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# Dramatic Effect of Lewis Acids on the Rhodium-Catalyzed Hydroboration of Olefins

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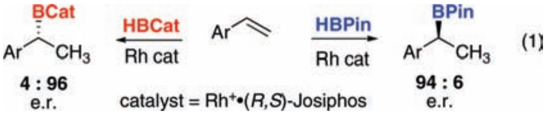
***Abstract:*** The addition of Lewis acids such as trispentafluoroboron as cocatalysts has been found to have a dramatic effect on the Rh-catalyzed hydroboration of olefins with pinacol borane. For example, aliphatic olefins do not react at all in noncoordinating solvents, but with the addition of 2% of $B(C_6F_5)_3$, the reaction is complete in minutes. Similarly, the reaction of aromatic olefins with HBPin occurs slowly and nonselectively in the absence of $B(C_6F_5)_3$, but is accelerated and occurs more selectively in its presence. Preliminary mechanistic studies suggest that the $B(C_6F_5)_3$ needs to be present throughout the course of the reaction, not just at the initiation stage, and implicate this species, along with THF, in the heterolytic cleavage of the B−H bond of HBPin.

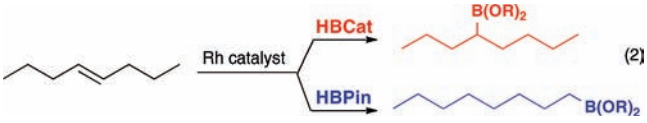
## Introduction

The application of transition metal catalysts in organic transformations provides the opportunity to affect reactions that are otherwise impossible, and to alter the chemo-, regio-, and stereoselectivity of the reaction as compared to the thermal counterpart.[1−3] The pioneering work of Hayashi and Ito demonstrated all of these features in the hydroboration of vinyl arenes.[4] Additionally, they and others have demonstrated that the reaction can be performed with high levels of enantioselectivity by the use of chiral ligands for rhodium, the metal of choice for this transformation.[4]

Although catechol borane (HBCat) is employed as the hydroborating reagent in the large majority of catalyzed hydroborations, recent studies from our group,[5] Fernandez,[6] Westcott,[7,8] Miyaura,[9,10] Gevorgyan,[11] and others[12−15] have shown that pinacol borane (HBPin) not only has the advantage of being significantly easier to handle, but it can also lead to complementary reactivities and selectivities. For example, in the hydroboration of vinyl arenes, using the same antipode of Binap or Josiphos, opposite enantiomers of the product are obtained depending on whether HBPin or HBCat is employed[5,6] (eq 1).



In the case of internal aliphatic olefins, the difference between hydroboration with HBCat and HBPin is even more extreme. In the former case, the hydroboration produces an internal, secondary boronate ester as expected, while in the latter case a linear terminal boronate is produced by a series of fast hydride shifts, which precede the eventual reductive elimination (eq 2).[13,16−18]



This reaction is of considerable utility because mixtures of olefins such as are commonly obtained from cracking processes can be employed directly to give a single product. This process is not only more cost-effective, but it is also considerably greener because energy need not be invested in purifying olefinic products prior to their conversion into value-added commodity chemicals.[17]

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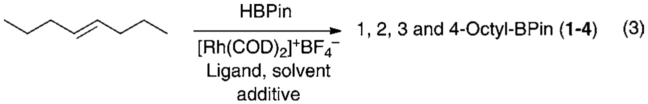
10.1021/ja904142m

***Table 1.*** Effect of Lewis Acids on the Regioselectivity of the Hydroboration Reaction[a]



| entry | ligand | solvent | Lewis acid, mol % | product distribution (**1**:**2**:**3**:**4**) | yield (%)[b] |
|---|---|---|---|---|---|
| **1** | **$PPh_3$** | **THF** | **0** | **99:0:0:1** | **95** |
| 2 | $PPh_3$ | DCE | 0 | | 0 |
| 3 | $PPh_3$ | DCE | $Sc(OTf)_3$, 2% | 75:5:4:16 | 65 |
| 4 | $PPh_3$ | DCE | $Sc(OTf)_3$, 4% | 56:8:7:29 | 55 |
| 5 | $PPh_3$ | DCE | $Sc(OTf)_3$, 8% | 37:9:13:41 | 71 |
| 6 | DPPB | DCE | $Sc(OTf)_3$, 2% | 10:2:14:73 | 81 |
| 7 | DPPB[c] | DCE | $Sc(OTf)_3$, 2% | 10:3:14:73 | 92 |
| 8 | DPPB[c] | DCE | FAB[d], 2% | 7:2:14:77 | 99 |
| **9** | **DPPB[c]** | **DCE** | **FAB, 2%** | **2:0:7:91** | **94[e]** |
| 10 | –[f] | DCE | $Sc(OTf)_3$, 2% | | 0 |
| 11 | –[f] | DCE | FAB, 2% | | 0 |

[a] Reaction conditions: 1 mol % Rh catalyst, 1.5 mol % ligand, 0.1 M, 30 °C, 24 h, nitrogen atmosphere (glovebox). [b] Yields obtained by GC analysis versus internal standards. Approximately 15% 2- and 3-isomers detected also, except in entry 9 where only 7% of the 3-isomer was observed. [c] Preformed $[Rh(COD)(DPPB)]BF_4 \cdot THF$ employed. [d] FAB = trispentafluorophenylboron. [e] Temp = −20 °C, 9 h. [f] No Rh catalyst.

