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Transfer Hydrosilylation

3-Silylated Cyclohexa-1,4-dienes as Precursors for Gaseous Hydrosilanes: The $B(C_6F_5)_3$-Catalyzed Transfer Hydrosilylation of Alkenes**

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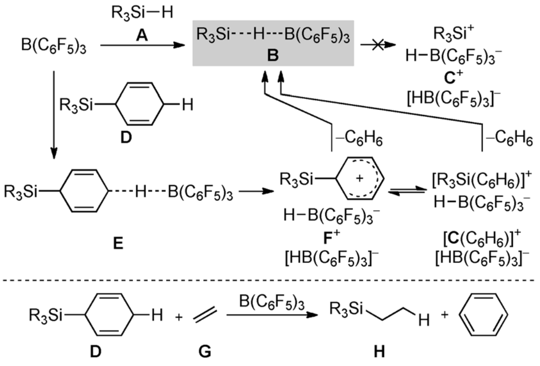
Alkene hydrosilylation is one of the prevalent methods for C–Si bond formation in academic as well as industrial settings, as reflected by a plethora of publications and patents.[1] Usually catalyzed by precious late-transition-metal complexes, substantial progress is currently being made in the design of catalysts based on more abundant transition metals.[2] Various triorganosilanes (R_3SiH) but also flammable trichlorosilane (Cl_3SiH) and harmful trialkoxysilanes ($(RO)_3SiH$ with $R =$ Me or Et) are commonly employed in these catalytic processes. Conversely, Me_3SiH and Me_2SiH_2 are rarely applied, as handling of these highly flammable and potentially explosive gases is, aside from safety concerns, particularly inconvenient on a laboratory scale. Practical methods avoiding these issues would, therefore, be relevant to several areas of silicon chemistry.

Our laboratory had shed light into the mechanism of the Si–H bond activation with the strong Lewis acid $B(C_6F_5)_3$[3,4] where the intermediacy of a silicon cation as a result of hydride abstraction was excluded (**A**→**B** but not $\mathbf{C}^+$, Scheme 1, upper).[5] We asked ourselves whether $B(C_6F_5)_3$ could be used for the deliberate generation of silicon cations by the activation of a bisallylic C–H bond in 3-silylated cyclohexa-1,4-dienes **D** (Scheme 1, upper). Formation of a transient intermediate **E** (**D**→**E**) would be followed by hydride abstraction ($\mathbf{E}\rightarrow\mathbf{F}^+$), arriving at the silicon-substituted Wheland complex $\mathbf{F}^+$ that could rearomatize with release of a benzene-stabilized silicon cation[6] ($\mathbf{F}^+\rightarrow[\mathbf{C}(\text{benzene})]^+$). Aware that neither $\mathbf{F}^+$ nor $[\mathbf{C}(\text{benzene})]^+$ are likely to exist in the presence of $HB(C_6F_5)_3^-$, the sequence would eventually produce intermediate **B**. The 3-silylated cyclohexa-1,4-dienes **D** would thus serve as viable hydrosilane precursors in $B(C_6F_5)_3$ catalysis,[4] and we planned to apply this new strategy to the in situ generation of otherwise gaseous Me_3SiH and Me_2SiH_2. The $B(C_6F_5)_3$-activated hydrosilanes **B** would then be reacted with an alkene **G**,[7,8] and the net reaction corresponds to an unprecedented ionic transfer hydrosilylation of alkenes (**D**→**H**, Scheme 1, lower).[9,10]



Scheme 1. Assumed pathway for the $B(C_6F_5)_3$-catalyzed release of hydrosilanes from 3-silylated cyclohexa-1,4-dienes (upper) and planned ionic transfer hydrosilylation of alkenes (lower).

To assess the validity of our hypothesis, we synthesized trimethylsilyl- and dimethylsilyl-substituted cyclohexa-1,4-dienes **1** and **2** as well as a series of representative triorganosilylated congeners **3**–**5** (Figure 1). These were all accessed in one step by the reaction of lithiated cyclohexa-1,4-diene with the corresponding chlorosilane (see the Supporting Information for details).

