

Tropylium Salt Promoted Hydroboration Reactions: Mechanistic Insights via Experimental and Computational Studies

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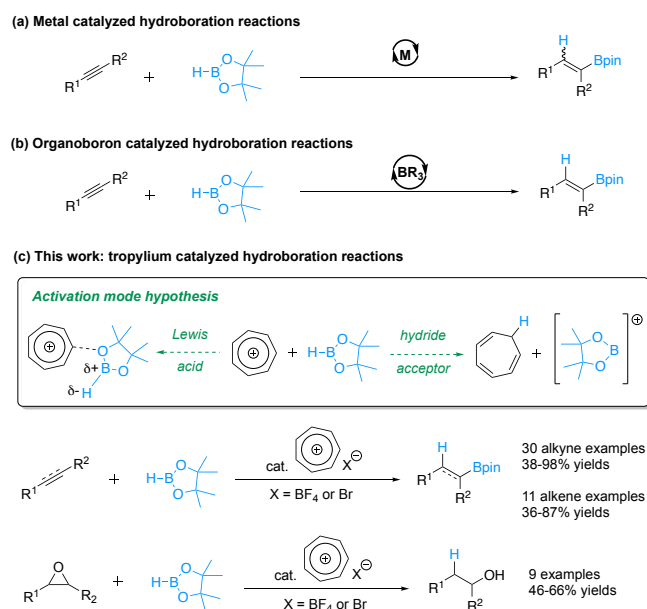
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Abstract: Hydroboration reaction of alkynes is one of the most synthetically powerful tools to access organoboron compounds, versatile precursors for cross coupling chemistry. This type of reaction has traditionally been mediated by transition metal or main group catalysts. Herein, we report a novel method using tropylium salts, typically known as organic oxidants and Lewis acids, to efficiently promote the hydroboration reaction of alkynes. A broad range of vinylboranes can be easily accessed via this metal-free protocol. Similar hydroboration reactions of alkenes and epoxides can also be efficiently catalyzed by the same tropylium catalysts. Experimental studies and DFT calculations suggested that the reaction follows an uncommon mechanistic paradigm, which is triggered by a hydride abstraction of pinacolborane with tropylium ion. This is followed by a series of *in situ* counterion-activated substituent exchanges to generate boron intermediates that promote the hydroboration reaction.

Introduction

Hydroboration of C-C multiple bonds is one of the most frequently used reactions in organic synthesis.^[1] It produces alkyl or alkenyl boranes, which are stable but versatile synthetic precursors for a wide range of coupling reactions.^[1] Since the early examples of uncatalyzed addition of borane to olefins by Brown,^[2] the field has evolved significantly over the last few decades to develop more efficient and practical catalytic systems for more challenging hydroborative processes. Among them, transition metal catalyzed hydroboration reaction remains the most thoroughly explored direction^[3] (Scheme 1a) with the focus slowly shifts from precious metals^[4] to more abundant ones.^[5] More recently, main group catalytic hydroboration has emerged as a new research field,^[6] with organoborane catalysts being the most attractive options (Scheme 1b).^[7] The quest to make hydroboration reaction completely metal-free ventures further into some scattered examples of organocatalytic systems such as carboxylic acids^[8] or amides.^[9] While the mechanism of transition metal and main group element catalyzed hydroboration reactions has been extensively studied, there is a limited understanding of activation mode and reaction design in organocatalytic systems. Therefore, a reliable and efficient organocatalyst, which is also robust and



Scheme 1. Tropylium catalyzed hydroboration of alkynes, alkenes and epoxides.

simple for necessary mechanistic studies, is in demand.

Given our ongoing interest in the chemistry of tropylium ion^[10] and our recent recognition of the similarity in Lewis acid catalyst activity of tropylium ion^[11] to boron Lewis acids $\text{B}(\text{Ar}^F)_3$, which are known as efficient catalysts for hydroboration reaction,^[7c, 7e-g, 7i, 7k] we envisioned that tropylium salts could potentially serve as suitable organocatalysts for the same chemical transformation. In addition to its Lewis acidity, tropylium ion is also known as an organic oxidant,^[12] which could abstract a hydride from borane reagents to trigger the reaction via the formation of borenium cation (Scheme 1c). If this works, it will offer a new catalytic paradigm in hydroborative chemistry, especially when the electrophilic tropylium ion is distinctively different from existing catalysts, many of which are nucleophiles or hydride donors.

