Studies on the Mechanism of B(C_{6}F_{5})_{3}-Catalyzed Hydrosilation of Carbonyl Functions

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The strong organoborane Lewis acid B(C_{6}F_{5})_{3} catalyzes the hydrosilation (using R_{3}SiH) 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 silylum species then coordinates the most basic function, which is selectively reduced by [HB(C_{6}F_{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_{6}F_{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_{6}F_{5})_{3} has emerged in recent years as a viable alternative.2 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_{6}F_{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_{6}F_{5})_{3} is an effective catalyst for the hydrosilation of a variety of aldehydes, ketones, and esters.8 BF_{3}·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_{6}F_{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_{6}F_{5})_{3}-Catalyzed Hydrosilation of Carbonyl Functions

In the presence of 1–4 mol % B(C_{6}F_{5})_{3}, addition of 1 equiv of R_{3}SiH 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 ary-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 reactions10 under all conditions examined. These

References

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(10) We see ref 12 and others have observed B(C_{6}F_{5})_{3}-catalyzed cleavage of ethers with silanes. See: Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. Tetrahedron Lett. 1999, 40, 8919.
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(C₆F₅)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(C₆F₅)₃/R₃SiH 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(C₆F₅)₃/R₃SiH 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(C₆F₅)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(C₆F₅)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(C₆F₅)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 constants for the para-X acetophenones (X = H, CH₃, Cl, NO₂) 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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Table 1. B(C₆F₅)₃-Catalyzed Hydrosilation of Carbonyl Functions Using Ph₃SiH

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>X</th>
<th>Conc.</th>
<th>Product</th>
<th>Yield</th>
</tr>
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<tr>
<td>1a</td>
<td></td>
<td>H</td>
<td>A</td>
<td>Ph₂CH₂OSiPh₃ + Ph₂SiOEt</td>
<td>87</td>
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<tr>
<td>1b</td>
<td></td>
<td>Cl</td>
<td>A</td>
<td>Ph₂CH₂OSiPh₃ + Ph₂SiOEt</td>
<td>82</td>
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<tr>
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<td></td>
<td>NO₂</td>
<td>A</td>
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<td>81</td>
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<tr>
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<td>A</td>
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<td>76</td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td>Cl</td>
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<td>84</td>
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<tr>
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<td>NO₂</td>
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<td>5</td>
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<td>Ph₂CH₂OSiPh₃ + Ph₂SiOEt</td>
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<td>6</td>
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<td>Ph₂CH₂OSiPh₃ + Ph₂SiOEt</td>
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<td>Ph₂CH₂OSiPh₃ + Ph₂SiOEt</td>
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<td>A</td>
<td>Ph₂CH₂OSiPh₃ + Ph₂SiOEt</td>
<td>45</td>
</tr>
</tbody>
</table>

*Conditions: A, 2% B(C₆F₅)₃, benzene or toluene; B, 1% B(C₆F₅)₃, toluene, syringe pump addition of silane over 1 h. Isolated yields. 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. Reaction via enol tautomer of substrate. cis diastereomer produced exclusively.

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Figure 1. Plot of $1/K_{obs}$ ($\times 10^{-4}$) vs acetophenone concentration for the hydrosilation of acetophenone with $\text{Ph}_3\text{SiH}$.

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 ($k_{obs} = 3.61(7) \times 10^{-4} \text{ s}^{-1}$ for $X = \text{Me}$; $2.01(5) \times 10^{-3} \text{ s}^{-1}$ for $X = \text{Cl}$; $1.35(3) \times 10^{-2} \text{ s}^{-1}$ for $X = \text{NO}_2$) 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 $\text{B}(\text{C}_6\text{F}_5)_3$ 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. In light of the above kinetic data, we propose a mechanism in which dissociation of borane from the substrate is necessary in order that $\text{B}(\text{C}_6\text{F}_5)_3$ may activate the silane. 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 silylum 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 core-

![Scheme 1](image)


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generated via hydride abstraction from Bu$_3$SnH using B(C$_6$F$_5$)$_3$.$^{18}$ By analogy to these phenomena, it is reasonable to propose that borane is able to abstract hydride, at least partially, from R$_3$SiH.