At the outset, we decided to focus on the use of **1**, as it is an attractive trimethylsilane precursor. We investigated its reactivity toward catalytic amounts of $B(C_6F_5)_3$ in $[D_8]$toluene as well as CD_2Cl_2. Species **1** rapidly transformed into Me_3SiH and benzene (see the Supporting Information for a time-dependent ^1H NMR analysis).[11] We then conducted the same experiments in the presence of 1-methylcyclohexene (**6a**; Table 1). While conducting the reaction in *n*-pentane led to complete recovery of the starting material (entry 1), we were delighted to find that transfer hydrosilylation is effective when switching to arene solvents, affording trimethyl(2-methylcyclohex-1-yl)silane (**7a**) with excellent *cis* selectivity in moderate yields (entries 2 and 3). Results were even more satisfying in halogenated solvents. The yield slightly improved in 1,2-dichloroethane (entry 4), and transfer hydrosilylation occurred in even higher yield in CH_2Cl_2 (entry 5). With this solvent, the amount of transfer reagent **1** was optimized. An increase of the equivalents of **1** from 1.15 to 1.30 afforded excellent 95% yield determined by GLC analysis, and 87% yield of isolated product was obtained at larger scale (entry 6). This result could not be improved any further by

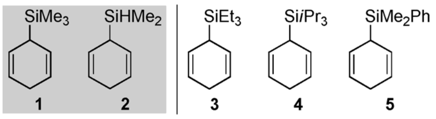


Figure 1. Various 3-silylated cyclohexa-1,4-dienes tested as transfer hydrosilylation reagents.

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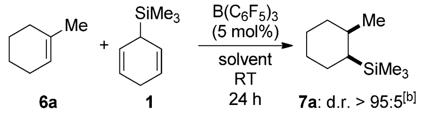
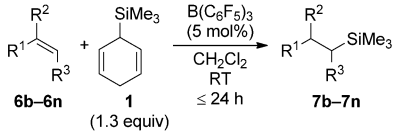
Table 1: Optimization of the transfer hydrosilylation employing trimethylsilane precursor **1**.[a]

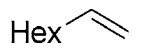
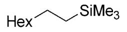
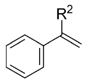
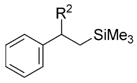
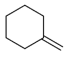
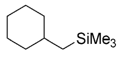
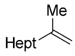
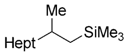
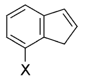
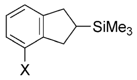
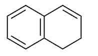
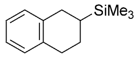
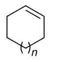
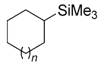
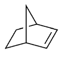
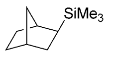
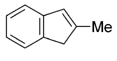
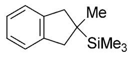


Entry	Equiv of **1**	Solvent	Yield of **7a** [%][c]
1	1.15	*n*-pentane	–[d]
2	1.15	toluene	48
3	1.15	benzene	53
4	1.15	1,2-dichloroethane	68
5	1.15	CH_2Cl_2	82
6	**1.30**	$\mathbf{CH_2Cl_2}$	**95 (87)**[e]
7	1.50	CH_2Cl_2	93
8[f]	1.30	CH_2Cl_2	–

[a] Unless otherwise noted, all reactions were conducted using $B(C_6F_5)_3$ (5 mol%) with a substrate concentration of 1.0 M in the indicated solvent at room temperature on a 0.2 mmol scale. [b] Obtained as a single diastereomer according to NMR spectroscopic analysis. Assigned by analogy with the related $B(C_6F_5)_3$-catalyzed hydrosilylation using $PhMe_2SiH$.[7] [c] Determined by GLC analysis using tetracosane as internal standard. [d] $B(C_6F_5)_3$-catalyzed liberation of Me_3SiH from **1** but no consumption of the alkene. [e] Yield of isolated product on a 0.5 mmol scale. [f] No catalyst.

