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# Journal Name

## ARTICLE

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

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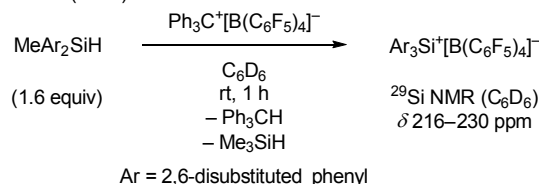
An in-depth experimental and theoretical study of the substituent exchange reaction of silylium ions is presented. Aside from the substitution pattern at the silicon atom, the selectivity of this process is predominantly influenced by the counteranion, which is introduced with the trityl salt in the 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 for the selective formation of trialkylsilylium 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-center transition state.
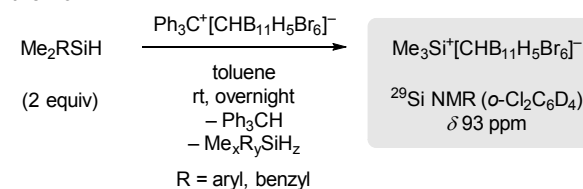
## Introduction

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–Condon–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.[4,5] 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.[6–8] Hence, hydrosilanes containing three identical substituents, *e.g.* $Et_3SiH$ or $iPr_3SiH$, 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 $MeAr_2SiH$ are used in the hydride abstraction with $Ph_3C^+[B(C_6F_5)_4]^-$, the formation of otherwise difficult to prepare triarylsilylium ions $Ar_3Si^+[B(C_6F_5)_4]^-$ is observed.[11] Notably, the use of less bulky hydrosilanes such as $MePh_2SiH$ or $Me(o\text{-Tol})_2SiH$ do not give triarylsilylium ions but mixtures of different silicon cations.[12]

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Müller (**2011**):

$$MeAr_2SiH \xrightarrow[\substack{C_6D_6 \\ rt,\ 1\ h \\ -\ Ph_3CH \\ -\ Me_3SiH}]{Ph_3C^+[B(C_6F_5)_4]^-} Ar_3Si^+[B(C_6F_5)_4]^-$$

(1.6 equiv)

$^{29}$Si NMR ($C_6D_6$)
$\delta$ 216–230 ppm

Ar = 2,6-disubstituted phenyl

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this work:

$$Me_2RSiH \xrightarrow[\substack{toluene \\ rt,\ overnight \\ -\ Ph_3CH \\ -\ Me_xR_ySiH_z}]{Ph_3C^+[CHB_{11}H_5Br_6]^-} Me_3Si^+[CHB_{11}H_5Br_6]^-$$

(2 equiv)

$^{29}$Si NMR ($o\text{-}Cl_2C_6D_4$)
$\delta$ 93 ppm

R = aryl, benzyl

**Scheme 1** Divergence in the generation of silylium ions by substituent redistribution (x+y+z = 4).

Herein, we report that treatment of hydrosilanes of type $Me_2RSiH$ (R = aryl, benzyl) with Reed's carborane-based trityl salt $Ph_3C^+[CHB_{11}H_5Br_6]^{-[13]}$ results in substituent exchange reactions selectively forming the elusive trimethylsilylium ion $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (Scheme 1, bottom). This method thus complements Müller's approach and offers a practical route to $Me_3Si^+$, avoiding the use of gaseous and highly flammable $Me_3SiH$.[14] A systematic experimental and computational investigation was performed to gain a full mechanistic picture of this phenomenon. DFT calculations revealed an unexpected mechanism and suggest an active role of the carborane counteranion in the outcome of these reactions.

**ARTICLE**

## Results and discussion

### Generation of the trimethylsilylium ion by substituent redistribution

When a mixture of $Me_2PhSiH$ and $Ph_3C^+[CHB_{11}H_5Br_6]^-$ 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 $o$-$Cl_2C_6D_4$ 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 for trialkylsilylium ions, indicated clean formation of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (Fig. 1). The structural integrity of the carborane counteranion was confirmed by ^{11}B NMR spectroscopy.

Unambiguous evidence for the structure of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ was eventually provided by its crystallographic characterization (Fig. 2).[15] Single crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion with $n$-hexane from a solution of the silylium salt in $o$-$F_2C_6H_4$ at room temperature. In accordance with reported molecular structures of silylium carboranes,[16] one bromine atom at the pentagonal belt of the icosahedral anion is bound to the silicon cation. Both the Si–Br bond distance of 2.435(6) Å and the sum of all C–Si–C bond angles of 346.3(6)° are comparable to the larger $Et_3Si^+[CHB_{11}H_5Br_6]^-$.

