Synthetic Methods

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Transfer Hydrosilylation

*Martin Oestreich**

cations · cyclohexa-1,4-dienes · hydrosilylation · radicals · silane transfer

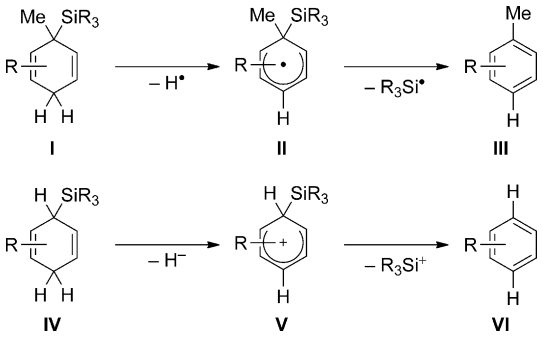
Dedicated to Professor Siegfried Blechert on the occasion of his 70th birthday

Transfer hydrogenation is without question a common technology in industry and academia. Unlike its countless varieties, conceptually related transfer hydrosilylations had essentially been unreported until the recent development of a radical and an ionic variant. The new methods are both based on a silicon-substituted cyclohexa-1,4-diene and hinge on the aromatization of the corresponding cyclohexadienyl radical and cation intermediates, respectively, concomitant with homo- or heterolytic fission of the Si–C bond. Both the radical and ionic transfer hydrosilylation are brought into context with one other in this Minireview, and early insight into the possibility of transfer hydrosilylation is included. Although the current state-of-the-art is certainly still limited, the recent advances have already revealed the promising potential of transfer hydrosilylation.

1. Concept and Strategy

A naive approach to understanding the chemistry of dihydrogen is to look at hydrosilanes. An extreme view is that the silicon atom is nothing but a "fat" hydrogen atom. Although this is clearly a gross oversimplification, the Si–H bond often serves as a useful model of the stronger H–H bond, particularly in cases where both participate in the same net reaction.

A core area of the dihydrogen arena without a counterpart in silicon chemistry is transfer hydrogenation. Known for more than a century, both heterogeneous and homogeneous methods have found broad application in industrial and academic settings.[1] Conversely, conceptually related transfer hydrosilylation processes had remained largely unknown until the research groups of Studer and Oestreich independently disclosed radical and ionic transfer hydrosilylations. Both techniques are based on silicon-substituted cyclohexa-1,4-dienes and exploit aromatization as the driving force (Scheme 1). The stepwise release of the hydrosilane provides equivalents of homolytically (**I**→**II**→**III**, top) or heterolytically (**IV**→**V**→**VI**, bottom) cleaved Si–H bonds. The radical sequence is initiated by hydrogen atom abstraction from the



Scheme 1. Silicon-substituted cyclohexa-1,4-dienes as hydrosilane surrogates in radical and ionic sequences.

methylene group in **I** (**I**→**II**) followed by fragmentation of **II** (**II**→**III**).[2] The ionic pathway consists of hydride abstraction from **IV** to yield the silicon-stabilized cyclohexadienyl cation **V**[3] (**IV**→**V**) and formal dissociation of the silicon cation (**V**→**VI**). As opposed to the heterolytic cleavage of the Si–C bond (**V**→**VI**), substitution at the silicon-bearing carbon atom in cyclohexadienyl radical **II** is required for selective Si–C bond homolysis (**II**→**III**) because otherwise release of a hydrogen atom competes.[4]

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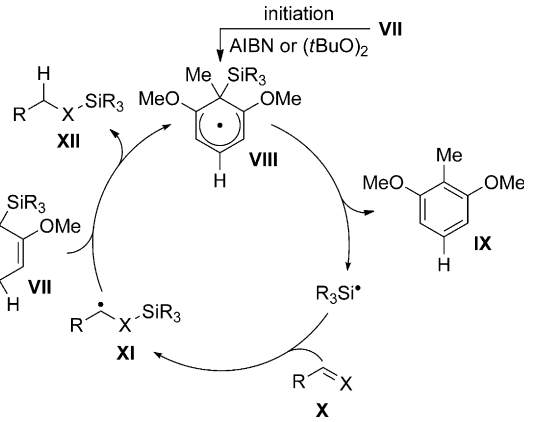
The strategy outlined above is the basis for the development of radical as well as ionic transfer hydrosilylations. This Minireview discusses and compares both approaches and highlights experimental findings that have gone almost unnoticed.

