

Catalytic Difunctionalization of Unactivated Alkenes with Unreactive Hexamethyldisilane through Regeneration of Silylium Ions

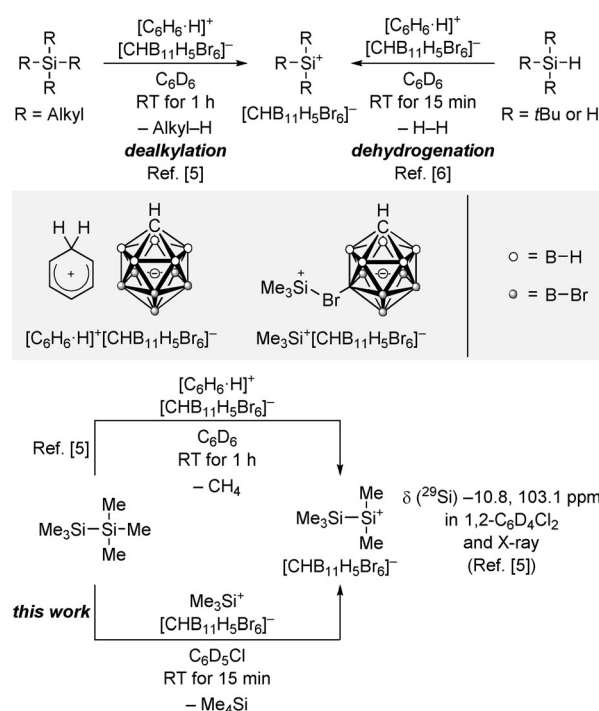
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Abstract: A metal-free, intermolecular syn-addition of hexamethyldisilane across simple alkenes is reported. The catalytic cycle is initiated and propagated by the transfer of a methyl group from the disilane to a silylium-ion-like intermediate, corresponding to the (re)generation of the silylium-ion catalyst. The key feature of the reaction sequence is the cleavage of the Si–Si bond in a 1,3-silyl shift from silicon to carbon. A central intermediate of the catalysis was structurally characterized by X-ray diffraction, and the computed reaction mechanism is fully consistent with the experimental findings.

There is a long-standing interest in the activation of the Si–Si bond in disilanes as evidenced by an ample body of literature.^[1] The vast majority of Si–Si bond-breaking reactions is mediated by transition-metal complexes to ultimately enable the catalytic transfer of both silicon units to an unsaturated molecule. Intermolecular additions across C≡C triple bonds are normally high-yielding but, unless conjugated or strained, C=C double bonds demand intramolecular delivery of the silyl groups. Also, oxidative addition of the Si–Si bond to a transition metal typically requires heteroatom substitution at the silicon atoms or incorporation of the Si–Si fragment into a small ring. There are just a few examples of the activation of unreactive hexamethyldisilane,^[2–4] and these were successfully applied to the difunctionalization of alkynes^[2] while alkenes do not react.^[3]

We recently developed a broadly applicable protolysis approach that reliably transforms otherwise inert fully alkylated silanes^[5] or hydrosilanes^[6] into counteranion-stabi-

lized silylium ions by making use of $[\text{C}_6\text{H}_6\text{-H}]^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ ^[7] as a super-strong Brønsted acid (Scheme 1, top). By this, we were able to generate $\text{Me}_2\text{-}(\text{Me}_3\text{Si})\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$, a previously elusive silyl-substituted silylium ion (Scheme 1, bottom).^[5] Interestingly, the same outcome was obtained with $\text{Me}_3\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ instead of the protonated benzene (Scheme 1, bottom); Me_3Si^+ acts like a fat proton.



Scheme 1. Dealkylative and dehydrogenative protolysis approaches to counteranion-stabilized silylium ions.

