**Thermodynamic versus kinetic control in substituent redistribution reactions of silylium ions steered by the counteranion†**

Lukas Omann, a,b Bimal Pudasaini, b Elisabeth Irran, b,c Hendrik F. T. Klare, d Mu-Hyun Baik *bc and Martin Oestreich *a

An in-depth experimental and theoretical study of the substituent exchange reaction of silylium ions is predominantly influenced by the counteranion, which is introduced with the trityl salt in the silylium ion generation. In contrast to Müller’s protocol for the synthesis of triarylsilylium ions under kinetic control, the use of Reed’s carborane anions leads to contact ion pairs, allowing selective formation of triarylsilylium ions under thermodynamic control. DFT calculations finally revealed an unexpected mechanism for the rate-determining alkyl exchange step, which is initiated by an unusual 1,2-silyl migration in the intermediate ipso-disilylated arenium ion. The resulting ortho-disilylated arenium ion can then undergo an alkyl transfer via a low-barrier five-centered transition state.

### Introduction

Silylium ions ($R_3Si^+$) have recently emerged as useful and versatile catalysts for synthetically attractive transformations.\(^1,2\) The most commonly used approach to generate silylium ions is the Bartlett–Condor–Schneider reaction,\(^3\) that is the silicon-to-carbon hydride transfer from a hydrosilane to the trityl cation ($Ph_3C^+$) paired with a weakly coordinating counteranion.\(^4\) However, substituent redistribution of the hydrosilane starting material can occur under these highly Lewis acidic reaction conditions, leading to undesired mixtures of various silicon compounds.\(^5–8\) Hence, hydrosilanes containing three identical substituents, e.g. Et3SiH or iPr3SiH, are usually employed in this reaction.\(^9\) Conversely, Müller and co-workers have turned this unselective process into a useful synthetic route to triarylsilylium ions (Scheme 1, top).\(^10\) When sterically demanding methyl(diaryl)silanes MeAr₂SiH are used in the hydride abstraction with Ph₃C⁺[B(C₆F₅)₄]⁻, the formation of otherwise difficult to prepare triarylsilylium ions Ar₃Si⁺[B(C₆F₅)₄]⁻ is observed.\(^11\) Notably, the use of less bulky hydrosilanes such as MePh₂SiH or Me(o-Tol)₂SiH does not give triarylsilylium ions but mixtures of different silicon cations.\(^12\)

Herein, we report that treatment of hydrosilanes of type Me₂RSiH (R = aryl, benzyl) with Reed’s carborane-based trityl salt Ph₃C⁺[CHB₁₁H₅Br₆]⁻ (ref. 13) results in substituent exchange reactions selectively forming the elusive trimethylsilylium ion Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (Scheme 1, bottom). This method thus complements Müller’s approach and offers a practical route to Me₃Si⁺, avoiding the use of gaseous and highly flammable Me₃SiH.\(^14\) A systematic experimental and computational investigation was performed to gain a full

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**Scheme 1** Divergence in the generation of silylium ions by substituent redistribution ($x + y + z = 4$).
mechanistic picture of this phenomenon. DFT calculations revealed an unexpected mechanism and suggested an active role of the carborane counteranion in the outcome of these reactions.

Results and discussion
Generation of the trimethylsilylium ion by substituent redistribution
When a mixture of Me$_2$PhSiH and Ph$_3$C$^+$$[$CHB$_{11}$H$_5$Br$_6$$]$ in toluene was stirred overnight at room temperature, a white suspension was obtained. The solid was collected by filtration, washed with n-pentane, and dissolved in o-Cl$_3$C$_6$D$_4$ for NMR spectroscopic analysis. Unexpectedly, only a singlet at 0.83 ppm was detected in the $^1$H NMR spectrum, while no aromatic resonances except for those of the deuterated solvent were observed. The low-field $^{29}$Si NMR chemical shift of 93 ppm in the corresponding $^1$H/$^{29}$Si HMQC spectrum, which is characteristic of trialkylsilylium ions, indicated clean formation of Me$_3$Si$^+$$[$CHB$_{11}$H$_5$Br$_6$$]$ (Fig. 1). The structural integrity of the carborane counteranion was confirmed by $^{11}$B NMR spectroscopy. Unambiguous evidence for the structure of Me$_3$Si$^+$$[$CHB$_{11}$H$_5$Br$_6$$]$ was eventually provided by its crystallographic characterization (Fig. 2).

