Studies on the Mechanism of $B(C_6F_5)_3$-Catalyzed Hydrosilation of Carbonyl Functions

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The strong organoborane Lewis acid $B(C_6F_5)_3$ catalyzes the hydrosilation (using R_3SiH) of aromatic and aliphatic carbonyl functions at convenient rates with loadings of 1−4%. For aldehydes and ketones, the product silyl ethers are isolated in 75−96% yield; for esters, the aldehydes produced upon workup of the silyl acetal products can be obtained in 45−70% yield. Extensive mechanistic studies point to an unusual silane activation mechanism rather than one involving borane activation of the carbonyl function. Quantitative kinetic studies show that the least basic substrates are hydrosilated at the fastest rates; furthermore, increased concentrations of substrate have an inhibitory effect on the observed reaction rate. Paradoxically, the most basic substrates are reduced selectively, albeit at a slower rate, in competition experiments. The borane thus must dissociate from the carbonyl to activate the silane via hydride abstraction; the incipient silylium species then coordinates the most basic function, which is selectively reduced by $[HB(C_6F_5)_3]^-$. In addition to the kinetic data, this mechanistic proposal is supported by a kinetic isotope effect of 1.4(5) for the hydrosilation of acetophenone, the observation that $B(C_6F_5)_3$ catalyzes H/D and H/H scrambling in silanes in the absence of substrate, computational investigations, the synthesis of models for proposed intermediates, and other isotope labeling and crossover experiments.

Introduction

The importance of Lewis acids in the catalysis of organic transformations involving carbonyl functions cannot be understated.[1] While the diversity of Lewis acids is extensive, boron-based reagents remain prominent as a result of their high Lewis acid strength and ready availability. While BF_3 remains the quintessential boron Lewis acid, the strong organometallic Lewis acid $B(C_6F_5)_3$[2] has emerged in recent years as a viable alternative.[3] Comparable in strength to BF_3,[4] it is considerably more hydrolytically stable and has indeed been shown to be active even under aqueous conditions.[5] Given that it is now commercially available, the number of applications in organic synthesis is growing; indeed, its use (as well as that of other pentafluorophenyl-substituted boranes) has recently been reviewed.[6] In general, for transformations involving the carbonyl function, it has been assumed that $B(C_6F_5)_3$ operates in a similar way to BF_3, serving to activate the carbonyl via coordination to one of the oxygen lone pairs.[7]

Some years ago, we found that $B(C_6F_5)_3$ is an effective catalyst for the hydrosilation of a variety of aldehydes, ketones, and esters.[8] $BF_3{\cdot}OEt_2$ has been reported to mediate this reaction also,[9] although not catalytically. In these studies, BF_3 activation of the carbonyl moiety is the starting point for mechanistic postulates and is included as a key step in the overall mechanistic scheme. It was therefore surprising that, for the $B(C_6F_5)_3$-mediated hydrosilation of these substrates, our preliminary mechanistic investigations strongly suggested that the borane/carbonyl adducts were not directly involved in the addition of Si−H across C═O. Since a detailed understanding of the intimate mechanism of such processes is crucial for the design of better and/or stereoselective catalysts, we have explored the mechanism of this reaction in detail and report a full account of this study herein.

Results and Discussion

$B(C_6F_5)_3$-Catalyzed Hydrosilation of Carbonyl Functions. In the presence of 1−4 mol % $B(C_6F_5)_3$, addition of 1 equiv of R_3SiH across the carbon−oxygen double bond of a variety of aldehydes, ketones, and esters is facile at room temperature, affording silyl ethers or silyl acetals in good isolated yields. In addition to the aryl-substituted compounds we initially employed,[8] aliphatic substrates were also found to undergo reduction under these conditions (Table 1). While aldehydes and ketones are hydrosilated quite cleanly, the silyl acetal products of ester reduction are susceptible to further silation reactions[10] under all conditions examined. These

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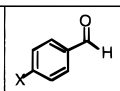
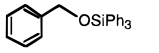
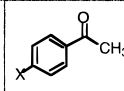
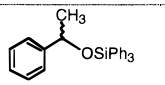
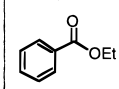
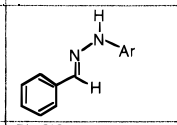
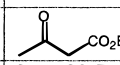
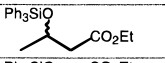
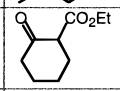
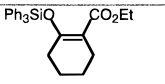
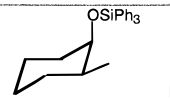
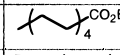
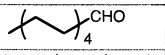
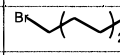
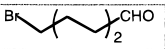
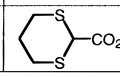
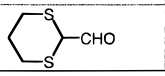
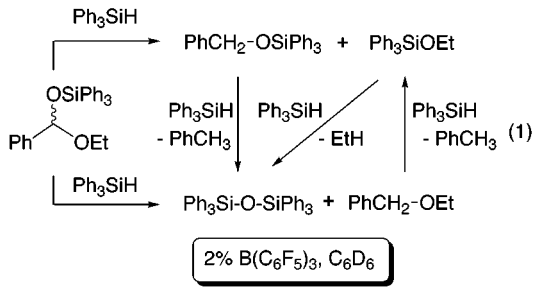
Table 1. $B(C_6F_5)_3$-Catalyzed Hydrosilation of Carbonyl Functions Using Ph_3SiH

Entry	Substrate	X	Cond.[a]	Product	Yield[b]
1a		H	**A**		87
1b		CH_3	**A**		82
1c		Cl	**A**		81
1d		NO_2	**A**		96
2a		H	**A**		76
2b		CH_3	**A**		84
2c		Cl	**A**		80
2d		NO_2	**A**		91
3[c]			**A**		80
4			**A**		84
5[d]			**A**		78
6[e]			**A**		75
7			**B**		69
8			**B**		70
9			**B**		45

[a] Conditions: **A**, 2% $B(C_6F_5)_3$, benzene or toluene; **B**, 1% $B(C_6F_5)_3$, toluene, syringe pump addition of silane over 1 h. [b] Isolated yields. [c] Yields of PhCHO were lower as a result of loss of product via evaporation and/or oxidation during workup; in situ conversion to the 2,4-dinitrophenylhydrazone was done to gauge the selectivity of the reaction for benzaldehyde more accurately. [d] Reaction via enol tautomer of substrate. [e] *cis* diastereomer produced exclusively.

processes compete effectively with carbonyl hydrosilation at later stages of the reaction and over-reduction products are in evidence. Careful examination of the reaction of ethylbenzoate with 1 equiv of silane and a catalytic amount of $B(C_6F_5)_3$ reveals a product mixture as shown in eq 1. The silyl ether and siloxane products result from



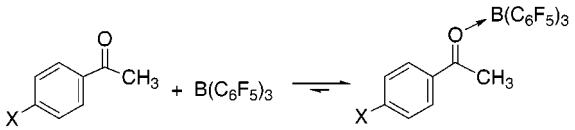
hydrosilation of the initial silyl acetal product; further reduction of these secondary products ultimately yields toluene and ethane, both of which are observed in trace amounts. Thus, while the silyl acetal is the major product, each of the other species in eq 1 is observed to some extent as well. Extensive variation in reaction conditions (temperature, solvent, and rate of silane addition) and the silane employed did not lead to more selective chemistry, so the yields as reported in Table 1 are optimized to the extent possible in our hands. Thus, maximum isolated yields of the products of ester hydrosilation (the analogous aldehydes upon workup with TBAF) are in the range of 60−70%. Nonetheless, this transformation (i.e., ester to aldehyde) is generally difficult to effect directly,[11] and for simple systems this represents an alternative worth considering.

