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$B(C_6F_5)_3$ catalyzed hydrosilation of enones and silyl enol ethers

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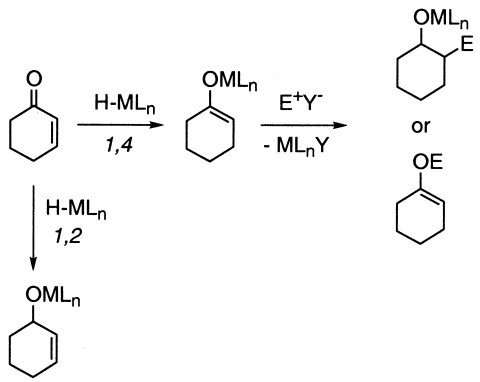
Abstract—The 1,4 hydrosilation of a variety of simple α,β-unsaturated enones as catalyzed by $B(C_6F_5)_3$ (1–2%) is described. For substrates with no steric hindrance near the β-carbon, 1,4 addition of silane is very clean; in other instances, 1,2 hydrosilation is competitive. The reaction is facile with five commercially available silane reagents. For two examples, a novel hydrosilation of the resulting silylenol ethers was also observed. The net *trans* stereochemistry of H–Si addition to the silylenol ether C=C bond was established and points to a stepwise mechanism for this reaction. This was supported by the observation and full spectroscopic characterization of a silylcarboxonium ion intermediate with an $[HB(C_6F_5)_3]^-$ counteranion in the hydrosilation of the silylenol ether derived from 4,4-dimethyl-2-cyclohexen-1-one and $PhMe_2SiH$.

1. Introduction

The selective reduction of α,β-unsaturated carbonyl compounds is an important transformation in organic synthesis and a number of methods exist for carrying out either selective 1,2[1,2] or 1,4-reductions[2] (Scheme 1). For the latter purpose, stoichiometric copper hydride[3] and alumino- or borohydride reductants[1,4] are particularly effective. Various strategies for effecting asymmetric conjugate reductions have also recently been described.[5] The resulting masked enolates have the potential to be synthetically elaborated by reaction with a variety of electrophiles and indeed, tandem reactions involving conjugate hydride addition followed by reaction with an electrophile have been effected successfully.[6]



Scheme 1.

A number of strategies in which hydrosilanes serve as the stoichiometric reductant have been reported[7–9] although Lewis acid catalyzed processes are rare.[2a,10] These reactions are noteworthy since the enolate produced is masked as a stable silyl enol ether which could be subsequently employed in a number of important C–C and C–X bond forming reactions.[6b,11] Developing new, experimentally convenient methods for the preparation of silyl enol ethers via conjugate reduction remains an important synthetic endeavor particularly using commercially available Lewis acid catalysts.

Tris-pentafluorophenylborane, $B(C_6F_5)_3$, has been shown by us and others to be a versatile Lewis acid capable of catalyzing a number of organic transformations.[12] In particular, this stable, highly electrophilic organometallic Lewis acid can catalyze the condensation or dehydrocoupling reactions of various group 14 reagents with common organic functions. For example, $B(C_6F_5)_3$ catalyzes the hydrosilation of carbonyl,[13] imine[14] and alkene[15] functions and the reductive silation of alcohols[16] and ethers.[17] The condensation of allylstannanes and hydrostannanes with alkyne[18] and carbonyl functions[19] has also been demonstrated. Finally, aldol-type reactions between silyl enol ethers or silylketene acetals with aldehydes and aldimines have been reported.[20]

Two general mechanistic pathways have been shown to be operative in $B(C_6F_5)_3$ catalyzed reactions depending on the particular group 14 reagent and/or organic compound being used. These pathways differ depending on whether $B(C_6F_5)_3$ first activates the organic function to nucleophilic attack by the Group 14 reagent, Scheme 2 path (a) or vice versa, Scheme 2 path (b). The former,

Keywords: Lewis acid catalysis; hydrosilation; enones; silylenol ethers; tris-(pentafluorophenyl)borane.

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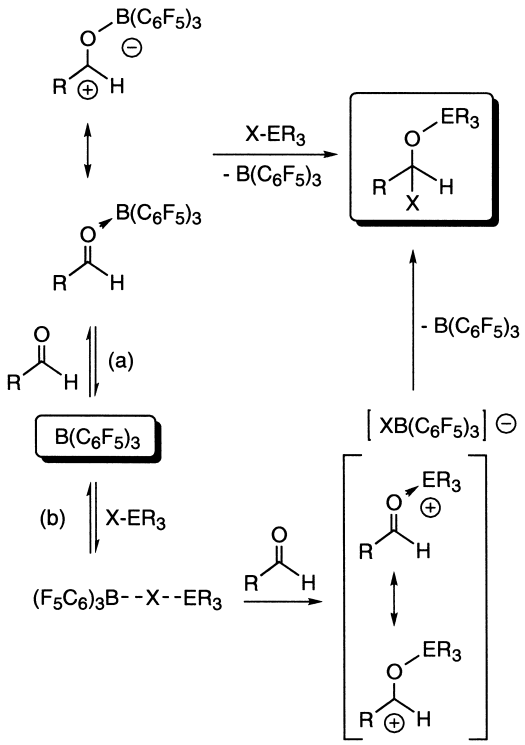


Scheme 2.

more conventional case, is tacitly assumed to occur in many cases such as in the addition of silyl enol ethers and silylketene acetals to aldehydes and aldimines.[20] We have shown that $B(C_6F_5)_3$ activates aromatic aldehydes to nucleophilic attack by allylstannane but that subsequent O–Sn bond formation with release of $B(C_6F_5)_3$ does not occur.[21] Instead, the resulting aldehyde-coordinated stannylium species propagates C–C bond making by reaction with another molecule of allylstannane, the initially formed alkoxyborate anion remaining intact throughout the catalytic cycle. This study illustrates that even when conventional mechanisms are operative, more complicated behavior may be occurring.