In contrast to the clean formation of Me$_3$Si$^+$, the non-polar n-pentane filtrate contained several tri- and tetraorganosilanes, such as Ph$_3$Si, MePh$_3$Si, Ph$_3$SiH, Me$_2$Ph$_2$Si, MePh$_2$SiH, Me$_3$PhSi, and Me$_2$PhSiH, as verified by GC-MS analysis. Since silylium ions are known to promote substituent redistribution, this result did not come as a surprise but raised the question why Me$_3$Si$^+$ was selectively formed in this reaction mixture, whereas Müller’s conditions cleanly afford sterically congested trialkylsilylium ions. 

Influence of the substituent pattern at the silicon atom on the selectivity of the substituent redistribution reaction
To understand the differences between Müller’s protocol$^{18}$ and our findings, we systematically studied the hydride transfer reaction of various hydrosilanes of type MeAr$_2$SiH and Me$_2$ArSiH using trityl salts Ph$_3$C$^+$$[$B(C$_6$F$_5$)$_4$$]$ and Ph$_3$C$^+$$[$CHB$_{11}$H$_5$Br$_6$$]$ (Table 1). Depending on the counteranion, slightly modified procedures were applied for the generation of the silicon cations (see the ESI$^*$ for details). For all reactions, an excess of hydrosilane (4 equiv.) was used, thereby optimizing for the hydrosilane and counteranion (Si = triorganosilyl).

![Image of molecular structure of Me$_3$Si$^+$$[$CHB$_{11}$H$_5$Br$_6$$]$](image-url)

**Table 1** Silylium ion generation by substituent redistribution: effect of the hydrosilane and counteranion (Si = triorganosilyl)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Si–H (4 equiv.)</th>
<th>X$^–$</th>
<th>Si$^+$</th>
<th>$\delta^{(29)}$ (ppm)</th>
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<tr>
<td>1</td>
<td>Me(C$_6$Me$_5$)$_3$SiH</td>
<td>B[(C$_6$F$_3$)$_4$]$^–$</td>
<td>(C$_6$Me$_5$)$_3$Si$^+$</td>
<td>217</td>
</tr>
<tr>
<td>2</td>
<td>Me(C$_6$Me$_5$)$_3$SiH</td>
<td>CHB$_{11}$H$_5$Br$_6$</td>
<td>(C$_6$Me$_5$)$_3$Si$^+$</td>
<td>217</td>
</tr>
<tr>
<td>3</td>
<td>MePh$_3$SiH</td>
<td>B[(C$_6$F$_3$)$_4$]$^–$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>MePh$_3$SiH</td>
<td>CHB$_{11}$H$_5$Br$_6$</td>
<td>MePh$_3$Si$^+$</td>
<td>57/76</td>
</tr>
<tr>
<td>5</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Me$_2$PhSiH</td>
<td>CHB$_{11}$H$_5$Br$_6$</td>
<td>Me$_2$PhSi$^+$</td>
<td>93</td>
</tr>
<tr>
<td>7</td>
<td>Me$_2$(C$_6$Me$_5$)$_2$SiH</td>
<td>B[(C$_6$F$_3$)$_4$]$^–$</td>
<td>(C$_6$Me$_5$)$_2$Si$^+$</td>
<td>217</td>
</tr>
<tr>
<td>8</td>
<td>Me$_2$(C$_6$Me$_5$)$_2$SiH</td>
<td>CHB$_{11}$H$_5$Br$_6$</td>
<td>Me$_2$Si$^+$</td>
<td>93</td>
</tr>
</tbody>
</table>