Despite the fact that pinacol boronate esters are more stable, the inherently lower activity of pinacol borane as compared to catechol borane does limit the widespread application of this reagent. For example, although high yields and high enantioselectivities are obtained with Quinap and Josiphos-based catalysts, hydroborations with binap-derived catalysts and HBPin proceed with only low enantioselectivity.[5,6] This is primarily because the low reactivity of HBPin does not permit the application of cryogenic reaction conditions to enhance enantioselectivity in the same fashion as is required to achieve high enantioselectivity with HBCat.[4] Additionally, HBPin cannot be employed to hydroborate internal olefins, unless the terminal product is desired. Thus, we began a study aimed at accelerating the hydroboration reaction with HBPin and widening the scope of this interesting reagent.

## Results and Discussion

Taking inspiration from the work of Hall[19] and Miyaura,[20] who demonstrated the significant effect of scandium triflate on allylborations with boronic esters, and Evans, who demonstrated the effect of $SmI_3$ on hydroborations,[21] we examined the effect of Lewis acids on the reaction shown in eq 3.[22] The air- and moisture-tolerant Lewis acid $Sc(OTf)_3$ was examined first.

We initially attempted the hydroboration of 4-octene in THF; however, the use of Lewis acids in combination with Rh catalysts led to polymerization of this solvent. Thus, we turned to dichloromethane (DCM) or dichloroethane (DCE). As shown in Table 1, entry 2, $[Rh(COD)_2]BF_4$/phosphine-based catalysts were unable to catalyze the reaction in this solvent. However, the addition of 2% $Sc(OTf)_3$ generated an active catalyst, which gave the linear isomer as the major product, along with minor amounts of the 2-, 3-, and 4-isomers (entry 3). As increasing amounts of $Sc(OTf)_3$ were added, the amount of branched product (**4**) increased until equal amounts of the 1- and 4-isomers were observed (entry 5). With DPPB as the ligand, the branched product (**4**) became the major isomer in the reaction (entry 6).

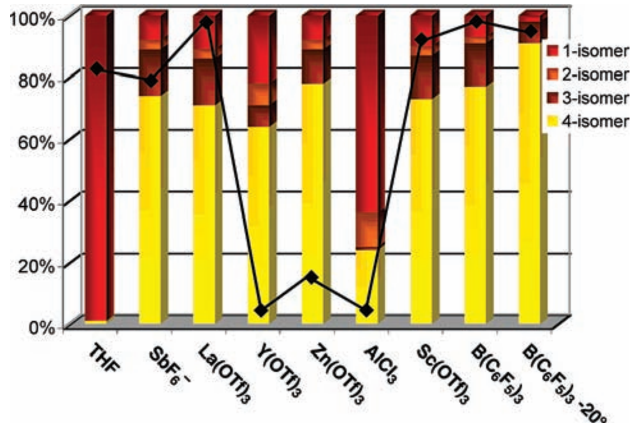


***Figure 1.*** Comparative study on the effect of Lewis acids on selectivity and yield in the hydroboration of *trans*-4-octene with pinacolborane. Yields given in black.

Other Lewis acids were screened using preformed $[Rh(COD)(DPPB)]^+BF_4^- \cdot THF$ as the catalyst (Figure 1). Like $Sc(OTf)_3$, most Lewis acids were found to give the 4-isomer as the major product, although in some cases the overall yield of the reaction was low. From these screens, the organic Lewis acid tris(pentafluorophenyl)boron (FAB) emerged as the most promising candidate, giving the product of direct hydroboration as 91% of the product distribution in 94% yield when the reaction was performed at −20 °C (Table 1, entry 9). Additionally, unlike $Sc(OTf)_3$, the solubility of FAB at lower temperatures was not an issue. In most cases, the 2- and 3-isomers were also observed in a combined yield of 10−15%; however, only 5% of these isomers was observed when FAB was employed at −20 °C (Figure 1). Finally, reactions run in the absence of Rh gave no reaction, indicating that the Lewis acid/HBPin combination alone did not catalyze the hydroboration (Table 1, entries 10, 11). This was an important control experiment considering the pioneering studies of Piers and Gevorgyan demonstrating the ability of FAB to catalyze the hydrosilylation of carbonyl compounds and olefins.[23,24]

Lewis acids also had a dramatic effect on the rate of the hydroboration of (*E*)-4-octene (Figure 2). Reactions employing 2% FAB are virtually complete within 15 min at 30 °C. Although the complete lack of activity observed in DCE in the absence of a Lewis acid makes the comparison difficult, when a catalyst is used with the $SbF_6^-$ counterion, the reaction does take place slowly, even in the absence of the Lewis acid (Figure 2). This provides some measure of the dramatic rate acceleration that is observed with the addition of a Lewis acid cocatalyst.

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(22) Note that Endo and co-workers have shown that Lewis bases accelerate the reaction with neutral Rh complexes:(a) Endo, K.; Hirokami, M.; Takeuchi, K.; Shibata, T. *Synlett* **2008**, *20*, 3231–3233. (b) Endo, K.; Hirokami, M.; Shibata, T. *Organometallics* **2008**, *27*, 5390–5393.