Experiments aimed at exploring the scope of the reaction showed that carbonyl hydrosilation occurs selectively only if more basic functions are absent from the substrate. Thus, while halogens, olefins, and internal alkynes are tolerated, nitrile and alcohol functions generally are not. This observation led us to develop in detail the utility of the $B(C_6F_5)_3/R_3SiH$ system for the dehydrogenative silation of alcohols as an alternative procedure for generating silyl ethers.[12] While the scope of alcohol silation is quite wide, the lower inherent basicity of carbonyl functions limits the carbonyl hydrosilation reaction to somewhat less functionalized substrates. Nonetheless, we have used this reaction to study the mechanism by which the $B(C_6F_5)_3/R_3SiH$ reagent operates in some detail.

Mechanistic Studies. Lewis acids are generally thought to activate carbonyl functions through coordination of the C=O moiety, which serves to further polarize the double bond and render the C atom even more electrophilic than in the uncomplexed species. There are some reports in the literature that suggest that Lewis acid catalyzed addition of Si−H to C=O proceeds in this fashion,[13] but these are generally unsupported by quantitative mechanistic data. While $B(C_6F_5)_3$ forms stable adducts with carbonyl-containing substrates,[14] we have made several observations that suggest a less conventional mechanism is operative for this system.

First, quantitative rate studies on the hydrosilation of benzaldehyde, acetophenone, and ethylbenzoate revealed that the order of reactivity was opposite to what would be expected on the basis of substrate basicity. That is, the least basic substrate toward $B(C_6F_5)_3$ (ethyl benzoate) was hydrosilated the fastest (TON = 637 hr^{-1}), followed by acetophenone (TON = 45 hr^{-1}) and benzaldehyde (TON = 19 hr^{-1}). If carbonyl adducts of $B(C_6F_5)_3$ were instrumental in bringing about hydrosilation, the least basic substrate would be the least active, since there would be a lower concentration of adduct present in solution to react and the level of substrate activation would be lower.

Second, the observed rates of hydrosilation for a series of *para*-substituted derivatives of acetophenone lead to a similar conclusion. As shown in eq 2, the equilibrium



X = CH_3, Cl, NO_2

X	K_{eq}
CH_3	$1.5(1)\times10^{3}$
Cl	$3.4(1)\times10^{2}$
NO_2	$6.0(1)\times10^{1}$

constants for the *para*-X acetophenones (X = H, CH_3, Cl, NO_2) vary as one would expect on the basis of the donor properties of the group. Thus, as the X group becomes

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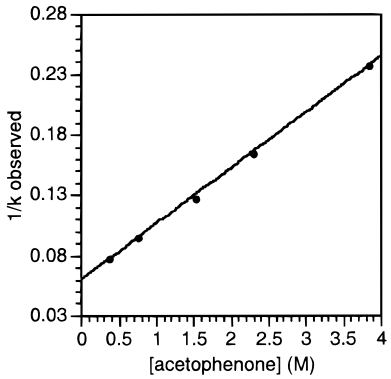


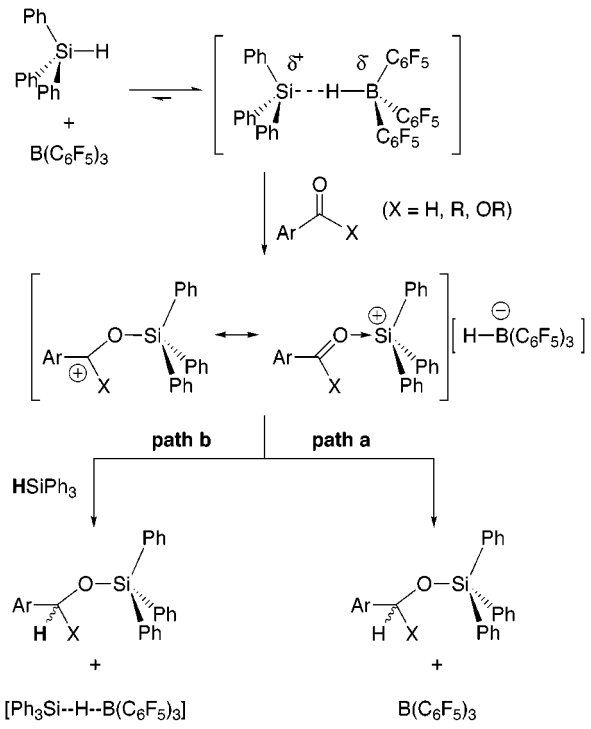
Figure 1. Plot of $1/k_{obs}$ ($\times 10^{-4}$) vs acetophenone concentration for the hydrosilation of acetophenone with Ph_3SiH.

more electron-withdrawing and makes the carbonyl group less basic, the equilibrium shifts away from the adduct. The observed rate constants for hydrosilation of these substrates ($k_{obs} = 3.61(7) \times 10^{-4}$ s^{-1} for X = Me; $2.01(5) \times 10^{-3}$ s^{-1} for X = Cl; $1.35(3) \times 10^{-2}$ s^{-1} for X = NO_2)[8] indicate that the rate of hydrosilation increases dramatically as X becomes more electron-withdrawing, again showing that less basic substrates are reduced more rapidly.

Third and perhaps most revealing, the rate of hydrosilation is inhibited by increases in the substrate concentration. Thus, in the hydrosilation of acetophenone, the observed rate constant is inversely proportional to the concentration of acetophenone (Figure 1). Since increases in the substrate concentration should push the equilibrium toward the adduct, the inhibitory effect of this on the overall rate of hydrosilation is perhaps the clearest indication that the carbonyl adducts of $B(C_6F_5)_3$ are not directly involved in the hydrosilation reaction.

While these equilibria strongly favor the carbonyl borane adducts, they are quickly established, and exchange processes between free and bound substrate are rapid on the chemical time scale.[14] In light of the above kinetic data, we proposed a mechanism in which dissociation of borane from the substrate is necessary in order that $B(C_6F_5)_3$ may activate the silane.[8] The manner in which we now believe this activation takes place is outlined in Scheme 1. In this picture, the resulting borane/silane complex then reacts with substrate, which displaces the hydridoborate counterion from the incipient silylium ion. At this point, reduction is consummated by one of two pathways, each of which is consistent with the observed kinetic behavior of the system. Transfer of a hydride to the carbonyl carbon of the substrate coordinated to R_3Si^+ occurs either from the hydridoborate (path a) or via another equivalent of R_3SiH (path b). Three issues regarding this mechanistic proposal arise: (1) What chemical evidence is there for silane activation via hydride abstraction by $B(C_6F_5)_3$? (2) How does substrate interact with the resulting borane/silane complex? (3) Which pathway for hydride delivery is operative in this system? Each of these questions is dealt with in turn in the following sections.