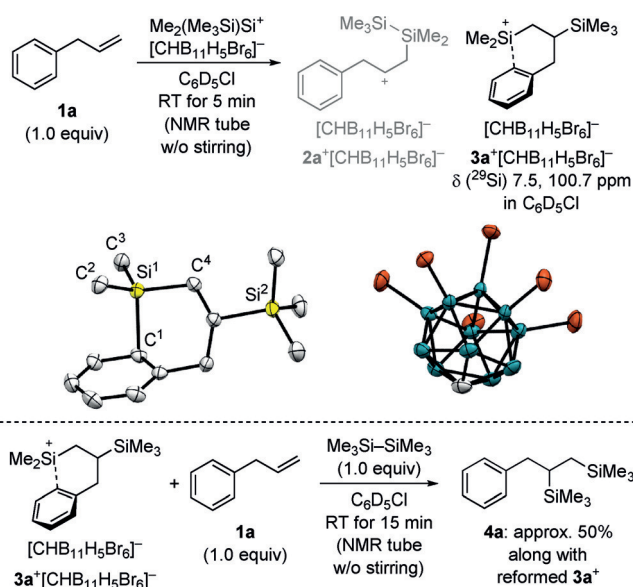
We then reacted $\text{Me}_2(\text{Me}_3\text{Si})\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ with allylbenzene (**1a**; Scheme 2, top), expecting the formation of carbenium ion **2a**⁺ stabilized by the β -silicon effect.^[8] However, we isolated silylium ion **3a**⁺ intramolecularly stabilized by the arene ring. The molecular structure of **3a**⁺ $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ was confirmed by X-ray diffraction,^[9] and the ²⁹Si chemical shifts of $\delta = 7.5$ and 100.7 ppm are consistent with a tetraalkyl-substituted silicon atom and an arene-stabilized silylium ion, respectively. There is no bond between the two silicon atoms in **3a**⁺ anymore. Knowing that silylium ions can chemoselectively cleave a Si–C(sp³) bond in hexamethyldisilane (see Scheme 1, bottom), we treated **3a**⁺

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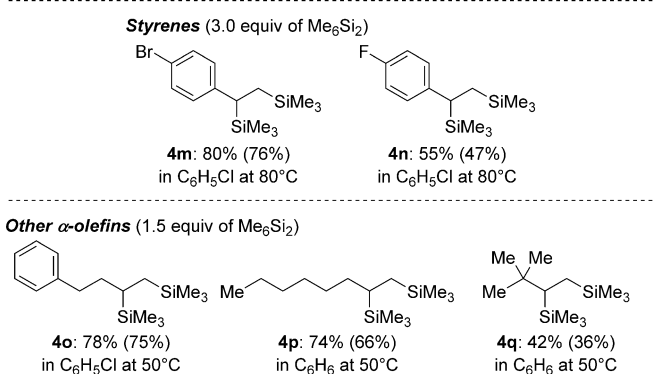
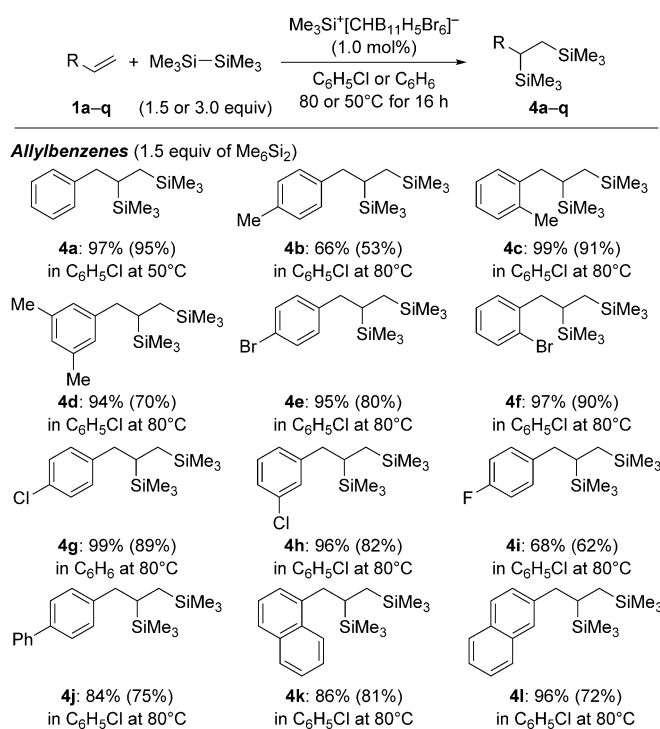
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Scheme 2. Key finding with molecular structure (top; thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity) and application to alkene difunctionalization (bottom). Selected bond lengths [Å] and angles [°]: Si^1-C^1 2.106(5), Si^1-C^2 1.848(5), Si^1-C^3 1.845(5), Si^1-C^4 1.859(4); $\text{C}^2-\text{Si}^1-\text{C}^3$ 114.9(2), $\text{C}^2-\text{Si}^1-\text{C}^4$ 115.0(2), $\text{C}^3-\text{Si}^1-\text{C}^4$ 113.3(2). B blue, Br red, C gray, Si yellow.

