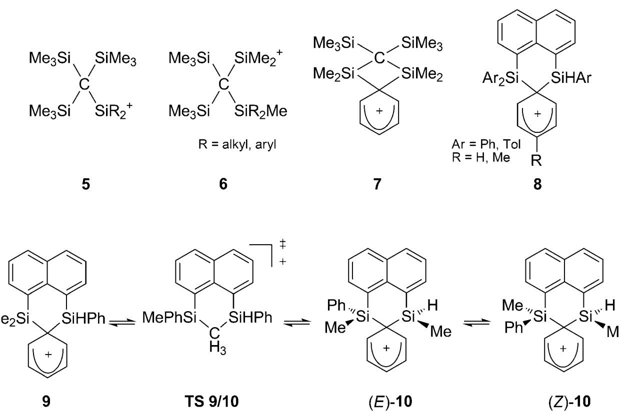


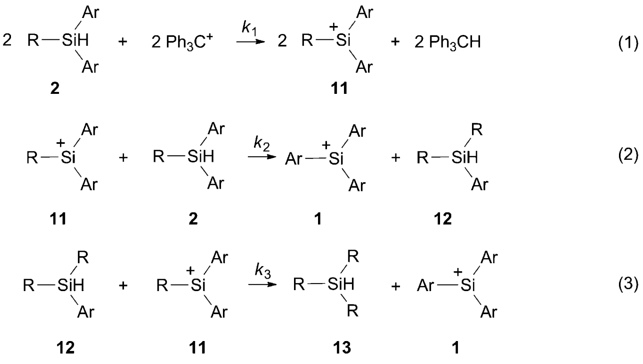
Figure 1. $^1H/^{29}Si$ HMQC spectrum of $\mathbf{4}[B(C_6F_5)_4]$ in [D$_6$]benzene at 305 K (● unreacted Ph_3C^+, + TippH). For a more detailed figure, see the Supporting Information, Figure S16.

Our mechanistic proposal for the intermolecular aryl–alkyl exchange reaction is based on previous results from Lickiss et al.[9] and our group.[10,11] Intramolecular alkyl–aryl exchange reactions for silyl cations of type **5** and **6** have been known since the work of Eaborn and co-workers.[12,13] Disilylated arenium ions **7** and **8**, which might be regarded as key intermediates in these ligand exchange reactions involving aryl groups, were recently isolated.[9,10] Quite recently, we established a mechanism that rationalized the reversible isomerisation of disilyl areniumions **9** and **10** (Scheme 3).[11] DFT computations suggested that in this case, the methyl group transfer proceeds via a methonium-like transition state **TS 9/10**.



Scheme 3. Isomerization reactions in arenium ions **9** and **10**.[11]

On the basis of these previous results, the following mechanistic scenario seems plausible: the first step, the



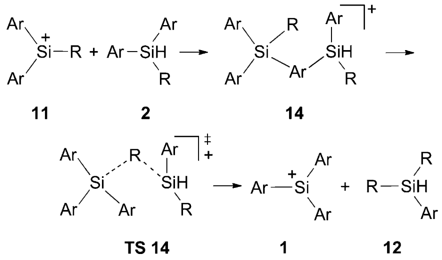
$$2\ \underset{\mathbf{2}}{R{-}SiHAr_2} + 2\ Ph_3C^+ \xrightarrow{k_1} 2\ \underset{\mathbf{11}}{R{-}Si^+Ar_2} + 2\ Ph_3CH \qquad (1)$$

$$\underset{\mathbf{11}}{R{-}Si^+Ar_2} + \underset{\mathbf{2}}{R{-}SiHAr_2} \xrightarrow{k_2} \underset{\mathbf{1}}{Ar{-}Si^+Ar_2} + \underset{\mathbf{12}}{R{-}SiHRAr} \qquad (2)$$

$$\underset{\mathbf{12}}{R{-}SiHRAr} + \underset{\mathbf{11}}{R{-}Si^+Ar_2} \xrightarrow{k_3} \underset{\mathbf{13}}{R{-}SiHR_2} + \underset{\mathbf{1}}{Ar{-}Si^+Ar_2} \qquad (3)$$

Scheme 4. Suggested reaction course for the formation of triarylsilylium ions **1** from alkyldiarylsilanes **2** (R=alkyl, Ar=aryl).

