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Mechanistic Aspects of Bond Activation with Perfluoroarylboranes

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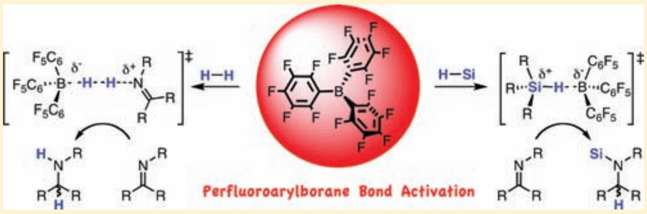
Supporting Information

ABSTRACT: In the mid-1990s, it was discovered that tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was an effective catalyst for hydrosilylation of a variety of carbonyl and imine functions. Mechanistic studies revealed a counterintuitive path in which the function of the borane was to activate the silane rather than the organic substrate. This was the first example of what has come to be known as "frustrated Lewis pair" chemistry utilizing this remarkable class of electrophilic boranes. Subsequent discoveries by the groups of Stephan and Erker showed that this could be extended to the activation of dihydrogen, initiating an intense period of activity in this area in the past 5 years. This article describes the early hydrosilylation chemistry and its subsequent applications to a variety of transformations of importance to organic and inorganic chemists, drawing parallels with the more recent hydrogen activation chemistry. Here, we emphasize the current understanding of the mechanism of this process rather than focusing on the many and emerging applications of hydrogen activation by fluoroarylborane-based frustrated Lewis pair systems.



INTRODUCTION

The activation of inert, nonpolar chemical bonds for useful functionalization has been a key research goal in many fields of catalysis and synthesis. For the most part, relevant activation processes have been the province of transition metals,[1] whether on heterogeneous surfaces or at metal centers in well-defined molecular compounds. Particularly in the latter arena, much is known regarding the mechanistic details of how various chemically inert bonds may be activated and reforged at transition-metal centers.

A textbook mechanistic picture involves the processes outlined in Scheme 1, utilizing the simplest substrate, dihydrogen (H_2), for illustration purposes. In most instances, the formation of a H_2 σ complex[2,3] is a likely first step, although this species may be a transition structure as opposed to a bona fide reacton intermediate. Two mechanisms for H−H cleavage emanate from this species: one path involving heterolytic cleavage of H_2 and the other featuring homolytic rupture of the H−H bond. In the former, an external or internal base may function as a deprotonating agent that accepts a proton from the polarized coordinated H_2 molecule in the σ complex. This path is typically followed in cationic species. Alternately, electrons in π-symmetric orbitals on the metal back-donate into the H_2 σ^* orbitals even as bonding electrons from the coordinated H_2 form a σ bond with the metal. This synergistic flow of electrons comprises the homolytic oxidative cleavage of the H−H bond concurrent with the formation of new M−H bonds. Both paths result in reactive metal hydrido complexes that are available for the functionalization of other substrates. Furthermore, the scheme may be generalized to include activation of other nonpolar bonds, such as Si−H, C−H, and B−H bonds.[4]

How is this relevant to a Forum Article on main-group chemistry? The recent renaissance of activity in main-group chemistry[5] that has, in part, led to this forum has in significant measure been driven by discoveries in the past decade[6−9] that show that systems consisting only of main-group elements can also activate the bonds discussed above in useful catalytic reactions.[10] These observations are significant on both economic and environmental grounds: main-group element-based catalysts are typically not as costly as transition-metal-based systems (which tend to rely on more expensive second- and third-row noble metals) and, especially for lighter main-group elements, toxicity issues are far less concerning. Thus, such main-group-element-based bond activation systems may be a cornerstone of potentially greener and more sustainable commercial processes.[11]

One class of main-group-element-based catalysts of considerable interest is the perfluoroarylboranes, typified by the parent compound tris(pentafluorophenyl)borane.[12−14] This compound, first reported in 1963,[15] is nearly 50 years old but is still going strong. It is characterized by strong Lewic acidity and excellent thermal stability and solubility in a wide range of solvents.[16,17] Moreover, and most remarkably, it is highly resistant to hydrolytic decomposition via B−C bond cleavage.[18] Although extremely hygroscopic, the water adducts formed via coordination of up to three water molecules[19] in the primary and secondary coordination spheres are quite stable, proceeding to $HOB(C_6F_5)_2$ and HC_6F_5 only slowly under ambient conditions. Despite this stability, awareness of this propensity to coordinate water is crucial for its use as a *Lewis* acid; the water adduct is a strong *Bronsted* acid,[20] and care must be taken to dry and store the reagent properly to avoid the introduction of trace amounts of H^+, which may or may not have an effect on the chemistry for

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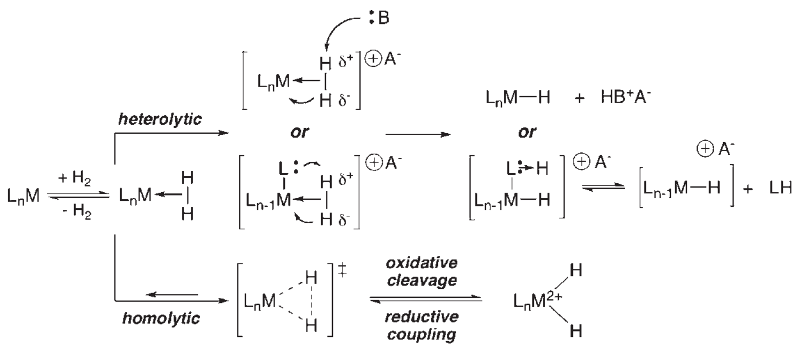
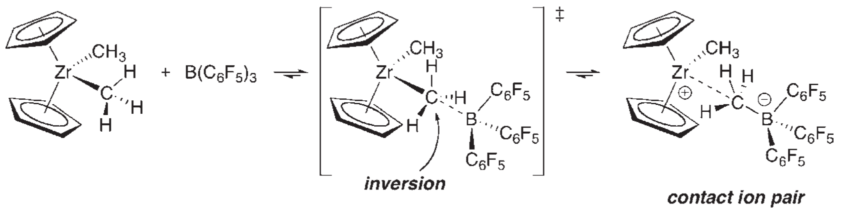
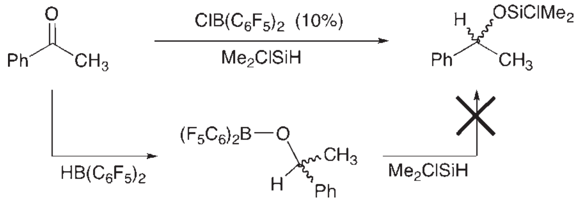
Scheme 1



Scheme 2



Scheme 3



which $B(C_6F_5)_3$ catalysis is intended. Finally, it should be recognized that $B(C_6F_5)_3$ is a reasonably powerful one-electron oxidant[21] in weakly donating solvents, with an estimated reduction potential of −0.64 V vs SCE.[22]