Optimization and Substrate Scope

We started our investigation by looking at the catalytic activity of tropylium tetrafluoroborate (**1a**) in the reaction between phenylacetylene (**1a**) and pinacolborane (HBpin, **3**). Gratifyingly, the initial reaction met with successful results. We proceeded further to optimize the reaction conditions on solvent, temperature, stoichiometry of HBpin and tropylium catalyst loading (for full optimization details, see the ESI).^[13] The optimal conditions were presented in Table 1, where best reaction outcomes were achieved with 2 mol% **1a** at 70 °C in neat condition. The use of relatively non-polar solvents such as 1,2-dichloroethane or toluene also led to excellent yields of hydroboration adduct **4a**, while acetonitrile or THF completely turned off the reaction (entries 6-7, Table 1). Our initial thought is that this can be attributed to the fact that these solvents can solvate or coordinate very well to tropylium or boron intermediates, rendering them much less reactive for the reaction to proceed.

Without the tropylium catalyst, it only led to 15% yield of **4a** as the background reaction (entry 1). Tropylium hexafluorophosphate seemed to be much less effective for this reaction (entry 8). Other tropylium salts such as chloride, bromide (**1b**) or triflate (**1c**) also proved to be capable of catalyzing the reaction with similar efficiency, however, tropylium chloride is too hygroscopic to be considered a practical catalyst. The important role of tropylium ion was highlighted by the fact that potassium or tetrabutylammonium salts of the same counterions either showed no catalytic activity or hindered the reaction. Furthermore, other hydride abstractors or organic Lewis acids such as tritylium^[14] or nitrosonium^[15] salts could also catalyze the reaction but with lower efficiencies than tropylium salts (entry 8).

The regioselectivity and stereochemistry of the reaction product was confirmed by comparison to literature data and also by a simple isotope labeling study. This study used our developed optimal reaction conditions on deuterated phenylacetylene (**2a-D**, 95%-D, Scheme 2), which gave product **4a-D** in 87% yield with 93% deuterium at the terminal carbon, confirming that the HBpin added to the C-C triple bond in *cis*-fashion with the indicated regioselectivity. We subsequently applied the optimized conditions towards the hydroboration of other alkyne substrates

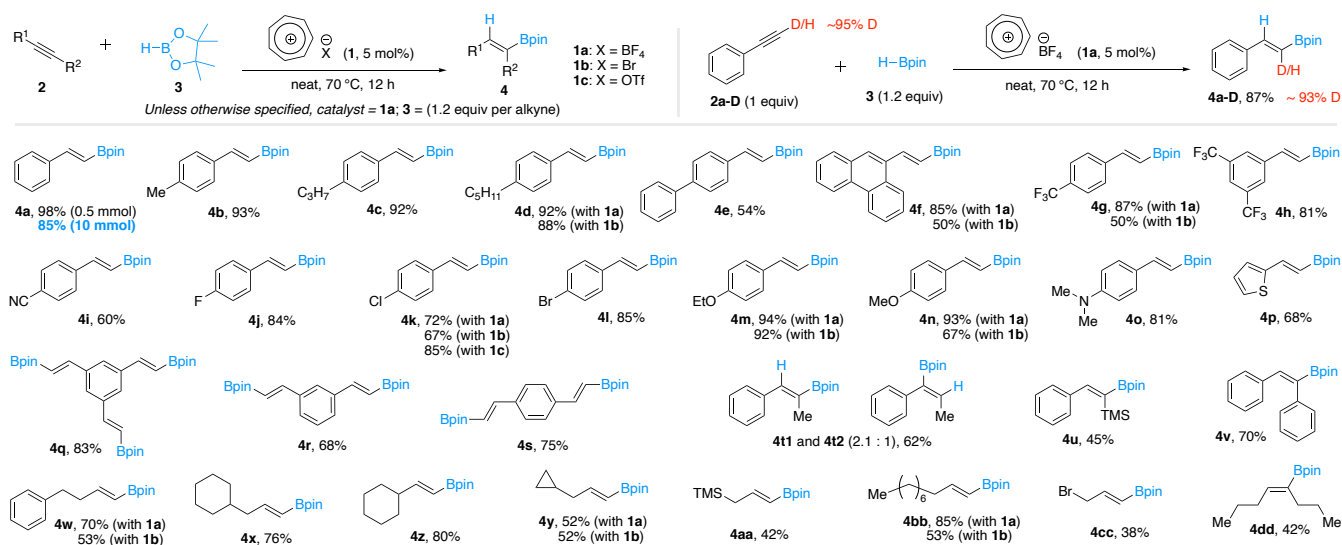
Table 1. Optimization of tropylium-catalyzed reaction between **2a** and **3**^[a]