In contrast to the clean formation of $Me_3Si^+$, the unpolar $n$-pentane filtrate contained several tri- and tetraorganosilanes, such as $Ph_4Si$, $MePh_3Si$, $Ph_3SiH$, $Me_2Ph_2Si$, $MePh_2SiH$, $Me_3PhSi$, and $Me_2PhSiH$, as verified by GC-MS analysis. Since silylium ions are known to promote substituent redistribution,[8] this result did not come as a surprise but raised the question why $Me_3Si^+$ was selectively formed in this reaction mixture, whereas Müller's conditions cleanly afford sterically congested triarylsilylium ions.[10]



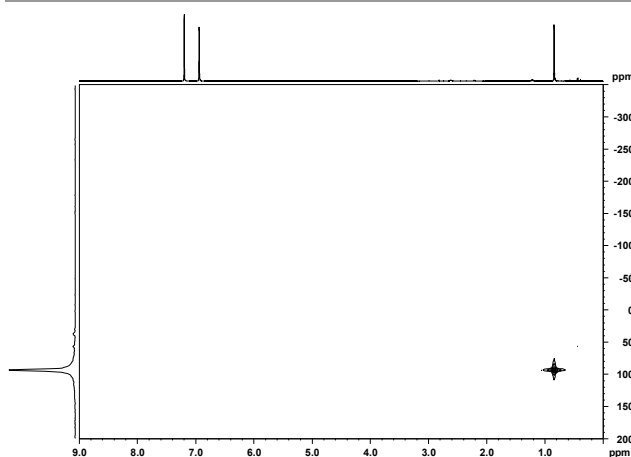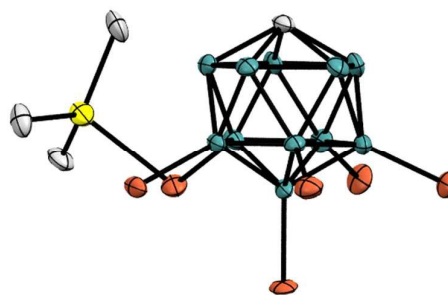**Fig. 2** Molecular structure of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (thermal ellipsoids at 50% probability level; H atoms omitted for clarity).

### Influence of the substituent pattern at the silicon atom on the selectivity of the substituent redistribution reaction

To understand the differences between Müllers's protocol[10] and our findings, we systematically studied the hydride transfer reaction of various hydrosilanes of type $MeAr_2SiH$ and $Me_2ArSiH$ using trityl salts $Ph_3C^+[B(C_6F_5)_4]^-$ and $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (Table 1). Depending on the counteranion, slightly modified procedures were applied for the generation of the silicon cations (see the see the ESI† for details). For all reactions, an excess of hydrosilane (4 equiv) was used, thereby excluding any influence of stoichiometry on the product formation. In accordance with Müller's report, bulky methyl(diaryl)silane $Me(C_6Me_5)_2SiH$ was converted to the corresponding triarylsilylium ion, regardless of which counteranion was used (entries 1 and 2). In contrast, hydride abstraction of sterically less hindered $MePh_2SiH$ with $Ph_3C^+[B(C_6F_5)_4]^-$ led to a complex reaction mixture as a result of anion decomposition (entry 3).[12,17] The use of the carborane counteranion $[CHB_{11}H_5Br_6]^-$ furnished the unscrambled silylium ion $MePh_2Si^+[CHB_{11}H_5Br_6]^-$, as confirmed by X-ray diffraction analysis (entry 4; see the ESI† for the molecular structure of $MePh_2Si^+[CHB_{11}H_5Br_6]^-$).[15]

**Table 1** Silylium ion generation by substituent redistribution: Effect of the hydrosilane and counteranion ($Si$ = Triorganosilyl).