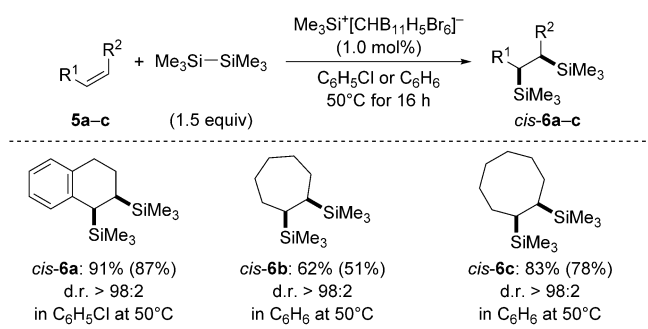
with hexamethyldisilane and alkene **1a** (1 equiv each) and found substantial formation of 1,2-bissilylated **4a** (Scheme 2, bottom). Based on this stoichiometric reaction sequence, we disclose here a catalytic alkene difunctionalization with unactivated hexamethyldisilane that does not require a metal catalyst.

The above stoichiometric experiments had established that chemoselective cleavage of one of the Si–C(sp³) bonds in hexamethyldisilane could be used to initiate and then maintain a catalytic cycle. Hence, the catalytic version of the alkene difunctionalization would rely on the self-regeneration of $\text{Me}_2(\text{Me}_3\text{Si})\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ from the disilane reactant.^[10] With 1.0 mol% of $\text{Me}_3\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ as the initiator,^[11] we quickly identified suitable reaction setups (Scheme 3). Both chlorobenzene and benzene could be employed as the solvent but yields were generally higher with chlorobenzene. However, the low boiling point of several alkenes and adducts made benzene the superior choice, particularly during purification. The reactions of volatile unfunctionalized substrates were performed at 50 instead of at 80 °C. Under these reaction conditions, the parent compound **1a** and various functionalized allylbenzenes **1b–j** as well as naphthyl-substituted **1k** and **1l** were converted into the 1,2-bissilylated adducts **4a–l** in good yields; the yields of isolated products were always slightly lower than those determined by ¹H NMR spectroscopy with an internal standard because of the low polarity of the adducts. The functional-group tolerance was as expected for silylium-ion chemistry: OMe and CF₃ groups were not compatible. An interesting case was *para*-chloro-substituted **1g**; no reaction was observed in chlorobenzene but **4g** formed quantitatively in benzene as the solvent. Styrene derivatives were prone to

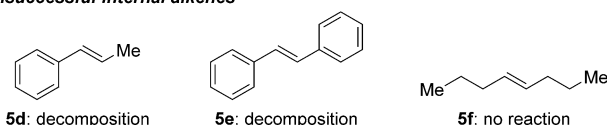


polymerization but **1m** and **1n** afforded decent yields of **4m** and **4n**, respectively, under more dilute conditions and using an excess of hexamethyldisilane. These results show that the allylic aryl group in alkene **1** and thus its coordination to the cationic silicon center attached to the γ -position in intermediate **3** are not necessary for the reaction to proceed. This was corroborated by the reaction of other α -olefins such as **1o–q**; these furnished bissilylated alkanes **4o–q** in acceptable yields.