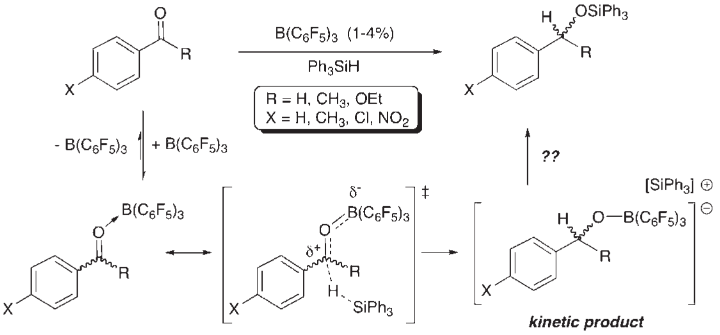
Tris(pentafluorophenyl)borane and its derivatives are employed in large-scale commercial processes that require the activation of catalyst precursors via abstraction of an X-type ligand to open up vacant coordination sites.[23] The strong Lewis acidity of $B(C_6F_5)_3$ allows it to do this effectively in, for example, early-transition-metal alkyl compounds, forming metal alkyl cations that serve as highly active olefin polymerization catalysts (Scheme 2). This application illustrates the Lewis acid strength of $B(C_6F_5)_3$ in that it is able to outcompete group 4 metallocenium cations, strong Lewis acids themselves, for alkide anions. The thermodynamic favorability of alkide transfer to boron is combined with a kinetically facile backside abstraction pathway that inverts the stereochemistry[24] of the abstracted alkide carbon (see Scheme 2). Finally, although the fluoroarylborate counteranion is weakly coordinating, the $[H_3CB(C_6F_5)_3]^-$ anion stabilizes the metallocenium cation through a contact ion-pair structure mediated by the bridging methyl group. The chemistry and dynamic properties of these types of ion pairs have been studied in great detail,[23] and this body of work offers insight into how boranes such as $B(C_6F_5)_3$ are able to activate nonpolar E−H bonds.

■ ACTIVATION OF SI−H BONDS

In the early 1990s, our group was engaged in the development of zwitterionic metallocenes[25] that could "self-activate" in the context of olefin polymerization catalysis. Accordingly, we developed routes to the new perfluoroarylborane bis(pentafluorophenyl)borane, $HB(C_6F_5)_2$,[26,27] to use as a reagent for the incorporation of Lewis acidic borane moieties into the ligand framework of group 4 metal-based metallocenes via the hydroboration of appropriate pendant functions.[28−31] Bis(pentafluorophenyl)borane turned out to be an excellent hydroboration reagent for a wide variety of olefins[27,32] by virtue of its relatively high Lewis acidity and its high tendency to dissociate into the monomeric boranes necessary to interact with hydroboration substrates, relative to other $[R_2BH]_2$ dimers.

We also found that it reacted rapidly with the carbonyl function of acetophenone, as depicted in Scheme 3. Because our original synthesis of the borane involved the treatment of $ClB(C_6F_5)_2$ with dimethylchlorosilane,[26] we postulated that the borinic ester produced via hydroboration of acetophenone might also be converted back to the borane in the presence of Me_2ClSiH, effectively making $HB(C_6F_5)_2$ a catalyst for the hydrosilylation of ketones. As predicted, when 10 mol % of the chloroborane was added to a mixture of acetophenone and Me_2ClSiH (1:1), catalytic formation of the hydrosilated ketone product was observed over the course of time, albeit slowly. However, when separately prepared, isolated borinic ester $(F_5C_6)_2BOCH(Ph)Me$ was *not* converted to $HB(C_6F_5)_2$ and silyl ether when treated with Me_2ClSiH, even at elevated temperatures, suggesting that the catalytic hydrosilylation was proceeding via another mechanism.

Scheme 4

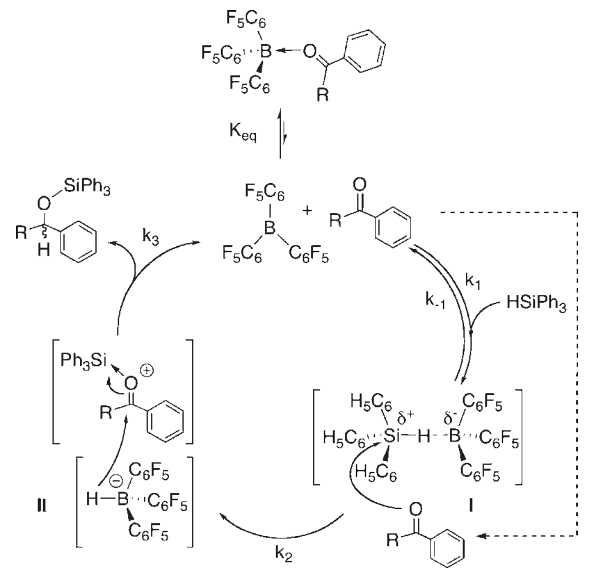


The most obvious alternative was via Lewis acid catalysis, wherein the boranes present would activate the carbonyl via coordination to the oxygen in a classic Lewis acid/Lewis base interaction. Indeed, scattered reports in the 1970s[33,34] suggested that $BF_3 \cdot OEt_2$ was an effective mediator of the hydrosilylation of carbonyl functions, and mechanistic postulates, although somewhat vague, invoked carbonyl—BF_3 adducts as key intermediates in the reaction. Thus, instead of using $HB(C_6F_5)_2$ as envisioned in Scheme 3, we employed $B(C_6F_5)_3$ as a catalyst and found that low loadings (1—4%) rapidly catalyzed the clean hydrosilylation of various aromatic aldehydes, ketones, and esters using $HSiPh_3$ as the silating reagent (Scheme 4).[35] When these substrates were reacted with stoichiometric amounts of borane in the absence of silane, equilibria resulted that strongly favored the $ArC(O)R \cdot B(C_6F_5)_3$ adducts[36] (K_{eq} is on the order of 10^2—10^4 depending on the basicity of the carbonyl compound) and, indeed, the X-ray structures of several of these isolated adducts were determinable. Given the previous literature on BF_3-mediated hydrosilylations and the obvious facility with which $B(C_6F_5)_3$ forms strong adducts with carbonyl functions, our initial mechanistic hypothesis for the $B(C_6F_5)_3$-facilitated reaction involved a classical Lewis acid activation pathway, as depicted in Scheme 4. However, admittedly without anything but a gut feeling, we felt that conversion of the presumed kinetic product of such a pathway, namely, the alkoxyborate—silylium ion pair shown, to the observed silyl ether thermodynamic products would face significant kinetic barriers, an issue not consistent with the rapid rates and high selectivities observed in these reactions. Adding to the unease concerning such a mechanism was the fact that we soon realized that the qualitative rate trends that we were witnessing showed that substrates of *lower* basicity toward $B(C_6F_5)_3$ were hydrosilated at much faster rates than the more strongly basic substrates, an observation completely inconsistent with the notion that the Lewis acid's function was to activate the carbonyl toward nucleophilic attack by the silane reagent. Quantitative kinetic studies confirmed these observations, establishing rate trends that not only showed that less basic substrates (as a function of both R and X in the aromatic carbonyl compounds of Scheme 4) were hydrosilated more rapidly than more basic substrates but that there was a substantial inhibitory effect of [substrate] on the observed rate of reaction. Thus, while k_{obs} was found to be directly proportional to the borane catalyst concentration, it was inversely proportional to the substrate concentration. Taken together, these observations led to the counterintuitive conclusion that borane activation of the carbonyl function, despite the favorable equilibria toward Lewis acid/base adducts, was *not* a key feature of the mechanism.