$$Si\!-\!H \xrightarrow[\substack{-\ Ph_3CH \\ -\ Me_xAr_ySiH_z}]{Ph_3C^+[X]^-} Si^+[X]^-$$

| Entry[a] | $Si$–H (4 equiv) | $[X]^-$ | $Si^+$ | $\delta(^{29}Si)$ [ppm][b] |
|---|---|---|---|---|
| 1 | $Me(C_6Me_5)_2SiH$ | $[B(C_6F_5)_4]^-$ | $(C_6Me_5)_3Si^+$ | 217 |
| 2 | $Me(C_6Me_5)_2SiH$ | $[CHB_{11}H_5Br_6]^-$ | $(C_6Me_5)_3Si^+$ | 217 |
| 3 | $MePh_2SiH$ | $[B(C_6F_5)_4]^-$ | –[c] | – |
| 4 | $MePh_2SiH$ | $[CHB_{11}H_5Br_6]^-$ | $MePh_2Si^+/Me_2PhSi^{+d}$ | 57/76 |
| 5 | $Me_2PhSiH$ | $[B(C_6F_5)_4]^-$ | –[c] | – |
| 6 | $Me_2PhSiH$ | $[CHB_{11}H_5Br_6]^-$ | $Me_3Si^+$ | 93 |
| 7 | $Me_2(C_6Me_5)SiH$ | $[B(C_6F_5)_4]^-$ | $(C_6Me_5)_3Si^+$ | 217 |
| 8[e] | $Me_2(C_6Me_5)SiH$ | $[CHB_{11}H_5Br_6]^-$ | $Me_3Si^+$ | 93 |

[a] All reactions were performed according to the General Procedure (GP) 1 for $X^-$ = $[B(C_6F_5)_4]^-$ ($C_6D_6$, room temperature, 60 min) or GP 2 for $X^-$ = $[CHB_{11}H_5Br_6]^-$ (toluene, room temperature, 18–24 h). See the ESI† for details. [b] Measured in $o$-$Cl_2C_6D_4$. [c] A complex mixture was obtained as a result of counteranion decomposition.[17] [d] Ratio of 79:21 determined by ^{1}H NMR spectroscopy. [e] Reaction performed at 50 °C for 72 h.



**Fig. 1** ^{1}H/^{29}Si HMQC NMR spectrum (500/99 MHz, $o$-$Cl_2C_6D_4$, 298 K, optimized for $J$ = 7 Hz) of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ from the reaction of $Me_2PhSiH$ with $Ph_3C^+[CHB_{11}H_5Br_6]^-$.

Journal Name

ARTICLE

However, the formation of the MePh$_2$Si$^+$ cation was accompanied by a substantial amount of a second silylium ion, which was assigned as Me$_2$PhSi$^+$ cation.[18] Notably, longer reaction times (7 days) or elevated temperatures (50 °C for 72 h) did not significantly change the product ratio of ~79:21 (not shown). In all cases, the generation of Me$_3$Si$^+$ was not observed. We then turned our attention to dimethyl(aryl)silanes (entries 5–8). The reaction of Me$_2$PhSiH with Ph$_3$C$^+$[B(C$_6$F$_5$)$_4$]$^-$ again resulted in decomposition of the borate counteranion (entry 5).[17] Conversely, treatment of Me$_2$PhSiH with trityl carborane Ph$_3$C$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$ exclusively afforded silylium salt Me$_3$Si$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$ without detectable formation of neither MePh$_2$Si$^+$ nor Me$_2$PhSi$^+$ (entry 6). Strikingly, hydride abstraction from sterically more demanding Me$_2$(C$_6$Me$_5$)SiH led to the corresponding 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 Me$_3$Si$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$ (entry 8).[19] However, heating of the reaction at 50 °C for 72 h was necessary.

Overall, these results indicate that hydride abstraction of hydrosilanes of type Me$_2$ArSiH with a carborane-based trityl salt tends to form the trimethylsilylium ion, whereas hydrosilanes of type MeAr$_2$SiH with a bulky aryl substituent favor triarylsilylium ion generation.

