## VIP Silylium Ions

## 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,<sup>[1,2]</sup> the ingenious use of their enormous electrophilicity for applications in synthesis or catalysis has attracted attention.<sup>[3]</sup> In view of the impressive success of the concept of frustrated Lewis pairs (FLPs) developed and popularized by the groups of Stephan and Erker,<sup>[4]</sup> we were intrigued by the idea to utilize the enormous Lewis acidity of silylium ions, R<sub>3</sub>Si<sup>+</sup>, 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.<sup>[5]</sup>

The only examples for triorganosubstituted silvlium 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 leavinggroup method.<sup>[1]</sup> 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<sub>3</sub>SiC<sub>3</sub>H<sub>5</sub>, we used diaryl (methyl)silanes Ar<sub>2</sub>(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.<sup>[6]</sup> Quite unexpectedly, a substituent exchange reaction took place under these conditions, and triarylsilylium ions Ar<sub>3</sub>Si<sup>+</sup> and trimethylsilane, Me<sub>3</sub>SiH, were formed (Scheme 1). This finding opens a new, feasible synthetic route to triarylsilylium ions. Further-

 $3 \operatorname{Ar}_2(\operatorname{Me})\operatorname{SiH} + 2 \operatorname{Ph}_3\operatorname{C}^+ \longrightarrow 2 \operatorname{Ar}_3\operatorname{Si}^+ + \operatorname{Me}_3\operatorname{SiH} + 2 \operatorname{Ph}_3\operatorname{CH}$ 2 1

**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)].

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more, the successful application of these triarylsilylium ions in dihydrogen activation was demonstrated.

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<sub>3</sub>CH. Inspection of the lower ionic phase by <sup>29</sup>Si NMR spectroscopy indicated the formation of a single silicon-containing species, which was characterized by a <sup>29</sup>Si NMR signal at very low field ( $\delta$ (<sup>29</sup>Si) = 225.3 ppm). This <sup>29</sup>Si NMR chemical shift is practically identical to the value reported previously for Mes<sub>3</sub>Si<sup>+</sup> (1a;  $\delta$ (<sup>29</sup>Si) = 225.5 ppm).<sup>[1]</sup> Further comparison of the <sup>1</sup>H and <sup>13</sup>C NMR data with that reported for  $1a^{[1]}$  confirmed that exclusively Mes<sub>3</sub>Si<sup>+</sup> was formed in the reaction.<sup>[7]</sup> Interestingly, the <sup>1</sup>H and the <sup>13</sup>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  $(nBu)_3$ SnH and the subsequent detection of trimesitylsilane, Mes<sub>3</sub>SiH. The only silicon-containing by-product of the reaction, trimethylsilane, Me<sub>3</sub>SiH, was detected in the nonpolar phase. The presence of excess trityl cation resulted in the ionization of trimethylsilane and the isolation of [Me<sub>3</sub>Si- $(C_7H_8)$  [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the form of colorless crystals from toluene.<sup>[7]</sup>

Three other diaryl(methyl) silanes 2c-e were found to yield triarylsilylium ions 1 c-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 2,4,6triisopropylphenyl (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 <sup>29</sup>Si, <sup>13</sup>C, and <sup>1</sup>H NMR spectroscopy.<sup>[7]</sup> Most characteristic for the formation of silvlium ions **1** is the <sup>29</sup>Si resonance of the positively charged silicon atom, which is shifted downfield significantly  $(\delta(^{29}\text{Si}) = 216-230 \text{ ppm}; \text{ Table 1})$ . The <sup>29</sup>Si NMR chemical shifts measured for silvlium ions 1c-e are independent of the arene solvent used (Table 1), indicating no significant interaction between the silvlium ion and the solvent molecules. In the case of silvlated arenium ions [R<sub>3</sub>SiArH]<sup>+</sup>, chemical shift differences  $\Delta \delta$ <sup>(29</sup>Si) between the benzenium and the toluenium species of more than  $\Delta \delta$ <sup>(29</sup>Si) = 10 ppm have been reported.<sup>[8]</sup> The substituent exchange is not restricted to methyl groups; that is, ethyldimesitylsilane 3(Ar=Mes) cleanly undergoes the transformation to give

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

lon	Ar/Ar′	$\delta$ ( <sup>29</sup> Si)	lon	Ar/Ar′	$\delta$ ( <sup>29</sup> Si)
1 a <sup>[b]</sup>	Mes/Mes	225.3	1 d <sup>[b]</sup>	Tipp/Tipp	229.8
<b>l</b> a <sup>[c]</sup>	Mes/Mes	223.8	<b>1</b> e <sup>[b]</sup>	Pemp/Pemp	216.2
1 a <sup>[d]</sup>	Mes/Mes	225.5	1 f <sup>[b]</sup>	Mes/Tipp	217.0
1 c <sup>[b]</sup>	Xylyl/Xylyl	229.9	<b>4</b> <sup>[b]</sup>	Тірр	244.7