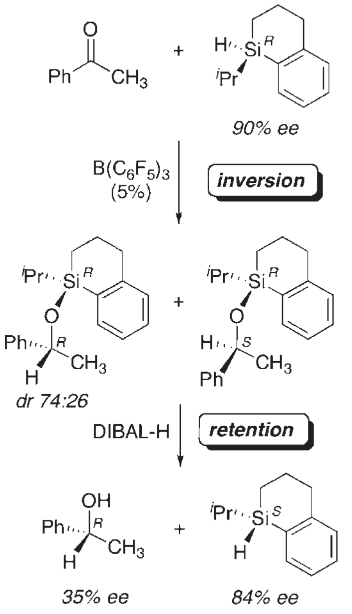
Instead, we proposed the mechanism shown in Scheme 5,[37] which invokes borane activation of the *silane* rather than the carbonyl function as the critical step in the reaction. Free borane is present, albeit in low concentrations, by virtue of the lability of the borane—carbonyl adducts; separate experiments show that the exchange between bound and free carbonyl functions is rapid in these systems. The key insight in this proposal was that the Lewis acid activates the silane in much the same way that dialkyl metallocene precatalysts are activated (Scheme 2), that is via an abstractive coordination of the Si—H bond to the Lewis acidic boron center via the silane—borane adduct **I**. This species is not observed in the absence of a Lewis base substrate, but under experimental conditions, the carbonyl compound present nucleophilically attacks the activated silicon center in **I** as indicated, forming an ion pair, **II**, in which a silylium cation is stabilized by the carbonyl substrate and partnered with the $[HB(C_6F_5)_3]^-$ anion. Collapse of this ion pair via hydride transfer to the highly electropositive carbonyl carbon consummates the reaction and regenerates free borane for re-entry into the catalytic cycle. Note that, in addition to accounting for the observed rate constant trends, this mechanism nicely circumvents the difficulties around the kinetic product of the more classical carbonyl activation mechanism shown in Scheme 4 in that there is no need to transmetallate the alkoxide group from boron to silicon in the final step: Si—O bond formation flows directly in the silane activation mechanism.

As mentioned above, attempts to observe a silane—borane adduct via NMR spectroscopy on 1:1 mixtures of $B(C_6F_5)_3$ and R_3SiH (R = Et, Ph) were unsuccessful, indicating that the adduct is present only in very small concentrations. Nonetheless, indirect evidence for adducts **I** was found in the observation that $B(C_6F_5)_3$ rapidly catalyzes H/D exchange between Et_3SiH and Ph_3SiD and that the borane $HB(C_6F_5)_2$ may be synthesized preparatively via the reaction of $B(C_6F_5)_3$ with Et_3SiH at moderate temperatures.[27] This latter reaction likely proceeds via the ion pair $[Et_3Si]^+[HB(C_6F_5)_3]^-$, where back-transfer of a C_6F_5 group to the silylium ion (producing the observed byproduct $Et_3Si—C_6F_5$) generates "Piers' borane".[38] Computational investigations, albeit performed at a low level of sophistication, also supported the existence of **I** by showing that these adducts are minima on the energy surface connecting R_3SiH and $B(C_6F_5)_3$ (R = Et, Ph). More sophisticated density functional theory (DFT) computations at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G* level corroborate these earlier findings; Figure S1 in the Supporting Information shows the computed structure of the $B(C_6F_5)_3$ adduct with Et_3SiH along with selected

Scheme 5



Scheme 6

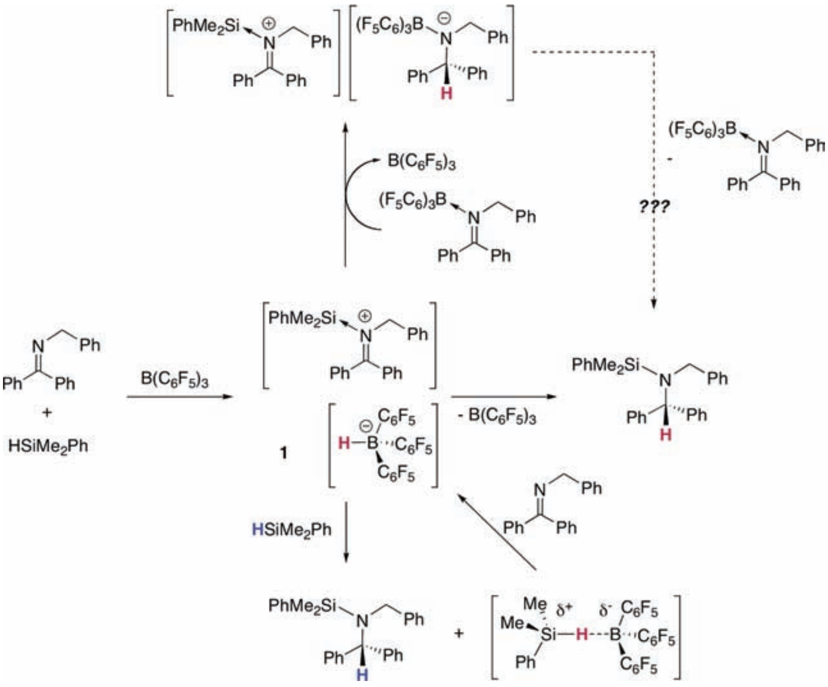


metrical parameters. Similar to what was found for the truncated Me_3SiH adduct of $B(C_6F_5)_3$,[39] the calculations show that the Et_3SiH adduct is lower in electronic energy by 3.6 kcal mol^{-1} compared to the two reactants and exhibits several close contacts between fluorine atoms on the perfluoroaryl groups and the C−H bonds of the silane methyl groups. These latter features are characteristic of many $B(C_6F_5)_3$ adducts with Lewis bases[36,40−42] and cumulatively serve to foster weak but crucial interactions between this borane and Lewis bases in bond-activating systems (vide infra).