## Mechanism of the substituent redistribution reaction with Me$_2$PhSiH

To gain insight into the reaction mechanism and to understand why the treatment of Me$_2$PhSiH with Ph$_3$C$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$ exclusively gives Me$_3$Si$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$, 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).[20] The hydride abstraction of Me$_2$PhSiH with Ph$_3$C$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$ 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 Me$_2$PhSi$^+$ (6A), which 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).[8e,21] 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 Me$_2$PhSiH to form hydride-bridged adduct 7A,[21] 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.
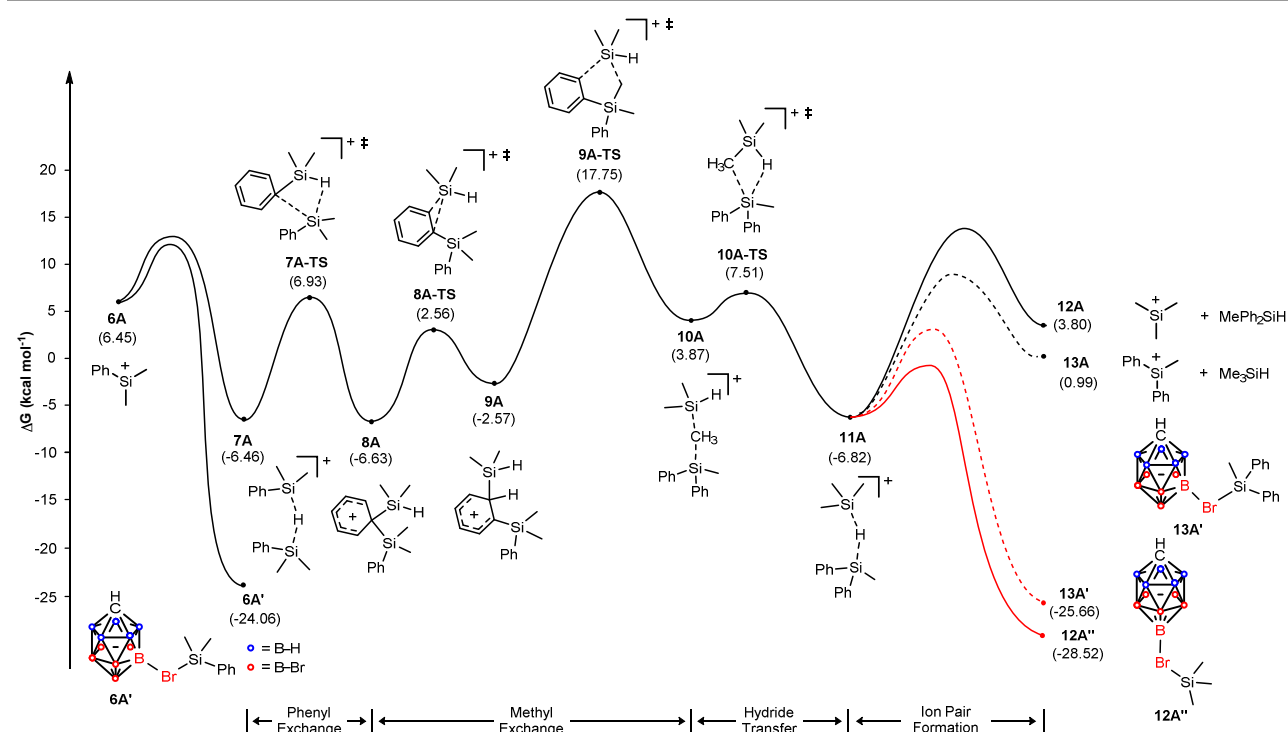


Fig. 3 Energy (kcal·mol$^{-1}$) profile of the substituent redistribution in the reaction of Me$_2$PhSiH (1A) with Ph$_3$C$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$ (2A). The energies are relative to the starting material 1A and 2A.
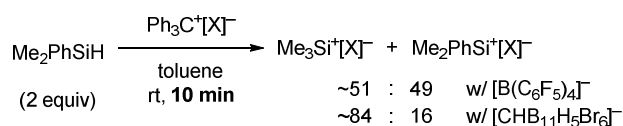
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Hydride-bridged adduct ion **7A** can undergo a phenyl group transfer to arrive at phenyl-bridged adduct **8A**[7c,8b,22] via the four-center transition state **7A-TS**, associated with a barrier of 13.4 kcal·mol^{−1}. Surprisingly, the subsequent methyl group transfer does not proceed via another typical four-membered transition state.[23] 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-center transition state **9A-TS** with an overall barrier of 24.2 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 (ΔG = 0.4 kcal·mol^{−1}), suggesting that both structures coexist in equilibrium. The formal dissociation of **11A** either gives Me₃Si⁺ or MePh₂Si⁺, 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. Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (**12A''**), which is located at −28.5 kcal·mol^{−1}, is 2.9 kcal·mol^{−1} lower in energy than MePh₂Si⁺[CHB₁₁H₅Br₆]⁻ (**13A'**) and also 4.5 kcal·mol^{−1} more stable than Me₂PhSi⁺[CHB₁₁H₅Br₆]⁻ (**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 R₃Si(toluene)⁺[CHB₁₁H₅Br₆]⁻. 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 ESI† for details).[24] This result was supported by independent control experiments (Scheme 2). The hydride abstraction of Me₂PhSiH with borate-based trityl salt Ph₃C⁺[B(C₆F₅)₄]⁻ 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*-Cl₂C₆D₄ revealed formation of a mixture of Me₃Si⁺[B(C₆F₅)₄]⁻ and Me₂PhSi⁺[B(C₆F₅)₄]⁻ in a ratio of ~51:49 along with small amounts of byproducts arising from counteranion decomposition. In contrast, stopping the reaction of Me₂PhSiH with Ph₃C⁺[CHB₁₁H₅Br₆]⁻ after stirring for 10 min in toluene furnished Me₃Si⁺[CHB₁₁H₅Br₆]⁻ as the major product along with only small amounts of unscrambled Me₂PhSi⁺[CHB₁₁H₅Br₆]⁻ (ratio ~84:16). In both reactions, full conversion of the trityl salt was observed.