2. Radical Transfer Hydrosilylation

Studer and co-workers introduced and established silicon-substituted cyclohexa-1,4-dienes of type **VII** as radical chain reducing reagents (Scheme 2).[5] As an alternative to conventional tin hydrides, reagents **VII** enable various reductive defunctionalizations.[2,5,6] Amrein and Studer also realized that unsaturated radical acceptors such as **X** would allow the formal transfer of a hydrosilane from the cyclohexa-1,4-diene **VII** to the π-system of **X** (Scheme 2).[7,8] After initiation, the cyclohexadienyl radical **VIII** transfers the silicon fragment to acceptor **X** (**VII**→**VIII**→**IX**) to yield β-silicon-substituted radical **XI.** **XI** then acts as the chain carrier, abstracting a hydrogen atom from **VII** (**VII**→**VIII**) concomitant with formation of the hydrosilylated acceptor **XII** (**XI**→**XII**).



Scheme 2. Radical chain of the radical transfer hydrosilylation. X = CH_2 (alkenes) and O (aldehydes). AIBN = azobisisobutyronitrile.

Representative examples of **VII** are resorcinol-derived cyclohexa-1,4-dienes **1**–**3** with trialkylsilyl or heteroatom-substituted dialkylsilyl groups; **4** is an attractive surrogate for gaseous Me_3SiH (Figure 1). As mentioned above, the methyl group at the silicon-bearing carbon atom in **1**–**4** is necessary to sustain the chain reaction.[2] Aryl substituents at the silicon atom are also tolerated (not shown).

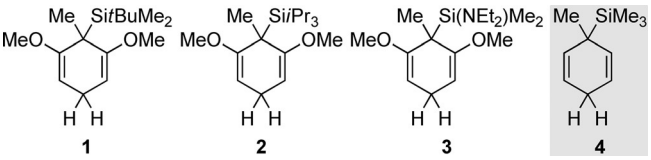
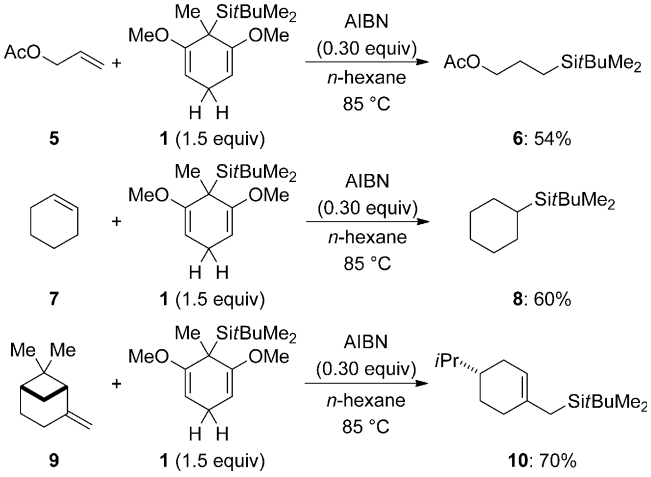


Figure 1. Typical silicon-substituted cyclohexa-1,4-dienes for radical transfer hydrosilylation.

The use of **1** (1.5 equiv) as a transfer reagent is illustrated for a few selected examples (Scheme 3).[7] Both terminal and internal alkenes react in decent yields (**5**→**6** and **7**→**8**). The acetate group is compatible with the radical process but will be too Lewis-basic for the ionic variant (see below). The 1,1-disubstituted double bond in β-pinene also accepts the silicon radical, but the initially formed radical intermediate undergoes fast ring opening prior to reduction with **1** (**9**→**10**). These transformations are the seminal examples of transfer hydrosilylation. The strength of this process is that it brings about radical hydrosilylation, which usually fails with trialkylsilanes as a result of their relatively strong Si–H bonds compared to, for example, $(Me_3Si)_3SiH$.