The second mode of reactivity involves initial Lewis acidic activation of the group 14 reagent to nucleophilic attack by the organic function, as illustrated by path b in Scheme 2. We have found this mechanism to be operative in $B(C_6F_5)_3$ catalyzed hydrosilation reactions. Extensive mechanistic studies show that $B(C_6F_5)_3$ polarizes the Si–H bond of hydrosilanes rendering the silicon susceptible to nucleophilic attack (ionization) by carbonyl functions.[13] The resulting hydridoborate anion, $[H–B(C_6F_5)_3]^-$, consummates hydrosilation regenerating $B(C_6F_5)_3$. Evidence has been provided that this type of mechanism likely occurs in the hydrosilation of imine,[14] alkene[15] and alcohol[16] functions as well.

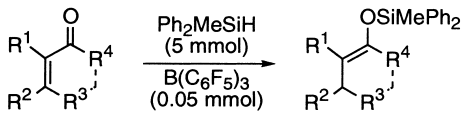
In this paper, we show that 1,4-hydrosilation of α,β-unsaturated ketones and the hydrosilation of silyl enol ethers can be appended to the list of useful reactions catalyzed by $B(C_6F_5)_3$. Both of these hydrosilation reactions are proposed to occur via a mechanistic pathway akin to that shown in Scheme 2(b).

2. Results and discussion

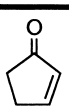
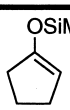
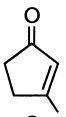
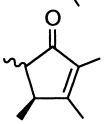
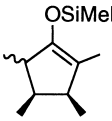
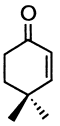
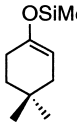
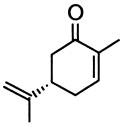
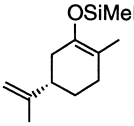
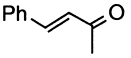
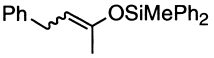
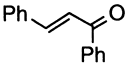
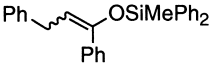
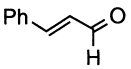
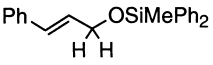
2.1. 1,4-Hydrosilation of enones

$B(C_6F_5)_3$ is an effective catalyst for carrying out 1,4-hydrosilation of unfunctionalized α,β-unsaturated ketones, Table 1. In general, these exothermic reactions are high yielding and only require small catalyst loadings. In cases where high yields of the 1,4-addition products are isolated, GC–MS analysis does indicate the presence of small amounts of an isomer which is presumably the 1,2-addition product. Reactions of 3-methyl-2-cyclopentenone (entry 3)

Table 1. $B(C_6F_5)_3$ catalyzed hydrosilation of enones

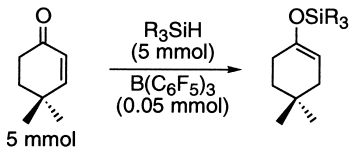


5 mmol

Entry	Enone	Product	Yield
1			81%
2			90%
3		complex mixture	--
4			55%
5			82%
6			96%
7			92%
8		 3:2 *E:Z*	85%
9		 1:10 *E:Z*	92%
10			88%
11		complex mixture	--

and methyl vinyl ketone (entry 11) lead to complex reaction mixtures containing both 1,2 addition products and oligomers.[22] Some oligomerization/polymerization[23] likely occurs in all cases, but the reactions can be biased towards the desired 1,4 reduction by manipulating reaction conditions. For example, in the case of 2-cyclopentenone (entry 1), clean 1,4-hydrosilation occurs at room temperature, whereas when the reaction is performed at low temperature, a complex reaction mixture indicative of these side reactions is observed. While linear α,β-unsaturated ketones undergo 1,4 hydrosilation under these conditions (entries 8 and 9), the corresponding aldehyde, *trans*-cinnamaldehyde, undergoes predominant 1,2-hydrosilation (entry 10); only small amounts of 1,4-hydrosilation are indicated by GC–MS analysis of the reaction mixtures. 1,2-Hydrosilation is also observed to predominate in substrates which incorporate steric bulk in the β-position (entry 3) but when both pathways are equally sterically problematic, the 1,4 addition is favored (for example, entry 4). The product mixture for the substrate of entry 4 consists of a 9:1 mixture of diastereomers (GC/MS and NMR spectroscopy), but both can be assigned as 1,4 addition products on the basis of the presence of only one vinylic methyl resonance for both diastereomers. The lower yield in this case was due to unavoidable product decomposition in the work-up procedure. Finally, as shown in Table 2, a variety of other commercially available silanes can be employed, although $^{i}Pr_3SiH$ does not react. We have previously noted the ineffectiveness of this silane in the silation of alcohols.[16]