Table 2: $B(C_6F_5)_3$-catalyzed transfer hydrosilylation of various alkenes employing reagent **1**.



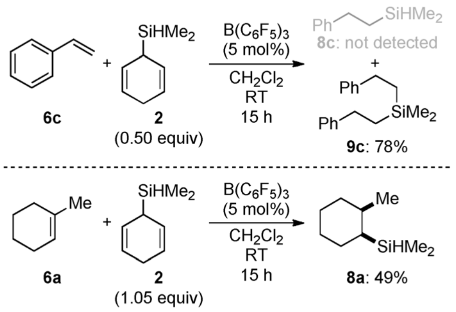
Entry	Alkene			Alkyltrimethylsilane		Yield [%][a]
1			**6b**		**7b**	84
2		$R^2 = H$	**6c**		**7c**	78
3		$R^2 = Me$	**6d**		**7d**	85
4		$R^2 = Ph$	**6e**		**7e**	94
5			**6f**		**7f**	85
6			**6g**		**7g**	81
7		X = H	**6h**		**7h**	69
8		X = Br	**6i**		**7i**	65
9			**6j**		**7j**	66
10		*n* = 1	**6k**		**7k**	61
11		*n* = 2	**6l**		**7l**	71
12			**6m**		**7m**	69[b]
13			**6n**		**7n**	73[c]

[a] Yield of isolated product after purification by flash chromatography on silica gel or Kugelrohr distillation. [b] *exo*:*endo* > 95:5 according to NMR spectroscopic analysis. [c] Obtained along with trace amounts of the other regioisomer (relative configuration not assigned).

adding more of **1** (entry 7). No reaction was seen in the absence of the $B(C_6F_5)_3$ catalyst (entry 8). It is remarkable that only little excess of **1** is necessary for high yield, because Me_3SiH is gaseous at room temperature. Another practical aspect of this reaction is that the byproducts, benzene and unreacted Me_3SiH, are easily removed from the crude reaction mixture.

With the optimized procedure in hand, we subjected various terminal and internal alkenes to the transfer hydrosilylation. Gratifyingly, our method emerged as widely applicable with all examples reacting at room temperature in acceptable reaction times (Table 2). The monosubstituted alkene oct-1-ene (**6b**) was converted in good yield of isolated product with complete *anti*-Markovnikov regioselectivity (entry 1). Typical styrenes **6c**–**6e** showed excellent reactivity, and the yield correlated with the cation-stabilizing ability of the α substituent in the order H < Me < Ph (entries 2–4). A few other 1,1-disubstituted alkenes were screened, and we were pleased to find that methylenecyclohexane (**6f**) furnished cyclohexylmethyl-substituted **7f** in high yield (entry 5); a comparable result was obtained with 2-methylnon-1-ene (**6g**; entry 6). We then turned to endocyclic alkenes. Applying our method to indenes **6h** and **6i** allowed us to isolate indanes **7h** and **7i** with a trimethylsilyl group at C2 (entries 7 and 8). Similarly, 1,2-dihydronaphthalene (**6j**) displayed regioselectivity in favor of C–Si bond formation in the homobenzylic position of **7j** (entry 9). Cyclic alkenes, such as cyclohexene (**6k**) and cycloheptene (**6l**), were converted into the corresponding cycloalkyltrimethylsilanes **7k** and **7l**, respectively (entries 10 and 11); the rather low yield of **7k** might be explained by its volatility. The transfer hydrosilylation of norbornene (**6m**) proceeded smoothly, exclusively yielding **7m** with *exo* selectivity (entry 12). This perfect *exo* selectivity is in agreement with that of another Lewis acid-catalyzed hydrosilylation.[12] Finally, indene **6n** with a methyl group at C2 showed an unexpected preference for selective C–Si bond formation in the more hindered position (entry 13) as opposed to the regioselective hydrosilylation of 1-methylcyclohexene (cf. **6a**→**7a**, Table 1). This finding indicates that stabilization of the positive charge developed at the (former) alkene carbon atoms during and after the transfer of the electrophilic silicon atom onto the trisubstituted double bond overrides steric factors. A secondary but benzylic carbocation outrivals a tertiary in this particular case (**6n**→**7n**). However, the C–C double bond is still sterically accessible in trisubstituted **6a** and **6n** whereas congested tetramethylethylene was too hindered to react with the $B(C_6F_5)_3$-activated Me_3SiH (not shown).[13]