Attempts to garner direct spectroscopic evidence for a B(C$_6$F$_5$)$_3$/silane interaction were only partially successful. When samples of B(C$_6$F$_5$)$_3$ and either Ph$_3$SiH or Et$_3$SiH (1:1 in C$_6$D$_6$) are monitored by $^1$H 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 resonance for the $^{29}$Si nucleus shifts from 0.5 ppm in free Et$_3$SiH to 1.2 ppm in the presence of 1 equiv of B(C$_6$F$_5$)$_3$. 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$_6$F$_5$)$_3$ in neat Et$_3$SiH was recorded at $-80$ °C. The chemical shift of the para-fluorines of the boron C$_6$F$_5$ rings are quite sensitive to the coordination environment about boron.$^{20}$ The value of $\Delta(\delta_{0p})$ for B(C$_6$F$_5$)$_3$ in neat Et$_3$SiH at room temperature is 16.6 ppm (cf. a value of 18.3 ppm for B(C$_6$F$_5$)$_3$ in C$_6$D$_6$)$^{20}$; at $-80$ °C, the value falls to 11.1 ppm, which is in the range expected for a weak Lewis base/B(C$_6$F$_5$)$_3$ 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$^{15,21}$), when B(C$_6$F$_5$)$_3$ is the abstracting agent, the process is incomplete and rapidly reversible.

There is, however, convincing indirect $^1$H NMR spectroscopic evidence that the chemistry in eq 3 is occurring. Although the chemical shift change for the silane hydrogen in Et$_3$SiH is insignificant when B(C$_6$F$_5$)$_3$ is added to the sample, the $^1$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 $^1$J Si–H coupling is no longer in evidence in these spectra. This phenomenon is reminiscent of that observed in the $^1$H 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$_3$Si][HB(C$_6$F$_5$)$_3$]$^-$. This is also manifested by the observed rapid scrambling of deuterium when a 1:1 mixture of Et$_3$SiH and Ph$_3$SiD is treated with 10% B(C$_6$F$_5$)$_3$ (eq 4). In the absence of ketone 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$_6$F$_5$)$_3$ with Ph$_3$SiH and Et$_3$SiH 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$_6$F$_5$)$_3$ and [HB(C$_6$F$_5$)$_3$]$^-$. 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.

Finally, the magnitude of the kinetic isotope effect observed in the B(C$_6$F$_5$)$_3$ catalyzed addition of Ph$_3$SiX (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 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 carboxylates with various silanes. Isotope effects of 1.4–1.9 have been reported for these reactions24 and interpreted in terms of hydride transfer24c (eq 6) rather than initial electron transfer followed by a hydrogen atom shift24a,b (eq 7) since 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(C6F5)3 followed by transfer of a hydrogen atom (eq 8), which must be considered since it has recently been shown that one-electron reduction of B(C6F5)3 is the first step in its reaction with a zirconaazacyclobutane derivative.

**Interation 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 acetonophene, when a 1:1 mixture of these two substrates is hydrosilated with Ph3SiH, 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) × 10^{-4} s^{-1}) is similar to that found for the hydrosilation of benzaldehyde itself (6.0(1)

\[
\text{Ph}_3\text{C} + \text{H-SiR}_3 \rightarrow \text{Ph}_3\text{C-H} + \text{SiR}_3
\]

(eq 6) rather than initial electron transfer:

\[
\text{Ph}_3\text{C} + \text{H-SiR}_3 \rightarrow [\text{Ph}_3\text{C}^- (\text{H-SiR}_3)^{+}]
\]

(eq 10). Most notably, the 13C resonance for the carbonyl carbon shifts downfield to 217.8 ppm from 196.8 ppm for free acetonophene in CD3Br, 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(C6F5)4]^{-} anion, ketone adducts of trialkylsilanylium ions are reasonable species and, like the olefin adducts of R3Si+ reported by Lambert et al.,29 have appreciable carbocationic character at the carbonyl carbon.


(26) We assume here that the relative basicities of benzaldehyde, acetonophene, and ethylbenzoate towards the borane/silane complex mirror that found for B(C6F5)3 itself.14

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


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 $[\text{HB(C}_6\text{F}_5\text{)_3}]$ (path a, Scheme 1) or by $\text{R}_3\text{SiH}$ (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 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 $\text{B(C}_6\text{F}_5\text{)_3}$ gives the silyl ether reduction product exclusively, a 1:1 mixture of ethylbenzene/hexaethyldisiloxane and unreacted acetophenone are produced when $[\text{Et}_3\text{Si}]^+\text{B}(-\text{C}_6\text{F}_5\text{)_4}]^{-}$, $[\text{Ph}_3\text{C}]^+\text{B}(-\text{C}_6\text{F}_5\text{)_4}]^{-}$, or the diborane $1,2-[\text{B(C}_6\text{F}_5\text{)_3}]_2\text{C}_6\text{F}_4$11 are employed as catalysts. In the latter case, abstraction of $\text{H}^-$ from silane presumably leads to silylium ion II, in which the hydride moiety in the counteranion is chelated by the two borane centers12 and is effectively unavailable for delivery to substrate; thus, in this system “$\text{Et}_3\text{Si}^+$” is again the true catalyst.