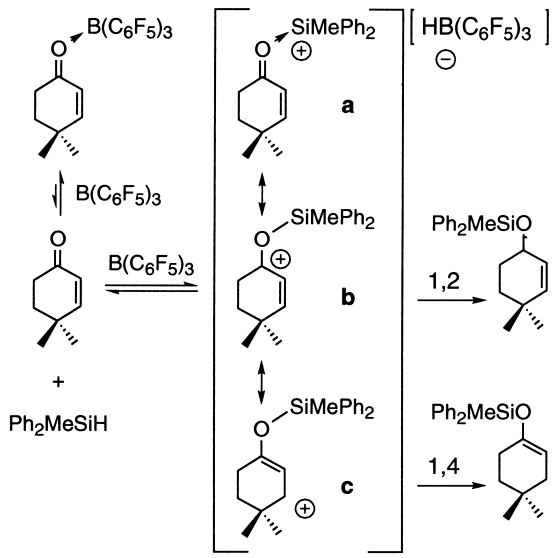
Table 2. $B(C_6F_5)_3$ catalyzed hydrosilation of 4,4-dimethyl-2-cyclohexen-1-one with various silanes



Entry	Silane	Yield (%)
1	Ph_2MeSiH	96
2	$^{t}BuMe_2SiH$	86
3	$PhMe_2SiH$	88
4	Et_3SiH	91
5	Ph_3SiH	86
6	$^{i}Pr_3SiH$	–

Although there exist many methods to effect the conjugate addition of hydride to enones, this method is attractive for a number of reasons. Small catalyst loadings are used (1%) and the products are readily purified by column chromatography using Et_3N/hexanes as eluent or by distillation. Unlike many other 1,4-reduction protocols, the products formed retain the 'enolate' functionality in the useful form of a silyl enol ether, an effective functional group for C–C bond formation via Lewis acid catalyzed aldol condensations.[20] The potential thus formally exists for developing tandem one-pot 1,4-hydrosilation/aldol or other alkylation reaction protocols where both reactions are catalyzed by $B(C_6F_5)_3$. Alternatively, the silyl enol ether products can be readily hydrolyzed leading to the saturated ketone derivatives providing a convenient method for the selective reduction of the 'ene' portion of enones. Finally, although extensive studies on more heavily functionalized substrates have not been done, previous work in our lab established that the $B(C_6F_5)_3$/silane reduction system is compatible with a variety of functions, provided they are not more basic than the enone moiety. This is exemplified here by the substrate in entry 7, which also contains a potentially reducible C–C double bond.[15]

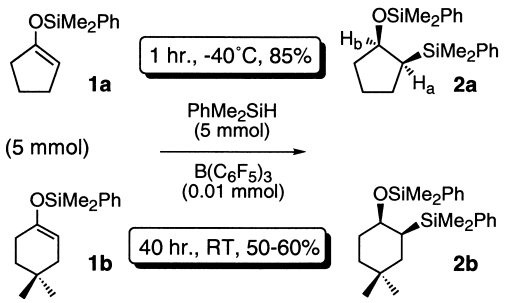
Based on the mechanistic work performed on saturated carbonyl[13] and imine[14] functions, we presume these reactions proceed similarly, i.e. via a silane activated pathway akin to that shown in Scheme 2(b). Thus, as depicted in Scheme 3, activation of silane by $B(C_6F_5)_3$ leads to silylcarboxonium intermediates stabilized by the hydridoborate counteranion $[HB(C_6F_5)_3]^-$; this ion pair then collapses to product via delivery of hydride from the hydridoborate. However, ^{19}F NMR analysis of a mixture of the substrate of entry 6, Table 1, 4,4-dimethyl-2-cyclohexen-1-one, $B(C_6F_5)_3$ and $PhMe_2SiH$ at −40°C (a temperature at which reaction is occurring) reveals only the presence of the borane/ketone adduct, and no evidence for formation of a hydridoborate stabilized silylcarboxonium ion pair is observed. Nonetheless, formation of the silylcarboxonium ion pair is the likely path to reduction, and hydride delivery to the silylcarboxonium ion can occur via three resonance structures, as shown in the Scheme. Attack at the silicon (**a**) results merely in starting materials, while hydride delivery which effects net 1,2 or 1,4 addition occurs via resonance structures **b** and **c**, respectively. This appears to be governed to some extent by steric effects in that 1,2 addition competes effectively for β-substituted enones (Table 1, entries 3 and 11) or aldehydic substrates (entry 10).



Scheme 3.

2.2. $B(C_6F_5)_3$-catalyzed hydrosilation of silyl enol ethers

In the above reactions, we found that careful control of the equivalency of the silane reagent is necessary since the silyl enol ether products are themselves susceptible to hydrosilation. This is particularly true for the more reactive silanes, for example $PhMe_2SiH$. With this silane, 1,4 hydrosilation of 2-cyclopenten-1-one or 4,4-dimethyl-2-cyclohexen-1-one is rapid, forming the silyl enol ethers

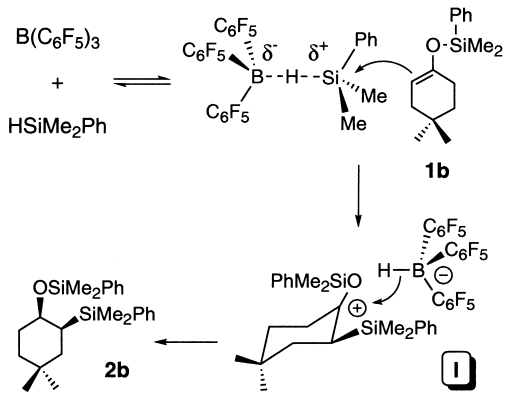


Scheme 4.

products **la** and **1b**, respectively, Scheme 4. These compounds can be elaborated further through a second, stereoselective hydrosilation step, to give the β-siloxy alkylsilanes **2a** and **2b** in good yields. Complete hydrosilation of the cyclohexyl silyl enol ether **1b** requires >40 h at room temperature with 2% catalyst loading and is accompanied by some $PhMe_2SiOSiMe_2Ph$ as a byproduct. By contrast, an NMR tube experiment has shown that hydrosilation of **1a** occurs rapidly even at −70°C. The products **2** were purified by column chromatography; **2b** isolated in this fashion was contaminated with $PhMe_2SiOSiMe_2Ph$, which in addition to being produced in the reaction, may be a result of partial decomposition of **2b** on the silica gel.