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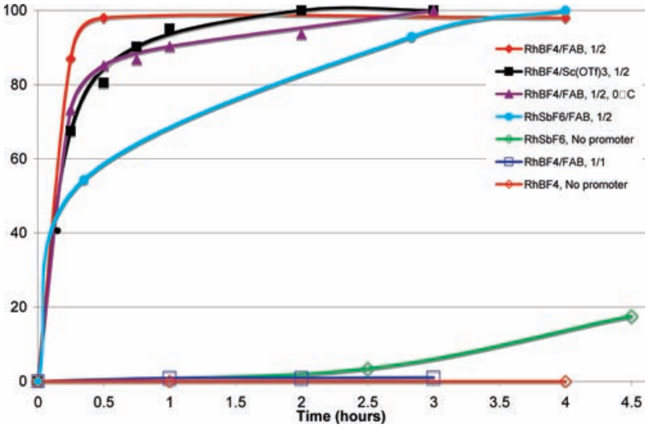
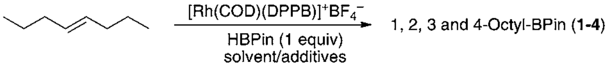


***Figure 2.*** Rate of hydroboration of 4-octene in the presence and absence of Lewis acids with $[Rh(COD)(DPPB)]BF_4^-$ and $[Rh(COD)(DPPB)]SbF_6^-$ catalysts. Unless otherwise noted, the reaction was performed at ambient glovebox temperature (30 °C).

***Table 2.*** Selectivity and Activity in the Hydroboration of 4-Octene[a]



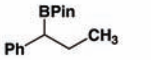
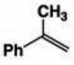
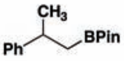
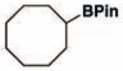
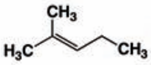
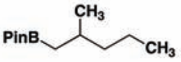
(4)

| entry | anion | additive | solvent | yield (time) | product distribution (**1**:**2**:**3**:**4**) |
|---|---|---|---|---|---|
| 1 | $BF_4^-$ | none | DCE | 0 | |
| 2 | $BF_4^-$ | none | THF | 80% (24 h) | 92:3:2:3 |
| 3 | $BF_4^-$ | none | $C_6H_6$ | 19% (22 h) | 91:4:0:5 |
| 4 | $BF_4^-$ | none | 2-MeTHF | 75% (10 h) | 92:3:2:3 |
| 5 | $SbF_6^-$ | none | DCE | 4% (3 h) 99% (24 h) | 8:3:15:74 |
| 6 | $SbF_6^-$ | FAB, 2% | DCE | 93% (3 h) | 7:3:14:75 |
| 7 | $SbF_6^-$ | none | THF | 93% (24 h) | 89:3:2:6 |
| 8 | $SbF_6^-$ | none | DCE/THF | 60% (24 h) | 85:3:3:9 |
| 9 | $BF_4^-$ | FAB, 2% | DCE | >99% (0.5 h) | 7:2:14:77 |
| 10 | $BF_4^-$ | FAB, 1% | DCE | 0 | |

[a] Reaction conditions: 1 mol % Rh catalyst, 0.1 M, 30 °C, 24 h, nitrogen atmosphere (glovebox).

The activity (albeit low) of the $SbF_6$ catalyst provided us the opportunity to compare the selectivity in the same solvent in the presence and absence of added Lewis acid. In addition, various solvents, counterions, and additives were examined (Table 2). As noted previously, the $BF_4^-$ catalyst is not active for the hydroboration of 4-octene in DCE, and in THF, the linear (1-) isomer predominates (Table 2, entries 1 and 2). Other coordinating solvents such as $C_6H_6$ and 2-MeTHF also give essentially complete isomerization to the 1-isomer (entries 3 and 4). It is important to note that even in the absence of added Lewis acid, when the reaction is performed in DCE, the $SbF_6^-$ complex yields the 4-isomer, albeit much more slowly than in the presence of the Lewis acid (compare entries 5 and 6). Interestingly, there is no change in selectivity between these two entries. Thus, although a rate acceleration is clearly ascribed to the addition of the Lewis acid, the change in selectivity for this substrate is most likely an effect of solvent. This hypothesis is confirmed by the experiment described in entries 7 and 8, where the reaction was performed in THF or a THF mixture, which provided the fully isomerized 1-isomer as the major product. Thus, in polar, noncoordinating solvents such as DCE, the product of direct hydroboration predominates, while in polar coordinating solvents such as THF, essentially complete isomerization to the linear isomer is observed. In solvent mixtures, the polar coordinating solvent dominates the reaction, and the linear isomer is the major product (entry 8). The reasons for the effect of solvent on the hydroboration versus isomerization manifold are not clear at this point, although complexation of THF to one or more of the intermediates seems entirely likely. This may be explained by stabilizing the Rh(III) oxidation state in the intermediate to allow reversible $\beta$-hydride elimination to out-compete reductive elimination.