Optimal conditions

Entry	Variations from optimal conditions	Yield of 4a (%) ^[b]
1	no catalyst (also see entry 8)	15
2	4 h	63
3	1 mol% catalyst 1a	92
4	5 mol% catalyst 1a	99
5	50 °C	94
6	solvent DCE or toluene (10 mol% 1a)	94 or 95
7	solvent MeCN or THF (10 mol% 1a)	traces
8 ^[c]	variation of catalyst	see below

[a] Reaction conditions: 0.5 mmol **2a**, 0.6 mmol **3** (1.2 equiv) and 0.01 mmol **1a** neat or in the indicated solvent (2 mL) at the indicated temperature for the indicated time.^[13] [b] Yield of the isolated **4a**. [c] All catalysts are anhydrous.

(Scheme 2). While these conditions work well for most substrates we tested, some of them showed unsatisfactory conversions. Therefore, we settled with a more suitable set of conditions from entry 4, Table 1 with 5 mol% tropylium catalyst and 12 hours reaction time to ensure good efficiency is achieved across the



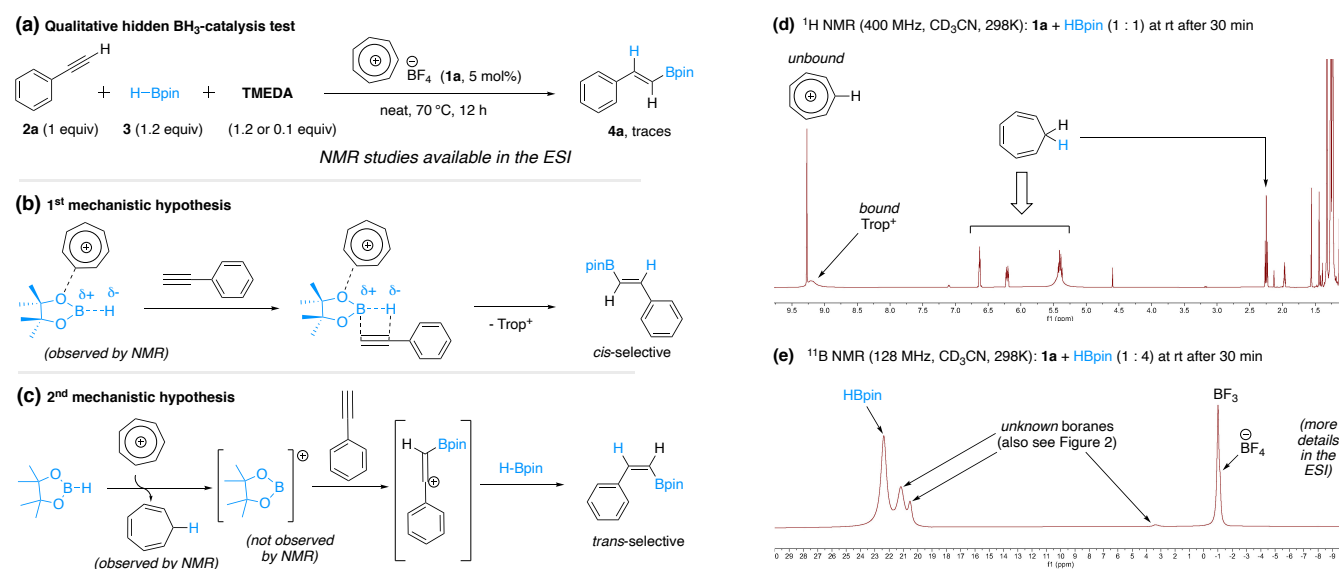
Scheme 2. Substrate scope of the hydroboration of alkynes. All products are *trans*-isomers, based on comparison of ¹H NMR spectra with literature data.

the whole substrate scope. Most of arylacetylene substrates reacted smoothly to give the (*E*)-alkenyl boronic ester products in good to excellent yield (**4a-4o**, Scheme 2). The reaction worked efficiently with heterocyclic as well as *bis* and *tris*(acetylenyl) substrates (**4p-4s**). Non-terminal aromatic alkynes also reacted but led to lower product yields (**4t-4v**) and mixture of regioisomers (**4t1** and **4t2**). Under these reaction conditions, alkyl-substituted alkynes resulted in generally lower conversions to the products than their aryl alkyne counterparts.