In these reactions, where $\text{Et}_3\text{SiH}$ is the only hydride donor present, abstraction of hydride by the carbocation-like ketone adducts of $\text{Et}_3\text{Si}^+$ regenerates the silylium ion in the proximity of the newly formed silyl ether oxygen (Scheme 2). Loss of $\text{Et}_3\text{SiOSiEt}_3$ 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 $\text{B(C}_6\text{F}_5\text{)_3}$-catalyzed process suggests that the $[\text{HB(C}_6\text{F}_5\text{)_3}]^{-}$ 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 $\text{B(C}_6\text{F}_5\text{)_3}$ is unable to mediate the hydrosilation of carbonyls (or the silation of alcohols12) when $\text{i-Pr}_3\text{SiH}$ 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 $[\text{i-Pr}_3\text{Si}]^+[\text{B(C}_6\text{F}_5\text{)_3}]^{-}$ is used as a catalyst for acetophenone reduction using $\text{i-Pr}_3\text{SiH}$ (2 equiv), rapid production of ethylbenzene is observed (eq 13). Indeed, $\text{i-Pr}_3\text{SiH}$ is a superior hydride donor toward $\text{Ph}_3\text{C}^+$ in comparison to $\text{Ph}_3\text{SiH}$ 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, $\text{PhCD}^-$ is observed as the sole product.33 A related experiment (eq 15) is also strongly supportive of borohydride delivery of hydride in the $\text{B(C}_6\text{F}_5\text{)_3}$-catalyzed reactions. A 1.5:0.5:0.5 mixture of acetophenone, ($\text{p-CH}_3\text{C}_6\text{H}_4)_3\text{SiH}$, and $\text{Ph}_3\text{SiH}$ was treated with a
catalytic amount of B(C6F5)3, and the reaction was monitored by 1H NMR spectroscopy. An excess of acetophenone was employed to suppress B(C6F5)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 PhCH(OSiPh3)CH3 and PhCH(OSiOMe)CH3,34 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(OSiPh3)CH3 and PhCH(OSiOMe)CH3 strongly argues against hydride donation by silane in the B(C6F5)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-labeling, and crossover experiments provide solid support for the silane activation mechanism by which the B(C6F5)3/Ph3SiH 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(C6F5)3-mediated reactions, such as the silation12 and deoxygenation10 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 diastereofacial and enantioselective hydrosilations. For example, if path b had been operative, a chiral silane (stochiometric 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(C6F5)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 products of entries 7, 39, 8, 10, and 94 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 Ph3SiH/2 mol % B(C6F5)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 boranepsilane mixture. Progress of the reaction was monitored by GC analysis of the reaction mixture. Upon completion of reaction, the crude reduced 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(C6F5)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 Ph3SiH (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 H2O (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 purged into saturated NH4Cl solution (25 mL), and the aqueous layer was extracted with Et2O (4 × 15 mL). The combined organic extracts were dried over anhydrous MgSO4, 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
hexanes/ethyl acetate eluants, followed by distillation at reduced pressure.

**General Procedure for Kinetic Studies.** Solutions containing known concentrations of Ph3SiH and the standard fluorene were prepared in toluene. Next, 1 μL of each solution was injected into Et3N (100 μL), the resulting solution was analyzed by GC using a standard temperature program, and the ratio of areas for the two peaks was obtained. This procedure was repeated three times for each concentration of Ph3SiH, and the average of the area ratios was calculated. The averages were used to obtain the response factor of Ph3SiH with respect to fluorene by plotting the concentration of Ph3SiH 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 R² = 0.997 and the response factor, RF = 0.69.

The kinetics of hydrosilation were followed quantitatively by GC by monitoring the loss of Ph3SiH. A stock solution consisting of Ph3SiH, 2 mol % B(C6F5)3, and fluorene was prepared in the drybox by dissolving 2.00 g of Ph3SiH, 0.079 mmol B(C6F5)3, and 0.5 mol % fluorene in toluene. Next, 1 mL of the stock solution (0.384 mmol Ph3SiH, 0.00772 mmol B(C6F5)3) was measured via GC by monitoring the loss of Ph3SiH. A stock solution of Et3SiH at rt: 128.1 (m, 2F, F reson; 143.6 (m, 1F, F reson); 160.2 (m, 2F, F reson). 19F NMR spectral data for 2 mg of B(CF3)3 in 500 μL of Et3SiH at -80 °C: 130.1 (m, 2F, F reson; 150.3 (m, 1F, F reson); 161.4 (m, 2F, F reson).

**Computational Studies.** All structures were built using the SPARTAN molecular modeling program. All structures were geometry-optimized with no constraints using semi-empirical 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.** Ph3SiH (57.0 mg, 0.218 mmol), Ph3SiD (57.0 mg, 0.218 mmol), and B(CF3)3 (2.0 mg, 0.0039 mmol) were dissolved in CD3OD (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 1H NMR spectrum was obtained. A mixture of products PhCHO(OSiPh3)CH2 and PhCH(O(OSiPh3)CH2)3 was observed, and the relative ratio of the two products was found to be 1:4.1, respectively, by integration, corresponding to a kinetic isotope effect found to be kHD/kH = 1.45).