[a] Spectra recorded at 305 K. [b] In [D<sub>6</sub>]benzene. [c] In [D<sub>8</sub>]toluene. [d] In [D<sub>5</sub>]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



**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.

atom  $(\delta(^{29}\text{Si}) = 244.7 \text{ ppm})$ , and in this case the <sup>1</sup>H/ <sup>29</sup>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<sub>2</sub>MeSi(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> upon reaction with trityl cation. This was indicated by a <sup>29</sup>Si NMR resonance at a frequency typical for silylarenium ions  $(\delta(^{29}\text{Si}) = 74.0 \text{ ppm}).^{[8]}$ 

Triarylsilylium borate  $1[B(C_6F_5)_4]$  and diaryl(ethyl) silylium borate  $4[B(C_6F_5)_4]$  are stable at room temperature in the



**Figure 1.**  ${}^{1}H/{}^{29}Si HMQC$  spectrum of **4**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in [D<sub>6</sub>]benzene at 305 K ( $\bullet$  unreacted Ph<sub>3</sub>C<sup>+</sup>, + TippH). For a more detailed figure, see the Supporting Information, Figure S16.

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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 tetra-kispentafluorophenylborate was isolated from a benzene solution of  $1a[B(C_6F_5)_4]$  after several days at room temperature.<sup>[7]</sup>

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



Scheme 3. Isomerization reactions in a renium ions  ${\bf 9}$  and  ${\bf 10}.^{[11]}$ 

case, the methyl group transfer proceeds via a methoniumlike transition state **TS 9/10**.

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

$$2 R - SiH + 2 Ph_{3}C^{+} \xrightarrow{k_{1}} 2 R - Si + 2 Ph_{3}CH$$
(1)  
Ar  
$$Ar$$

$$R \xrightarrow{+}_{Ar} Ar + R \xrightarrow{+}_{SiH} Ar \xrightarrow{+}_{Ar} Ar + R \xrightarrow{-}_{SiH} Ar \xrightarrow{+}_{Ar} Ar + R \xrightarrow{-}_{SiH} Ar \xrightarrow{(2)}_{Ar}$$

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$$R = SiH + R = Si \xrightarrow{+} Ar \xrightarrow{k_3} R = SiH + Ar = Si$$

$$Ar = Ar = R = Ar$$

$$R = Ar$$

$$Ar = R$$

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

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## Communications

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.<sup>[11]</sup> The aryl exchange then proceeds and the products are formed via alkonium-like TS14. 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 silvlium ions 1a and 1d, Mes<sub>2</sub>TippSi<sup>+</sup> (1 f) was obtained as the only cross-product.<sup>[14]</sup> In particular, no MesTipp<sub>2</sub>Si<sup>+</sup> (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 silvlium ions 1a and 1f are formed. At the time the concentration of the intermediate silvlium ion Tipp<sub>2</sub>MeSi<sup>+</sup> 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

$$e[B(C_6F_{5})_4] + PMes_3 + H_2 \longrightarrow 1e(H) + [HPMes_3][B(C_6F_{5})_4]$$
  
15 16

**Scheme 6.** Dihydrogen activation by a silylium/phosphane Lewis pair (conditions: 0.1013 MPa, H<sub>2</sub>, RT, benzene).

activation (Scheme 6) and yielded silane **1** e(H) quantitatively according to NMR spectroscopy ( $\delta$ (<sup>29</sup>Si) = -38.9 ppm, <sup>1</sup>J<sub>Si,H</sub> = 195 Hz) and trimesitylphosphonium borate [Mes<sub>3</sub>PH][B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**16**;  $\delta$ (<sup>31</sup>P) = -27.2 ppm, <sup>1</sup>J<sub>PH</sub> = 478 Hz). The identity of both compounds was further confirmed by complete analysis including XRD.<sup>[7]</sup>

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- [14] Cation **1 f** was identified in the mixture by its NMR data. In particular, the relative intensities of the proton signals at  $\delta({}^{1}\text{H}) = 2.85 (1 \text{ H}, p\text{-CH}(\text{CH}_3)_2), 2.41 (2 \text{ H}, o\text{-CH}(\text{CH}_3)_2), 2.04 (6 \text{ H}, p\text{-CH}_3), 1.98 \text{ ppm} (12 \text{ H}, o\text{-CH}_3)$  were decisive in its identification.