Scheme 1



Hydride Abstraction from R_3SiH by $B(C_6F_5)_3$. It is well-known in the literature that $B(C_6F_5)_3$ is a strong enough Lewis acid to abstract alkide[15] and hydride[16] ions from neutral organometallic precursors.[3] Indeed, this process is the key activating step for generation of cationic olefin polymerization catalysts.[17] Furthermore, it has been shown that the tributylstannyl cation can be

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(20) Typically, neutral, three-coordinate pentafluorophenyl borane compounds exhibit a peak separation between the *para* and *meta* fluorine resonances of >15 ppm. As the environment about boron proceeds through neutral, four coordinate to anionic, four coordinate geometries, this parameter gets smaller as the resonance for the *para* fluorine shifts upfield. This was first observed by Horton and de With[20a] and used to assess the extent of ion pairing between organometallic cations and $[MeB(C_6F_5)_3]^-$. It is a sensitive tool for assessing the coordination environment around boron in $-C_6F_5$-substituted boranes.[20b–d] (a) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424. (b) Köhler, K.; Piers, W. E.; Xin, S.; Feng, Y.; Bravakis, A. M.; Jarvis, A. P.; Collins, S.; Clegg, W.; Yap G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557. (c) Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W. C.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, in press. (d) Köhler, K.; Piers, W. E. *Can. J. Chem.* **1998**,*76*, 1249.

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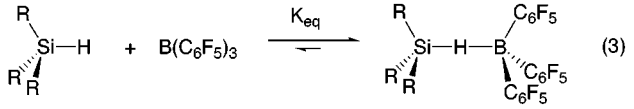
generated via hydride abstraction from Bu_3SnH using $B(C_6F_5)_3$.[18] By analogy to these phenomena, it is reasonable to propose that borane is able to abstract hydride, at least partially, from R_3SiH.

Attempts to garner direct spectroscopic evidence for a $B(C_6F_5)_3$/silane interaction were only partially successful. When samples of $B(C_6F_5)_3$ and either Ph_3SiH or Et_3SiH (1:1 in C_6D_6) are monitored by ^1H NMR spectroscopy, little perturbation in the chemical shift of the resonances for the silane hydrogen are observed. This indicates that, in the absence of a substrate, borane/silane adduct formation is only partial and that its concentration is low under these conditions (i.e., for eq 3, $K_{eq} \ll 1$). The

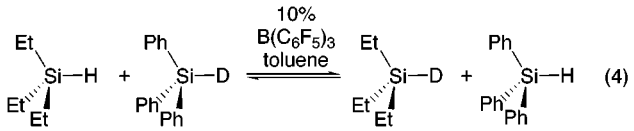


(3)

resonance for the ^{29}Si nucleus shifts from 0.5 ppm in free Et_3SiH to 1.2 ppm in the presence of 1 equiv of $B(C_6F_5)_3$. While the trend is in the expected direction,[19] the change is too small to be conclusive.

In an effort to drive the equilibrium to the right, the ^{19}F NMR spectrum of $B(C_6F_5)_3$ in neat Et_3SiH was recorded at −80 °C. The chemical shift of the *para*-fluorines of the boron C_6F_5 rings are quite sensitive to the coordination environment about boron.[20] The value of $\Delta(\delta_{m,p})$ for $B(C_6F_5)_3$ in neat Et_3SiH at room temperature is 16.6 ppm (cf. a value of 18.3 ppm for $B(C_6F_5)_3$ in C_6D_6[20d]); at −80 °C, the value falls to 11.1 ppm, which is in the range expected for a weak Lewis base/$B(C_6F_5)_3$ adduct.[14] Nonetheless, even under these conditions, the equilibrium likely favors the constituent reagents. Thus, while hydride abstraction from silanes using the isoelectronic trityl ion is irreversible (and the method of choice for generating silylium-like ions in the condensed phase[19,21]), when $B(C_6F_5)_3$ is the abstracting agent, the process is incomplete and rapidly reversible.

There is, however, convincing indirect ^1H NMR spectrocopic evidence that the chemistry in eq 3 is occurring. Although the chemical shift change for the silane hydrogen in Et_3SiH is insignificant when $B(C_6F_5)_3$ is added to the sample, the J coupling between Si−H and the CH_2 protons of the ethyl groups is lost within minutes of borane contact with silane (Figure 2). Similarly, the $^1J_{Si-H}$ coupling is no longer in evidence in these spectra. This phenomenon is reminiscent of that observed in the ^1H NMR spectra of alcohols before and after the addition of catalytic amounts of H^+.[22] In this instance, the borane catalyzes the rapid exchange of Si−H protons by generating small amounts of "$[Et_3Si]^+[HB(C_6F_5)_3]^-$". This is also manifested by the observed rapid scrambling of deuterium when a 1:1 mixture of Et_3SiH and Ph_3SiD is treated with 10% $B(C_6F_5)_3$ (eq 4). In the absence of ketone



(4)

Lewis bases (vide infra), the deuterium is essentially equally distributed between the two silanes within minutes of borane addition.

Further evidence for the borane/silane adduct was obtained via computational studies. Calculations at the AM1 level showed that the adducts of $B(C_6F_5)_3$ with Ph_3SiH and Et_3SiH fall into energy minima; geometry optimization in the absence of any restraints gave the metrical parameters and Mulliken charges collected in Table 2. For comparison, similar level calculations were done on the free silanes, $B(C_6F_5)_3$ and $[HB(C_6F_5)_3]^-$. As expected on the basis of steric considerations, the B−H−Si angles in these adducts are essentially 180°. The B−H and Si−H distances are elongated relative to the values calculated for the hydridoborate and silane species, indicating incomplete transfer of the hydride from silane to borane. Comparison of the atomic charges for Si and B in the adducts, which increase and decrease relative to the uncomplexed silane and borane, respectively, attests to significant charge separation occurring as the adduct forms. Higher level ab initio computations (MP2/6-31G**) on the adduct formed from SiH_4 and BH_3 lead to similar conclusions.