The siloxy and silyl groups in **2a** example are assigned a *cis*-disposition by nOe experiments and the magnitude of the $^3J_{HH}$ coupling constant. Irradiation of H_a leads to enhancement in H_b and vice versa, while the coupling constant of 5.5 Hz is most consistent with a *cis*-orientation; vicinal *trans*-hydrogens on a cyclopentane ring are expected to experience little coupling compared to ≈8 Hz coupling expected for vicinal *cis*-hydrogens.[24] For comparison, Fleming has prepared *cis*-2-(dimethylphenylsilyl)cyclopentanol via another route and observed a $^3J_{HH}$ of 4.8 Hz.[25] Treatment of **2a** with TBAF in THF gave *cis*-2-(dimethylphenylsilyl)cyclopentanol with identical data to that reported by Fleming.[25] Similar considerations for product **2b** indicate a *cis* stereochemistry (see Section 4). Thus, the Si–H bond has added to the enol ether C=C bond in a *trans* fashion, implying a stepwise reaction for this reduction.

Hydrosilation of silyl enol ethers has not, to our knowledge, been reported. Larson and co-workers have shown that hydroboration of silyl enol ethers is possible but this reaction did not require Lewis acid activation and gave *trans* products resulting from concerted *cis* addition of B–H to the silyl enol ether C=C bond.[26] Given that hydrosilation catalyzed by $B(C_6F_5)_3$ effects *trans* addition of Si–H to the substrate double bond, a likely mechanism again involves borane activation of silane followed by reaction with the silyl enol ether, particularly since the silyl enol ethers do not appear to interact with $B(C_6F_5)_3$ in solution as judged by ^{19}F NMR spectroscopy (vide infra). A stepwise mechanism such as that proposed in Scheme 5 would also account for the observed stereochemistry of the products **2**. Also consistent with this proposal is the spectroscopic observation of a silylcarboxonium intermediate when a mixture of $B(C_6F_5)_3$, **2b** and $PhMe_2SiH$ is probed via multinuclear NMR spectroscopy.



Scheme 5.

The formation of an ion pair, **I**, can be observed by ^{19}F NMR spectroscopy (Fig. 1). The ketone 4,4-dimethyl-2-cyclohexen-1-one was mixed with approximately 20% $B(C_6F_5)_3$ in C_7D_8 in an NMR tube at −40°C, Fig. 1(a). Under these conditions, the borane is mostly sequestered as the ketone adduct. Addition of one equivalent of $PhMe_2SiH$ leads rapidly to the silyl enol ether **lb** as described above (Table 2) and, as shown in Fig. 1(b), signals for free $B(C_6F_5)_3$ are observed indicating that at −40°C, an adduct between **lb** and $B(C_6F_5)_3$ is not formed. In light of the poor basicity of silyl enol ethers, this is perhaps not too surprising. Addition of a second equivalent of $PhMe_2SiH$ to the sample resulted in the formation of another species, present as an undissolved oil at the bottom of the NMR tube. This behavior is common to many reactions where a perfluoroaryl borate counterion is formed.[27] Spectroscopic analysis of this oil revealed that, in the ^{19}F NMR spectrum (Fig. 1(c)) a new set of signals has arisen. Significantly, a much

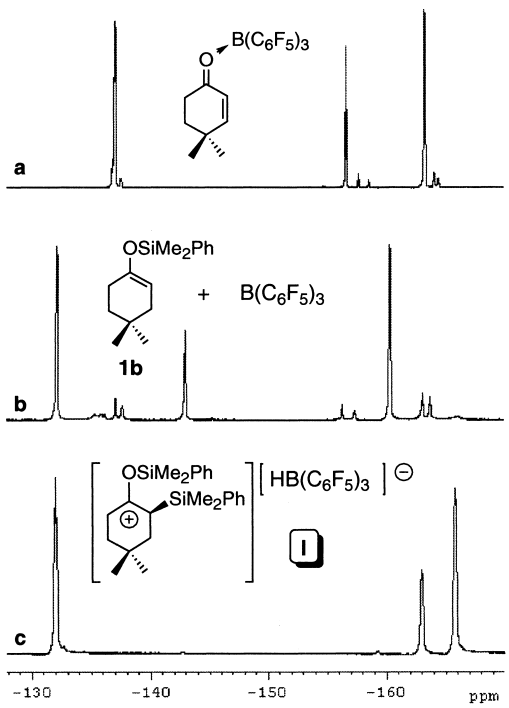


Figure 1. 282 MHz ^{19}F NMR spectra at −40°C showing (a) 4,4-dimethyl-2-cyclohexen-1-one and 20% $B(C_6F_5)_3$; (b) sample in (a) plus 1 equiv. of $PhMe_2SiH$; (c) sample in (b) plus a second equivalent of $PhMe_2SiH$.

lowered value for $\Delta\delta_{p,m}$ of 2.8 ppm indicates that an anionic borate had been formed, which we take as evidence for the formation of an intermediate like **I**.[28]