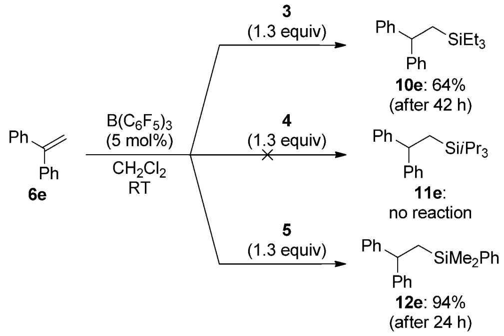
Encouraged by this success, we addressed the release and transfer of Me_2SiH_2 from precursor **2** (Scheme 2). The silicon atom in **2** is decorated with an Si–H bond that could participate in another $B(C_6F_5)_3$-catalyzed hydrosilylation.[7] Indeed, its reaction with equimolar amounts of styrene (**6c**) in the presence of 5 mol% $B(C_6F_5)_3$ led to both single and double hydrosilylation, as evidenced by GLC-MS analysis (**6c**→**8c**/**9c**; not shown). Adjusting the stoichiometry to 0.5 equiv of **2** allowed us to form **9c** arising from double addition selectively (Scheme 2, upper). We then reasoned that reaction with a sterically more demanding alkene would stop at the stage of monoaddition. Transfer hydrosilylation of the trisubstituted alkene **6a** with a slight excess of **2** yielded **8a**



Scheme 2. Reactivity of dimethylsilane precursor **2**: double (upper) versus single hydrosilylation (lower) governed by steric factors.

with the Si–H bond still intact as the major product along with unidentified heavier compounds (Scheme 2, lower).

To further demonstrate the generality of our method, we examined the transfer hydrosilylation from cyclohexa-1,4-dienes **3**–**5** onto alkene **6e** (Scheme 3). Compared to **1** with its trimethylsilyl group, **3** and **4** are more bulky. Transfer of the triethylsilyl group was possible, but required prolonged reaction time (**6e**→**10e** using **3**); the triisopropyl moiety did not transfer at all[7] (**6e**→**11e** using **4**). Complete conversion of **4** into *i*Pr$_3$SiH and benzene by $B(C_6F_5)_3$ was however observed. As the trimethylsilyl group is not easily functionalized,[14] we included precursor **5** with a phenyl-substituted silicon atom into our survey. That would later allow for oxidative degradation of the C–Si bond. The reaction with **5** afforded the target compound in near quantitative yield (**6e**→**12e** using **5**).



Scheme 3. Transfer hydrosilylation with triorganosilylated cyclohexa-1,4-dienes **3**–**5**.

To summarize, we disclosed herein an unprecendented ionic transfer hydrosilylation of alkenes. The ability of the commercially available Lewis acid $B(C_6F_5)_3$ to catalyze the release of hydrosilanes from 3-silylated cyclohexa-1,4-dienes was instrumental for this. The hydrosilylation of alkenes is promoted by the same catalyst.[7] With the easy-to-handle 3-trimethylsilyl- or 3-dimethylsilylcyclohexa-1,4-dienes **1** and **2**, we applied this method to the in situ generation of gaseous Me$_3$SiH and Me$_2$SiH$_2$, silanes that are often prohibited from laboratories for safety considerations.

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