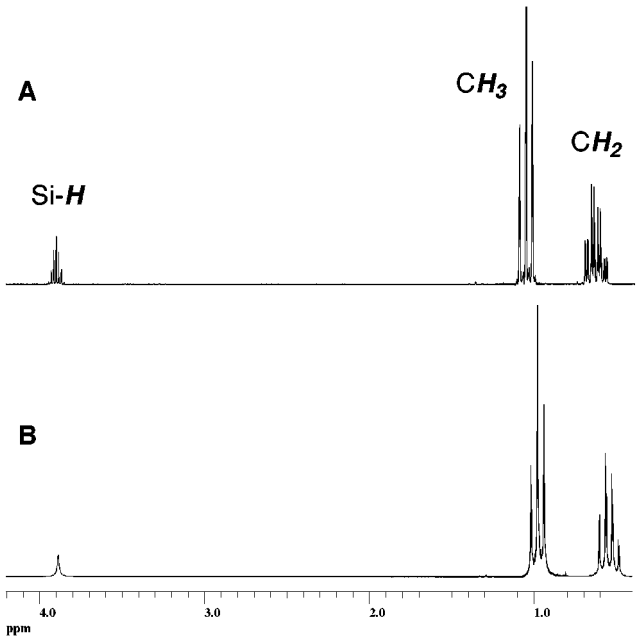


Figure 2. 300 MHz ^1H NMR spectra (C_6D_6, room temperature) of (**A**) Et_3SiH and (**B**) Et_3SiH plus 10% $B(C_6F_5)_3$ (10 min of mixing).

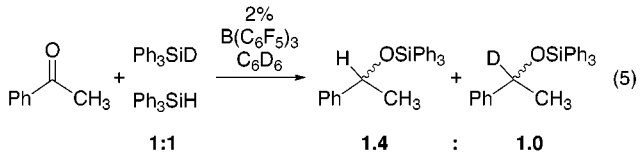
Table 2. AM1 Optimized Parameters for $B(C_6F_5)_3$/R_3SiH Adducts

species	R_{B-H} (Å)	R_{Si-H} (Å)	q_B (e)[a]	q_H (e)[a]	q_{Si} (e)[a]
Ph_3SiH		1.4695		−0.24	1.31
$Ph_3SiH-B(C_6F_5)_3$	1.3938	1.7119	0.31	−0.23	1.57
$[HB(C_6F_5)_3]^-$	1.2164		0.00	−0.05	
$Et_3SiH-B(C_6F_5)_3$	1.3929	1.6672	0.32	−0.24	1.41
Et_3SiH		1.4701		−0.23	1.09
$B(C_6F_5)_3$			0.50		
ΔPh_3SiH[b]	0.1774	0.2424	−0.19	0.01	0.26
ΔEt_3SiH[b]	0.1765	0.1971	−0.18	−0.01	0.32

[a] q_x represents the charge of atom x in terms of an electron. [b] Δ refers to the difference between the property of the adduct and free species.

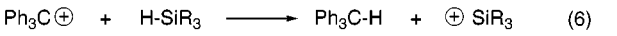
Finally, the magnitude of the kinetic isotope effect observed in the $B(C_6F_5)_3$ catalyzed addition of Ph_3SiX (X = H, D) to acetophenone is also consistent with hydride abstraction. While the availability of free borane to a large degree controls the overall rate of the reaction, in the two reactions that are actually involved in the hydrosilation, abstraction of the hydride from the silane is likely rate-limiting. Thus, a primary KIE (k_H/k_D) of

1.40(5) is observed for this reaction, as measured by the experiment shown in eq 5. On the basis of zero point

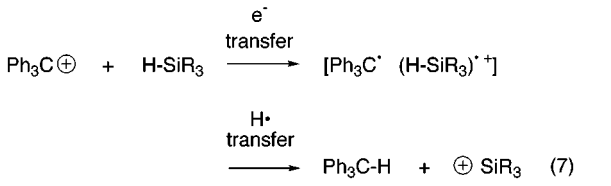


(5)

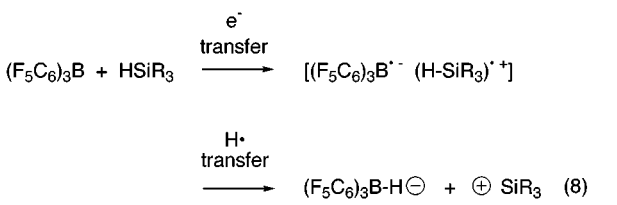
energy considerations, the maximum isotope effect to be expected for Si−(H,D) cleavage is ~3.8,[23] so the observed magnitude is significant. Furthermore, it is in the same range measured for the reactions of carbocations with various silanes. Isotope effects of 1.4−1.9 have been reported for these reactions[24] and interpreted in terms of hydride transfer[24c] (eq 6) rather than initial electron


(6)

transfer followed by a hydrogen atom shift[24a,b] (eq 7) since

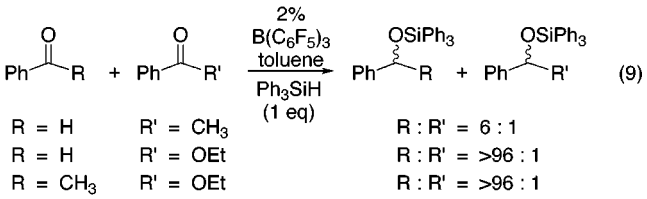

(7)

transfer of H• from silane generally leads to larger isotope effects (>2).[23] The magnitude of the isotope effect observed in the present hydrosilation reaction therefore is more consistent with direct hydride abstraction than with a pathway involving initial electron transfer from the silane to $B(C_6F_5)_3$ followed by transfer of a hydrogen atom (eq 8), which must be considered since it has recently


(8)

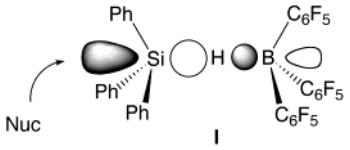
been shown that one-electron reduction of $B(C_6F_5)_3$ is the first step in its reaction with a zirconaazacyclobutane derivative.[25]

Interaction of Substrate with the Borane/Silane Adduct. As indicated in Scheme 1, once the borane/silane complex is formed, we believe the carbonyl substrate nucleophilically attacks the silicon center. This is indicated by several competition experiments that show that it is the most basic substrate that is reduced selectively, albeit at a slower rate.[26] For instance, while we have established that benzaldehyde is hydrosilated at a slower rate than acetophenone, when a 1:1 mixture of these two substrates is hydrosilated with Ph_3SiH, the benzaldehyde is hydrosilated preferentially by a 6:1 margin (eq 9). The observed rate constant for the consumption of silane in this experiment ($3.02(9) \times 10^{-4}$ s^{-1}) is similar to that found for the hydrosilation of benzaldehyde itself ($6.0(1) \times 10^{-4}$ s^{-1}).[27] The selectivities are even better in competition experiments involving the less basic substrate ethylbenzoate; in these reactions, no products of ester hydrosilation are detected. This phenomenon is also observed in mixed substrates such as that shown in entry 4, Table 1. In this ketoester, it is the more basic ketone function which is exclusively reduced. The rate of the reaction is consistent with the presence of a group with the basicity of a ketone; when a further equivalent of silane is added to the solution, the rate of silane consumption increases dramatically as hydrosilation of the ester function ensues.