The ^{11}B NMR chemical shift for **I** was measured to be −25 ppm, again consistent with an anionic borate.[29] Comparison of spectral data of **I** to separately prepared $[Bu_4N]^+[H-B(C_6F_5)_3]^-$, which showed identical ^{11}B and ^{19}F NMR data to that observed for **I** (see Section 4), helped to confirm that this species indeed contained the hydridoborate anion $[H-B(C_6F_5)_3]^-$. The ^{29}Si NMR spectrum of **I** showed two signals at 46 and 7 ppm. The former signal is consistent with the silicon from a silylcarboxonium intermediate,[30] while the latter is in the expected region for tetraalkyl substituted silanes. The corresponding values for the hydrosilated product, **2b** are 3.4 ppm (O–Si) and −1.1 ppm (C–Si). Clearly, a significant shift in the value for the O–Si NMR shift is reflective of the partial positive charge on the Si atom. Species with similar structural characteristics to **I** have been proposed and generated in situ previously.[31,32] In the present case, spectroscopic observation of a chemically stable silylcarboxonium intermediate is unusual. As it is warmed, **I** proceeds to products by selective attack of the hydride *trans* to the bulky silyl group leading to the *cis* products in the second part of this stepwise process.

3. Conclusions

In summary, we have observed clean 1,4 hydrosilation of several α,β unsaturated enones utilizing $B(C_6F_5)_3$ as a catalyst. Mechanistically, the reactions are proposed to be related to the reduction of saturated carbonyl functions and imines by the same $B(C_6F_5)_3$/silane reagent system. Since the silyl enol ether products of these reactions are themselves susceptible to $B(C_6F_5)_3$ catalyzed addition to, for example, aldehydes, the potential for tandem reactions exists.

Perhaps more intriguing is the observation that the cyclic silyl enol ether products can also undergo $B(C_6F_5)_3$ mediated hydrosilation, providing new avenues for one-pot transformations of enone substrates. For example, the β-silylalkoxy functionality is prone to acid or base induced elimination reactions,[33] as indicated by the loss of $PhMe_2SiOSiMe_2Ph$ upon attempted silica gel purification of **2b**. Thus, this protocol could provide a means of effecting a novel transformation, enone to alkene with vinylic group transposition in one pot.

Reactions of silyl enol ethers with electrophiles are generally thought to take place via initial C-attack by the electrophile. Hence, silylcarboxonium species are the presumed intermediates, the electrophilic Si subsequently being attacked by a nucleophile to generate a C=O double bond. However, until now, direct spectroscopic observation of these intermediates by NMR spectroscopy or other means is without precedent. The characterization of intermediate ion pair **I** supports the general mechanistic picture we have developed for the $B(C_6F_5)_3$/silane reagent system in which the key function of the borane is to activate the silane by partial abstraction of the silane hydride.

4. Experimental

4.1. Starting materials and solvents

$B(C_6F_5)_3$ was purchased from Boulder Scientific and was dried with $Cl(H)SiMe_2$, sublimed under vacuum at ~100°C and stored in a glove box. Other chemicals were purchased from Aldrich and used as received or purified using standard procedures. Toluene was purified using the Grubbs/Dow method.[34] C_7D_8 and C_6D_6 were purchased from Cambridge Isotopes and were distilled from Na/benzophenone. NMR spectra were obtained on either a Bruker AMX300 or Bruker AM-400 spectrometer. All ^1H and ^{13}C spectra were referenced externally to Me_4Si at 0 ppm by referencing the solvent peak. ^{11}B NMR spectra were referenced relative to $BF_3{\cdot}Et_2O$ at 0 ppm. ^{19}F NMR spectra were referenced externally to C_6F_6 at −163 ppm relative to $CFCl_3$ at 0 ppm. ^{29}Si NMR spectra were referenced relative to Me_4Si at 0 ppm. NMR tube reactions were generally carried out by charging an NMR tube with the initial reagents in glove box under an argon atmosphere using scrupulously dried deuterated solvents. Subsequent reagents were introduced by syringe to the septa-sealed NMR tubes at the appropriate temperature. For low temperature reactions, reactants were typically mixed at −78°C and the placed in NMR probe at appropriate temperature. In some cases, the NMR tube, after being submerged in dry ice/acetone, was shaken once to ensure proper mixing mindful of the potential for premature heating.[35] In cases where premature reaction occurs, the reactions were repeated. IR spectra were obtained on neat samples for liquids and as KBr disks for solids using a Matteson Instruments 4030 Galaxy Series spectrometer. Elemental analyses were performed using a Control Equipment Corporation 440 Elemental Analyzer. High resolution mass spectra were obtained using a Kratos MS-80 spectrometer.

4.2. General procedure for enone hydrosilation (Tables 1 and 2)

A round bottom flask or 10 dram vial was charged with the enone (5.0 mmol), $B(C_6F_5)_3$ (51 mg, 0.01 mmol) and toluene (5.0 mL). The silane (5.0 mmol) was then added to the reaction mixture via syringe (except for Ph_3SiH which is a solid) all at once. Typically, after 1–5 min period of time, the reaction mixture heated up considerably and turned yellow or orange in color. Stirring was continued for 30–60 min and the reaction mixtures were analyzed by GC–MS, which usually indicated the reaction was complete. The products were purified by column chromatography (silica gel, 2% Et_3N/hexanes as eluent) and characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy or by comparison of ^1H NMR data to literature values. The purity of the samples was generally greater than 95%. In some cases, small amounts of $R_3SiOSiR_3$ formed via hydrolysis of the silyl enol ether was observed.