In Situ Generation of [Ph(CH3)C=O]SiEt3][B(CF3)3] (1) ([PhC]=B(CF3)3) (0.24 mg, 0.026 mmol) was suspended in CD3OD, and Et3SiH (4.2 μL, 0.026 mmol) was added via syringe. Upon shaking, a clear liquid clathrate separated from the benzene, and 1H NMR analysis revealed the presence of PhCH. To this sample was added acetophenone (3.0 μL, 0.026 mmol) via syringe. Upon shaking, the liquid clathrate layer turned light orange. The CD3OD was decanted from the oil, and the oil was washed twice with 0.2 mL of CD3OD. The oil was subsequently dissolved in CD3OD and analyzed by NMR spectroscopy. 1H NMR: 7.68 (m, 2H); 7.44 (m, 1H); 7.09 (m, 2H); 2.44 (s, 3H); 0.7–1.3 (m, 15H). 13C(1H) NMR: 217.8, 144.7, 134.6, 131.9, 130.9, 149.1 (J C-F = 245.7 Hz), 137.1 (J C-F = 246.3 Hz), 25.6, 6.1, 5.1. 19F NMR: -19.9 (FTMS), -162.1 (F para, -166.1 (F meta), -168.36.

Deoxygencnation of Acetophenone with Et3SiH with Various Catalysts (eq 12). Et3SiH (48 μL, 0.3 mmol) was dissolved in CD3OD, and catalyst (0.066 mmol) was added. Then PhCO(O)Me (35 μL, 0.3 mmol) in CD3OD was added via syringe, and the reaction was followed by 1H NMR spectroscopy. In each case, this analysis showed unreacted PhCO(O)Me and production of PhCH2CH3 with no PhCHO(OSiEt3)CH2 observable.

Deoxygencnation of Acetophenone with i-Pr3SiH Catalyzed by [i-Pr3Si][B(CF3)3]. To an orange-red, two-phase solution of [Ph(CH3)C=O]SiEt3][B(CF3)3] (24 mg, 0.03 mmol) in CD3OD, was added i-Pr3SiH (60 μL, 0.30 mmol). The mixture remained biphasic but became pale yellow in color. To this mixture was added PhCO(O)Me (15 mg, 0.13 mmol). 1H NMR analysis of the top bright yellow layer within 5 min of mixing showed that all PhCO(O)Me was consumed and that PhCH2CH3 was formed quantitatively.

Hydrolysis of Acetophenone Using i-Pr3Si/Ph3Si Mixture. To PhCO(O)Me (6 mg, 0.05 mmol), Ph3SiD (13 mg, 0.05 mmol), and i-Pr3SiH (10 μL, 0.05 mmol) dissolved in CD3OD, was added B(CF3)3 (5 mg, 0.01 mmol) as a solution in CD3OD. NMR analysis of the product mixture showed the formation of PhCHO(OSiPh3)Me and only trace quantities of PhCHO(OSiPr3)Me. 1H NMR analysis of the top bright yellow layer within 5 min of mixing showed that all PhCO(O)Me was consumed and that PhCH2CH3 was formed quantitatively.

Hydrolysis of Acetophenone Using (tolylo)Si/Ph3Si Mixture. PhCO(O)Me (18 μL, 0.15 mmol) was added by a solution of B(CF3)3 in CD3OD, 5 mg, 0.01 mmol in 100 μL) A 1H NMR spectrum was immediately obtained (1 min after mixing), and spectra were collected periodically over a 75 min time period. 1H NMR analysis revealed that only PhCHO(OSiSiMe3)Me and PhCHO(OSiPr3)Me were formed. The identity of the former compound was confirmed by independent synthesis via B(CF3)3-catalyzed silylation of PhCHO(OH)Me using (24) Spartan Version 3.1; Wave function Inc.: Irvine, CA.
\((\text{tol})_2\text{SiH}\). \(^1\text{H}\) NMR \((\text{C}_6\text{D}_6)\): 7.75 \(\text{d, 6H, } J = 8.0\) \(\text{Hz}\); 7.39–7.35 \(\text{m, 2H}\); 7.17–7.00 \(\text{m, 9H}\); 5.19 \(\text{q, 1H, } J = 6.3\) \(\text{Hz}\); 2.08 \(\text{s, 9H}\); 1.46 \(\text{d, 3H, } J = 6.3\) \(\text{Hz}\). \(^{13}\text{C}\) NMR \((\text{C}_6\text{D}_6)\): 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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