(9)

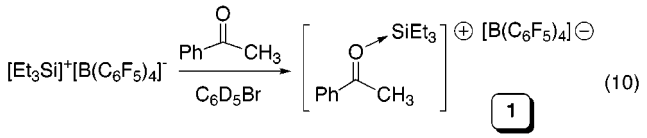
These observations imply that the relative strength of the Lewis base plays a critical role in determining the selectivity of the reaction as well as the overall rate. The computational studies described above show that the LUMO of $R_3Si-H-B(C_6F_5)_3$ lies along the Si−H−B axis, with a large orbital lobe protruding from the silicon *trans* to the Si−H bond (**I**). This would likely be the preferred



I

site of nucleophilic attack on the adduct and would furthermore aid in displacement of the hydrido borate from silicon.

The chemical viability of a ketone adduct of R_3Si^+ was tested experimentally by generating the arene-stabilized triethylsilylium ion in bromobenzene (using $[Ph_3C]^+$-$[B(C_6F_5)_4]^-$ according to the methodology developed by Lambert[19,21]) and treating with 1 equiv of acetophenone. In bromobenzene, the resulting species is soluble and stable for several hours and can thus be examined spectroscopically, although we were unable to procure its isolation. ^1H and ^{13}C NMR spectroscopic studies are completely consistent with clean formation of adduct **1** (eq 10). Most notably, the ^{13}C resonance for the carbonyl



(10)

carbon shifts downfield to 217.8 ppm from 196.8 ppm for free acetophenone in C_6D_5Br, while the methyl protons move upfield to 2.44 ppm as compared to 2.55 ppm in unbound ketone.[28] Clearly, when the counteranion is the weakly coordinating $[B(C_6F_5)_4]^-$ anion, ketone adducts of trialkylsilylium ions are reasonable species and, like the olefin adducts of R_3Si^+ reported by Lambert et al.,[29] have appreciable carbocationic character at the carbonyl carbon.

(25) Harlan, C. J.; Hascall, T.; Fujita, E.; Norton, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 7275.

(26) We assume here that the relative basicities of benzaldehyde, acetophenone, and ethylbenzoate towards the borane/silane complex mirror that found for $B(C_6F_5)_3$ itself.[14]

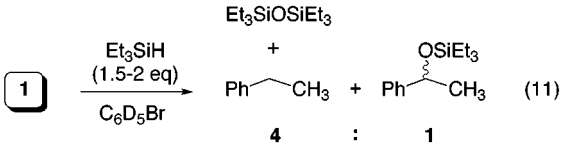
(27) The smaller rate constant in the competition experiment is due to the substrate inhibition phenonmenon.

(28) Hartman, J. S.; Stilbs, P.; Forsen, S. *Tetrahedron Lett.* **1975**, 3497.

(29) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.

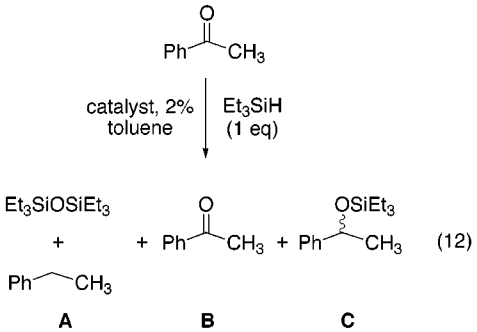
Mode of Hydride Delivery. As mentioned above, two routes for consummation of hydrosilation are plausible, distinguished by whether hydride delivery to the coordinated carbonyl function is performed by $[HB(C_6F_5)_3]^-$ (path **a**, Scheme 1) or by R_3SiH (path **b**). Although we are unable to conclusively prove which path is operative, several lines of experimentation point strongly toward the former path, i.e., borohydride attack of silylium activated ketone.

That being said, reaction of acetophenone adduct **1** with a 1.5- to 2-fold excess of triethylsilane clearly indicates that such an adduct is capable of abstracting hydride from silane. However, as eq 11 shows, the



(11)

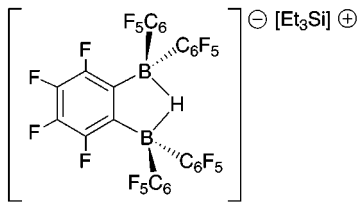
product distribution in this stoichiometric reaction is quite different from that observed in the borane-catalyzed process. The major acetophenone-derived product is ethylbenzene, formed along with hexaethyldisiloxane and arising from full deoxygenation of the ketone.[10] Furthermore, these are the exclusive products of acetophenone hydrosilation in reactions where silane is the only hydride source in the system (eq 12). Whereas $B(C_6F_5)_3$



(12)

catalyst	A : B : C
$B(C_6F_5)_3$	0 : 0 : 1
$[Ph_3C]^+[B(C_6F_5)_4]^-$	1 : 1 : 0
$[Et_3Si]^+[B(C_6F_5)_4]^-$	1 : 1 : 0
1,2-$[B(C_6F_5)_2]_2C_6F_4$	1 : 1 : 0

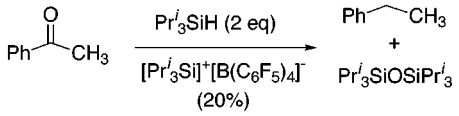
gives the silyl ether reduction product exclusively, a 1:1 mixture of ethylbenzene/hexaethyldisiloxane and unreacted acetophenone are produced when $[Et_3Si]^+[B(C_6F_5)_4]^-$,[19] $[Ph_3C]^+[B(C_6F_5)_4]^-$,[30] or the diborane 1,2-$[B(C_6F_5)_2]_2C_6F_4$[31] are employed as catalysts. In the latter case, abstraction of H^- from silane presumably leads to silylium ion **II**, in which the hydride moiety in the counteranion is chelated by the two borane centers[32] and is effectively unavailable for delivery to substrate; thus, in this system "Et_3Si^+" is again the true catalyst.



II

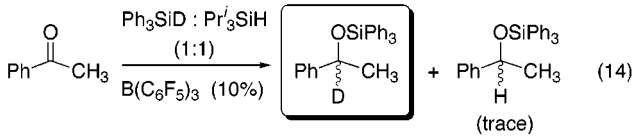
In these reactions, where Et_3SiH is the only hydride donor present, abstraction of hydride by the carbocation-like ketone adducts of Et_3Si^+ regenerates the silylium ion in the proximity of the newly formed silyl ether oxygen (Scheme 2). Loss of $Et_3SiOSiEt_3$ from this species, which is likely quite facile and irreversible,[10] gives a carbocation that rapidly abstracts hydride from silane to complete the full deoxygenation of ketone. Because the product distribution is so different in these reactions, the production of silyl ether products exclusively in the $B(C_6F_5)_3$-catalyzed process suggests that the $[HB(C_6F_5)_3]^-$ counteranion is not simply a spectator but provides the hydride necessary to complete hydrosilation of the carbonyl group.