A significant prediction of the mechanism as depicted in Scheme 5 concerns the stereochemistry at silicon, which should undergo inversion if a stereochemically pure silane were employed because of S_N2 displacement of the $[HB(C_6F_5)_3]^-$ anion by the incoming carbonyl substrate. Access to suitable silicon-based stereoprobes at the time of our original publications was limited, and so this was an experiment we reluctantly left on the cutting room floor. However, in 2007, Oestreich devised a convenient and reliable silane stereoprobe[43] and deployed it in an illuminating series of experiments that provided conclusive evidence for the S_N2 silicon mechanism for $B(C_6F_5)_3$-catalyzed hydrosilylation.[44] The key experiment is summarized in Scheme 6. The stereoenriched *R* isomer (90% ee) can be used to hydrosilate the prochiral substrate acetophenone using 5 mol % $B(C_6F_5)_3$ to form a 74:26 mixture of diastereomeric silyl ethers. The treatment of these isomers with DIBAL-H (a reaction known to proceed via retention of the configuration at silicon) regenerated the silane, which was shown to have an *S* configuration at silicon, with 84% ee. Thus, overall, the reaction proceeds with a 97% inversion in the first step, consistent with Scheme 5, and 99% retention in the reductive cleavage step. Interestingly, the 1-phenylethanol product is formed with the *R* enantiomer present in 38% ee, suggesting that the chiral silicon center remains coordinated to the carbonyl ligand and to some extent induces a preferential transfer of hydride from $[HB(C_6F_5)_3]^-$ to the *si* face of the ketone. At around the same time, Kawakami and co-workers reported a similar overall inversion of stereochemistry using the optically active silane (*R*)-(Np)PhMeSiH (Np = naphthyl) to hydrosilate benzaldehyde and cyclohexanone, albeit with some loss of ee in the product silyl ethers.[45]

Further support for the “silane activation” mechanism came in subsequent studies, in which we found that $B(C_6F_5)_3$ is also an effective Lewis acid catalyst for the hydrosilylation of imines. In a report published in 2000,[46] we noted that a variety of imines are subject to reduction with silanes under conditions similar to those under which carbonyl compounds are reduced. Again, stable imine−$B(C_6F_5)_3$ adducts form readily and can be characterized in detail via NMR spectroscopy and crystallography,[40] but because they exhibit substantial lability toward imine dissociation, free borane is liberated to activate suitable silanes toward nucleophilic attack by an imine. For certain ketimines, the delivery of hydride to the imine carbon (step k_3 in Scheme 5) becomes rate-limiting and iminium ion pairs related to the unobserved intermediate **II** (Scheme 5) in the carbonyl hydrosilylations are the dominant boron-containing species in solution. Thus, silyliminium ion **1** (Scheme 7) was fully characterized by ^1H, ^{11}B, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopy upon mixing of $B(C_6F_5)_3$, $BnN{=}CPh_2$, and $HSiMe_2Ph$ in toluene-d_8. Here, the bulkier groups on the imine carbon raise the barrier to the hydride transfer necessary for product formation and catalyst speciation pools at the silyliminium ion pair. Although less well-established than in the carbonyl hydrosilylation reactions, we believe hydride delivery occurs via the $[HB(C_6F_5)_3]^-$ anion (the red hydride) rather than from silane (the blue hydride) because hydrosilylation reactions catalyzed by $[PhMe_2Si(arene)]^+[B(C_6F_5)_4]^-$, where hydride delivery necessarily comes from silane, occur at significantly slower rates that those catalyzed by $B(C_6F_5)_3$ (hours versus minutes).[47] Hog and Oestreich have observed that, unlike for prochiral ketones, hydrosilylation of imines with enantiotopic faces does not exhibit any enantioselectivity when using enantiomerically pure silanes.[48] They speculate that this is a result of ion pairs akin to **1** reacting with $B(C_6F_5)_3$ imine adducts rather than the silyliminium salt, as shown in the top of Scheme 7. However, it is not clear how the ion pair formed from such a reaction would be

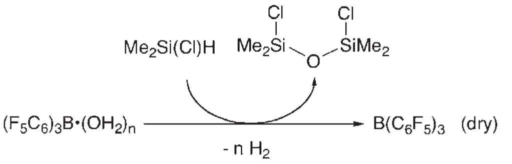
Scheme 7



transformed into product; kinetic difficulties similar to those pointed out in connection with Scheme 4 would arise from such an ion pair, which would likely be as stable, if not more so, than **1**. More study is required to address this issue, but for simple substrates, the evidence so far best supports hydride transfer from the hydridoborate counteranion in much the same way as is observed in the carbonyl reductions.

OTHER APPLICATIONS

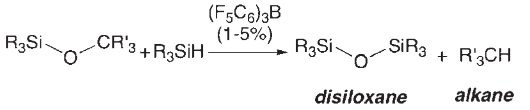
The discovery of this metal-free silane activation system has led to its application in a number of transformations that chemists would normally turn to transition-metal catalysts to bring about. In all cases, the mechanism proposed originally by our group appears to be operative, in that, generally, higher activities are observed in systems wherein more free borane should be available to activate silane. Rosenberg et al. have shown that hydrosilylation of both carbonyl[49] and thiocarbonyl[50] compounds using disilanes can give controlled access to new disilane materials. Our group,[51] and others,[52] have utilized the $B(C_6F_5)_3$/silane system to perform selective 1,4-conjugate addition reductions to a number of α,β-unsaturated carbonyl functions and, indeed, even some olefins can be hydrosilated selectively using $B(C_6F_5)_3$ as a catalyst.[53] Borane/silane can also be used to catalyze the reductive amination[47] and the reductive etherification[54] of carbonyl functions; here, in addition to reactivity with the carbonyl group, the borane/silane combination is used to silate the water produced in these reactions to the corresponding disiloxane ($R_3Si-O-SiR_3$), an extremely facile reaction. In fact, the reaction shown in eq 1, in which water is silated by $Me_2Si(Cl)H$, is so effective that we routinely use it to dry the wet borane samples that are received from various vendors. The silane employed is one for which the disiloxane is volatile enough to be effectively removed during sublimation of the dried $B(C_6F_5)_3$.