Scheme 3. Radical transfer hydrosilylation of alkenes.

Radical transfer hydrosilylation coupled with 5-*exo*-*trig* cyclizations is shown for different transfer reagents in Scheme 4.[7,8] The level of diastereocontrol is generally low, but the slight preference for the *cis* relative configuration is explained with the Beckwith–Houk model for these ring closures. The transfer of $tBuMe_2SiH$ released from **1** proceeds under the previously employed setup (AIBN at 85 °C; **11**→**12**). However, the reaction of a twofold excess of Me_3SiH surrogate **4** required harsher reaction conditions [$(tBuO)_2$ at 140 °C; **11**→**13**)]. It is noteworthy that even the transfer of Tamao's $(Et_2N)Me_2SiH$ from **3** works in reasonable yield, thereby providing a handle for further functional group manipulations (**11**→**14** after treatment with isopropanol).

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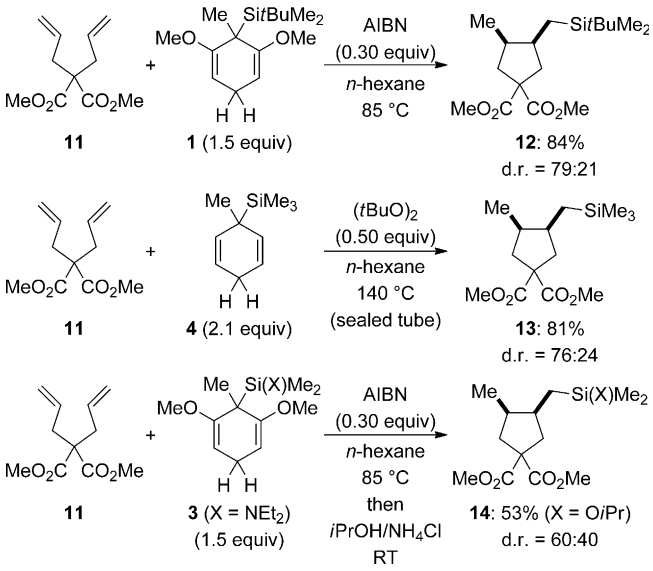
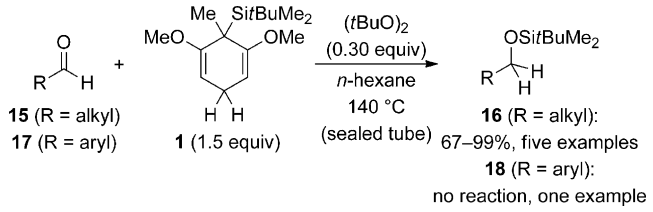


Scheme 4. Radical transfer hydrosilylation coupled with radical cyclization.

Selected triple bonds also participated in the radical transfer hydrosilylation (not shown).[8]

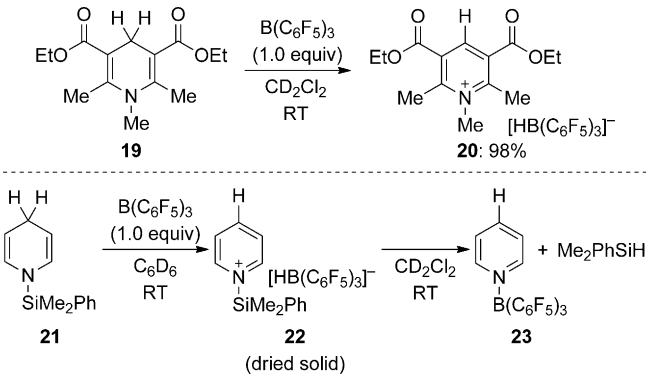
As part of their investigations, Amrein and Studer demonstrated the possibility of radical transfer hydrosilylation of aldehydes (Scheme 5).[8] These reactions had to be performed at 140 °C in a sealed tube with di-*tert*-butyl peroxide as initiator. Alkyl aldehydes **15** and even cyclohexanone (not shown) reacted readily under these conditions (**15**→**16**). Conversely, aryl aldehydes **17**, for example, benzaldehyde, were not converted into **18**, presumably because of the stability of the intermediate benzyl radical, which cannot be reduced by cyclohexa-1,4-diene **1**.