***Table 3.*** Effect of Lewis Acid on Yield and Distribution in the Hydroboration of Various Olefins[a]

| Entry | Starting Material | Product | No Lewis acid | FAB (2%) |
|---|---|---|---|---|
| 1 |  |  | 15% yield<br>2.5 : 1 | 84% yield<br>75 : 1 |
| 2 |  |  | 12% yield | 87% yield<br>> 99:1 |
| 3 |  |  | 19% yield<br>9 : 1 | 70% yield<br>32 : 1 |
| 4 |  |  | no reaction | 90% yield |
| 5 |  |  | no reaction | 84% yield<br>> 99 : 1 |

[a] Reaction conditions as in Table 1 using preformed $[Rh(COD)(DPPB)]BF_4\cdot THF$ (1 mol %) and FAB (2 mol %) in DCE. Entries 1, 2, and 4, 9 h, 70 °C; entry 5, 3 h, 30 °C; and entry 3, 24 h, 30 °C. Times/temps are identical for reactions with and without FAB (tris-(pentafluorophenyl)boron).

Finally, the effect of loading of FAB on the reaction was examined (entries 9, 10). Intriguingly, at 1% loading, which is equivalent to the amount of Rh catalyst added, FAB has no effect, and there is no reaction. However, at 2% loading, the expected rate acceleration occurs. The rationale for these results will be described below.

To determine the generality of the Lewis acid effect, the hydroboration of other alkenes was examined (Table 3). The same trend was observed, where activity and selectivity increased dramatically upon the addition of the Lewis acid cocatalyst. In the case of $\beta$-methyl styrene (entry 1), upon addition of the Lewis acid, selectivity increased from 2.5:1 to 75:1. In the case of 1-alkenes such as allylbenzene, the selectivity for the linear product increases from 9:1 to 32:1, with a significant increase in yield at comparative reaction times (entry 3). This is a particularly interesting reaction, in which the only two products observed are the branched boronate ester where boron is placed proximal to the phenyl ring, and the linear boronate ester from direct reaction. Finally, trisubstituted olefins, which are completely unreactive in the absence of the Lewis acid, give high yields in the presence of a Lewis acid cocatalyst (entry 5). Even with the more reactive HBCat, trisubstituted olefins are typically difficult substrates; however, it should be noted that direct hydroboration is not observed, even in the presence of the Lewis acid. Instead, the product results from isomerization and hydroboration yielding a primary boronic ester as the observed product.

It should be noted that Table 3 contains two types of substrates, arene-containing substrates in entries 1−4 and internal aliphatic olefins in entries 4 and 5. Aliphatic olefins behave similarly to 4-octene: they do not react in DCE in the absence of the Lewis acid catalyst.[25] Arene-containing substrates

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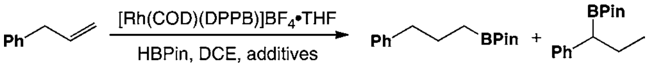
(25) Reactions of aliphatic olefins catalyzed by $[Rh(COD)(DPPB)]BF_4$ do proceed in THF solvent yielding linear boronate esters.

***Scheme 1.*** Yield and Selectivity of Hydroboration of Allylbenzene under Various Catalytic Conditions



| additive | yield | L : B |
|---|---|---|
| none | 19% | 9 : 1 |
| FAB (2:1) | 70% | 32 : 1 |
| FAB (1:1) | 19% | 9 : 1 |

(entries 1−3), however, show low activity in DCE under catalytic conditions without added Lewis acid and display greatly improved yields and selectivities upon the addition of FAB.

As previously noted, for the hydroboration of 4-octene, the amount of FAB added is critical. At 2% loading, which is a 2:1 molar ratio with the catalyst, high activity is observed, while at a 1:1 ratio, the added Lewis acid had no apparent effect. The same was observed in the hydroboration of allylbenzene (Scheme 1). At a 1:1 ratio with the catalyst, the Lewis acid had no discernible effect on the activity or selectivity of the hydroboration.

Examination of a 1:1 mixture of $[Rh(COD)(DPPB)]^+BF_4^-\cdot THF$ and FAB by $^{19}F$ and $^{31}P$ NMR gave some insight into these phenomena. At a 1:1 ratio, no free $BF_4^-$ or FAB were observed in solution. Instead, a strong interaction between the Lewis acid and the outer sphere $BF_4^-$ anion was observed. A series of $^{19}F$ NMR NOESY and COSY experiments (Supporting Information) indicated that this interaction is best described either as a bridging interaction via a $\mu$-fluoride or as complete transfer of $F^-$ from $BF_4^-$ to generate $FB(C_6F_5)_3^-$, which, based on the NOESY data, is interacting with the $BF_3$ species.[26] Because there is no hydroboration of 4-octene when the added FAB is tied up by interaction with $BF_4^-$, it is clear that free FAB must be present in solution to see a change in activity and/or selectivity.

The catalyst precursor was unchanged by $^{31}P$ NMR when 1 equiv of FAB was added, consistent with the lack of catalytic activity. However, upon the addition of excess FAB, the catalyst precursor was converted in new species as evidenced by the appearance of signals at ca. 40 ppm (Figure 3). Although clearly more than one species is present, the observation of new peaks in the $^{31}P$ NMR implies that an active catalyst has been generated by the addition of the second equivalent of FAB. The same results were observed when the catalyst was treated with $Sc(OTf)_3$. Upon warming, additional signals appeared in the same region, indicating either catalyst decomposition or the generation of new species (Supporting Information).