(1)

The dehydrogenative silation of water is a reaction that can be extended to the silation of a wide variety of alcohols and using a variety of commercially available silanes. This reaction provides a convenient and more atom economical alternative to the standard method for introduction of this common alcohol protecting group,[55] which generally employes silyl chlorides and an amine base. There are, however, limits to the scope of silane that can be used in the $B(C_6F_5)_3$-catalyzed process; the desirable triisopropylsilyl group, for example, cannot be introduced using this method. The steric bulk of the silane precludes effective borane activation of the Si−H bond and/or the backside attack of substrate necessary to displace the $[HB(C_6F_5)_3]^-$ anion. Nonetheless, this is a method with wide scope[56] that can also be used to silate thiols.[57]

Care must be taken in many of the above reactions not to utilize an excess of silane reagent because the silyl ether products are prone to further reaction, involving C−O bond cleavage (eq 2). The products of this reaction, alkanes and disiloxanes, are both of interest depending on the perspective of the chemist utilizing the chemistry. For example, organic chemists interested in functional group manipulation find utility in the complete deoxygenation of the various oxygen-containing functions[55,58−61] (R−OH, ArOR, ketones, aldehydes, esters, carboxylic acids, and acid chlorides), wherein the borane/silane system provides mild alternatives to harsher reductive deoxygenation protocols such as the Wolff–Kishner or Clemmensen reductions. The disiloxane byproduct provides the thermodynamic driving force for the reaction through the formation of strong Si–O bonds; volatile alkane products can also improve the favorability of the process. In fact, we have recently utilized these features to catalytically convert CO_2 to CH_4, using triethylsilane as the sacrificial reductant.[62,63]



(2)

On the other hand, from the perspective of the silicon chemist, the reaction of eq 2 was recognized by scientists at General Electric to have significant potential to construct complex siloxane and silicone structures very conveniently. Cella and Rubinsztajn[64−66] conducted seminal studies in this area to prepare macromolecular siloxanes, while Brook et al. have subsequently exploited this "Piers–Rubinsztajn reaction"[67] for the selective preparation of dendritic silicon structures with high monodispersity and containing a variety of functional groups.[68−70] Chiral siloxanes have also been prepared using this methodology,[71] as well as polysiloxanes containing periodically dispersed main-chain silsesquioxane units.[72] Detailed mechanistic studies on this reaction[39] reveal some complexities involving Si–H/SiOR group exchange in addition to the desired generation of new Si–O–Si linkages and alkane but strongly corroborate the mechanistic findings from our group that were focused on the organic applications of this reaction. These investigators also reported a sophisticated computational treatment of the adduct between $B(C_6F_5)_3$ and Me_3SiH, utilizing the B3LYP/6-311+G-(2d,p)//B3LYP/6-31G* level, a treatment that indicates that the interaction between the two is very weak and features a nonlinear Si–H–B angle of 155.7°. This adduct thus shows features very similar to those established computationally for the $Et_3SiH/B(C_6F_5)_3$ adduct discussed above (see Figure S1 in the Supporting Information). It is remarkable that such a weak adduct, which because of its complete spectroscopic transparency must be present in extremely low concentrations, is so highly reactive toward organic bases, but there is no denying the utility of the borane/silane system.

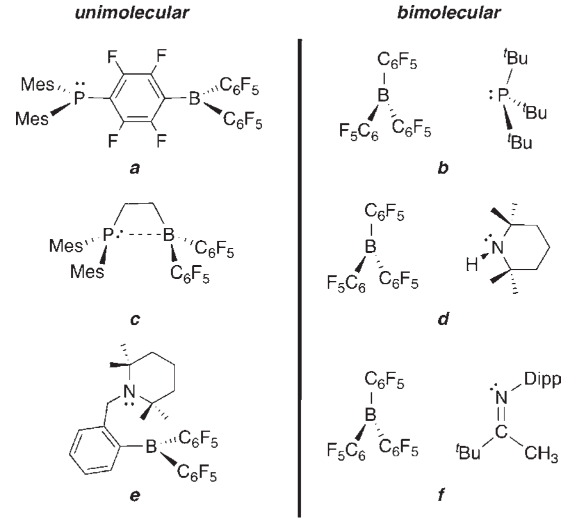
■ ACTIVATION OF H_2

The Si–H bond activation triggered by $B(C_6F_5)_3$ in the presence of oxygen and nitrogen bases as described above is a direct antecedent of the metal-free H_2 activations by what have come to be known as "frustrated Lewis pairs".[10] Given that many organotransition-metal catalysts active for the hydrogenation of unsaturated functions also act as hydrosilylation catalysts, the relationship between $B(C_6F_5)_3$/silane hydrosilylations and $B(C_6F_5)_3/H_2$ hydrogenations should not come as a surprise. However, H_2 is a much more economically viable and "greener" reductant than silanes and so the significance of the discoveries by Stephan, Erker, and others[73−77] lie in the potential to conduct metal-free hydrogenations on a large, commercially viable scale.

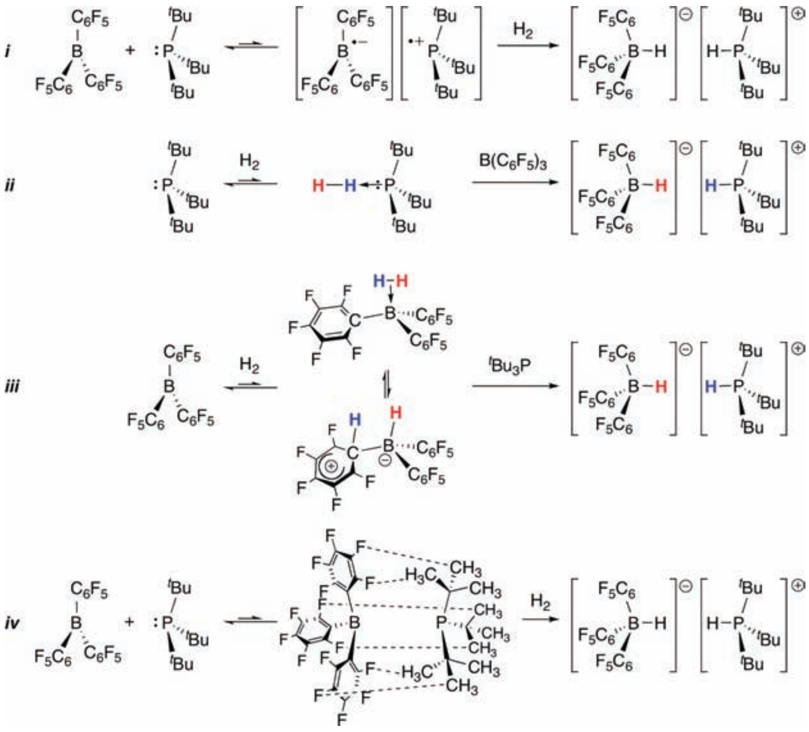
A selected roster of recently uncovered hydrogen activation systems is given in Chart 1, and they may be classified as unimolecular (left) or bimolecular (right) depending on whether or not the Lewis acid/base pair is tethered or not. All are based on fluoroarylboranes; the first such compound to split hydrogen—reversibly—was the tethered compound **a**, which was discovered somewhat serendipitously in the exploration of the reactions of $B(C_6F_5)_3$ with bulky secondary phosphines.[7] These observations led rapidly to the discovery of the analogous bimolecular $R_3P/B(C_6F_5)_3$ systems, exemplified by **b**.[78] In addition to $^tBu_3P$, bulky trimesitylphosphine is an effective partner in this chemistry, and hydroboration of dimesitylvinylphosphine using $HB(C_6F_5)_2$ leads to the highly effectual unimolecular system **c**.[79] It was soon recognized that bulky nitrogen bases were also able to activate H_2 in the presence of $B(C_6F_5)_3$, with tetramethylpiperidine (**d**) being especially successful,[80] along with its unimolecular analogue **e**.[81] Here, the basicity of the amine partner is important in governing the direction of H_2 activation/elimination; the less basic amino borane *o*-$Ph_2N-C_6H_4-B(C_6F_5)_2$ does not react with hydrogen, but the putative zwitterionic product of H_2 activation rapidly eliminates H_2.[82] Finally, and most relevant to the implementation of this activation to useful hydrogen-transfer chemistry, bulky imines, as exemplified in **f**, are also capable of participating as the Lewis base in the frustrated Lewis pair.[83]