Mechanistic studies

Apart from demonstration of practicality, it is also important to elucidate the mechanistic pathway of our newly developed tropylium salt catalyzed hydroboration of alkynes. While we carried out this project, the Thomas group reported important recognitions of hidden pathways in hydroboration chemistry,^[16] which actually involve the catalytic activity of *in situ* generated BH₃

from nucleophilic catalysts or ligands and HBpin. These reports prompted us to carefully reconsider our original hypotheses and perform an in-depth investigation into the activation mode of our tropylium catalysts (Scheme 3). Thomas and co-workers nominated a qualitative 'hidden BH₃ catalysis' test, involving the addition of tetramethylethylenediamine (TMEDA) to the reaction. This additive will supposedly complex with any BH₃ formed in the reaction mixture, making it easier to identify by characteristic signals in NMR spectra. Thus, this was the first mechanistic control study that we did and we learned straightaway that it turned off the reaction completely, as no hydroboration product was formed in the reaction (Scheme 3a). In hindsight, this was not surprising, as tropylium ion is known to coordinate to the nitrogen centre of the amino group and even remove hydride from tertiary amines.^[10e, 12a, 12b] The coordination of tropylium to TMEDA was observed by NMR spectroscopy (see page S39 in the experimental ESI); this presumably rendered our catalytic system inactive. Therefore, Thomas's qualitative test is, unfortunately, not applicable to our reaction conditions in this work.



Scheme 3. Experimental mechanistic studies and original hypotheses of reaction mechanism: (a) Control study with TMEDA; (b) Lewis acid activation hypothesis; (c) Hydride abstraction activation hypothesis; (d) ¹H NMR complexation studies and (e) ¹¹B NMR complexation studies between HBpin and **1a**.

Our first original hypothesis was that the Lewis-acidic tropylium ion could coordinate to the oxygen centres on HBpin, enhancing the polarization of the B-H bond and promote the addition to the triple bond (Scheme 3b). This will likely produce the *cis*-selective addition product (*trans*-isomer), which agrees with our actual results. Our complexation NMR studies between tropylium salts and HBpin did show some supporting evidence for this Lewis coordination (Scheme 3d). However, there is a more predominant transformation happening between these two species. The ¹H NMR spectrum (in CD₃CN) of a 1 : 4 mixture of Trop.BF₄ **1a** or Trop.Br **1b** with HBpin (to mimic 5 mol% catalyst vs. 0.2 equiv = 20 mol% in excess of HBpin in optimal reaction conditions) also showed clear evidence of the formation of cycloheptatriene, even when the analysis was done instantly after mixing the two compounds. Similar outcomes were observed with longer reaction times or at 70 °C (see Scheme 3d for a representative spectrum of the mixture after 30 minutes at room temperature). It

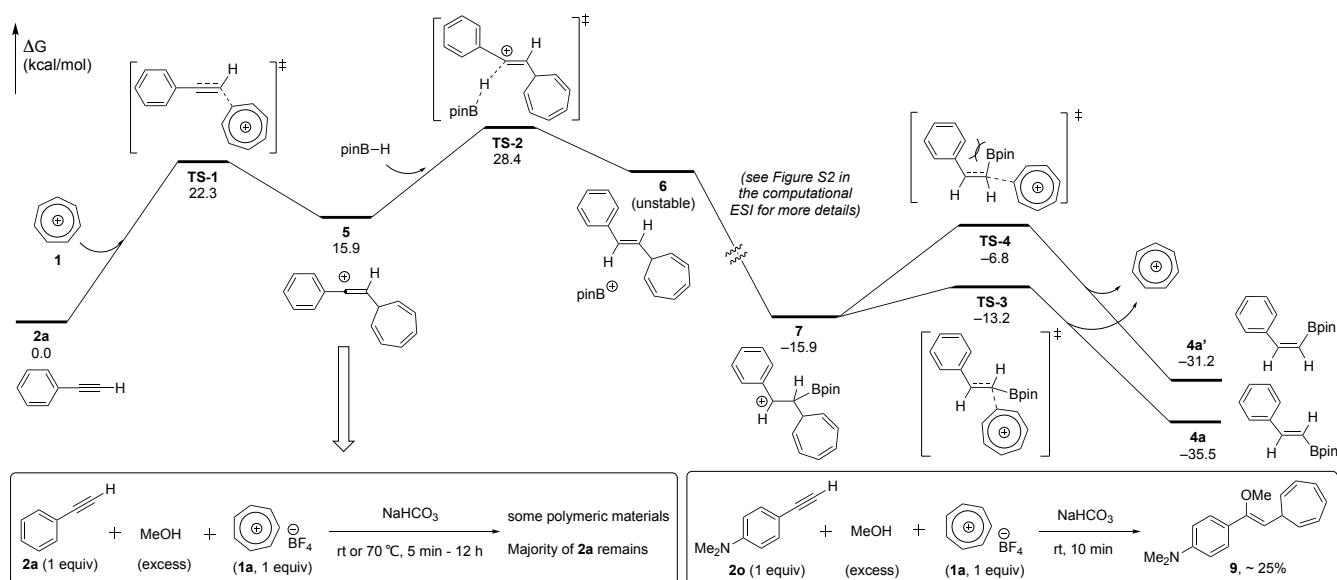
beckoned another hypothesis we had at the beginning of this work that tropylium ion could act as a hydride abstractor^[12a, 12b] to generate a borenium ion from HBpin.^[4e, 17] This could then quickly react with the alkyne to form a vinyl cation intermediate,^[17b, 18] which subsequently take a hydride from another molecule of HBpin to generate the target product and start another reaction cycle (Scheme 3c).^[7d] It should be noted that this reaction pathway would tentatively produce the *trans*-selective hydroboration product (*cis*-isomer), which contradicts our experimental outcomes.