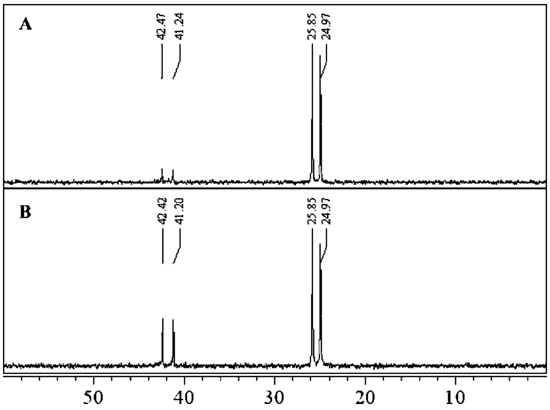


***Figure 3.*** $^{31}P$ NMR spectra of (A) $[Rh(COD)(DPPB)]BF_4\cdot THF$ and HBPin with 2 equiv of FAB and (B) as above with 2 equiv of $Sc(OTf)_3$.

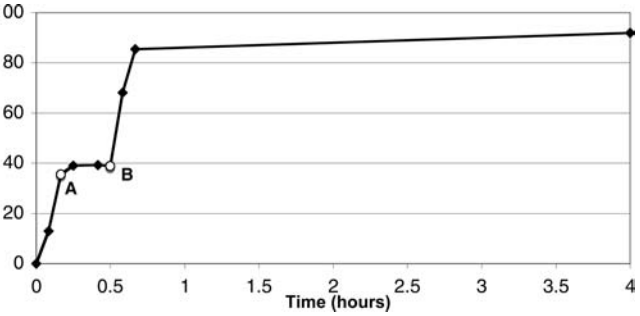
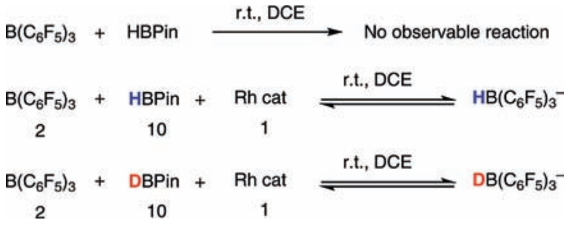


***Figure 4.*** Catalyzed hydroboration of 4-octene using preformed $[Rh(COD)(DPPB)]BF_4$ (1 mol %) and FAB (2 mol %) in DCE. The reaction was inhibited by the addition of $Bu_4NBF_4$ (4 mol %) at point A, and then reactivated by addition of additional FAB (4 mol %) at point B.

***Scheme 2.*** Hydride Abstraction Occurs from Pinacolborane and Requires FAB and $[Rh(COD)(DPPB)]BF_4\cdot THF$ To Proceed



To determine whether or not the presence of free FAB is only required to initiate the reaction, an inhibition study was carried out. Because the $BF_4^-$ anion quenches FAB by fluoride transfer, it was employed to remove free Lewis acid from reactions that have already begun. As shown in Figure 4, the hydroboration of 4-octene with 1% $[Rh(COD)(DPPB)]^+BF_4^-\cdot THF$ and 2% FAB was allowed to proceed to ca. 40% conversion, at which point $Bu_4N^+BF_4^-$ was added to complex the free FAB. This resulted in complete cessation of reaction. To ensure that catastrophic catalyst death had not accompanied the $Bu_4N^+BF_4^-$ addition, a second aliquot of FAB was added after 30 min, which reinitiated the reaction. These experiments clearly illustrate that FAB does not act solely as an initiator and is required throughout the course of the reaction.

Considering the ability of FAB to catalyze the hydrosilylation of alkenes and carbonyl compounds in the absence of a metal catalyst,[23] we examined the reaction of 4-octene with HBPin and FAB, and found no reaction between FAB and HBPin by proton or boron NMR, consistent with the lack of catalytic activity in the absence of the metal. However, when

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(26) The interaction was confirmed by 1D, 2D-COSY, and 2D-NOESY fluorine NMR. On the basis of the $^{19}F$ NMR spectrum, in comparison with the spectra for independently prepared $F-B(C_6F_5)_3^-$ (Chen, M.-C.; Roberts, J.; Marks, T. *Organometallics* **2004**, *23*, 932−935), it is likely that the fluoride has been completely transferred. However, cross peaks are observed in the $^{19}F$ NOESY spectrum between the signal at −192 ppm (integrating to one fluorine, and assigned to the bridging or transferred $F^-$) and that at −156 ppm (integrating to three fluorines, showing an isotopic shift for binding to $^{10}B$ and $^{11}B$, and assigned to the $BF_3$ remnant of the $BF_4^-$ counterion). This can be interpreted either as exchange of fluoride between $BF_3$ and FAB or as a bridging interaction. It should be noted that the signal at −192 ppm is similar to a bridging fluoride between two boron Lewis acids, observed to resonate at −188 ppm (Solé, S.; Gabbaï, F. P. *Chem. Commun.* **2004**, 1284−1285). It should also be noted that the hydroboration was not accelerated by the addition of $BF_3$ etherate even at 20% loading. See the Supporting Information for spectra.