Despite the efficacy of H_2 activation and the intensity of activity in this area, details concerning the intimate mechanism of how the H–H bond is cleaved by these systems are lacking, especially from the experimental perspective. A priori, at least four possible mechanisms might be envisioned, illustrated in Scheme 8 for the $^tBu_3P/B(C_6F_5)_3$ pair. All involve a preequilibrium between free phosphine and/or borane and a (presumably) highly reactive intermediate from which hydrogen cleavage emanates. In mechanism **i**, which postulates oxidation of the Lewis base by $B(C_6F_5)_3$,[22] this intermediate is a radical anion/radical cation ion pair that forms upon electron transfer from phosphine to borane, which then homolytically cleaves hydrogen. It has been observed that solutions of *N*,*N*-dialkylanilines and $B(C_6F_5)_3$ indicate the partial formation of classical adducts but that hydride abstraction to yield iminium salts of $[HB(C_6F_5)_3]^-$ also occurs. Solutions of these mixtures exhibit a pale-pink color and are electron spin resonance active;[13] however, the nature of the paramagnetic materials present is not clear. These observations suggest that mechanism **i** is plausible, but although both $[B(C_6F_5)_3]^{\bullet-}$[84] and $[^tBu_3P]^{\bullet+}$[85] have been generated and observed, the disparity in the reduction potential of $B(C_6F_5)_3$[22] and the oxidation potential of $^tBu_3P$ suggest that any formation of this

Chart 1



Scheme 8



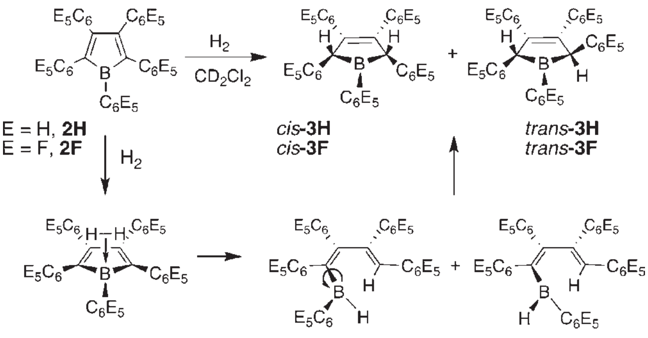
radical cation/anion ion pair would be limited to subnanomolar concentrations.

Mechanisms **ii** and **iii** are similar in character in that they invoke activation of the H_2 by one or the other of the Lewis base (**ii**) or acid (**iii**), forming an adduct that then undergoes hydride or proton abstraction to form the product ion pair. These are clearly heterolytic pathways. Mechanism **ii** finds plausibility in the observation of phosphine−hydrogen adducts via low-temperature matrix-isolation techniques, but this option has not received serious consideration because of the extremely fleeting nature of such adducts. Mechanism **iii**, on the other hand, seems more reasonable, especially in light of the mechanistic picture developed for the activation of Si−H bonds, in which silane−borane adducts play a key role. There is also an obvious connection to related heterolytic mechanisms in the transition-metal-mediated cleavage of H_2 (Scheme 1). As in the silane case, however, attempts to observe such a $B(C_6F_5)_3 \cdot H_2$ adduct spectroscopically have failed to provide any indication of significant concentrations of it in solution. Computations have shown that a van der Waals complex between $B(C_6F_5)_3$ and H_2 forms, but it is not believed to lay on the H_2 activation pathway.[86] However, the addition of side-on-bonded H_2 to one of the three B−C bonds would lead to the Wheland-type structure shown in Scheme 8**iii**, which, although stabilized by the π-donating fluorine substituents,[87] would still be expected to exhibit substantial Bronsted acidity; deprotonation of this species by the Lewis base partner would lead to observed products.

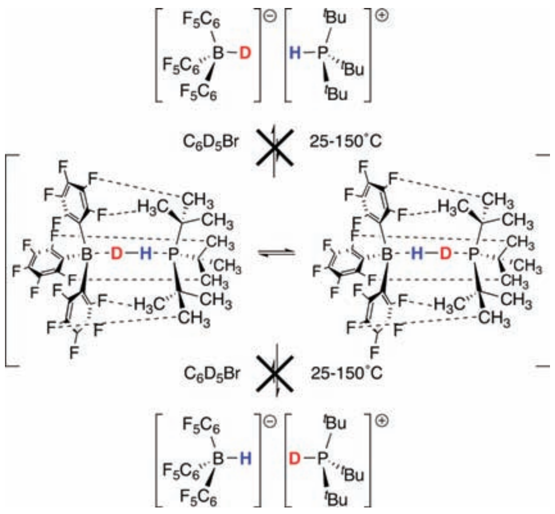
Support for a mechanism of this character is found in the reactivity of pentaarylboroles with H_2. Recently, we have shown that the two borole compounds **2-H**[88] and **2-F**[89] undergo facile reaction with H_2 to yield cis and trans isomers of the boracyclopentenes **3-H** and **3-F** in the *absence* of an external Lewis base (Scheme 9).[90] Experimental and computational studies strongly suggest that H_2 forms a side-on adduct with these highly Lewis acidic boranes, which leads to cleavage of one of the internal B−C bonds of the somewhat strained and antiaromatic borole ring. The resulting *cisoid*-borylbutadiene compounds undergo rapid recyclization to yield the observed products,[91,92] a mechanism that nicely explains the observation of both *cis*- and *trans*-boracyclopentene products **3-H**/**F**. These results show explicitly that highly Lewis acidic boron centers can engage in chemically consequential interaction with H_2, as is invoked in the mechanism depicted in Scheme 8**iii**. While $B(C_6F_5)_3$ may indeed form a weak adduct with H_2, the reverse process appears to be more favorable than, for example, B−C bond cleavage in the absence of a Lewis base. In compounds **2**, the enhanced Lewis acidity of the antiaromatic borole ring, along with the presence of ring strain, lowers the barrier to B−C bond rupture from the H_2 adduct.