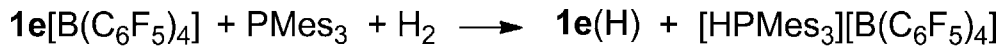
hydride transfer reaction [Scheme 4, Eq. (1)] is rate-determining ($k_1 < k_2$). Therefore, alkyl diaryl silylium ions **11** cannot be detected. They undergo a fast alkyl–aryl exchange reaction with neutral starting silane **2** to form more stable triaryl silylium ions **1**, and the less sterically hindered dialkyl aryl silane **12** [Eq. (2)]. As silane **12** is less sterically congested, the reaction described by Equation (3) is even faster ($k_3 > k_2$), and only the products triaryl silylium **1** and trialkylsilane **13** can be detected.



Scheme 5. Proposed reaction mechanism for the alkyl–aryl exchange.

The key step, the alkyl–aryl exchange [Eq. (2), Scheme 4] is believed to progress via disilylated arenium ions **14** (Scheme 5), which show close resemblance to disilyl cation **10** from our previous work.[11] The aryl exchange then proceeds and the products are formed via alkonium-like **TS 14**. Although this mechanistic proposal is based on conclusions by analogy, there are experimental facts which support this mechanism: 1) According to our proposal, only $^2/_3$ equivalents of trityl cation is needed for a complete consumption of silane **2** (Schemes 1 and 4), which is in agreement with the detection of excess trityl cation in our first experiments when a 1:1 stoichiometry was applied; 2) In a cross experiment which uses silanes **2a** and **2d**, only three different triarylsilylium ions are formed upon reaction with trityl cation. Apart from silylium ions **1a** and **1d**, $Mes_2TippSi^+$ (**1f**) was obtained as the only cross-product.[14] In particular, no $MesTipp_2Si^+$ (**1g**) was formed. The silanes **2a** and **2d** show a significantly different reactivity versus the trityl cation. The sterically less-hindered silane **2a** is consumed much more rapidly than **2d**. Consequently, at short reaction times, only silylium ions **1a** and **1f** are formed. At the time the concentration of the intermediate silylium ion $Tipp_2MeSi^+$ becomes significant, no dimesityl(methyl)silane (**2a**) is available, and therefore only $Tipp_3Si^+$ (**1d**) is formed as a third species.

Triarylsilylium ions **1** form frustrated Lewis pairs with bulky triaryl phosphanes. This is indicated by the unchanged NMR spectroscopic parameter when triarylsilylium borates are mixed with triaryl phosphanes in benzene. For effective dihydrogen activation, however, the properties of the phosphane base must be adjusted. For example, stirring a 1:1 mixture of the silylium borate **1e**$[B(C_6F_5)_4]$ with tris(pentafluorphenyl)phosphane in benzene under a dihydrogen atmosphere at room temperature resulted in no detectable formation of products. In contrast, when trimesityl phosphane **15** was applied, the FLP underwent irreversible dihydrogen activation (Scheme 6) and yielded silane **1e**(H) quantitatively according to NMR spectroscopy ($\delta(^{29}Si) = -38.9$ ppm, $^1J_{Si,H} = 195$ Hz) and trimesitylphosphonium borate $[Mes_3PH][B(C_6F_5)_4]$ (**16**; $\delta(^{31}P) = -27.2$ ppm, $^1J_{P,H} = 478$ Hz). The identity of both compounds was further confirmed by complete analysis including XRD.[7]



$$\mathbf{1e}[B(C_6F_5)_4] + \underset{\mathbf{15}}{PMes_3} + H_2 \longrightarrow \mathbf{1e}(H) + \underset{\mathbf{16}}{[HPMes_3][B(C_6F_5)_4]}$$

Scheme 6. Dihydrogen activation by a silylium/phosphane Lewis pair (conditions: 0.1013 MPa, H_2, RT, benzene).

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