However, the ¹¹B NMR of the Trop.BF₄ **1a**/HBpin mixture (Scheme 3e) did not show the presence of a borenium species. This is most likely due to the fact that the borenium ion would immediately combine with a nucleophilic species in the reaction mixture, such as the fluoride from tetrafluoroborate or the bromide, to form more stable boranes. Apart from remaining HBpin and BF₄ anion, we initially could only identify the presence of BF₃, plus the

formation of some unidentified boranes in the ^{11}B NMR spectrum (Scheme 3e, also see Figure 2 and discussion later). On the other hand, we have carried out an extensive Density Functional Theory (DFT) calculation^[19] to validate our hypotheses in either Scheme 3b or 3c. Our DFT calculations showed that the activation barrier for the uncatalyzed hydroboration between HBpin and alkyne **2a** is approximately 42.5 kcal/mol, which is consistent with the fact that this hydroboration cannot occur without catalyst (see Figure S1 in the computational ESI for details). However, all transition states and intermediates related to mechanistic hypotheses in Schemes 3b and 3c are too energetically unfavorable to be feasible (see Figure S1 in the computational ESI); therefore, they could be considered unlikely for the reaction.

In our substrate scope study discussed above in Scheme 2, tropylium bromide (**1b**) and triflate (**1c**) catalysts were also employed for a selected number of substrates and gave comparable or slightly lower efficiencies than tropylium

tetrafluoroborate. It should be noted that we chose not to carry out more examples with these catalysts due to their hygroscopic and difficult-to-handle nature. On the other hand, as discussed earlier in Table 1, potassium or tetrabutylammonium salts of the same counterions either showed no catalytic activity or hindered the reaction while tritylium or nitrosonium salts could also catalyze the reaction but with lower efficiencies than tropylium salts. It prompted us to investigate the possibility of a more direct role of tropylium ion in triggering the reaction, which is depicted in Scheme 4. We hypothesized that the electrophilic tropylium ion could add to the C-C triple bond to generate a vinyl cation intermediate **5**, which can take a hydride from HBpin similar to the borenium pathway in Scheme 3c. This would result in closely associated pair **6**, which would lead to the formation of carbocation **7**. Intermediate **7** could then eliminate a tropylium ion to form the hydroboration product.



Scheme 4. The third mechanistic hypothesis and supporting computational and experimental studies.

A combination of computational and experimental studies was then carried out to find supporting arguments for this new hypothesis (Scheme 4). The addition of tropylium ion to the C-C triple bond of **2a** has an activation energy of 22.3 kcal/mol and that of the subsequent hydride abstraction step between vinyl cation **5** and HBpin is calculated to be 28.4 kcal/mol (Scheme 4). The hydride transfer presumably leads to the formation of the associated pair **6**. Our attempt to optimize **6** always generate carbocation **7**, which suggests that **6** is unstable and will transform into **7** barrierlessly. To confirm this result, Born-Oppenheimer molecular dynamics (BOMD) simulations were carried out. We found that after **TS-2**, **6** is formed and rapidly converted to **7** without crossing any barrier at around 248 fs (see Figure S2 in the computational ESI), which is consistent with our DFT calculations on this species.