Scheme 5. Radical transfer hydrosilylation of aldehydes.

3. Ionic Transfer Hydrosilylation

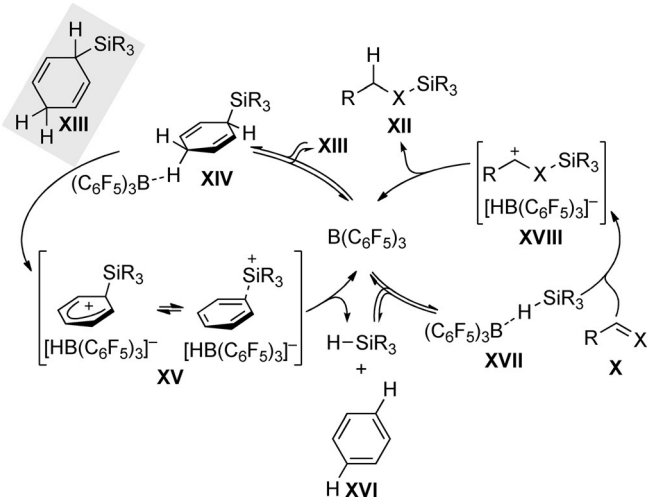
The origin of ionic transfer hydrosilylation can be seen in the $B(C_6F_5)_3$-promoted hydride abstraction from 1,4-dihydropyridines (Scheme 6). Stephan, Crudden, and co-workers systematically investigated the abstraction of hydride from Hantzsch-type dihydropyridines by the strong Lewis acid $B(C_6F_5)_3$.[9] Clean formation of the pyridinium ion with $[HB(C_6F_5)_3]^-$ as counteranion was found for Hantzsch hydride donors with an NMe rather than a free NH group (**19**→**20**, Scheme 6, top). An experiment hidden in publications by Nikonov and co-workers is even more pertinent to



Scheme 6. Hydride abstraction from 1,4-dihydropyridines by $B(C_6F_5)_3$.

ionic transfer hydrosilylation.[10] Hydride abstraction from *N*-silylated 1,4-dihydropyridine **21** generated the ion pair **22** (Scheme 6, bottom). Adduct **22** is a (reversible) frustrated Lewis pair/hydrosilane system[11] composed of pyridine/$B(C_6F_5)_3$ and Me_2PhSiH, from which the hydrosilane is slowly released (**22**→**23**, Scheme 6, bottom).

Nikonov's experiment is intriguing in the sense that the electron-deficient borane employed for the hydrosilane release from the partially reduced silicon-substituted hetarene is also a superb Lewis acid for the activation of Si–H bonds.[12] A broad spectrum of hydrosilylation reactions is in fact catalyzed by $B(C_6F_5)_3$.[13] However, pyridine and $B(C_6F_5)_3$ form Lewis pair **23**, which will hamper the subsequent Si–H bond activation. This obstacle would be overcome by using 3-silylated cyclohexa-1,4-dienes instead of *N*-silylated 1,4-dihydropyridines. The arene formed as waste in the hydrosilane release step would not interfere with $B(C_6F_5)_3$-catalyzed hydrosilylations. The overall strategy, therefore, consists of two consecutive catalytic cycles, both promoted by $B(C_6F_5)_3$ (Scheme 7).[14] A quantum-chemical treatment by Sakata and Fujimoto later confirmed the mechanism proposed for π-basic alkenes by Simonneau and Oestreich.[15] It still needs to be verified whether the concecutive process also applies to σ-basic aldehydes as these could competitively



Scheme 7. Consecutive catalytic cycles of ionic transfer hydrosilylation. X = CH_2 (alkenes) and O (aldehydes).