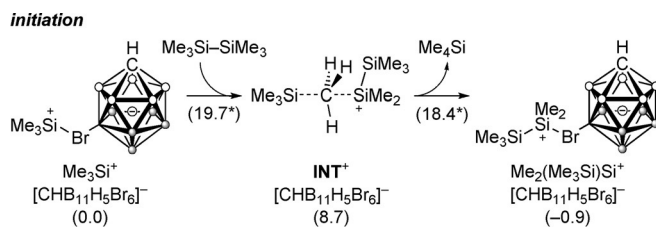
Extension of the procedure to internal alkenes was possible but limited (Scheme 4). Cyclic 1,2-disubstituted alkenes **5a–c** reacted in good yields and with superb diastereoselectivity but acyclic substrates **5d–f** did not. Tri- and tetrasubstituted alkenes decomposed. The *cis* relative configuration of *cis*-**6a–c** is rationalized by our mechanistic



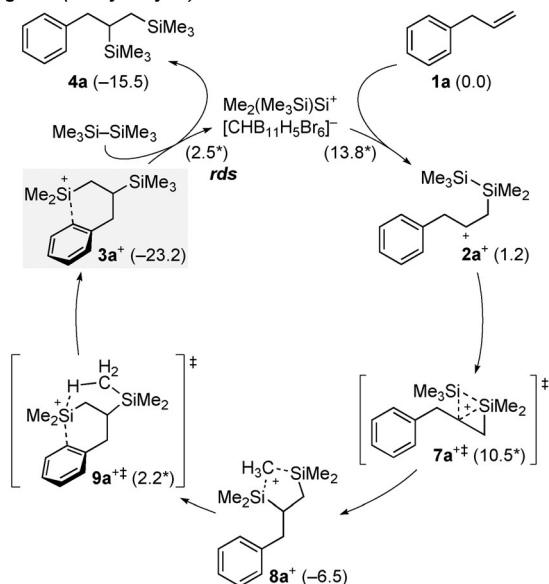
unsuccessful internal alkenes



Scheme 4. Catalytic difunctionalization of internal alkenes with hexamethyldisilane involving silylium ion self-regeneration. Yields determined by ^1H NMR spectroscopy with CH_2Br_2 as an internal standard; yields of isolated products after flash chromatography on silica gel given in parentheses.



propagation (catalytic cycle)



Scheme 5. Initiation and catalytic cycle of the silylium-ion-promoted bissilylation of allylbenzene (see the Supporting Information for calculated structures of relevant intermediates and transition states). For each reaction step, the Gibbs free reaction energies and barriers (labeled with an asterisk) in kcal mol^{-1} were computed at the PW6B95-D3 level of theory. The counteranion $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ is omitted for clarity when not acting as a stabilizing donor. rds = rate-determining step.

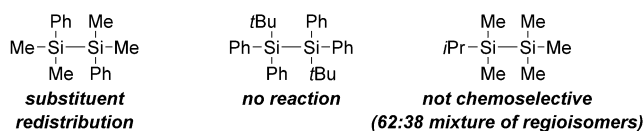


Figure 1. Other disilanes investigated.

model (see Scheme 5 and the Supporting Information for an illustration).

Disilanes other than hexamethyldisilane were also tested in the model reaction with allylbenzene (Figure 1). However, heteroleptic disilanes such as 1,1,2,2-tetramethyl-1,2-diphenyldisilane suffered from substituent redistribution.^[12] A *tert*-butyl group at the silicon atom(s) prevents this but, relying on dearylation, 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane did not participate; a stoichiometric experiment showed that $\text{Me}_3\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ cannot facilitate the dearylation step. Notably, unsymmetrically substituted 1-isopropyl-1,1,2,2,2-pentamethyldisilane furnished both regioisomers of the bissilylated alkane with a 62:38 ratio in 47% combined yield. The chemoselectivity of the demethylation obtained from a stoichiometric experiment was low (40:60 for *i*PrMe(Me_3Si) Si^+ and $\text{Me}_2(\text{iPrMe}_2\text{Si})\text{Si}^+$; see the Supporting Information for details).

Density functional theory (DFT) calculations were performed at the PW6B95-D3/def2-QZVP + COSMO-RS(chlorobenzene)//TPSS-D3/def2-TZVP + COSMO(chlorobenzene) level of theory^[13] to provide insight into the mechanism of the alkene difunctionalization in chlorobenzene solution using hexamethyldisilane as the reagent and $\text{Me}_3\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ as the initiator. The computed Gibbs free energy profiles (in kcal mol^{-1} at 298 K and 1 mol L^{-1} reference state) for the initiation and the catalytic bissilylation of allylbenzene (**1a**) and but-1-ene (model compound for alkyl-substituted α -olefins) are shown in the Supporting Information. The initiation step as well as the catalytic cycle for **1a** as the substrate are depicted in Scheme 5.

