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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. Apart 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 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-centered transition state.

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Introduction

Silvlium ions (R₃Si⁺) have recently emerged as useful and versatile catalysts for synthetically attractive transformations.^{1,2} The most commonly used approach to generate silvlium ions is the Bartlett-Condon-Schneider reaction,3 that is the silicon-tocarbon 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. 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 $Ph_3C^+[B(C_6F_5)_4]^-$, the formation of otherwise difficult to prepare triarylsilylium ions $Ar_3Si^+[B(C_6F_5)_4]^-$ is

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observed.¹¹ Notably, the useof 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 Me_2RSiH (R = aryl, benzyl) with Reed's carborane-based trityl salt $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (ref. 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_* .⁴ A systematic experimental and computational investigation was performed to gain a full

Müller (2011): MeAr ₂ SiH (1.6 equiv) A	$\begin{array}{c} Ph_{3}C^{+}[B(C_{6}F_{5})_{4}]^{-} \\ \hline \\ \hline \\ C_{6}D_{6} \\ rt, 1 h \\ - Ph_{3}CH \\ - Ph_{3}CH \\ - Me_{3}SiH \\ r = 2,6-disubstituted phenylemetric pheny$	Ar ₃ Si ⁺ [B(C ₆ F ₅) ₄] [−] ²⁹ Si NMR (C ₆ D ₆) δ216–230 ppm
this work:		
Me ₂ RSiH	Ph ₃ C ⁺ [CHB ₁₁ H ₅ Br ₆] [−]	Me ₃ Si ⁺ [CHB ₁₁ H ₅ Br ₆] ⁻
- (2 equiv)	toluene rt, overnight – Ph ₃ CH – Me _x R _y SiH _z	²⁹ Si NMR (o -Cl ₂ C ₆ D ₄) δ 93 ppm
	R = aryl, benzyl	

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



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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 Me₂PhSiH and Ph₃C⁺[CHB₁₁H₅Br₆]⁻ 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*-Cl₂C₆D₄ for NMR spectroscopic analysis. Unexpectedly, only a singlet at 0.83 ppm was detected in the ¹H NMR spectrum, while no aromatic resonances except for those of the deuterated solvent were observed. The low-field ²⁹Si NMR chemical shift of 93 ppm in the corresponding ¹H/²⁹Si HMQC spectrum, which is characteristic of trialkylsilylium ions, indicated clean formation of Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (Fig. 1). The structural integrity of the carborane counteranion was confirmed by ¹¹B 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*-F₂C₆H₄ 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 Et₃Si⁺[CHB₁₁H₅Br₆]⁻.

In contrast to the clean formation of Me₃Si⁺, the non-polar *n*pentane filtrate contained several tri- and tetraorganosilanes, such as Ph₄Si, MePh₃Si, Ph₃SiH, Me₂Ph₂Si, MePh₂SiH, Me₃PhSi, and Me₂PhSiH, as verified by GC-MS analysis. Since silylium



Fig. 1 1 H/ 29 Si HMQC NMR spectrum (500/99 MHz, o-Cl₂C₆D₄, 298 K, optimized for J = 7 Hz) of Me₃Si⁺[CHB₁₁H₅Br₆]⁻ from the reaction of Me₂PhSiH with Ph₃C⁺[CHB₁₁H₅Br₆]⁻.



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

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

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

To understand the differences between Müller's protocol¹⁰ and our findings, we systematically studied the hydride transfer reaction of various hydrosilanes of type MeAr₂SiH and Me₂ArSiH 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 ESI† for details). For all reactions, an excess of hydrosilane (4 equiv.) was used, thereby

 $\label{eq:stable1} \begin{array}{ll} \mbox{Silylium ion generation by substituent redistribution: effect of the hydrosilane and counteranion (Si = triorganosilyl) \end{array}$

	Ph ₃ C⁺[X] [−]	D 0:+IVI-
R ₃ SI—H	– Ph ₃ CH – Me _x Ar _y SiH _z	R321 [X]

Entry ^a	Si-H (4 equiv.)	$[X]^-$	Si^+	δ(²⁹ Si) ^b [ppm]
1	Me(C ₆ Me ₅) ₂ SiH	$[B(C_6F_5)_4]^-$	(C ₆ Me ₅) ₃ Si ⁺	217
2	Me(C ₆ Me ₅) ₂ SiH	$[CHB_{11}H_5Br_6]^-$	$(C_6Me_5)_3Si^+$	217
3	MePh ₂ SiH	$[B(C_6F_5)_4]^-$	c	_
4	MePh ₂ SiH	$[CHB_{11}H_5Br_6]^-$	MePh ₂ Si ⁺ / Me ₂ PhSi ^{+d}	57/76
5	Me ₂ PhSiH	$[B(C_6F_5)_4]^-$		_
6	Me ₂ PhSiH	[CHB ₁₁ H ₅ Br ₆] ⁻	Me_3Si^+	93
7	Me ₂ (C ₆ Me ₅)SiH	$[B(C_6F_5)_4]^-$	$(C_6Me_5)_3Si^+$	217
8 ^e	Me ₂ (C ₆ Me ₅)SiH	$[CHB_{11}H_5Br_6]^-$	Me ₃ Si ⁺	93