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capture the silicon electrophile at an earlier stage that is interrupting the hydrosilane-release cycle.

The hydrosilane-release cycle (Scheme 7, left) commences with coordination of $B(C_6F_5)_3$ to the methylene C–H group opposite to the face with the silicon group (**XIII**→**XIV**).[15] This reversible interaction eventually leads to hydride abstraction and formation of silicon-stabilized cyclohexadienyl cation **XV** (**XIV**→**XV**).[3] Intermediate **XV** was our source of inspiration, as we had initially been interested in making arene-stabilized silicon cations such as **XV** by hydride abstraction from cyclohexa-2,5-dien-1-yl-substituted silanes **XIII** with the trityl cation (the "cyclohexadienyl-leaving-group" approach).[16] Neutral $B(C_6F_5)_3$ yields, however, $[HB(C_6F_5)_3]^-$, which reduces the silicon cation in ion pair **XV** to afford the hydrosilane and arene **XVI**. That hydrosilane then enters the hydrosilylation cycle (Scheme 7, right) to form adduct **XVII**[12] in equilibrium. The $B(C_6F_5)_3$-activated hydrosilane **XVII** reacts with various π- and σ-basic substrates **X**, for example, alkenes[17] and aldehydes[18]. Formal transfer of the silicon cation onto the Lewis base is followed by borohydride reduction (**X**→**XVIII**→**XII**).

To test this above strategy, several cyclohexa-1,4-diene-based hydrosilane surrogates were prepared, for example, **24** and **25** (Figure 2, left).[14,19] Variation of the substitution

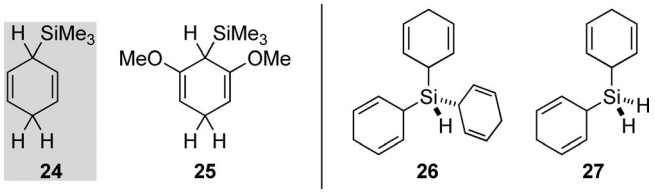
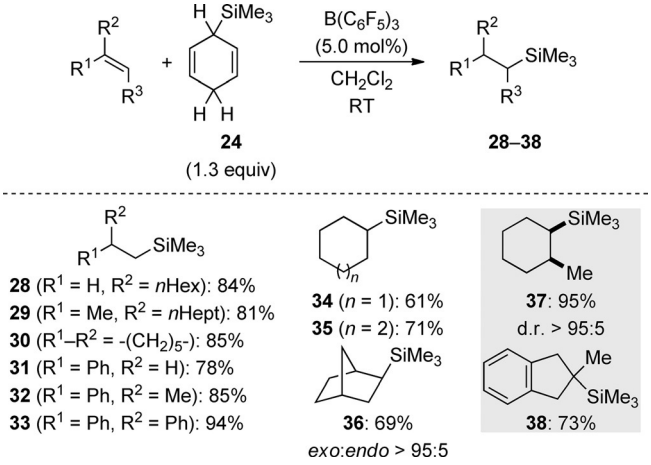


Figure 2. Silicon-substituted cyclohexa-1,4-dienes for ionic transfer hydrosilylation.

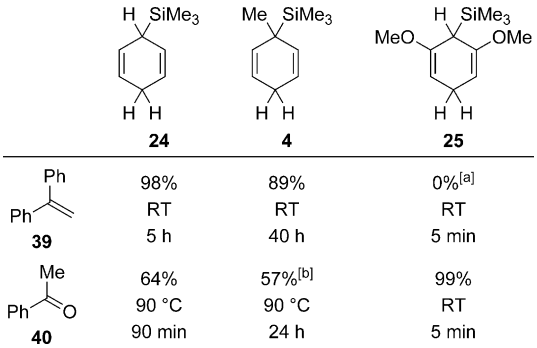
pattern at the silicon atom was also investigated, but the focus of Oestreich and co-workers was on the transfer of otherwise gaseous hydrosilanes such as Me_3SiH, Me_2SiH_2, and difficult-to-handle SiH_4. **26** and **27** are such surrogates for monosilane (Figure 2, right).[20]