$^a$ All reactions were performed according to General Procedure (GP) 1 for X$^–$ = B[(C$_6$F$_3$)$_4$]$^–$ (C$_6$D$_6$, room temperature, 60 min) or GP 2 for X$^–$ = CHB$_{11}$H$_5$Br$_6$ (toluene, room temperature, 18–24 h). See the ESI$^*$ for details. $^b$ Measured in o-Cl$_3$C$_6$D$_4$. $^c$ A complex mixture was obtained as a result of counteranion decomposition.$^{19}$ $^d$ Ratio of 79:21 determined by $^1$H NMR spectroscopy. $^e$ Reaction performed at 50 $^\circ$C for 72 h.
excluding any influence of stoichiometry on the product formation. In accordance with Müller’s report, bulky meth-
yl(diaryl)silane Me(C₆Me₅)₂SiH was converted to the corre-
sponding triarylsilylium ion, regardless of which coun-
teranion was used (entries 1 and 2). In contrast, hydride 
abstraction from sterically less hindered MePh₂SiH with 
Ph₃C⁺[B(C₆F₅)₄]⁻ led to a complex reaction mixture as a result 
of anion decomposition (entry 3). The use of the carborane 
counteranion [CHB₁₁H₅Br₆]⁻ furnished the unscrambled 
silylium ion MePh₂Si⁺[CHB₁₁H₅Br₆], as confirmed by X-ray 
diffraction analysis (entry 4; see the ESI† for the molecular 
structure of MePh₂Si⁺[CHB₁₁H₅Br₆]). However, the forma-
tion of the MePh₂Si⁺ cation was accompanied by a substantial 
amount of a second silylium ion, which was found to be the 
Me₃Si⁺ cation. Notably, longer reaction times (7 days) or 
elevated temperatures (50 °C for 72 h) did not signi-
ficantly change the product ratio of ~79 : 21 (not shown). In all cases, 
the generation of Me₃Si⁺ was not observed. We then turned 
our attention to dimethyl(aryl)silanes (entries 5–8). The 
reaction of Me₂PhSiH with Ph₃C⁺[CHB₁₁H₅Br₆]⁻ again resulted 
in decomposition of the borate counteranion (entry 5). 
Conversely, treatment of Me₂PhSiH with trityl carborane 
Ph₃C⁺[CHB₁₁H₅Br₆] exclusively afforded silylium salt Me₃-
Si⁺[CHB₁₁H₅Br₆] without detectable formation of MePh₂Si⁺ 
or Me₂PhSi⁺ (entry 6). Strikingly, hydride abstraction from 
stERICALLY more demanding Me₂(C₆Me₅)SiH led to the corre-
sponding triarylsilylium ion in the presence of the borate 
counteranion (entry 7), while substituent redistribution into 
the ‘opposite direction’ was induced by the carborane anion,
now affording Me₃Si⁺[CHB₁₁H₅Br₆] (entry 8). However, 
heating of the reaction at 50 °C for 72 h was necessary.

Overall, these results indicate that hydride abstraction from 
ydrosilanes of type Me₂ArSiH with a carborane-based trityl salt 
tends to form the trimethylsilylium ion, whereas hydrosilanes 
of type Me₃Ar₂SiH with a bulky aryl substituent favor triar-
ysilylium ion generation.

Mechanism of the substituent redistribution reaction with 
Me₂PhSiH
To gain insight into the reaction mechanism and to understand 
why the treatment of Me₂PhSiH with Ph₃C⁺[CHB₁₁H₅Br₆]⁻ 
exclusively gives Me₃Si⁺[CHB₁₁H₅Br₆]⁻, we constructed 
a complete reaction energy profile using DFT calculations at the 
M06/cc-pVTZ(-f)//6-31G** level of theory (Fig. 3; see the ESI† 
for details of the computational method). The hydride abstraction 
from Me₂PhSiH with Ph₃C⁺[CHB₁₁H₅Br₆]⁻ was found to have a 
barrier of 15.5 kcal mol⁻¹ and is therefore expected to occur 
rapidly at room temperature (not shown). In the condensed 
phase, the resulting silylium ion Me₂PhSi⁺ (6A) is located 
at a relative free energy of 6.5 kcal mol⁻¹, is stabilized through 
coordination by the solvent, another hydrosilane molecule, or 
by the counteranion (see the ESI† for a comparison of the 
association energies). Coordination of one of the bromine 
atoms of the carborane counteranion to the silicon cation 
results in the highest binding energy, and the resulting ion pair 
6A⁺ is predicted to be at a relative free energy of 
−24.1 kcal mol⁻¹. Silylium ion 6A⁺ can also interact with another 
equivalent of Me₂PhSiH to form hydride-bridged adduct 7A⁺.
located at −6.5 kcal mol$^{-1}$. Note that these energies are not adjusted for the different concentrations of the components and assume normal conditions. Given that Me$_2$PhSiH (1A) is present in excess, these normal energies suggest that adduct 7A will be encountered easily in significant quantities.