As shown in Scheme 5, top, the methyl transfer from hexamethyldisilane to $\text{Me}_3\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ is exergonic by $-0.9 \text{ kcal mol}^{-1}$ over an overall barrier of $19.7 \text{ kcal mol}^{-1}$ to form $\text{Me}_2(\text{Me}_3\text{Si})\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ along with Me_4Si . The methyl-group exchange proceeds through intermediate INT^+ over two transition states (see the Supporting Information). Counteranion-stabilized $\text{Me}_2(\text{Me}_3\text{Si})\text{Si}^+$ then enters the catalytic cycle (Scheme 5, bottom). An $\text{S}_{\text{N}}2$ -like attack of alkene **1a** at the electrophilic silicon center of $\text{Me}_2(\text{Me}_3\text{Si})\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ is endergonic by $1.2 \text{ kcal mol}^{-1}$ over a low barrier of $13.8 \text{ kcal mol}^{-1}$ to release the anion $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ and the unstable carbocation 2a^+ . A rapid 1,3-silyl shift occurs via transition state $7\text{a}^{+\ddagger}$, rearranging 2a^+ into 8a^+ with a bridging methyl group. This transformation is exergonic by $-7.7 \text{ kcal mol}^{-1}$ over a barrier of $9.3 \text{ kcal mol}^{-1}$. Another $16.7 \text{ kcal mol}^{-1}$ of stabilization is gained from reorganization of 8a^+ into intramolecular arene-silylium ion adduct 3a^+ ; the barrier with transition state $9\text{a}^{+\ddagger}$ is again low ($8.7 \text{ kcal mol}^{-1}$). The coordination of $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ to 3a^+ by a Si-Br bond is endergonic by $10.3 \text{ kcal mol}^{-1}$ and thus

unfavorable in solution. This reaction cascade is in full agreement with the experimental observation that $2\mathbf{a}^+$ was not detected and $3\mathbf{a}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ is a bench-stable separated ion pair (see Scheme 2, top). This ion pair could be viewed as a frustrated Lewis pair that subsequently engages in a propagating methyl transfer from hexamethyldisilane similar to the initiation (see Scheme 5, top). This step is endergonic by 7.7 kcal mol^{-1} over a rate-limiting barrier of $25.7\text{ kcal mol}^{-1}$ and regenerates the catalyst $\text{Me}_2(\text{Me}_3\text{Si})\text{Si}^+[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ with release of the 1,2-bissilylated alkane $4\mathbf{a}$. The catalytic cycle is exergonic by $-15.5\text{ kcal mol}^{-1}$ with an overall barrier of $25.7\text{ kcal mol}^{-1}$, consistent with the gentle heating required in the experiment.^[14]

The unreactive Si–Si bond in hexamethyldisilane is usually activated by transition-metal complexes^[2] or during a transition-metal-catalyzed process.^[4] Its intermolecular addition across unactivated alkenes is unprecedented.^[3] We have disclosed here a silylium-ion-promoted reaction that enables the catalytic bissilylation of electronically unbiased α -olefins and selected disubstituted internal alkenes. Supported by quantum-chemical calculations, the reactions mechanism is fully understood and in line with experimental observations. The transfer of a methyl group from a methyl-substituted silicon atom to a silylium-ion-like intermediate maintains catalytic turnover in this transformation, and the cleavage of the Si–Si bond occurs in a 1,3-silyl shift from silicon to carbon.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkenes · density functional calculations · homogeneous catalysis · silylium ions · Si–Si activation

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assumes the role of the Lewis base, thereby intermolecularly stabilizing the rearranged silylium ion as an adduct with the counteranion. It is less stable ($-12.0 \text{ kcal mol}^{-1}$ relative to but-1-ene) than the intramolecular arene adduct ($-23.2 \text{ kcal mol}^{-1}$ relative to allylbenzene), resulting in a lower overall barrier of

$19.2 \text{ kcal mol}^{-1}$ (vs. $25.7 \text{ kcal mol}^{-1}$), and the catalytic cycle is exergonic by $-14.2 \text{ kcal mol}^{-1}$.

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