The ionic transfer hydrosilylation emerged as broadly applicable to unfunctionalized alkenes (Scheme 8).[14] The reaction conditions were mild, just maintaining the reactants together with the catalyst in CH_2Cl_2[15] at room temperature. Terminal, that is, mono- and 1,1-disubstituted, alkenes reacted smoothly (→**28**–**33**), as did internal alkenes (→**34**–**38**). The *exo* selectivity seen for norbornene (→**36**) and the predominant *cis* diastereoselectivity in the hydrosilylation of 1-methylcyclohexene (→**37**) were evidence of the involvement of carbenium ion intermediates. The hydrosilylation of another trisubstituted alkene, 2-methyl-1*H*-indene, showcased the better stabilization of a benzylic compared to a tertiary carbenium ion (→**38**).

Oestreich and co-workers recently reported a systematic study of the ionic transfer hydrosilylation.[19,21] This work includes screenings of representative π- and σ-donating substrates, electronically and sterically modified surrogates, and partially or fully fluorinated triarylboranes. Selected



Scheme 8. Ionic transfer hydrosilylation of alkenes.



Scheme 9. Gauging the reactivity of surrogate/substrate combinations in ionic transfer hydrosilylation. [a] **25** completely consumed. [b] Partial deoxygenation to styrene.

representative data are depicted in Scheme 9. The reduction of σ-basic acetophenone (**40**) using standard **24** requires higher temperature than that of π-basic 1,1-diphenylethylene (**39**) because **40** forms a stronger Lewis acid/base adduct with $B(C_6F_5)_3$ (column 1). Cognate **4**, previously used by Studer and co-workers in the radical transfer hydrosilylation,[7] with an additional methyl group at the silicon-bearing carbon atom is less reactive (column 2). Resorcinol-derived **25**, which mimics Studer's reagents (cf. Figure 1), is far more reactive than **24** because of its enhanced hydricity (column 3). However, the Lewis-basic methoxy groups in **25** compete with the substrate for the transfer of the silicon electrophile (cf. **XVII**→**XVIII**, Scheme 7). The π-basic alkene is not sufficiently nucleophilic, and demethylation of the resorcinol dimethyl ether was observed. Conversely, the carbonyl hydrosilylation was complete at room temperature within minutes.

A crucial test of transfer hydrosilylation is whether it would enable the transfer of monosilane. The serious safety issues associated with handling SiH_4 have deterred synthetic chemists from its use, and conventional hydrosilylation with this dangerous gas is barely researched. Simonneau and Oestreich introduced solid **26** and liquid **27** as monosilane surrogates to ionic transfer hydrosilylation (Figure 2, right and Scheme 10).[20] It was shown that $B(C_6F_5)_3$ unleashes SiH_4

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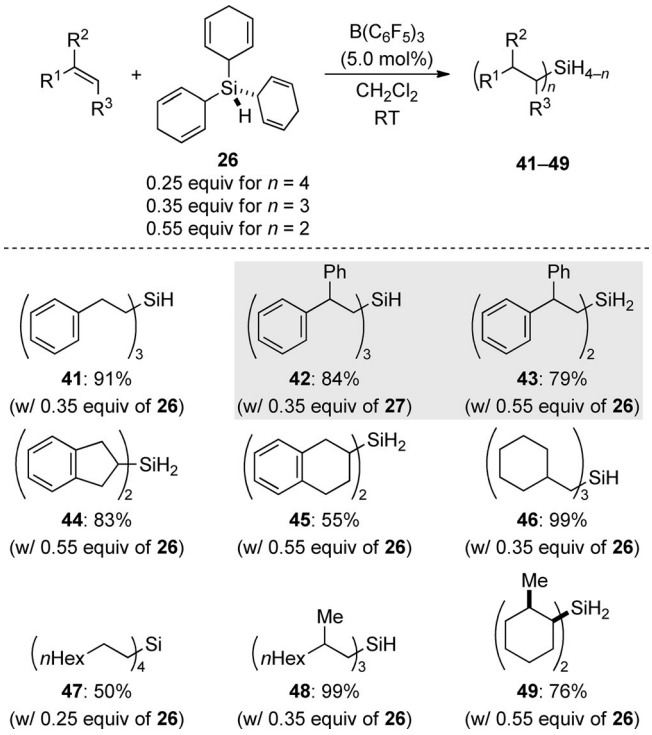