Further evidence for this notion exists in the following set of experiments. Borane $B(C_6F_5)_3$ is unable to mediate the hydrosilation of carbonyls (or the silation of alcohols[12]) when *i*-Pr_3SiH is the silane employed, presumably because the front strain associated with hydride abstraction is too great to effect activation of this sterically demanding silane. Nevertheless, when $[i\text{-}Pr_3Si]^+[B(C_6F_5)_4]^-$[19] is used as a catalyst for acetophenone reduction using *i*-Pr_3SiH (2 equiv), rapid production of ethylbenzene is observed (eq 13). Indeed, *i*-Pr_3SiH is a



(13)

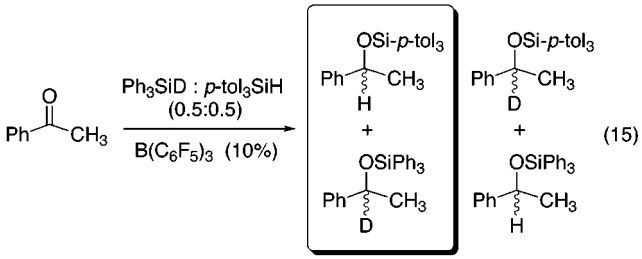
superior hydride donor toward Ph_3C^+ in comparison to Ph_3SiH according to the scale developed by Mayr et al.[24c] Thus, it is convincing evidence for hydridoborate delivery of hydride that in the experiment shown in eq 14, PhCD-



(14)

$(OSiPh_3)CH_3$ is observed as the sole product.[33]

A related experiment (eq 15) is also strongly supportive



(15)

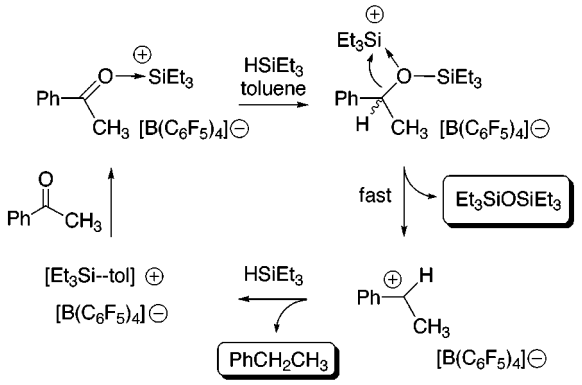
of borohydride delivery of hydride in the $B(C_6F_5)_3$-catalyzed reactions. A 1.5:0.5:0.5 mixture of acetophenone, $(p\text{-}CH_3C_6H_4)_3SiH$, and Ph_3SiH was treated with a

(30) (a) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1. (b) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

(31) Williams, V. C.; Piers, W. E.; Clegg, W.; Collins, S.; Marder, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 3244.

(32) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755.

Scheme 2



catalytic amount of $B(C_6F_5)_3$, and the reaction was monitored by ^1H NMR spectroscopy. An excess of acetophenone was employed to suppress $B(C_6F_5)_3$ mediated H/D scrambling between the silanes,[33] which we have shown is facile in the absence of Lewis bases (eq 4). Initial spectra revealed peaks attributable to the products PhC**H**(OSitol$_3$)CH$_3$ and PhC**D**(OSiPh$_3$)CH$_3$[34] in a ~4:1 ratio.[35] As the reaction progressed to completion, the two silyl ethers were ultimately present in a 1:1 ratio. The absence of the other possible isotopomeric products, i.e., PhCD(OSitol$_3$)CH$_3$ and PhCH(OSiPh$_3$)CH$_3$ strongly argues against hydride donation by silane in the $B(C_6F_5)_3$-catalyzed reaction, which would be expected to yield a mixture of all four of these possible products.

Conclusions

Taken together, the above kinetic, competition, intermediate modeling (i.e., the preparation of **1**), isotopic labeling, and crossover experiments provide solid support for the silane activation mechanism by which the $B(C_6F_5)_3$/R_3SiH hydrosilating system operates. Although this Lewis acid binds to carbonyl functions in the usual sense,[14] the actual mechanism of addition of Si−H to the C═O double bond follows the general path depicted in Scheme 1. Contrary to expectations based on the general perception that reactions such as this proceed through the LA/carbonyl adduct, the key step in this reaction is borane activation of the Si−H bond rather than C═O. Although the results of this study caution against sweeping generalizations, it appears that this type of mechanism is operative in other $B(C_6F_5)_3$-mediated reactions, such as the silation[12] and deoxygenation[10] of alcohols, the hydrosilation of imines,[36] the hydrostannation of carbonyl substrates,[37] and allylsilation and stannation reactions.[38]

We have taken pains to show that the final step in the reduction involves addition of H^- to the carbonyl carbon from the hydridoborate counteranion, rather than free silane and believe that the cumulative evidence obtained provides strong support for this proposal. This mechanistic issue has implications for devising strategies aimed at developing catalysts for performing diastereo and enantioselective hydrosilations. For example, if path **b** had been operative, a chiral silane (stoichiometric reagent) would presumably be necessary. However, the fact that path **a** most likely predominates provides hope that a chiral borane catalyst may be able to effect these transformations asymmetrically; efforts are currently being directed toward this goal.

Experimental Section

General. General procedures were as described previously.[12,14] Substrates were purchased from Aldrich-Sigma and dried and purified prior to use. Equilibrium constants for adduct formation between $B(C_6F_5)_3$ and the *para*-substituted acetophenone substrates were measured using ^1H NMR spectroscopy as described previously.[14] NMR data for the products of hydrosilation of the substrates in entries 1−3, Table 1, were reported in the Supporting Information deposited along with the original communication.[8] Data for the aldehyde products of entries 7,[39] 8,[40] and 9[41] were identical to reported data for these compounds. LRMS was done on a Varian Star 3400 CX GC with a Varian Saturn 2000 mass spec detector (electron impact ionization); HRMS was performed on a Kratos MS-80 spectrometer.

General Procedure for Ketone and Aldehyde Hydrosilations. A stock Ph_3SiH/2 mol % $B(C_6F_5)_3$ solution was prepared by dissolving 2.00 g of triphenylsilane and 0.079 g of tris(pentafluorophenyl)borane in toluene in a 10.0 mL volumetric flask. For each substrate, 0.5 mL of the stock solution was placed into a 3 mL vial containing a magnetic stir bar. For liquid substrates, 0.5 mL of toluene was added to the vial prior to sealing with a rubber septum; reaction was initiated by injection of 1 equiv of substrate. For solid substrates, 1 equiv was dissolved in 0.5 mL of toluene, and this solution was injected into the borane/silane mixture. Progress of the reaction was monitored by GC analysis of the reaction mixture. Upon completion of reaction the crude reaction mixture was introduced directly onto a silica gel liquid chromatography column and purified by column chromatography using hexanes/ethyl acetate mixtures.