Hydride-bridged adduct ion 7A can undergo a phenyl group transfer to arrive at phenyl-bridged adduct 8A$^+$ via the four-centered transition state 7A-TS, associated with a barrier of 13.4 kcal mol$^{-1}$. Surprisingly, our subsequent methyl group transfer does not proceed via another typical four-membered transition state. Instead, our calculations suggest that 1,2-migration of the silicon group in 8A occurs via the low barrier transition state 8A-TS, leading to ortho-disilylated arenium ion 9A. This seemingly unfavorable intermediate is only 4.1 kcal mol$^{-1}$ higher in energy than arenium ion 8A. Finally, 9A facilitates the exchange of one methyl group, passing through five-centered transition state 9A-TS with an overall barrier of 24.3 kcal mol$^{-1}$ relative to 7A. This energetically most demanding reaction step forms methonium ion 10A, which is metastable and rapidly rearranges to hydride-bridged adduct 11A via low barrier transition state 10A-TS. The hydrosilane-stabilized silylium ions 7A and 11A are almost isoenergetic ($\Delta G = 0.4$ kcal mol$^{-1}$), suggesting that both structures coexist in equilibrium. The formal dissociation of 11A gives either Me$_3$Si$^+$ or MePh$_2$Si$^+$, the former being calculated to be 2.8 kcal mol$^{-1}$ higher in energy. However, coordination by the carborane anion changes the energy landscape decisively, as ion pair formation reverses the energy ordering. Me$_3$Si$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (12A$^-$), which is located at −28.5 kcal mol$^{-1}$, is 2.9 kcal mol$^{-1}$ lower in energy than MePh$_2$Si$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (13A$^-$) and also 4.5 kcal mol$^{-1}$ more stable than Me$_2$PhSi$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (6A$^-$), thus predicting the silylium salt 12A$^-$ as the major product of the substituent redistribution reaction.

It should be noted that silylium ions are significantly more stabilized by coordination of the carborane counteranion than by formation of solvent adducts such as R$_3$Si(toluene)$[\text{CHB}_{11}H_2\text{Br}_6]$ . Moreover, the energy differences between these arenium ions are small, predicting a mixture of different silylium ions in the absence of the carborane counteranion (see the ESIF for details). This result was supported by independent control experiments (Scheme 2).

The hydride abstraction from Me$_2$PhSiH with borate-based trityl salt Ph$_3$C$^-$[B(C$_6$F$_5$)$_3$] was repeated but stopped after stirring for 10 min in toluene (cf. Table 1, entry 5). NMR spectroscopic analysis of the polar phase in o-C$_6$D$_4$ revealed the formation of a mixture of Me$_3$Si$^+$[B(C$_6$F$_5$)$_3$] and Me$_2$PhSi$^+$[B(C$_6$F$_5$)$_3$] in a ratio of ~51 : 49 along with small amounts of byproducts arising from counteranion decomposition. In contrast, stopping the reaction of Me$_2$-PhSiH with Ph$_3$C$^-$[CHB$_{11}$H$_2$Br$_6$] after stirring for 10 min in toluene furnished Me$_3$Si$^+$[CHB$_{11}$H$_2$Br$_6$] as the major product along with only small amounts of unscrambled Me$_2$-PhSi$^+$[CHB$_{11}$H$_2$Br$_6$] (ratio ~84 : 16). In both reactions, full conversion of the trityl salt was observed.

As shown in Fig. 4, the silylium ions can be bound either to the apical or one of the equatorial bromine atoms of the carborane counteranion, with a slight preference of 1.1 kcal mol$^{-1}$ for the apical position in Me$_3$Si$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (12A$^-$). This result is in contrast to the molecular structure in the solid state, which shows the equatorial isomer (cf. Fig. 2). We speculate that either packing effects or a statistical preference for the equatorial isomer is the reason for this discrepancy. Notably, the equatorial isomer 12A$^-$ is still 1.8 kcal mol$^{-1}$ lower in energy than the equatorial isomer of MePh$_2$Si$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (13A$^-$).