As shown in Fig. 4, the silylium ions can either be bound 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 Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (**12A''**). This result is in contrast to the molecular structure in the solid state, which shows the equatorial conformer (*cf.* Fig. 2). We speculate that either packing effects or a statistical preference for the equatorial conformer are the reason for this discrepancy. Notably, the equatorial conformer **12A'** is still 1.8 kcal·mol^{−1} lower in energy than the equatorial conformer of MePh₂Si⁺[CHB₁₁H₅Br₆]⁻ (**13A'**). The higher ion pairing energy in **12A'** can be ascribed to the low steric demand of Me₃Si⁺, 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 Me₂PhSi⁺ (**6A**) and MePh₂Si⁺ (**13A**) with the carborane counteranion is less tight, and the ion pairing is therefore slightly less favorable. This trend is reflected in the corresponding Si–Br bond lengths of these silylium carborane salts, which were computed to be shortest in both conformers of Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (**12A'** and **12A''**).
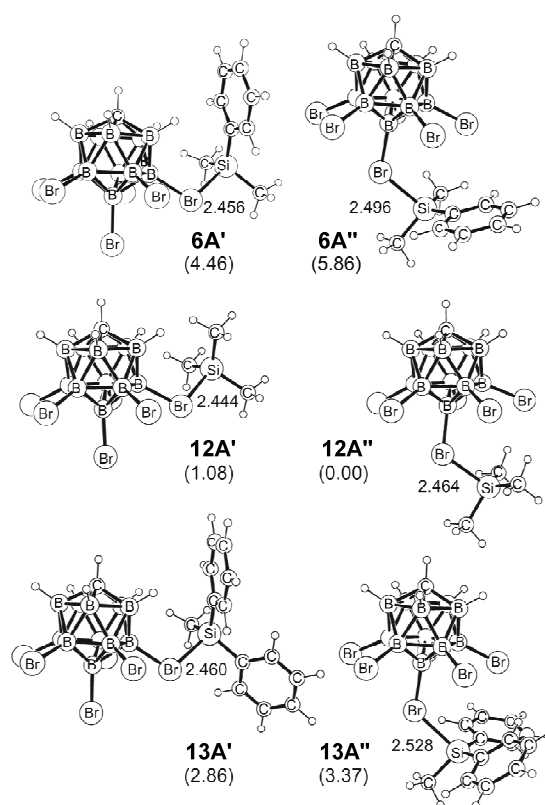


**Fig. 4** Computed apical and equatorial conformers of Me₂PhSi⁺[CHB₁₁H₅Br₆]⁻ (top), Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (middle) and MePh₂Si⁺[CHB₁₁H₅Br₆]⁻ (bottom). Si–Br bond distances given in Å and relative free energy differences (kcal·mol^{−1}) shown in parenthesis.