While **TS-2** is associated with high activation energy, making this a challenging pathway, the rest of this reaction profile looks rather feasible. Because of the steric repulsion between Bpin and phenyl moieties, **TS-3** is calculated to be 6.4 kcal/mol lower in energy

than that of **TS-4**, resulting in the *cis*-selective **4a** as the favored product, which is consistent with our experiments. However, we failed to find experimental evidence of the formation of vinyl cation **5** by trapping it with other nucleophiles. As a representative example, we could not find the methoxy-cycloheptatrienylation adduct when we replaced the borane reagent with methanol (Scheme 4, bottom-left). Interestingly, a similar trapping reaction with the electron-rich aromatic alkyne **2o** successfully led to the formation of adduct **9** in decent efficiency without optimization of reaction conditions (Scheme 4, bottom-right). The formation of **9** indicates that when there is a strong stabilization effect, in this case coming from the conjugation of *p*-NMe₂ group, it is possible to form a vinyl cation intermediate (**5o**), which reacts with methanol to form **9**. However, this type of reactivity might not be general for the other alkyne substrates, as observed with the standard substrate **2a**. In addition to the high activation energy to **TS-2**, although this does not rule out completely but casts some doubts over our third hypothesis of this tropylium-promote hydroboration reaction mechanism.

Another revisit to our catalyst scope in Table 1 revealed that tropylium salts with chloride, bromide, triflate and tetrafluoroborate counterions catalyzed the reaction efficiently, while those with hexafluorophosphate or BARF counterions gave unsatisfactory results. Furthermore, while tropylium tetrafluoroborate led to almost the same efficiency as the tropylium counterpart, tropylium hexafluorophosphate completely suppressed this hydroboration reaction. These results indicated that while tropylium ion is an essential component, the counterions have an undeniable role in their catalytic activity. So to further unravel the mechanism of our chemistry, we carried out kinetic studies of reactions catalyzed by 5 mol% of tropylium bromide (**1b**) and different loadings of tropylium tetrafluoroborate (**1a**) under optimal conditions. The conversion to the hydroboration product was monitored by ^1H NMR spectroscopy over time (Figure 1a). The interesting thing we learned from these studies is that most reactions (except the one with high catalyst loading – 15 mol% of **1a**) seemed to undergo a catalyst pre-activation period of 5-10 minutes. The lower catalyst loading was, the longer the reaction took to start showing some conversion. The pre-activation time of 5 mol% tropylium bromide was similar to that of 10 mol% tropylium tetrafluoroborate. This prompted us to look deeper into the reaction between tropylium salts and HBpin, which was presumably the only chemical process that caused this pre-activation period.

As discussed before, it was obviously evident that tropylium ion abstracted a hydride from HBpin and turned into cycloheptatriene, but what became of the rest eluded us earlier. The pinacoloborenium ion intermediate (see Scheme 3c) was never observed so we believed it was captured by some nucleophiles in the reaction mixture. This is presumably where the counterions from tropylium salts came into play. With tropylium tetrafluoroborate, it was previously reported that the BF_4 anion can dissociate to form BF_3 and fluoride, which can capture the borenium ion into the corresponding fluoropinacolato borane.^[10] Similar reaction can presumably happen with tropylium bromide to form bromopinacolato borane.

Therefore, we decided to carry out further ^{11}B and ^{19}F NMR spectroscopic analyses of the reaction between tropylium salts and HBpin to get more insights. The pertinent sections of ^{11}B NMR spectra of HBpin and tropylium tetrafluoroborate (**1a**) mixture at

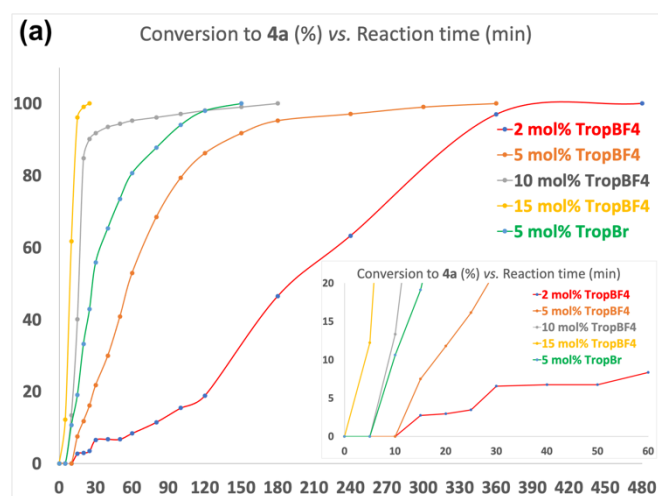


Figure 1. (a) Kinetic studies of the conversion of **2a** to reaction product **4a** with different catalyst loadings, (inset) zoom-in version of initial reaction stage.