General Procedure for Ester Hydrosilations. $B(C_6F_5)_3$ (0.0023 mmol) was added to a 25 mL round-bottom flask equipped with a magnetic stir bar. Benzene (3 mL) was added to the flask followed by the ester (2.15 mmol), and then the flask was sealed with a rubber septum. A solution of Ph_3SiH (2.4 mmol) in benzene (3 mL) was prepared and stored in a syringe. The flask was clamped to a stir plate and the solution was rapidly stirred. The silane solution was slowly added dropwise over a period of 5 min to the ester solution. The reaction was monitored by TLC and was quenched by the addition of THF (9 mL) and H_2O (1 mL) after all of the starting material was consumed. The heterogeneous solution was cooled to −8 °C, and then TBAF (5.4 mmol) in THF was added to the stirred solution via syringe. The reaction mixture was stirred at −8 °C for 30 min, then allowed to warm to room temperature, and stirred for an additional 3 h. The reaction mixture was poured into saturated NH_4Cl solution (25 mL), and the aqueous layer was extracted with Et_2O (4 × 15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, and then the solid was removed by suction filtration. The solvent was removed in vacuo, giving the crude product. Purification was performed by column chromatography using

(33) Although a trace of the proteo silyl ether is observed, this arises from the trace amounts of Ph_3SiH present in the d_1-triphenylsilane. It should also be noted that the rate of $B(C_6F_5)_3$-catalyzed H/D scrambling is very slow when one of the partners is *i*-Pr_3SiH. Furthermore, the rate of scrambling for silanes which are susceptible to exchange is slowed considerably when a Lewis base is present.

(34) These products were easily distinguishable at 400 MHz and were positively identified by separate synthesis and characterization.

(35) This observation is an indication that (*p*-$CH_3C_6H_4)_3SiH$ is a superior hydride donor in comparison to Ph_3SiD, as expected on the basis of both the isotope effect and the electronic properties of *p*-$CH_3C_6H_4-$ vs C_6H_5-.

(36) Sonmor, E.; Blackwell, J. M.; Piers, W. E. unpublished results.

(37) (a) Ooi, T.; Uraguchi, D.; Maruoka, K. *Tetrahedron Lett.* **1998**, *39*, 8105. (b) Ooi, T.; Uraguchi, D.; Kagoshima, N.; Maruoka, K. *J. Am. Chem. Soc.* **1998**, *120*, 5327. (c) Maruoka, K.; Ooi, T. *Chem. Eur. J.* **1999**, *5*, 829.

(38) Lambert, J. B.; Zhao, Y.; Wu. H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001.

(39) Ceruti, M.; Pegani, I.; Fochi, R. *Synthesis* **1987**, *1*, 79.

(40) Le Borgne, J.-F. *J. Organomet. Chem.* **1976**, *122*, 123.

(41) Koch, S. S. C.; Chamberlin, A. R. *J. Org. Chem.* **1993**, *58*, 2725.

hexanes/ethyl acetate eluants, followed by distillation at reduced pressure.

General Procedure for Kinetic Studies. Solutions containing known concentrations of Ph_3SiH and the standard fluorene were prepared in toluene. Next, 1 μL of each solution was injected into Et_3N (100 μL), the resulting solution was analyzed by GC using a standard temperature program, and the ratio of areas for the two peaks were obtained. This procedure was repeated three times for each concentration of Ph_3SiH, and the average of the area ratios was calculated. The averages were used to obtain the response factor of Ph_3SiH with respect to fluorene by plotting the concentration of Ph_3SiH versus the ratio of areas multiplied by the concentration of fluorene. The slope of the line obtained corresponds to the response factor of the system. Linear regression analysis of the data gave $R^2 = 0.997$ and the response factor, RF = 0.68(2).

The kinetics of hydrosilation were followed quantitatively by GC by monitoring the loss of Ph_3SiH. A stock solution consisting of Ph_3SiH, 2 mol % $B(C_6F_5)_3$, and fluorene was prepared in the drybox by dissolving 2.00 g of Ph_3SiH. 0.079 g of $B(C_6F_5)_3$, and 0.5−1.0 g of fluorene in toluene in a 10.0 mL volumetric flask. Next, 0.5 mL of the stock solution (0.384 mmol Ph_3SiH, 0.00772 mmol $B(C_6F_5)_3$) was measured via syringe and placed into a 1 dram vial containing a magnetic stir bar, and the vial was sealed with a rubber septum. One equivalent of substrate was dissolved in 0.5 mL of toluene, and this solution was injected into the vial (total volume = 1.0 mL). After completion of addition of the substrate solution, the time was recorded. Aliquots (1 μL) were extracted from the reaction mixture with a microsyringe at various time intervals and injected into a vial containing 100 μL of Et_3N. The moment at which the aliquot was injected into the Et_3N quenching solution was recorded. The quenched samples were subsequently analyzed by gas chromatography. The ratios of integrated area of Ph_3SiH to fluorene (internal standard) were calculated for the samples and then converted to concentrations of Ph_3SiH using the standardization curve obtained as described above. The natural logarithm of the silane concentration was plotted versus the time of quenching (in seconds) giving a straight line over several half-lives.

Ethyl 3-Triphenylsiloxybutanoate (Table 1, entry 4). The general procedure described above was used to prepare this product as a white solid in 84% yield after column chromatography. IR (KBr): 1735 (vs). ^{1}H NMR ($CDCl_3$): 7.61 (dd, J = 1.9 Hz and J = 7.5 Hz, 6H); 7.45−7.30 (m, 9H); 4.44 (ddq, J = 5.7 Hz, J = 6.1 Hz, and J = 7.2 Hz, 1H,); 3.99 (ABX_q, J = 7.1 Hz and J_{AB} = 10.8 Hz, 1H); 3.95 (ABX_q, 1H); 2.60 (ABX_q, J = 7.2 Hz and J_{AB} = 14.7 Hz, 1H); 2.41 (ABX_q, 1H); 1.21 (d, J = 6.1 Hz, 3H); 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): 171.2, 134.6, 135.5, 129.9, 127.8, 67.1, 60.2, 44.6, 23.7, 14.1. HRMS calcd for $C_{24}H_{26}O_3Si$: 390.1651. Found: 390.1632. Anal. Calcd for $C_{24}H_{26}O_3Si$: C, 73.81; H, 6.71. Found: C, 73.91; H, 6.54.

Ethyl 2-Triphenylsiloxy-1-cyclohexenecarboxylate (Table 1, entry 5). The general procedure described above was used to prepare this product as a white solid in 78% yield after column chromatography. IR (neat): 1713 (s). ^{1}H NMR: 7.85 (m, 6H); 7.18 (m, 9H); 3.93 (q, J = 7.0 Hz, 2H); 2.35 (m, 2H); 2.01 (m, 2H); 1.19 (m, 4H); 0.89 (t, 3H). ^{13}C NMR 167.0, 157.9, 136.0, 130.3, 128.1, 134.8, 110.7, 59.5, 32.7, 25.9, 22.9, 22.4, 14.4. HRMS calcd for $C_{27}H_{28}O_3Si - C_2H_5O$: 383.1467. Found: 383.1477. Exact mass calcd for $C_{27}H_{28}O_3Si - C_6H_5$: 351.1416. Found: 351.1420.