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

Hence, this ion pair is the most stable silylium salt despite the lack of stabilizing phenyl groups. Both conformers of $Me_2PhSi^+[CHB_{11}H_5Br_6]^-$ (**6A'** and **6A''**) are higher in energy than the corresponding $MePh_2Si^+[CHB_{11}H_5Br_6]^-$ (**13A'** and **13A''**), indicating that the stabilization of these silylium carborane salts is determined by a delicate balance of electronic and steric effects. It should be also noted here that the DFT optimized structures for $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (**12A'**) and $MePh_2Si^+[CHB_{11}H_5Br_6]^-$ (**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 MePh₂SiH

To understand why the reaction of $MePh_2SiH$ with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ does not furnish $Me_3Si^+[CHB_{11}H_5Br_6]^-$, 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 as in the case of $Me_2PhSiH$ due to the slightly higher hydride donor strength of $MePh_2SiH$ (see Table S1 in the ESI† for details). The resulting silylium ion $MePh_2Si^+$ (**6B**) with a relative free energy of 0.75 kcal·mol$^{-1}$ is almost isoenergetic to the reactant state. Adduct formation with another equivalent of $MePh_2SiH$ affords hydrosilane-stabilized silylium ion **7B**, which undergoes a methyl/phenyl exchange reaction following a very similar reactivity pattern as described above, leading to
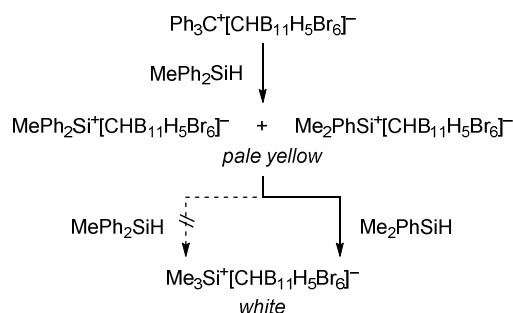
scrambled hydride-bridged adduct **11B**. The transformation of **7B** to **11B** via intermediates **8B**, **9B**, and **10B** is again reversible, since **7B** and **11B** have similar free energies ($\Delta G$ = 0.7 kcal·mol$^{-1}$). As before, the methyl group transfer via five-membered transition state **9B-TS** shows the highest barrier, which is 24.2 kcal·mol$^{-1}$ relative to **7B**. In this equilibrium, unscrambled $MePh_2Si^+[CHB_{11}H_5Br_6]^-$ (**6B'**) with a relative free energy of $-$25.9 kcal·mol$^{-1}$ is predicted to be the major species, followed by scrambled $Me_2PhSi^+[CHB_{11}H_5Br_6]^-$ (**12B'**) and $Ph_3Si^+[CHB_{11}H_5Br_6]^-$ (**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 $MePh_2Si^+[CHB_{11}H_5Br_6]^-$ being the main product of the reaction (*cf.* Table 1, entry 4).[25]

Our calculations suggest that a subsequent methyl exchange reaction leading to $Me_3Si^+$ is unlikely (**11B** → **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 $MePh_2SiH$ with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ stops at the above mentioned mixture of silicon cations rather than undergoing exhaustive substituent redistribution to furnish low energy $Me_3Si^+[CHB_{11}H_5Br_6]^-$.
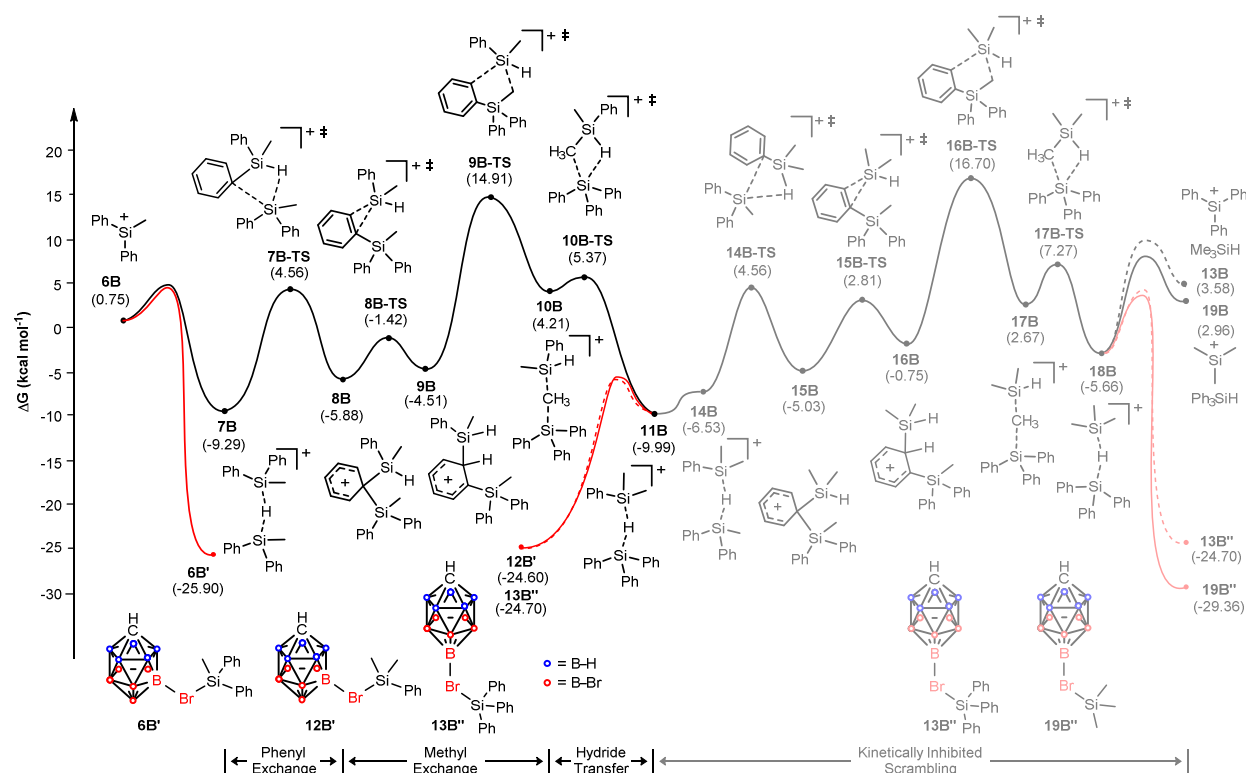