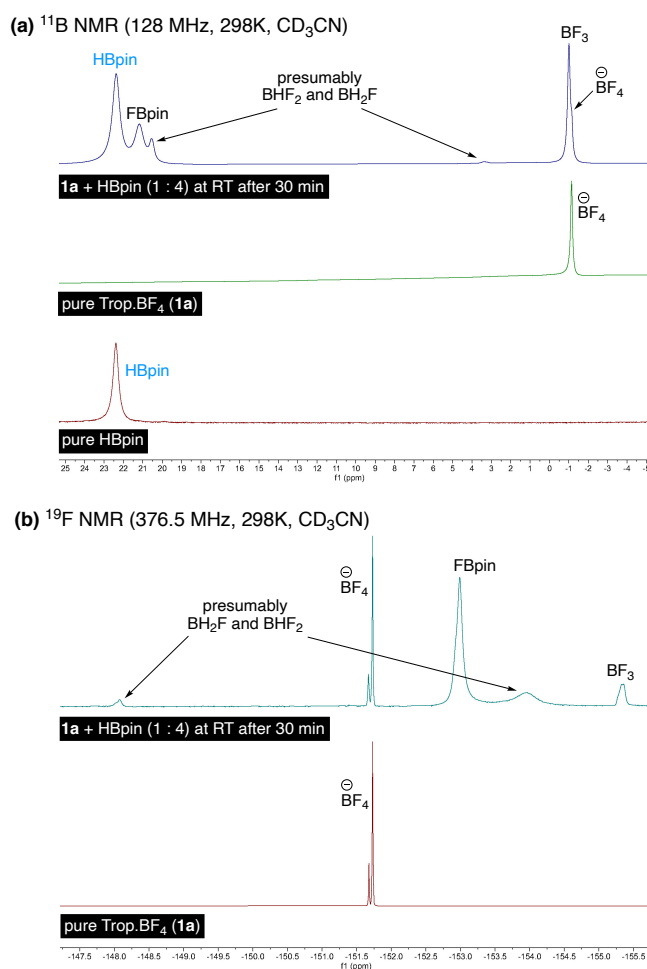


Figure 2. ^{11}B (128 MHz, CD_3CN , 298K) and ^{19}F (376.5 MHz, CD_3CN , 298K) NMR spectra of HBpin and **1a** (pure and mixture at 4 : 1 ratio, rt, 30 min).

4 : 1 ratio after 30 minutes at room temperature can be seen in Figure 2.^[20] After matching signals with known boron species in literature, we were able to identify FBpin^[21] (~ 21 ppm in ^{11}B and ~ -153 ppm in ^{19}F NMR) at all ratios. We did not observe any signals corresponding to $[\text{FHBpin}]^-$, formed by the coordination of fluoride to HBpin, which was reported by the Thomas group in their work with iron and cobalt tetrafluoroborate salts.^[22] There were signals corresponding to some remaining BF_4 anion (~ -1 ppm and ~ -151.7 ppm) and the by-product BF_3 (~ -1 and ~ -155.3 ppm). There were two more new boron compounds formed in this mixture. Although we could not fully interpret these signals, we believe that they correspond to BHF_2 ^[23] and BH_2F (never been characterized by experimental NMR spectroscopy before),^[24] which were presumably produced via substituent exchange reactions between HBpin and BF_3 (*vide infra*).^[7e, 25] It should be noted that in ^{19}F NMR spectra, there are signals corresponding to ^{10}B (small peaks or shoulders) and ^{11}B (major peaks) isotopes for each species (see page S41 in the experimental ESI). With our experimental data pointing towards the formation of a complex mixture of a range of borane species in the presence of HBpin and tropylium tetrafluoroborate, we carried out computational studies to rationalize these results. Interestingly, our DFT calculations^[19] show that HBpin can indeed react with tropylium tetrafluoroborate via hydride transfer transition state **TS-**

5 to form cycloheptatriene, FBpin, and BF_3 species with the calculated barrier of 25.3 kcal/mol (Figure 3a). This result is consistent with experimental finding that other hydride acceptors, including tritylium and nitrosonium tetrafluoroborate, can also promote this hydroboration reaction albeit with lower efficiency; whereas, potassium and tetrabutylammonium salts show no activity (Table 1). We also found that BF_3 species can further react with HBpin via two transborylation transition states **TS-6** and **TS-7** (B–H/B–F σ -bond metathesis), giving BHF_2 and BH_2F species with the activation barriers calculated to be 27.6 kcal/mol relative to BF_3 intermediate (Figure 3a).