The higher ion pairing energy in 12A$^-$ can be ascribed to the lower steric demand of Me$_3$Si$^+$, leading to a closer carborane coordination and to attractive van der Waals interactions between the methyl moieties and the carborane anion. Especially in the apical position, the methyl functionality can interact with the highly polarizable bromine atoms. In contrast, the molecular fit of the sterically more demanding silylium ions Me$_2$PhSi$^+$ (6A$^-$) and MePh$_2$Si$^+$ (13A$^-$) with the carborane counteranion is less

![Scheme 2](image)

**Scheme 2** Influence of the counteranion on the selectivity of the trimethylsilylium ion formation.

![Fig. 4](image)

**Fig. 4** Computed apical and equatorial isomers of Me$_2$PhSi$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (top), Me$_3$Si$^+[\text{CHB}_{11}H_2\text{Br}_6]$ (middle) and Me$_2$PhSi$^+$$[\text{CHB}_{11}H_2\text{Br}_6]$ (bottom). Si–Br bond lengths are given in Å and relative free energy differences (kcal mol$^{-1}$) are shown in parentheses.
tight, and the ion pairing is therefore slightly less favorable. This trend is reflected in the corresponding Si–Br bond lengths of these silylum carborane salts, which were computed to be shortest in both isomers of Me$_3$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (12A' and 12A’). Hence, this ion pair is the most stable silylum salt despite the lack of stabilizing phenyl groups. Both isomers of Me$_2$PhSi$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (6A’ and 6A”) are higher in energy than the corresponding MePh$_2$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (13A’ and 13A”), indicating that the stabilization of these silylum carborane salts is determined by a delicate balance of electronic and steric effects. It should also be noted here that the DFT optimized structures for Me$_3$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (12A”) and MePh$_2$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (13A”) are in good agreement with the corresponding molecular structures obtained by X-ray diffraction analysis (see the ESI† for details).

**Mechanism of the substituent redistribution reaction with MePh$_2$SiH**

To understand why the reaction of MePh$_2$SiH with Ph$_3$C$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (2B) does not furnish Me$_3$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (1B), we constructed again a complete energy profile employing DFT simulations (Fig. 5). The initial hydride transfer of the hydrosilane to the trityl cation has a calculated barrier of 14.3 kcal mol$^{-1}$ (not shown), which is 1.2 kcal mol$^{-1}$ lower in energy compared to the case of Me$_2$PhSiH due to the slightly higher hydride donor strength of MePh$_2$SiH (see Table S1 in the ESI† for details). The resulting silylum ion MePh$_2$Si$^+$ (6B) with a relative free energy of 0.8 kcal mol$^{-1}$ is almost isoenergetic to the reactant state. Adduct formation with another equivalent of MePh$_2$SiH affords hydrogen-stabilized silylum ion 7B, which undergoes a phenyl/methyl exchange reaction following a very similar reactivity pattern as described above, leading to scrambled hydride-bridged adduct 11B. The transformation of 7B to 11B via intermediates 8B, 9B, and 10B is again reversible, since 7B and 11B have similar free energies ($\Delta G = 0.7$ kcal mol$^{-1}$). As before, the methyl group transfer via five-membered transition state 9B-TS shows the highest barrier, which is 24.2 kcal mol$^{-1}$ relative to 7B. In this equilibrium, unscrambled MePh$_2$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (6B) with a relative free energy of $-25.9$ kcal mol$^{-1}$ is predicted to be the major species, followed by scrambled Me$_2$PhSi$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (12B’) and Ph$_3$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ (13B’), which are basically isoenergetic at $-24.6$ kcal mol$^{-1}$ and $-24.7$ kcal mol$^{-1}$, respectively. This finding is in good agreement with the experimental observation of unscrambled MePh$_2$Si$^+$(CH$_{11}$H$_5$Br$_6$)$_-$ being the main product of the reaction (cf. Table 1, entry 4).

Our calculations suggest that a subsequent methyl exchange reaction leading to Me$_3$Si$^+$ is unlikely (11B $\rightarrow$ 18B, gray energy profile in Fig. 5). The transition state for this methyl group transfer, 16B-TS, is located 26.7 kcal mol$^{-1}$ relative to 11B, which is 1.8 kcal mol$^{-1}$ higher in energy than the barrier of the backward reaction via transition state 9B-TS. Consequently, the
reaction of MePh₂SiH with Ph₃C⁺[CHB₁₁H₅Br₆]⁻ stops at the above-mentioned mixture of silicon cations rather than undergoing exhaustive substituent redistribution to furnish low energy Me₃Si⁺[CHB₁₁H₅Br₆]⁻.