**Fig. 5** Energy (kcal·mol$^{-1}$) profile of the substituent redistribution in the reaction of $MePh_2SiH$ (**1A**) with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (**2B**). The energies are relative to the starting material **1B** and **2B**.

$Ph_3C^+[CHB_{11}H_5Br_6]^-$

$MePh_2SiH$

$MePh_2Si^+[CHB_{11}H_5Br_6]^-$ + $Me_2PhSi^+[CHB_{11}H_5Br_6]^-$
*pale yellow*

$MePh_2SiH$ —//—                $Me_2PhSiH$

$Me_3Si^+[CHB_{11}H_5Br_6]^-$
*white*

**Scheme 3** Probing kinetic inhibition in the substituent redistribution reaction with $MePh_2SiH$.

This kinetic inhibition was further proven by another mechanistic control experiment (Scheme 3). When a mixture of $Ph_3C^+[CHB_{11}H_5Br_6]^-$ and $MePh_2SiH$ in toluene was stirred overnight at room temperature, a pale yellow suspension was obtained, which is characteristic for silylium ions with aromatic substituents (*cf.* Table 1, entry 4). Addition of less bulky $Me_2PhSiH$ 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 $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

### Scope of the substituent redistribution reaction

The hydride abstraction of various dialkyl(phenyl)silanes with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ finally revealed that the redistribution reaction is not restricted to methyl groups (Table 2). Although $Et_2PhSiH$ reacted much slower compared to $Me_2PhSiH$, exclusive formation of trialkylsilylium ion $Et_3Si^+[CHB_{11}H_5Br_6]^-$ was observed (entries 1 and 2). Employing more bulky $iPr_2PhSiH$ led to clean generation of unscrambled dialkyl(aryl)silylium ion $iPr_2PhSi^+[CHB_{11}H_5Br_6]^-$, as verified by X-ray crystallography (entry 3; see the ESI† for for the molecular structure of $iPr_2PhSi^+[CHB_{11}H_5Br_6]^-$).[15] These results are in accordance with our calculations, predicting high energy barriers for the transfer of bulky alkyl groups. Sterically even more shielded $tBu_2PhSiH$ then completely thwarted the hydride abstraction, and only the trityl salt was recovered from the reaction mixture (entry 4).

**Table 2** Silylium ion generation from hydrosilanes of type $R_2PhSiH$.

$R_2PhSiH$ $\xrightarrow[\text{rt, overnight}]{Ph_3C^+[CHB_{11}H_5Br_6]^-}$ $R_3Si^+[CHB_{11}H_5Br_6]^-$
(2 equiv)          toluene            or
$R_2PhSi^+[CHB_{11}H_5Br_6]^-$

| Entry[a] | R | $Si^+$ | $\delta(^{29}Si)$ [ppm][b] |
|---|---|---|---|
| 1 | Me | $Me_3Si^+$ | 93 |
| 2[c] | Et | $Et_3Si^+$ | 100 |
| 3 | iPr | $iPr_2PhSi^+$ | 76 |
| 4 | tBu | – | – |

[a] All reactions were performed according to GP 2. See the ESI† for details. [b] Measured in $o$-$Cl_2C_6D_4$. [c] With 4 equiv of $Et_2PhSiH$ and 7 days reaction time. [d] No reaction, only $Ph_3C^+[CHB_{11}H_5Br_6]^-$ was recovered.