On the other hand, it should be noted that computational exploration of the mechanism of H_2 splitting by compound **a** in Chart 1 indicates that a path akin to mechanism **iii** in Scheme 8 (which was postulated in the seminal D. W. Stephan *Science* paper[7]) has a relatively high computed barrier because of dearomatization of the linking C_6F_4 ring.[93,94] In fact, these barriers (>50 kcal mol^{-1}) are too high to be reconciled with the experimentally observed facility of the H_2 addition reaction to *p*-$Mes_2P-C_6F_4-B(C_6F_5)_2$, which occurs rapidly even at temperatures below 0 °C. Furthermore, one might expect B−C bond cleavage to be a significant side reaction if addition of H_2 across a B−C bond were occurring in these systems, but the products of such a cleavage (i.e., C_6F_5H and $HB(C_6F_5)_2$) are not observed when $B(C_6F_5)_3$ is treated with 4 atm of H_2 even for long periods of time. Thus, the relevance of the mechanism in

Scheme 9



Scheme 10



Scheme 8**iii** for the splitting of hydrogen by the systems shown in Chart 1 is questionable.

The mechanistic proposal for hydrogen cleavage by $B(C_6F_5)_3$ and ${}^tBu_3P$ (and other Lewis base partners) that currently enjoys the most widespread appeal is that depicted in Scheme 8**iv**, although the evidence for it is largely based on theoretical studies, albeit utilizing highly sophisticated, state-of-the-art computational methods.[86,95] In this mechanism, the frustrated Lewis pair, unable to form a classical adduct for steric reasons, comes together in what has been termed an “encounter complex”, which is held together by several weak H···F interactions. The pocket comprised of the region where a normal dative bond would form in sterically less challenged Lewis pairs is able to accept a H_2 molecule, and the electric field generated by the proximal but noninteracting occupied orbital of the phosphine and unoccupied orbital of the borane is strong enough to rapidly and heterolytically cleave the H_2 molecule, yielding the observed phosphonium borate product.

While supported by quantum chemical computations,[94] convincing experimental evidence for the encounter complex between $B(C_6F_5)_3$ and ${}^tBu_3P$ (or any other frustrated Lewis pair for that matter) has not, to our knowledge, been forthcoming. Attempts to observe the adduct via ^{11}B, ^{19}F, or ^{31}P NMR spectroscopic experiments on $B(C_6F_5)_3/{}^tBu_3P$ mixtures reportedly reveal spectra that appear essentially unchanged from those of the separate reagents.[78,96] We have attempted to access the encounter complex from the other side of the equation by preparing the selectively labeled ion pair $[{}^tBu_3PH]^+[DB(C_6F_5)_3]^-$ and determining the extent (if any) of label exchange between the two sites (Scheme 10). While it has been reported that thermal elimination of H_2 from $[{}^tBu_3PH]^+[HB(C_6F_5)_3]^-$ is not observed,[78] if the encounter complex is accessible, and then one might expect to observe H/D exchange in the labeled ion pair. The required ion pair is easily prepared from $[K]^+[DB(C_6F_5)_3]^-$ and $[{}^tBu_3PH]^+[Cl]^-$ in acetonitrile (see the Experimental Section) and exhibited no J_{HD} coupling in a C_6D_5Br solution or exchange of label at room temperature. Indeed, heating at 100 °C for 24 h resulted in no change in the NMR spectra. The ion pair began to degrade when the sample was heated further to 150 °C, yielding several unidentified products; no evidence for P−D bond formation was found in the ^{31}P NMR spectrum, although some indication of B−F bond formation (broad resonance at −189 ppm in the ^{19}F NMR spectrum) was observed. Thus, it appears that other decomposition pathways ensue before an encounter complex can be accessed from $[{}^tBu_3PH]^+[DB(C_6F_5)_3]^-$. Experimental confirmation regarding the validity of the “encounter complex mechanism” in the splitting of H_2 by bimolecular frustrated Lewis pair systems, and indeed by unimolecular systems, thus awaits further study and is a key area for future research in this exciting area.

■ CONCLUSIONS

The above account shows that $B(C_6F_5)_3$ (and related fluoroarylboranes with sufficient Lewis acidity) is able to activate the strong, nonpolar bonds of silanes and H_2 with remarkable facility in the presence of a suitable Lewis base. The ability of the $B(C_6F_5)_3$/base pair (whether tethered or not) to split hydrogen or activate Si−H hinges or the pair’s inability to form a classical Lewis acid/Lewis base adduct *or* ability to dissociate to an extent allows for free borane and free Lewis base to activate the substrate. This latter scenario is clearly operative in the hydrosilylation chemistry described above, and the mechanistic picture developed there is surely related to what must be occurring in the activation of H_2 by these systems. Indeed, for moderately bulky bases, such as lutidine, classical Lewis acid/base adducts are observed to form with $B(C_6F_5)_3$ but are labile enough to dissociate to a great enough extent that splitting of hydrogen is eventually observed.[97]

Not surprisingly, in light of the mechanism presented for the hydrosilylation of imines above, this scenario is also commonly observed in the hydrogenation of imines as mediated by $B(C_6F_5)_3$.[98,99] Because most desirable imine substrates are less bulky than what is required to completely defeat dative bond formation, the necessity to have the imine dissociate from $B(C_6F_5)_3$ to allow for hydrogen to access the unquenched p orbital on boron is imperative. Although precisely analogous to the imine hydrosilylation chemistry shown in Scheme 7, in the context of hydrogenation, this phenomenon has been referred to as “thermally induced frustration”[100] and is contrasted with the “inherent” frustration felt by partners who cannot get together in a classical sense. In these labile imine/borane adducts, rupture of the dative bond is proposed to lead to the higher energy encounter complex, where secondary interactions such as C−H−F hydrogen bonds or $\pi-\pi$-stacking interactions hold the imine and borane together long enough for hydrogen activation to occur. The decampment of the dative adduct to the encounter complex finds plausibility in the fact that both types of secondary interactions thought to stabilize this encounter complex have been observed in many structurally characterized carbonyl,[36] imine,[40] and other[13,101] adducts of $B(C_6F_5)_3$.

Despite these many studies, intriguing mechanistic questions remain, particularly with respect to the intimate mechanism of hydrogen activation by these systems. Furthermore, the number of applications of frustrated Lewis pair activation of small molecules continues to rise dramatically.[102] The high level of activity in this area speaks to its potential and serves as a clear recent example of the renaissance in main-group element chemistry occurring in the chemical community.