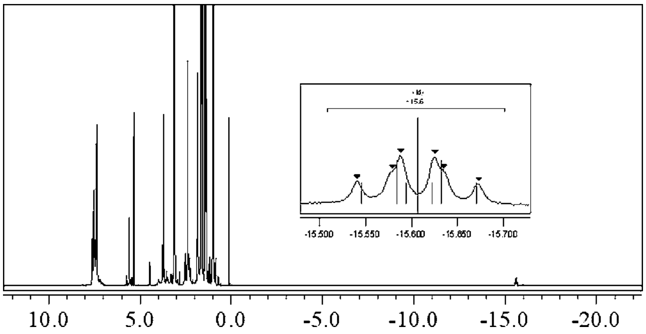


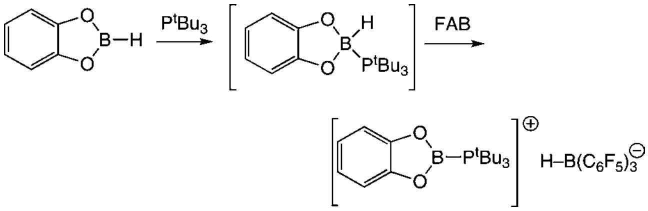
***Figure 5.*** Reaction between $HB(C_6F_5)^-$ and $[Rh(COD)(DPPB)]BF_4 \cdot THF$ showing the presence of at least one strong Rh−H signal with coupling to Rh and two equivalent phosphorus atoms.

$[Rh(COD)(DPPB)]BF_4 \cdot THF$ was added to a mixture of these two species, $HB(C_6F_5)_3^-$ was detected in the $^1H$ and $^{11}B$ NMR spectra. Carrying out the same reaction with DBPin resulted in the observation of $DB(C_6F_5)_3^-$ and the loss of the doublet in the boron NMR (Supporting Information).[27] These experiments demonstrated that in the presence of the Rh catalyst, the hydride of pinacolborane is partially transferred to FAB (see Scheme 2).

Independently generated $HB(C_6F_5)_3^-$, when reacted with $[Rh(COD)(DPPB)]BF_4 \cdot THF$, yields rhodium hydrides as observed by $^1H$ NMR (Figure 5). The observation of a doublet of triplets suggests that the two phosphorus atoms are magnetically equivalent in the major species. This is consistent with the work of duBois,[28] who has shown that there is an equilibrium between rhodium hydrides and borohydrides. This transfer was only observed in the presence of an excess of the hydride reagent, also consistent with duBois's results in which the equilibrium has been shown to favor the borohydride.[29] Although it should be emphasized that it is still unclear whether this reaction is relevant to the catalytic cycle, it is clear that under stoichiometric conditions, FAB is able to mediate the partial transfer of hydride from HBPin to Rh.

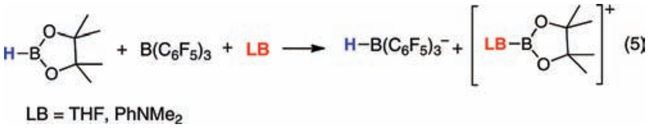
Intrigued by the similarity of this system to the hydrosilylation chemistry described by Piers[30−32] and Gevorgyan,[23] we considered whether THF cocrystallized with the Rh complex was the true species responsible for mediating the hydride transfer from HBPin to FAB. This reaction has considerable precedence in the cleavage of other H-element bonds in the frustrated Lewis acid/Lewis base systems of Stephan.[33−36] Of particular relevance to this discussion, the Stephan group has demonstrated that catechol borane reacts with FAB and bulky phosphines to give $HB(C_6F_5)_3^-$ and the corresponding boryl phosphonium cation (Scheme 3).[37]

***Scheme 3.*** Hydride Abstraction from HBCat by FAB and a Bulky Phosphine As Described by Stephan and Co-workers[37]



Indeed, when HBPin (10 equiv) and $B(C_6F_5)_3$ (1 equiv) are mixed in the presence of 10 equiv of THF, $HB(C_6F_5)_3^-$ is observed. Other Lewis bases such as DABCO and $PhNMe_2$ also promote the formation of $HB(C_6F_5)_3^-$ from HBPin (Figure 6). In both cases, an additional signal is observed in the region expected for a borenium cation. In the case of THF-mediated cleavage, a signal is observed at 22.2 ppm, which is distinguishable from the decomposition product $B_2Pin_3$ at 20.99 ppm (Figure 7). When $PhNMe_2$ is employed, a signal is observed at 26.4 ppm in the $^{11}B$ NMR, which may also represent $[PhNMe_2BPin]^+$.[41−43] Consistent with this, when a THF-free catalyst prepared in dichloromethane was employed, no $HB(C_6F_5)_3^-$ was observed, and no hydroboration activity was observed regardless of the amount of FAB added, illustrating the importance of a catalytic amount of THF to mediate this transfer. It should be noted that, although there are examples of borohydride accelerated hydroboration,[38] the combination of THF, FAB, and HBPin did not catalyze the hydroboration reaction, indicating that regardless of what role these species play in splitting the B−H bond, the presence of the Rh catalyst is required for overall hydroboration of olefins.[39]

Although we have not been able to isolate the stabilized borenium ion, based on the work of Stephan,[37] Piers,[40] and Gevorgyan,[23] a Lewis base-stabilized borenium ion is a likely intermediate (eq 5). Considering the necessity of the Rh catalyst to affect the overall hydroboration, the boryl cation may be ultimately transferred to Rh, such that the effect of the catalytic amount of FAB is to act as a mediator of oxidative addition, although we cannot rule out direct transfer to the olefin at this point.