This kinetic inhibition was further proven by another mechanistic control experiment (Scheme 3). When a mixture of Ph₃C⁺[CHB₁₁H₅Br₆]⁻ and MePh₂SiH in toluene was stirred overnight at room temperature, a pale yellow suspension was obtained, which is characteristic of silylium ions with aromatic substituents (cf. Table 1, entry 4). Addition of less bulky Me₂-PhSiH to this mixture resulted in a quick decolorization and formation of a white suspension. NMR spectroscopic analysis of the solid now confirmed exclusive formation of Me₃Si⁺[CHB₁₁H₅Br₆]⁻.

Scope of the substituent redistribution reaction

The hydride abstraction from various dialkyl(phenyl)silanes with Ph₃C⁺[CHB₁₁H₅Br₆]⁻ finally revealed that the redistribution reaction is not restricted to methyl groups (Table 2). Although Et₂PhSiH reacted much slower compared to Me₂-PhSiH, exclusive formation of trialkylsilylium ion Et₃-Si⁺[CHB₁₁H₅Br₆]⁻ was observed (entries 1 and 2). Employing more bulky iPr₂PhSiH led to clean generation of unscrambled dialkyl(aryl)silylium ion iPr₃PhSi⁺[CHB₁₁H₅Br₆]⁻, as verified by X-ray crystallography (entry 3; see the ESI† for the molecular structure of iPr₂PhSi⁺[CHB₁₁H₅Br₆]⁻). These results are in accordance with our calculations, predicting high energy barriers for the transfer of bulky alkyl groups. Sterically even more shielded tBu₂PhSiH then completely thwarted the hydride abstraction, and only the trityl salt was recovered from the reaction mixture (entry 4).

To investigate whether the phenyl group in Me₂PhSiH can be replaced by other ‘leaving groups’, we also tested a benzyl and an alkyl substituent in Me₂RSiH (Table 3). As in the case of Me₂PhSiH (entry 1), clean formation of Me₃Si⁺[CHB₁₁H₅Br₆]⁻ was observed with Me₂BnSiH (entry 2), showing that the phenyl group is not essential for the exchange process. In contrast, the bulky tert-butyl group in Me₂tBuSiH completely prevented substituent redistribution, and silylium ion Me₂tBuSi⁺[CHB₁₁H₅Br₆]⁻ was formed as the only product (entry 3). This result again demonstrates that the intermolecular substituent exchange reaction is sensitive towards sterically demanding alkyl groups (cf. entry 3 in Table 2).

Table 3 Silylium ion generation from hydrosilanes of type Me₂RSiH

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Si⁺</th>
<th>δ²⁹Si [ppm]</th>
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<tr>
<td>1</td>
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<td>3</td>
<td>tBu</td>
<td>Me₂tBuSi⁺</td>
<td>98</td>
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</table>

All reactions were performed according to GP 2. See the ESI for details.

Conclusion

It has been known for decades that silylium ions can undergo redistribution reactions of their substituents. The present combined experimental and detailed computational study finally provides a full mechanistic picture of this phenomenon. The mechanism involves a series of phenyl and alkyl exchange reactions, the latter being calculated to be the energetically most demanding steps. While the transfer of phenyl groups proceeds via common four-centered transition states, the corresponding alkyl exchange was found to pass through unusual five-membered transition states. These are accessible after 1,2-silyl migration at the stage of the intermediate disilylated arenium ions.