^{*a*} All reactions were performed according to 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*-Cl₂C₆D₄. ^{*c*} A complex mixture was obtained as a result of counteranion decomposition.¹⁷ ^{*d*} Ratio of 79:21 determined by ¹H NMR spectroscopy. ^{*e*} Reaction performed at 50 °C for 72 h. excluding any influence of stoichiometry on the product formation. In accordance with Müller's report, bulky methyl(diaryl)silane Me(C6Me5)2SiH was converted to the corresponding triarylsilylium ion, regardless of which counteranion was used (entries 1 and 2). In contrast, hydride abstraction from sterically less hindered MePh₂SiH 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 [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]⁻).¹⁵ However, the formation of the MePh₂Si⁺ cation was accompanied by a substantial amount of a second silvlium ion, which was found to be the Me₂PhSi⁺ cation.¹⁸ Notably, longer reaction times (7 days) or elevated temperatures (50 °C for 72 h) did not significantly change the product ratio of \sim 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⁺[B(C₆F₅)₄]⁻ again resulted in decomposition of the borate counteranion (entry 5).17 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 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 $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (entry 8).¹⁹ However, heating of the reaction at 50 °C for 72 h was necessary.

Overall, these results indicate that hydride abstraction from hydrosilanes of type Me_2ArSiH with a carborane-based trityl salt tends to form the trimethylsilylium ion, whereas hydrosilanes of type $MeAr_2SiH$ with a bulky aryl substituent favor triarylsilylium 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).²⁰ 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 silvlium ion Me₂PhSi⁺ (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 Me₂PhSiH to form hydride-bridged adduct 7A,²¹



Fig. 3 Energy (kcal mol⁻¹) profile of the substituent redistribution in the reaction of Me_2PhSiH (1A) with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (2A). The energies are relative to the starting materials 1A and 2A.

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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 Me₂PhSiH (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 8A7c,8b,22 via the fourcentered 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 1,2migration 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 hydridebridged adduct 11A via low barrier transition state 10A-TS. The hydrosilane-stabilized silvlium ions 7A and 11A are almost isoenergetic ($\Delta G = 0.4 \text{ kcal mol}^{-1}$), suggesting that both structures coexist in equilibrium. The formal dissociation of **11A** gives either 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. $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (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 $Me_2PhSi^+[CHB_{11}H_5Br_6]^-$ (6A'), thus predicting the silvlium 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)⁺[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 from 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 the 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

	Ph₃C⁺[X] [_]		т	Mol	⊃he;+iv1-
Me ₂ PhSiH	toluono		т	ivie ₂ i	
(2 equiv)	rt, 10 min	~51	:	49	w/ [B(C ₆ F ₅) ₄] ⁻
(Z cquiv)		~84	:	16	w/ [CHB ₁₁ H ₅ Br ₆] ⁻

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

decomposition. In contrast, stopping the reaction of Me_2 -PhSiH with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ after stirring for 10 min in toluene furnished $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as the major product along with only small amounts of unscrambled Me_2 -PhSi⁺[CHB₁₁H₅Br₆]⁻ (ratio ~84 : 16). In both reactions, full conversion of the trityl salt was observed.

As shown in Fig. 4, the silvlium 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 $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ (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 $MePh_2Si^+[CHB_{11}H_5Br_6]^-$ (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 silvlium ions Me₂PhSi⁺ (6A) and MePh₂Si⁺ (13A) with the carborane counteranion is less



Fig. 4 Computed apical and equatorial isomers of Me₂PhSi⁺[CHB₁₁-H₅Br₆]⁻ (top), Me₃Si⁺[CHB₁₁H₅Br₆]⁻ (middle) and MePh₂Si⁺[CHB₁₁H₅-Br₆]⁻ (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 silylium carborane salts, which were computed to be shortest in both isomers of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (12A' and 12A"). Hence, this ion pair is the most stable silylium salt despite the lack of stabilizing phenyl groups. Both isomers 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 also be 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 $\mbox{MePh}_2\mbox{SiH}$