4.2.1. Table 1, entry 1. Yield: 81% of colorless oil. HRMS: mass calcd for $C_{18}H_{20}OSi$, 280.1283; found, 280.1294. Identified by comparison to published data.[36]

4.2.2. Table 1, entry 2. Yield: 90% of colorless oil. ^1H

NMR ($CDCl_3$, 400 MHz): δ 7.74–7.69 (m, 4H), 7.51–7.40 (m, 6H), 2.25 (app. td, 4H, *J*=1.6, 7.2 Hz), 1.79 (m, 2H), 1.65 (s, 3H), 0.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.12, 136.27, 134.19, 129.85, 127.78, 113.29, 33.58, 33.39, 19.73, 11.92, −1.99. HRMS: mass calcd for $C_{19}H_{22}OSi$, 294.1440; found, 294.1413.

4.2.3. Table 1, entry 4. Yield: 55% of colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66–7.62 (m, 4H), 7.42–7.37 (m, 6H), 2.30 (m, 1H), 1.96 (m, 1H), 1.76 (m, 1H), 1.40 (dm, 2H, *J*=2.05 Hz), 0.93 (d, 3H, *J*=6.87 Hz), 0.85 (d, 3H, *J*=7.16 Hz), 0.74 (d, 3H, *J*=7.02 Hz), 0.70 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2, 136.2, 134.4, 129.9, 127.9, 118.2, 45.4, 42.2, 41.5, 16.8, 14.4, 13.2, 10.9, −2.2. HRMS: mass calcd for $C_{22}H_{28}OSi$, 336.19094; found, 336.19133. The isolated product was determined to be an 8.7:1 mixture of two diastereomers by GC/MS analysis. The NMR data reported above is for the major diastereomer. The enone starting material, 2,3,4,5-tetramethyl-2-cyclopentenone (Aldrich), was determined to be an 8:1 ratio of *trans*/*cis* diastereomers by GC/MS and ^1H NMR analysis.[37]

4.2.4. Table 1, entry 5. Yield: 82% of colorless oil. HRMS: mass calcd for $C_{19}H_{22}OSi$, 294.1256; found, 294.1439. Identified by comparison to published data.[38]

4.2.5. Table 1, entry 6; Table 2, entry 1. Yield: 96% of colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.75–7.70 (m, 4H), 7.48–7.42 (m, 6H), 4.90 (tt, 1H, *J*=1.3, 4.1 Hz), 2.13 (m, 2H), 1.84 (td, 2H, *J*=2.3, 3.8 Hz), 1.46 (t, 2H, *J*=6.4 Hz), 0.95 (s, 6H), 0.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.19, 136.26, 134.28, 129.79, 127.78, 104.04, 37.80, 35.84, 28.52, 27.85, 27.51, −2.48. HRMS: mass calcd for $C_{21}H_{26}OSi$, 322.1753; found, 322.1751.

4.2.6. Table 1, entry 7. Yield 92% of colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65–7.62 (m, 4H), 7.44–7.34 (m, 6H), 4.64 (m, 1H, vinyl CH_2), 4.58 (m, 1H, vinyl CH_2), 2.17–1.82 (m, 5H, $2CH_2$ groups and CH), 1.60 (s, 3H), 1.59 (s, br, 3H), 1.31 (m, 2H), 0.71 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 142.4, 136.5, 134.2, 129.8, 127.8, 111.8, 108.6, 42.3, 35.6, 30.1, 27.7, 20.7, 16.3, −1.8. HRMS: mass calcd for $C_{23}H_{28}OSi$, 348.19094; found 348.19003.

4.2.7. Table 1, entry 8. Yield: 85% as 3:2 mixture of *E*/*Z* isomers. Both identified by comparison to published data.[38]

4.2.8. Table 1, entry 9. Yield 90% of colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.58 (m, 4H), 7.42–7.19 (m, 16H), 5.32 (t, 1H, *J*=7.18 Hz, vinyl CH), 3.38 (d, 2H, *J*=7.18 Hz, CH_2), 0.56 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.6, 141.3, 138.6, 135.6, 134.4, 130.0, 128.4, 128.2, 127.9, 127.8, 127.6, 126.0, 125.7, 110.6, 32.4, −2.2. HRMS: mass calcd for $C_{28}H_{26}OSi$, 406.17529; found, 406.17358. The product mixture was found to be a 10:1 mixture of *Z*/*E* isomers by NMR and GC/MS analysis. Only data for the major *Z* isomer is reported above. Assignment of the major isomer as *Z* was made on the basis of nOe experiments and comparison of data to the closely related silyl enol ethers containing (*Z*)-dimethylphenyl silyloxy,[39] and (*Z*)-trimethyl silyloxy groups.[40]

4.2.9. Table 1, entry 10. Yield: 88% of colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80–7.67 (m, 2H), 7.55–7.26 (m, 6H), 6.69 (dt, 1H, *J*=1.5, 15.9 Hz, H_a), 6.39 (dt, 1H, *J*=5.3, 15.9 Hz, H_b), 4.52 (dd, 1H, *J*=1.6, 5.3 Hz, CH_2O), 0.80 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.92, 135.81, 134.37, 133.95, 130.26, 129.86, 128.44, 127.87, 127.37, 126.38, 64.22, −2.85. HRMS: mass calcd for $C_{22}H_{22}OSi$, 330.1268; found, 330.1281.

4.2.10. Table 2, entry 2. Yield: 86% of colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 4.75 (t, 1H, *J*=3.9 Hz, C=CH), 1.98 (m, 2H), 1.79 (dt, 2H, *J*=2.2, 4.0 Hz), 1.38 (t, 2H, *J*=6.5 Hz), 0.90 (s, 9H), 0.90 (s, 6H, CH_3), 0.64 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ l49.44, 103.20, 37.94, 35.97, 28.62, 28.03, 27.55, 25.77, 18.02, −4.38. HRMS: mass calcd for $C_{14}H_{28}OSi$, 240.1909; found, 240.1912.