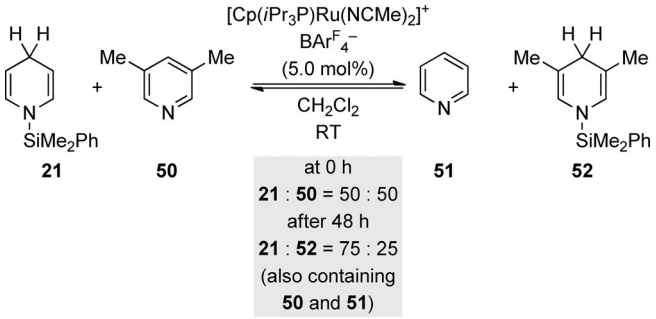
Scheme 10. Ionic transfer hydrosilylation of alkenes with monosilane.

prior to *n*-fold hydrosilylation of typical alkenes. The chemoselectivity is determined by steric demand and cannot be controlled by the ratio of the reactants. In one case, the use of **27** (0.35 equiv) or **26** (0.55 equiv) led to the selective formation of monohydrosilane **42** ($n=3$) and dihydrosilane **43** ($n=2$), respectively (gray box). An α-olefin afforded the tetraorganosilane (→**47**), but the other transfer reactions yielded either mono- or dihydrosilanes with synthetically useful selectivities, including styrene (→**41**).

4. Outlook

Transfer hydrosilylation is at the early stages of development, but the variants disclosed by the groups of Studer[7,8] and Oestreich[14,19,20] have already indicated its potential. The radical process is superior to $B(C_6F_5)_3$ catalysis because of its compatibility with Lewis-basic functional groups, carboxyl groups in particular. Moreover, the ionic pathway cannot transfer silicon groups with bulky substituents, for example, tBuMe$_2$Si and iPr$_3$Si.[14] The reaction temperature of the cationic process is, however, an advantage when transferring gaseous and hence difficult-to-handle hydrosilanes, for example, Me$_3$SiH, Me$_2$SiH$_2$, and SiH$_4$. The focus of the work of Simonneau and Oestreich is on these pyrophoric and explosive hydrosilanes, and the monosilane surrogates finally allow safe synthetic chemistry with this hazardous smallest member of the hydrosilane family.

These transfer hydrosilylations are transition-metal free, and this naturally raises the question whether transition metals are also able to catalyze the transfer of a hydrosilane from one molecule to another. Reversibility of the hydrosilylation would be a basic requirement for this. It was again the groups of Nikonov[10] and later Oestreich[22] who demonstrated such reversibility for 1,4-selective pyridine hydrosilylation (Scheme 11). Nikonov's fundamental discovery is



Scheme 11. Reversible hydrosilylation of pyridines: An example of a transition-metal-catalyzed transfer hydrosilylation. BAr$^F_4{}^-$ = tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate.

again buried in his method-oriented publications (cf. Scheme 6, bottom). A ruthenium catalyst promotes hydrosilane transfer from an *N*-silylated 1,4-dihydropyridine to 3,5-lutidine (**21**→**52**, Scheme 11); a nitrile also served as an acceptor (not shown).[10] This proof of concept of a transition-metal-catalyzed transfer hydrosilylation could prove viable in the future.

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