***cis*-2-Methylcyclohexanoxytriphenylsilane (Table 1, entry 6).** The general procedure described above was used to prepare this product as a white solid in 75% yield after column chromatography. ^{1}H NMR: 7.80 (m, 6H); 7.20 (m, 9H); 4.03 (m, 1H); 1.90−1.10 (m, 9H); 0.96 (d, J = 6.7 Hz, 3H). ^{13}C NMR: 135.7, 136.0, 130.1, 128.1, 73.5, 37.2, 33.0, 29.7, 24.9, 21.5, 17.8. HRMS calcd for $C_{25}H_{28}OSi$: 372.1909. Found: 372.1894. Anal. Calcd for $C_{25}H_{28}OSi$: C, 80.59; H, 7.58. Found: C, 80.46; H, 7.29.

Evidence for $Et_3SiH/B(C_6F_5)_3$ Interaction. ^{19}F NMR spectral data for 2 mg of $B(C_6F_5)_3$ in 500 μL of Et_3SiH at rt: 128.1 (m, 2F, F_{ortho}); 143.6 (m, 1F, F_{para}); 160.2 (m, 2F, F_{para}). ^{19}F NMR spectral data for 2 mg of $B(C_6F_5)_3$ in 500 μL of Et_3SiH at −80 °C: 130.1 (m, 2F, F_{ortho}); 150.3 (m, 1F, F_{para}); 161.4 (m, 2F, F_{meta}).

Computational Studies. All structures were built using the SPARTAN molecular modeling program.[42] All structures were geometry-optimized with no constraints using semiempirical methods at the AM1 level of theory. Charges were calculated at the AM1 level using Mulliken population analysis.

Measurement of the Deuterium Kinetic Isotope Effect. Ph_3SiH (57.0 mg, 0.218 mmol), Ph_3SiD (57.0 mg, 0.218 mmol), and $B(C_6F_5)_3$ (2.0 mg, 0.0039 mmol) were dissolved in C_6D_6 (0.6 mL) in a dry NMR tube. Acetophenone (25.4 μL, 0.218 mmol) was added to the solution via syringe. The resulting solution was vigorously shaken to ensure complete mixing,and then the ^{1}H NMR spectrum was obtained. A mixture of products $PhCH(OSiPh_3)CH_3$ and $PhCD(OSiPh_3)CH_3$ was observed, and the relative ratio of the two species was found to be 1.4:1, respectively, by integration, corresponding to a kinetic isotope effect found to be k_H/k_D = 1.4(5).

In Situ Generation of $[Ph(CH_3)C{=}O{\bullet}SiEt_3]^+[B(C_6F_5)_4]^-$ (1). $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.24 mg, 0.026 mmol) was suspended in C_6D_6, and Et_3SiH (4.2 μL, 0.026 mmol) was added via syringe. Upon shaking, a clear liquid clathrate separated from the benzene, and ^{1}H NMR analysis revealed the presence of Ph_3CH. To this sample was added acetophenone (3.0 μL, 0.026 mmol) via syringe. Upon shaking, the liquid clathrate layer turned light orange. The C_6D_6 was decanted from the oil, and the oil was washed twice with 0.2 mL of C_6D_6. The oil was subsequently dissolved in C_6D_5Br and analyzed by NMR spectroscopy. ^{1}H NMR: 7.68 (m, 2H); 7.44 (m, 1H); 7.09 (m, 2H); 2.44 (s, 3H); 0.7−1.3 (m, 15H). $^{13}C\{^1H\}$ NMR: 217.8, 144.7, 134.6, 131.9, 130.9, 149.1 (J_{C-F} = 242.6 Hz), 139.0 (J_{C-F} = 245.7 Hz), 137.1 (J_{C-F} = 243.6 Hz), 25.6, 6.1, 5.1. ^{19}F NMR: −131.9 (F_{ortho}); −162.1 (F_{para}); −166.1 (F_{meta}). $^{11}B\{^1H\}$ NMR: −16.8.

Deoxygenation of Acetophenone with Et_3SiH with Various Catalysts (eq 12). Et_3SiH (48 μL, 0.3 mmol) was dissolved in C_6D_6, and catalyst (0.006 mmol) was added. Then PhC(O)Me (35 μL, 0.3 mmol) in C_6D_6 was added via syringe, and the reaction was followed by ^{1}H NMR spectroscopy. In each case, this analysis showed unreacted PhC(O)Me and production of $PhCH_2CH_3$ with no $PhCH(OSiEt_3)Me$ observable.

Deoxygenation of Acetophenone with *i*-Pr_3SiH Catalyzed by $[i\text{-}Pr_3Si]^+[B(C_6F_5)_4]^-$. To an orange-red, two-phase solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (24 mg, 0.03 mmol) in C_6D_6 was added *i*-Pr_3SiH (60 μL, 0.30 mmol). The mixture remained biphasic but became pale yellow in color. To this mixture was added PhC(O)Me (15 mg, 0.13 mmol). ^{1}H NMR analysis of the top bright yellow layer within 5 min of mixing showed that all PhC(O)Me was consumed and that $PhCH_2CH_3$ was formed quantitatively.

Hydrosilation of Acetophenone Using *i*-Pr_3SiH/Ph_3SiD Mixture. To PhC(O)Me (6 mg, 0.05 mmol), Ph_3SiD (13 mg, 0.05 mmol), and *i*-Pr_3SiH (10 μL, 0.05 mmol) dissolved in C_6D_6 was added $B(C_6F_5)_3$ (5 mg, 0.01 mmol) as a solution in C_6D_6. NMR analysis of the product mixture showed the formation of $PhCD(OSiPh_3)Me$ and only trace quantities of $PhCH(OSiPh_3)_3$ interpreted to arise from a small amount of Ph_3SiH contaminant.

Hydrosilation of Acetophenone Using $(tolyl)_3SiH/Ph_3SiD$ Mixture. Ph_3SiD (13 mg, 0.05 mmol) and $(p\text{-}CH_3C_6H_4)_3SiH$ (15 mg, 0.05 mmol) were dissolved in C_6D_6 in an NMR tube. Acetophenone (18 μL, 0.15 mmol) was added followed by a solution of $B(C_6F_5)_3$ in C_6D_6 (5 mg, 0.01 mmol in 100 μL). A ^{1}H NMR spectrum was immediately obtained (1 min after mixing), and spectra were collected periodically over a 75 min time period. ^{1}H NMR analysis revealed that only $PhCH(OSitol_3)Me$ and $PhCD(OSiPh_3)Me$ were formed. The identity of the former compound was confirmed by independent synthesis via $B(C_6F_5)_3$-catalyzed silation of PhCH(OH)Me using

(42) Spartan Version 3.1; Wave function Inc.: Irvine, CA.

$(tol)_3SiH$. ^1H NMR (C_6D_6): 7.75 (d, 6H, J = 8.0 Hz); 7.39−7.35 (m, 2H), 7.17−7.00 (m, 9H); 5.19 (q, 1H, J = 6.3 Hz); 2.08 (s, 9H); 1.46 (d, 3H, J = 6.3 Hz). ^{13}C NMR (C_6D_6): 147.1, 140.2, 136.4, 132.5, 129.4, 127.5, 126.2, 72.6, 27.8, 22.0 (one aromatic carbon missing).

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