4.2.11. Table 2, entry 3. Yield: 88% of colorless oil. ^1H NMR (C_7D_8, 400 MHz): δ 7.60–7.50 (m, 2H), 7.20–7.10 (m, 3H), 4.82 (tt, 1H, *J*=1.3, 4.0 Hz), 2.02 (m, 2H), 1.71 (dt, 2H, *J*=2.1, 4.2 Hz), 1.26 (t, 2H, *J*=6.6 Hz), 0.82 (s, 6H), 0.39 (s, 3H). Identified by comparison to published data.[41]

4.2.12. Table 2, entry 4. Yield: 91% of colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 4.74 (tt, 1H, *J*=1.2, 4.0 Hz, C=CH), 1.99 (m, 2H), 1.78 (dt, 2H, *J*=2.2, 4.1 Hz), 1.38 (t, 2H, *J*=6.6 Hz), 0.96 (t, 9H, *J*=8.0 Hz, $SiCH_2CH_3$), 0.90 (s, 6H, CH_3), 0.64 (q, 6H, *J*=8.0 Hz, $SiCH_2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.31, 102.72, 37.90, 35.97, 28.58, 27.94, 27.46, 6.69, 4.92. HRMS: mass calcd for $C_{14}H_{28}OSi$, 240.1909; found, 240.1918.

4.2.13. Table 2, entry 5. Yield: 86% of white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.69–7.61 (m, 6H), 7.46–7.33 (m, 9H), 4.84 (t, 1H, *J*=4.1 Hz), 2.01 (m, 2H), 1.68 (dt, 2H, *J*=2.2, 3.8 Hz), 1.32 (t, 2H, *J*=6.4 Hz), 0.78 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.16, 135.43, 134.34, 129.99, 127.74, 104.69, 37.76, 35.81, 28.46, 27.80, 27.56. HRMS: mass calcd for $C_{26}H_{28}OSi$, 384.1909; found, 384.1947.

4.2.14. 1-(Dimethylphenylsiloxy)-1-cyclopentene, 1a. ^1H NMR ($CDC1_3$, 400 MHz): δ 7.69–7.61 (m, 6H), 7.46–7.33 (m, 9H), 4.84 (t, 1H, *J*=4.1 Hz), 2.01 (m, 2H), 1.68 (dt, 2H, *J*=2.2, 3.8 Hz), 1.32 (t, 2H, *J*=6.4 Hz), 0.78 (s, 6H). δ HRMS: mass calcd for $C_{13}H_{18}OSi$, 218.1127; found, 218.1137.

4.2.15. 1-(Dimethylphenylsilyl)-2-(dimethylphenylsiloxy) cyclopentane, 2a. A round-bottom flask was charged with $B(C_6F_5)_3$ (51 mg, 0.10 mmol), 2-cyclopenten-1-one (420 μL, 5.0 mmol) and toluene (5.0 mL). $PhMe_2SiH$ (1.61 mL, 10.5 mmol) was added via syringe all at once. An exothermic reaction ensues after which the mixture was stirred at room temperature for 30 min. The mixture was concentrated in vacuo and then purified by column chromatography (silica gel, hexanes then 2% ethyl acetate/hexanes as eluent) affording a colorless oil (1.5 g, 85%). A small amount of $PhMe_2SiOSiMe_2Ph$ was present but could be removed by purifying a second time by column chromatography. ^1H NMR (C_6D_6, 400 MHz): δ 7.55 (dd, 2H, *J*=1.9, 7.3 Hz), 7.48 (dd, 2H, *J*=3.6, 6.6 Hz), 7.29–7.17 (m, 6H), 4.36 (ddd, 1H, *J*=2.2, ~5.0, ~5.0 Hz, H_a), 1.85–1.67 (m, 2H), 1.65–1.51 (m, 2H), 1.47–1.29 (m, 2H),

1.12 (ddd, 1H, J=5.5, 8.8, 10.4 Hz, H_b), 0.41 (s, 3H), 0.36 (s, 3H), 0.27 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (C_6D_6, 100 MHz): δ 141.10, 139.08, 134.59, 134.26, 130.08, 129.21, 128.33 (one aryl C missing), 78.36, 38.05, 35.43, 26.94, 25.29, −0.28, −1.14, −1.72, −2.42. Anal. calcd for $C_{16}H_{30}OSi_2$: C, 71.12%; H, 8.53%. Found: C, 71.45%; 8.23%. ^{1}H NMR decoupling experiments showed that $J(H_a/H_b)$=5.5 Hz. In nOe experiments, irradiation of H_a led to enhancement in H_b (8.0%) and vice versa (11.0%).