To understand why the reaction of MePh₂SiH with Ph₃- $C^{+}[CHB_{11}H_5Br_6]^{-}$ does not furnish Me₃Si⁺[CHB₁₁H₅Br₆]⁻, 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 Me₂PhSiH due to the slightly higher hydride donor strength of MePh₂SiH (see Table S1 in the

ESI^{\dagger} for details). The resulting silvlium ion MePh₂Si^{\dagger} (**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 MePh₂SiH affords hydrosilane-stabilized silvlium 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 (ΔG = 0.7 kcal mol⁻¹). As before, the methyl group transfer *via* fivemembered transition state 9B-TS shows the highest barrier, which is 24.2 kcal mol^{-1} relative to 7B. In this equilibrium, unscrambled MePh₂Si⁺[CHB₁₁H₅Br₆]⁻ (**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 MePh₂Si⁺[CHB₁₁H₅Br₆]⁻ 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** \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



Fig. 5 Energy (kcal mol⁻¹) profile of the substituent redistribution in the reaction of MePh₂SiH (**1A**) with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (**2B**). The energies are relative to the starting materials **1B** and **2B**.

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 Me_3Si^+ [CHB₁₁H₅Br₆]⁻.

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 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 $Ph_3C^+[CHB_{11}H_5Br_6]^-$ 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 iPr₂PhSi⁺[CHB₁₁H₅Br₆]⁻, as verified by X-ray crystallography (entry 3; see the ESI† for the molecular



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

Table 2	Silylium ion	generation	from	hydrosilanes	of type R ₂ PhSiH
				2	

	R ₂ PhSiH (2 equiv)	Ph ₃ C ⁺ [CHB ₁₁ H ₅ toluene rt, overnigh	5 ^{Br} 6] [−] ►	R ₃ Si ⁺ [CHB ₁₁ H₅Br ₆] [−] or R ₂ PhSi ⁺ [CHB ₁₁ H₅Br ₆]_
Entry ^a		R	Si^+	$\delta(^{29}S)$	i) ^b [ppm]
1		Ме	Me ₃ Si ⁺	93	
2^{c}		Et	Et_3Si^+	100	
3		iPr	iPr ₂ PhS	Si ⁺ 76	
4		<i>t</i> Bu	d	_	

^{*a*} All reactions were performed according to GP 2. See the ESI for details. ^{*b*} Measured in o-Cl₂C₆D₄. ^{*c*} With 4 equiv. of Et₂PhSiH and 7 days reaction time. ^{*d*} No reaction; only Ph₃C⁺[CHB₁₁H₅Br₆]⁻ was recovered.

Table 3 Silylium ion generation from hydrosilanes of type Me₂RSiH

	Me ₂ RSiH (2 equiv)	Ph ₃ C ⁺ [CHB ₁₁ toluene rt, overnig	H ₅ Br ₆] [−] ∍ ght	Me₃Si ⁺ [CHB ₁₁ H₅Br ₆] ⁻ or Me₂RSi ⁺ [CHB ₁₁ H₅Br ₆] ⁻
Entry ^a		R	Si^+	$\delta(^{29}\text{Si})^b$ [ppm]
1		Ph	Me_3Si^+	93
2		Bn	Me ₃ Si ⁺	93
3		<i>t</i> Bu	Me ₂ tBu	Si ⁺ 98

 a All reactions were performed according to GP 2. See the ESI for details. b Measured in $o\text{-}Cl_2C_6D_4.$

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).

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 Me₂*t*BuSiH completely prevented substituent redistribution, and silylium ion Me₂*t*BuSi⁺[CHB₁₁-H₅Br₆]⁻ 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-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 $(R_3Si^+[CHB_{11}H_5Br_6]^-)$ than by formation of toluenium $(R_3Si(toluene)^+[CHB_{11}H_5Br_6]^-)$ or hydrosilane-stabilized silylium ions $([R_3Si-H-SiR_3]^+[CHB_{11}H_5-Br_6]^-)$. 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 Me₂PhSiH turned out to be replaceable by other 'leaving groups', such as a benzyl or even a sterically demanding C₆Me₅ group. However, two alkyl groups must be preinstalled in the hydrosilane starting material to steer the reaction towards formation of Me₃Si⁺[CHB₁₁H₅Br₆]⁻. In contrast, hydride abstraction from MePh₂SiH with only one alkyl substituent leads to a mixture of different silylium ions, as exhaustive scrambling to Me₃Si⁺ is kinetically inhibited. Exchanging the phenyl groups in MePh₂SiH by 2,6-disubstituted aryl groups (*e.g.* C₆Me₅) 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.

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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 MePh₂SiH with $Ph_3C^+[CHB_{11}H_5Br_6]^-$, we were not able to detect this silylium ion by ${}^1H/{}^{29}Si$ HMQC NMR spectroscopy.