A potential mechanism that would accommodate all of our data is shown in Scheme 4. This proposed mechanism includes

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(27) The $J_{D-B}$ is too small to be observed by $^{11}B$ NMR, resulting in a broad singlet.

(28) DuBois, D. L.; Blake, D. M.; Miedaner, A.; Curtis, C. J.; DuBois, M. R.; Franz, J. A.; Linehan, J. C. *Organometallics* **2006**, *25*, 4414–4419.

(29) The position of this equilibrium relates to the relative hydride affinities of the specific Rh and boron species in question. In the actual catalytic system, even a small equilibrium can lead to constructive reaction because the Rh hydride is transferred to the olefin in the hydroboration reaction.

(30) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887–4892.

(31) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921–3923.

(32) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247–8254.

(33) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433–7437.

(34) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535–1539.

(35) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P. R.; Stephan, D. W. *Dalton Trans.* **2007**, 3407–3414.

(36) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.

(37) Dureen, M. A.; Lough, A.; Gilbert, T. M.; Stephan, D. W. *Chem. Commun.* **2008**, 4303–4305.

(38) Arase, A.; Nunokawa, Y.; Masuda, Y.; Hoshi, M. *J. Chem. Soc., Chem. Commun.* **1992**, 51–52.

(39) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968–4971.

(40) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090–3098.

(41) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016–5036.

(42) Kolle, P.; Noth, H. *Chem. Rev.* **1985**, *85*, 399–418.

(43) Noth, H.; Weber, S.; Rasthofer, B.; Narula, C.; Konstantinov, A. *Pure Appl. Chem.* **1983**, *55*, 1453–1461.

(44) Line-broadening, a common characteristic of these species, may also hinder observation.

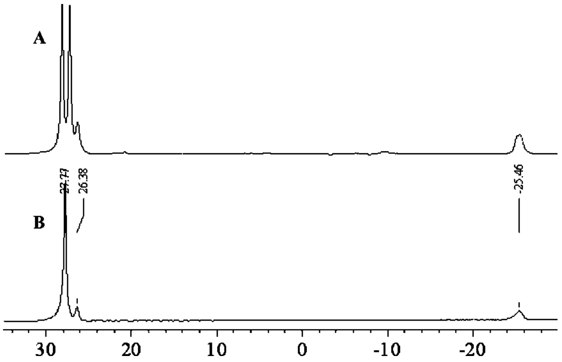


***Figure 6.*** $^{11}$B and $^{11}$B{$^1$H} NMR of HBPin in the presence of $PhNMe_2$ and FAB.

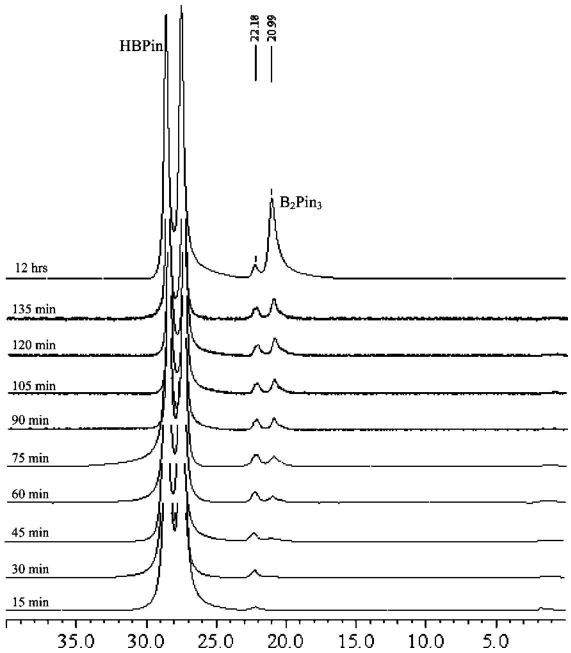
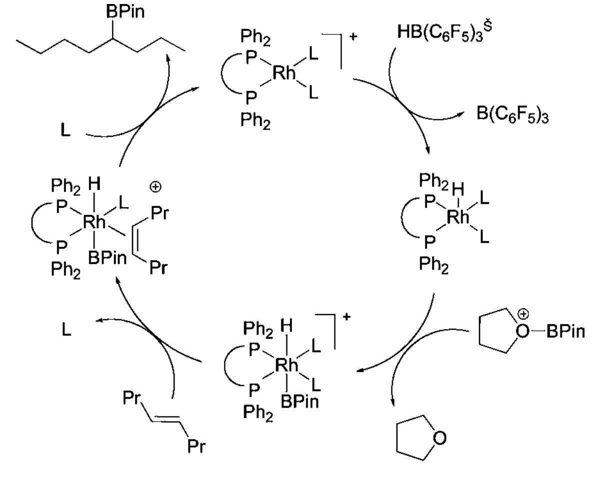


***Figure 7.*** $^{11}$B NMR of HBPin in the presence of THF and FAB at different times, showing the increase in the signal at 20.99 ppm attributable to $B_2Pin_3$, and the signal at 22.18 ppm, which is in the correct region for a borenium ion stabilized by THF.