■ EXPERIMENTAL SECTION

General Procedures. An argon-filled MBraun glovebox was employed for manipulation and storage of all oxygen- and moisture-sensitive compounds. All reactions were performed on a double-manifold high-vacuum line using standard techniques.[103] Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber from Matheson Gas Products. Toluene and hexanes solvents were dried and purified using the Grubbs/Dow purification system[104] and stored in evacuated 500 mL bombs over sodium tetraglyme/benzophenone ketyl. Acetonitrile was dried, distilled, and stored in an evacuated 500 mL bomb over CaH_2. Tetrahydrofuran (THF) and diethyl ether were dried, distilled, and stored in evacuated 500 mL bombs over sodium benzophenone ketyl. All solvents were distilled prior to use. THF-d_8 was dried over and distilled from sodium benzophenone ketyl and stored in a glass bomb in the glovebox. CD_3CN and C_6D_5Br were dried over and distilled from CaH_2 and stored in glass bombs in the glovebox. ^1H and ^{13}C chemical shifts were referenced to residual proton and naturally abundant ^{13}C resonance of the deuterated solvent, respectively. ^{19}F NMR spectra were externally referenced to C_6F_6 (δ −163.0) in C_6D_6. ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 (δ 0). ^{11}B NMR spectra were externally referenced to BF_3OEt_2 (δ 0). Assignments of chemical shifts are based on ^1H, ^2H, $^{13}C\{^1H\}$, ^{11}B, ^{19}F, ^{31}P, and $^{31}P\{^1H\}$ NMR spectra recorded on a Bruker RDQ-400 spectrometer. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was sublimed at 65 °C in an oil bath under high dynamic vacuum, then stirred over $Me_2Si(H)Cl$ for 4 h, and resublimed under the same conditions after vacuum removal of volatiles. Tri-*tert*-butylphosphine $[P(^tBu)_3]$ was purchased from Aldrich and distilled under a high static vacuum prior to use. Solutions of HCl (2.0 M in Et_2O) were purchased from Aldrich and used as received. A potassium hydride suspension in mineral oil (Aldrich) was washed three times with hexanes and dried under a high dynamic vacuum to give an off-white powder that was used without further purification. All compounds were stored in the glovebox. Deuterium, grade 2.7, was obtained from Praxair and used as received. $[^tBu_3PD]^+[DB(C_6F_5)_3]^-$ was synthesized via an identical route reported in the synthesis of $[^tBu_3PH]^+[HB(C_6F_5)_3]^-$,[78] using D_2 in place of H_2.

Synthesis of $[^tBu_3PH]^+[Cl]^-$. To a stirring solution of $P(^tBu)_3$ (0.200 g, 0.99 mmol, in 6 mL of Et_2O) under argon was added a solution of HCl (2.0 M in Et_2O, 0.50 mL), immediately forming a white precipitate. The mixture was stirred for 30 min at room temperature, whereupon the solid was filtered and washed with hexanes (3 × 20 mL) using a swivel frit assembly. The solid was then dried under vacuum, providing $[^tBu_3PH]^+[Cl]^-$ as a white solid (0.215 g, 90%). NMR spectral data were in agreement with a previously reported synthesis of $[^tBu_3PH]^+[Cl]^-$.[105]

Synthesis of $[K]^+[DB(C_6F_5)_3]^-$. In a glovebox, a glass bomb was charged with $[^tBu_3PD]^+[DB(C_6F_5)_3]^-$ (0.200 g, 0.278 mmol) and dissolved in THF (10 mL). Solid KH (0.017 g, 0.418 mmol) was added to the flask in several portions, and the flask was stirred at room temperature under argon for 1 h. Residual solids were filtered away with an Acrodisc, and the solution was transferred to a round-bottomed flask, whereupon the solvent was removed under vacuum to give a tacky solid. Hexanes (20 mL) were condensed into the flask, which was then sonicated for 30 min, during which time a white precipitate formed. The solid was filtered using a swivel frit assembly, washed with hexanes (3 × 20 mL), and dried under vacuum, providing $[K]^+[DB(C_6F_5)_3]^-$ as a white powder (0.100 g, 65%). ^2H NMR (61.4 MHz, THF-d_8): δ 3.71 (br app s). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8) partial: δ 148.5 (dm, $^1J_{CF}$ = 243 Hz), 136.5 (dm, $^1J_{CF}$ = 242 Hz). ^{11}B NMR (128.4 MHz, THF-d_8): δ −27.4 (br app s). ^{19}F NMR (376.5 MHz, THF-d_8): δ −135.4 (app d, $^3J_{FF}$ = 23 Hz, 6F), −168.5 (t, $^3J_{FF}$ = 19 Hz, 3F), −171.0 (m, 6F).

Synthesis of $[^tBu_3PH]^+[DB(C_6F_5)_3]^-$. In a glovebox, a solution of $[^tBu_3PH]^+[Cl]^-$ (0.032 g, 0.136 mmol, in 0.5 mL of MeCN) was added dropwise to a solution of $[K]^+[DB(C_6F_5)_3]^-$ (0.075 g, 0.136 mmol, in 0.5 mL of MeCN), whereupon a white precipitate immediately formed. The suspension was filtered through an Acrodisc, and the solvent was removed, providing $[^tBu_3PH]^+[DB(C_6F_5)_3]^-$ as a white solid (0.075 g, 77%). ^1H NMR (400 MHz, CD_3CN): δ 5.39 (d, $^1J_{HP}$ = 443 Hz, 1H), 1.59 (d, $^3J_{HP}$ = 15.6 Hz, 27H). No H−D coupling was observed between the P−*H* and B−*D* atoms in the ^1H NMR spectrum. ^2H NMR (61.4 MHz, CH_3CN): δ 3.69 (br app s). ^{11}B NMR (128.4 MHz, CD_3CN): δ −24.9 (br app s). ^{19}F NMR (376.5 MHz, CD_3CN): δ −134.7 (app d, $^3J_{FF}$ = 23 Hz, 6F), −165.0 (t, $^3J_{FF}$ = 19 Hz, 3F), −168.3 (m, 6F). ^{31}P NMR (162 MHz, CD_3CN): δ 56.68 (s). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ 56.68 (dm, $^1J_{PH}$ = 440 Hz). Samples of $[^tBu_3PH]^+[DB(C_6F_5)_3]^-$ (0.015 g, 0.021 mmol) and C_6D_5Br (0.8 mL) were combined in a J. Young NMR tube, which was sealed and heated to 100 °C for 24 h. NMR analysis (^1H, ^{11}B, and $^{31}P\{^1H\}$) indicated that no H/D exchange or other reaction had occurred in the ion pair. When the sample was heated to 150 °C for 24 h, degradation to several unidentified species was observed in the ^{19}F NMR spectrum.

Computational Methods. Coordinates from the work of Chojnowski et al.[39] on the trimethylsilane derivative were used as a starting point for $[Et_3SiHB(C_6F_5)_3]$. The starting materials and adduct were optimized on *Gaussian 03* at the B3LYP/6-31G(d,p) level of theory, and then frequency calculations were carried out at this level. Single-point energy calculations were further run at the B3LYP/6-311G+(2d,p) level of theory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Computed structure of $[Et_3SiHB(C_6F_5)_3]$ and its *x*,*y*, and *z* coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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