**Table 3** Silylium ion generation from hydrosilanes of type $Me_2RSiH$.

$Me_2RSiH$ $\xrightarrow[\text{rt, overnight}]{Ph_3C^+[CHB_{11}H_5Br_6]^-}$ $Me_3Si^+[CHB_{11}H_5Br_6]^-$
(2 equiv)          toluene            or
$Me_2RSi^+[CHB_{11}H_5Br_6]^-$

| Entry[a] | R | $Si^+$ | $\delta(^{29}Si)$ [ppm][b] |
|---|---|---|---|
| 1 | Ph | $Me_3Si^+$ | 93 |
| 2 | Bn | $Me_3Si^+$ | 93 |
| 3 | tBu | $Me_2tBuSi^+$ | 98 |

[a] All reactions were performed according to GP 2. See the ESI† for details. [b] Measured in $o$-$Cl_2C_6D_4$.

To investigate whether the phenyl group in $Me_2PhSiH$ can be replaced by other `leaving groups´, we also tested a benzyl and alkyl substituent in $Me_2RSiH$ (Table 3). As in the case of $Me_2PhSiH$ (entry 1), clean formation of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ was observed with $Me_2BnSiH$ (entry 2), showing that the phenyl group is not essential for the exchange process. In contrast, the bulky *tert*-butyl group in $Me_2tBuSiH$ completely prevented substituent redistribution, and silylium ion $Me_2tBuSi^+[CHB_{11}H_5Br_6]^-$ 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).

## Conclusion

It has been known for decades, that silylium ions can undergo redistribution reactions of their substituents.[8] 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-center transition states, the corresponding alkyl exchange was found to pass 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 ($R_3Si^+[CHB_{11}H_5Br_6]^-$) than by formation of toluenium ($R_3Si(toluene)^+[CHB_{11}H_5Br_6]^-$) or hydrosilane-stabilized silylium ions ($[R_3Si–H–SiR_3]^+[CHB_{11}H_5Br_6]^-$). 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 ($\Delta G \geq 2.9$ kcal·mol$^{-1}$ for R = Me). These energy differences account for the highly selective formation of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ and $Et_3Si^+[CHB_{11}H_5Br_6]^-$ from the reaction of the corresponding hydrosilanes $R_2PhSiH$ (R = Me, Et) with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ under thermodynamic control.

The phenyl group in $Me_2PhSiH$ turned out to be exchangeable by other `leaving groups´, such as a benzyl or even a sterically demanding $C_6Me_5$ group. However, two alkyl groups must be preinstalled in the hydrosilane starting material to steer the reaction towards formation of $Me_3Si^+[CHB_{11}H_5Br_6]^-$. In contrast, hydride abstraction of $MePh_2SiH$ with only one alkyl substituent leads to a mixture of different silylium ions, as exhaustive scrambling to $Me_3Si^+$ is kinetically inhibited. Exchanging the phenyl groups in $MePh_2SiH$ by 2,6-disubstituted aryl groups (*e.g.* $C_6Me_5$) eventually provides access to sterically congested triarylsilylium ions, as previously demonstrated by Müller and co-workers.[10]

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 trityl salt.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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25 Although our calculations predict formation of small amounts of $Ph_3Si^+[CHB_{11}H_5Br_6]^-$ in the reaction of $MePh_2SiH$ with $Ph_3C^+[CHB_{11}H_5Br_6]^-$, we were not able to detect this silylium ion by $^1H/^{29}Si$ HMQC NMR.

**TOC**

$Me_5C_6$ — $\overset{C_6Me_5}{\underset{C_6Me_5}{Si}}{}^+$

$Ph_3C^+$
$[B(C_6F_5)_4]^-$

$R$ — $\overset{C_6Me_5}{\underset{Me}{Si}}$ — $H$

$Ph_3C^+$
$[CHB_{11}H_5Br_6]^-$

$R = Me$

$R = C_6Me_5$