***Scheme 4.*** Proposed Catalytic Cycle for FAB-Promoted Hydroboration Catalyzed by Rh$^+$ Catalyst[a]



L = THF, or COD or (E)-4-octene

[a] Note that the olefin is drawn as cis when coordinated to the metal for convenience sake, and also note that the geometry of the complexes in question is only speculative.

the indirect transfer of HBPin to the catalyst via heterolytic B−H bond cleavage to $HB(C_6F_5)_3^-$ and $[PinB\text{-}THF]^+$. Following this reaction, transfer of hydride from $HB(C_6F_5)_3^-$ to Rh$^+$ yields a Rh(I) neutral hydride, which then undergoes formal oxidative addition of the borenium THF species to yield a cationic Rh(III) species. From here, hydroboration of the olefin proceeds as expected (Scheme 4). It should be noted that the addition of the borenium species may proceed with subsequent loss of THF (as drawn), or THF may be retained as a ligand until later in the cycle where it would be lost to affect another heterolytic B−H bond cleavage of HBPin. Yet another possibility is that the oxidative addition of the borenium ion to Rh would precede hydride transfer. Although the precise reasons for the increase in selectivity with aryl alkenes are unclear at this point, it is possible that the two-step oxidative addition generates a complex with a geometry different from that observed in the case of direct oxidative addition, which may explain the observed differences in selectivity.[45] It should be emphasized that other potential mechanisms, for example, involving Rh(V) intermediates, cannot be ruled out at this point. Considering that the equilibrium for the transfer of hydride between Rh and FAB lies toward the FAB hydride, it is also conceivable that a slow oxidative addition is accelerated by removal of hydride from Rh by FAB. The reaction with the olefin substrate might then be initiated by addition of the Rh boryl species rather than a Rh hydride. The precise mechanism of action of FAB on the hydroboration is currently in progress.

Preliminary kinetic evidence shows that in the absence of Lewis acid, the rhodium-catalyzed hydroboration of allylbenzene occurs faster than the corresponding deuterioboration carried out with DBPin. However, in the presence of the Lewis acid, no kinetic isotope effect is observed, consistent with acceleration of the oxidative addition step such that another step in the catalytic cycle becomes turnover limiting.

## Conclusions

Lewis acids such as FAB have a clear effect on the hydroboration of olefins with pinacol borane. Although the nature of the effect is slightly different depending on the substrate class and solvent, the overall result is the same: increases in activity and selectivity are observed. In the case of aliphatic olefins, when reactions are run in coordinating solvents, the linear product predominates. In noncoordinating solvents, 4-octene undergoes hydroboration, yielding the 4-isomer in the presence of FAB. In the absence of FAB, reactivity in these solvents is low or nonexistent. The differences in selectivity for these substrates appear to be related to a solvent effect because the $SbF_6$- catalyst gives the linear isomer in THF and the branched (4-isomer) in DCE. However, a dramatic enhancement in activity is observed such that the reaction is complete in less than 30 min under normal conditions. When aromatic alkenes are employed, such as $\beta$-methyl styrene, the addition of FAB leads again to an improvement in selectivity and activity. With this substrate class, the selectivity increase does not appear to be solvent-related, but is likely a consequence of the shift in mechanism observed upon the addition of FAB.

$^{19}$F NMR studies indicated that at a 1:1 ratio of FAB to Rh catalyst, there is no free FAB present in solution, as it is

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(45) Interactions between FAB and the aromatic moiety cannot be ruled out at this time.

subjugated to complexation with the $BF_4^-$ counterion of the catalyst. $^{31}P$ NMR studies of this 1:1 system confirmed that there was no observable change upon addition of HBPin to this system. Upon addition of an additional free equivalent of FAB, changes were observed in the catalyst, concomitant with the observation of catalytic activity. Poisoning studies using $Bu_4NBF_4$ added to scavenge any free FAB in reactions that are in progress confirmed that the FAB effect was not merely confined to initiation and was required over the course of the reaction.

On the basis of hydride-transfer reactions between FAB and $HSiR_3$ pioneered by Piers[40] and Gevorgyan,[23] the reaction between FAB and HBPin was examined. The combination of these reagents in the absence of catalyst was not active in the hydroboration and gave no change by NMR. However, upon addition of the catalyst, $HB(C_6F_5)_3^-$ was observed by boron NMR. Co-crystallized THF was determined to be the likely mediator of this transfer.

Similarly, preformed $HB(C_6F_5)_3^-$ was shown to transfer hydride reversibly to the Rh catalyst. Thus, it is conceivable that the role of $B(C_6F_5)_3$ in the hydroboration of unreactive substrates is to facilitate oxidative addition of HBPin to the Rh catalyst. Although the equilibria likely do not lie in the direction of hydride transfer to Rh, the eventual hydroboration of the olefin may act as a sink driving this reaction. Efforts are underway to clarify the nature of this step and the mechanism of eventual boryl transfer to complete the hydroboration reaction.

In conclusion, we have clearly shown that in metal-catalyzed hydroborations with HBPin, the addition of catalytic amounts of Lewis acids such as $B(C_6F_5)_3$ has a dramatic effect, accelerating the rate of reaction in all cases examined and improving the regioselectivity in some cases. The observation of $HB(C_6F_5)_3^-$ in these reactions implicates this species in the overall transformation, although further work is required to firmly establish the role of this species in the catalytic cycle. The generality of the use of Lewis acids as cocatalysts in metal-catalyzed reactions is currently under study in our lab.

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**Supporting Information Available:** Experimental procedures, relevant NMR spectra, and supporting experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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