Additionally, our DFT calculations revealed that the silicon cations are significantly more stabilized by ion pair formation with the carborane counteranion (R₃Si⁺[CHB₁₁H₅Br₆]⁻) than by formation of toluenium (R₃Si(toluene)⁺[CHB₁₁H₅Br₆]⁻) or hydrosilane-stabilized silylium ions ([R₃Si–H–SiR₃]⁺[CHB₁₁H₅Br₆]⁻). More importantly, purely aliphatic silylium carboranes with small substituents, i.e., methyl or ethyl groups, were found to be distinctly lower in energy than the corresponding mixed aliphatic/ aromatic or purely aromatic silylium ion pairs as
a result of stronger attractive interactions ($\Delta G \approx 2.9$ kcal mol$^{-1}$ for $R = \text{Me}$). These energy differences account for the highly selective formation of $\text{Me}_3\text{Si}^+\text{[CHB}_{11}\text{H}_{5}\text{Br}_6]^-$ and $\text{Et}_3\text{Si}^+\text{[CHB}_{11}\text{H}_{3}\text{Br}_3]^-$ from the reaction of the corresponding hydrosilanes $\text{R}_3\text{PhSiH}$ ($R = \text{Me, Et}$) with $\text{Ph}_3\text{C}^+[\text{CHB}_{11}\text{H}_3\text{Br}_3]^-$ under thermodynamic control.

The phenyl group in $\text{Me}_2\text{PhSiH}$ turned out to be replaceable by other ‘leaving groups’, such as a benzyl or even a sterically demanding $\text{Cy}_3\text{Me}_2$ group. However, two alkyl groups must be preinstalled in the hydrosilane starting material to steer the reaction towards formation of $\text{Me}_3\text{Si}^+\text{[CHB}_{11}\text{H}_3\text{Br}_3]^-$.

Contrast, hydride abstraction from $\text{MePh}_2\text{SiH}$ with only one alkyl substituent leads to a mixture of different silylium ions, as exhaustive scrambling to $\text{Me}_3\text{Si}^+$ is kinetically inhibited. Exchanging the phenyl groups in $\text{MePh}_2\text{SiH}$ by 2,6-disubstituted aryl groups ($e.g.$ $\text{Cy}_3\text{Me}_2$) eventually provides access to sterically congested triarylsilylium ions, as previously demonstrated by Müller and co-workers.$^{16}$

These general trends provide a solid foundation for the mechanistic understanding of the substituent redistribution of silylium ions, thereby enabling the prediction of the outcome of these exchange reactions. Thus, this process can be used as a reliable synthetic route not only to triaryl- but also to trialkylsilylium ions by deliberate choice of the hydrosilane and counteranion of the triyl salt.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references


12638; (b) A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, *Organometalics*, 2013, **32**, 4713–4722.


15 CCDC 1818576 for Me3Si+[CHB11H5Br6]−, CCDC 1818582 for MePh3Si+[CHB11H5Br6]−, and CCDC 1818581 for iPr3PhSi+[CHB11H5Br6]− contain the supplementary crystallographic data for this paper.


17 The decomposition of the [B(C6F5)3]− counteranion is likely to proceed via an S8Ar reaction of the formed silylium ions with the borate. The formation of B(C6F5)3 was verified by 19F NMR spectroscopic analysis, and GC-MS analysis revealed formation of several silanes containing a C6F5 unit.

18 The generated silylium ions were converted to the corresponding fluorosilanes using (C6F5)3PF2 (1.0 equiv.), thereby facilitating product characterization by both NMR spectroscopic and GC-MS analysis. For the preparation of [C6F5]3PF2, see: C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374–1377.

19 Small amounts of the triarylsilylium ion (C6Me3)3Si[CHB11H5Br6]− were also detected (cf. ref. 10).

20 The mechanism of intermolecular substituent exchange reactions at related ferrocene-stabilized silylium ions had already been studied by quantum-chemical analyses (cf. ref. 8d). However, the calculated barriers for the transition states were relatively high. For the calculated mechanism of an intramolecular substituent exchange reaction at a silicon cation with a rigid naphthalene-1,8-diyl backbone, see: ref. 8c.


23 We were not able to locate a four-centered transition state from 8A to directly arrive at 10A. See Fig. S67 in the ESI† for geometric scan calculations.

24 Me3Si(toluene)+[CHB11H5Br6]− was calculated to be only 0.7 kcal mol−1 lower in energy than MePh3Si(toluene)+[CHB11H5Br6]− (see the ESI† for details).

25 Although our calculations predict formation of small amounts of Ph3Si+[CHB11H5Br6]− in the reaction of MePh3SiH with Ph3C+[CHB11H5Br6]−, we were not able to detect this silylium ion by 1H/29Si HMQC NMR spectroscopy.