4.2.16. 4,4-Dimethyl-1-(dimethylphenylsilyl)-2-(dimethylphenylsiloxy)cyclohexane, 2b. A round-bottom flask was charged with $B(C_6F_5)_3$ (51 mg, 0.10 mmol), 4,4-dimethyl-2-cyclohexen-1-one (658 μL, 5.0 mmol) and toluene (5.0 mL). $PhMe_2SiH$ (1.61 mL, 10.5 mmol) was added via syringe all at once. An exothermic reaction ensues after which the mixture was stirred at room temperature for 40 h. The mixture was concentrated in vacuo and then purified by column chromatography (silica gel, 2% ethyl acetate/hexanes as eluent) affording a colorless oil (1.41 g). $PhMe_2SiOSiMe_2Ph$ was present but could not be removed by purifying again by column chromatography. The yield of **2b** is approximately 60% taking this into account. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.60 (m, 4H), 7.54–7.49 (m, 6H), 4.03 (m, 1H, H_a), 1.84 (t, 1H, J=13.1 Hz), 1.66 (td, 1H, J=4.1, 13.7 Hz), 1.50 (dq, 1H, J=3.2, 14.5 Hz), 1.32 (tdd, 1H, J=2.6, 3.8, 14.2 Hz), 1.21–1.09 (m, 2H, one of them H_b), 0.92 (s, 3H), 0.80 (s, 3H), 0.35 (s, 6H), 0.33 (s, 3H), 0.31 (s, 3H). ^{13}C NMR (C_6D_6, 100 MHz): δ 140.29, 139.84, 134.67, 134.29, 130.09, 130.02, 129.38, 128.48, 69.63, 35.19, 33.81, 33.61, 31.31, 30.44, 28.20, 24.14, −0.12, −0.61, −2.90, −3.44. ^{29}Si NMR: (C_6D_6, 79.5 MHz): δ 3.4, −1.1. ^{1}H, ^{13}C NMR and ^{29}Si resonances from $PhMe_2SiOSiMe_2Ph$ are not included. HRMS: calcd for $C_{24}H_{34}OSi_2$, 396.2305; found, 396.2312. ^{1}H NMR nOe experiments were used to establish the *cis*-relationship of H_a and H_b. First, H_b was assigned using a DEPT ^{13}C NMR experiment to identify the two CH carbons and an HMQC NMR experiment to identify the attached ^{1}H. Irradiation of H_a led to a 6.3% nOe in H_b. The coupling constant between H_a and H_b could not be obtained, but is less than 3 Hz based on the appearance of H_a in the ^{1}H NMR spectrum. If the silyl and siloxy groups were *trans*-disposed they would be expected to occupy equatorial sites whereas H_a and H_b would both occupy axial sites; the expected coupling constant would be 10–14 Hz.[24] In a *cis*-substituted cyclohexane, one of H_a/H_b would be axial and the other equatorial leading to a small coupling constant (0–3 Hz).

4.2.17. Characterization of ion-pair I by NMR spectroscopy. An NMR tube was charged with 4,4-dimethyl-2-cyclohexen-1-one (28 μL, 0.20 mmol), $B(C_6F_5)_3$ (20 mg, 0.04 mmol) and C_7D_8 (~500 μL). $PhMe_2SiH$ (32 μL, 0.20 mmol) was added via syringe causing the solution to heat up immediately. ^{1}H NMR confirmed that clean hydrosilation to silylenol ether **1b** had occurred. ^{19}F NMR at −40°C showed NMR signals predominantly for uncoordinated $B(C_6F_5)_3$. A second equivalent of $PhMe_2SiH$ (32 μL, 0.20 mmol) was added at to the NMR tube cooled to −78°C. The tube was placed in the NMR probe precooled to −60°C and ^{1}H, ^{19}F and ^{11}B NMR showed that reaction had taken place. A two-layer reaction mixture is formed under these conditions. All of $B(C_6FS)_3$ was incorporated into new compound with the following ^{19}F and ^{11}B NMR spectroscopic data. ^{19}F NMR (C_7D_8, 282 MHz, −60°C): δ −132.0 (br., 2F, *o*-F's), −62.8 (br., lF, *p*-F's), −165.6 (br., 2F, *m*-F's). ^{11}B NMR (C_7D_8, 128.4 MHz, −60°C): δ −25. ^{29}Si NMR (C_7D_8, 76.5 MHz, −60°C): δ 46, 7. ^{1}H and ^{13}C NMR spectra are very broad in toluene, but can be recorded at −80°C in CD_2Cl_2.

4.2.18. Separate synthesis of $[Bu_4N]^+[H-B(C_6F_5)_3]^-$. This ion pair was generated in situ by mixing $B(C_6F_5)_3$, Bu_4NBr and Et_3 SiH in 1:1:1 molar ratio (0.20 mmol) in C_6D_6. ^{1}H NMR (400 MHz): δ 4.16 (br. d, 1H, B*H*), 2.44 (m, 8H, NCH_2), 1.01 (m, 16H), 0.74 (br. t, 12H, J=6.9 Hz). ^{13}C NMR (100 MHz): δ 149.4 (dm, J=235 Hz, C–F), 138.9 (dm, J=240 Hz, *C*–F), 137.5 (dm, J=246 Hz, *C*–F), 126.7 (br., *C*–B), 58.98 (NCH_2), 24.02, 19.97, 13.58. ^{19}F NMR (282 MHz): δ −133.0 (d, 2F, *o*-F's), −163.9 (t, 1F, *p*-F's), −166.9 (m, 2F, *m*-F's). ^{11}B NMR (128.34 MHz): δ −25.5 (d, J=58 Hz). The ion pair can be isolated as a solid by mixing reactants together (1:1:1) in CH_2Cl_2 under argon atmosphere, removing CH_2Cl_2 in vacuo, and adding hexane to the resulting oily residue which leads to a white solid upon sonication. The hexane is removed by filtration, more hexane is added and removed by filtration. ^{19}F NMR and elemental analysis of the resulting white powder confirmed that it was $[Bu_4N]^+[H-B(C_6F_5)_3]^-$: This material decomposes at room temperature over weeks. Anal. calcd for $C_{34}H_{37}NBF_{15}$: C, 54.05%; H, 4.94%; N, 1.85%. Found: C, 53.68%; 4.65%, N, 1.85%.

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