Our DFT calculations demonstrate that for this hydroboration of alkyne, the formation of *in situ* BH_2F species is very important and BH_2F can potentially act as a hidden boron catalyst. The catalytic cycle for the hydroboration is shown in Figure 3b. From BH_2F , the 1,2-*syn*-addition to **2a** via **TS-8** is found to occur giving boron alkene intermediate **10** with the calculated barrier of 9.9 kcal/mol relative to BH_2F . To proceed, transborylation (B–C/B–H σ -bond metathesis) between **10** and HBpin can then take place in a stepwise fashion via **TS-9** and **TS-10** giving product **4a** with the retention of *E*-configuration. The activation barriers of **TS-9** and **TS-10** are calculated to be 22.4 and 22.7 kcal/mol relative to intermediate **10**. The transborylation involves a transient μ -H

bridged species **11** consisting of two three-center two-electron (“3c-2e”) bonds, which are employed by the sp^2 hybrid orbital of bridging carbon atom and the 1s orbital of bridging hydrogen atom^[7] (see Figure S3 in the computational ESI for the intrinsic bond orbital analysis of intermediate **11**). Our DFT calculations are in agreement with a recent study by Thomas and Lloyd-Jones for the Arase-Hoshi alkyne hydroboration.^[7]

The activation barrier for the formation of BH_2F catalyst from HBpin and tropylium tetrafluoroborate is calculated to be 27.6 kcal/mol (Figure 3a); whereas, the rate-determining step for the hydroboration of alkyne by BH_2F catalyst is 22.7 kcal/mol (Figure 3b). These results suggest that the reaction has to suspend until the formation of BH_2F . Once BH_2F species is generated, the hydroboration of alkyne can take place efficiently. This finding is consistent with our experimental data that an “activation period” exists at the beginning of the reaction (Figure 1). Furthermore, solvents that can strongly bind to the boron intermediates in Figure 3a are likely to hinder the reaction. For example, the binding energy of THF to BF_3 is calculated to be 12.9 kcal/mol, which thus increases the activation barrier of **TS-6** in THF to be 40.5 kcal/mol relative to BF_3 –THF complex. This result gives a rationalization for the negative effect of solvents on this hydroboration reaction (Table 1).

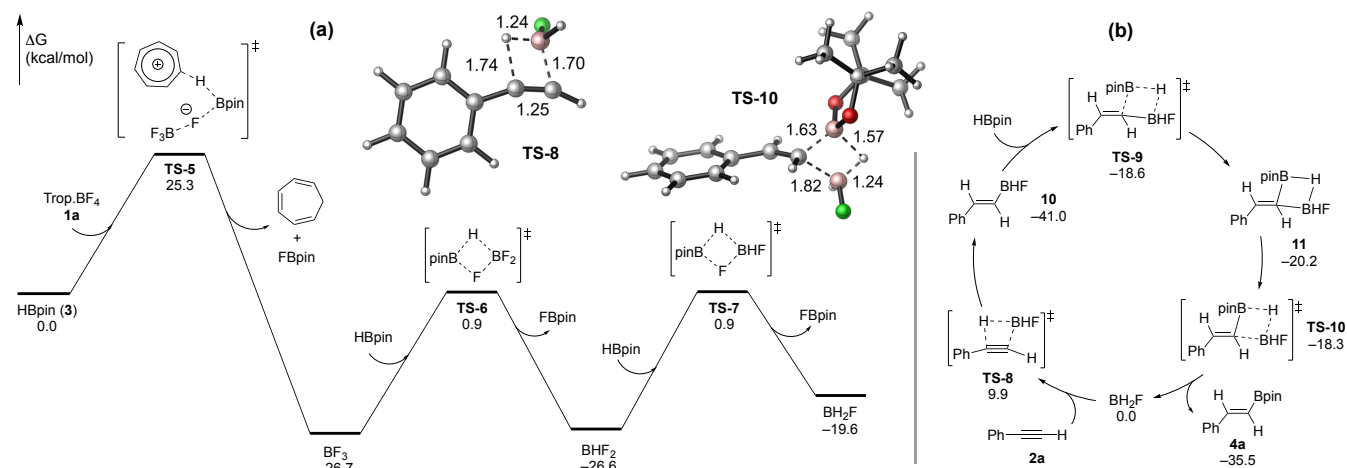


Figure 3. (a) Free energy profile (kcal/mol) for the formation of BH_2F from HBpin and tropylium tetrafluoroborate (b) catalytic cycle for the hydroboration of alkyne catalyzed by BH_2F . In Figure 3b, energy values (kcal/mol) are relative to BH_2F . All bond distances are in Ångstrom.

Here, it should be mentioned that we have also carried out DFT calculations for various hydroboration pathways that could be triggered by each boron intermediate of the reaction, including the possibilities that (i) BHF_2 intermediate acts as the hydroboration catalyst and (ii) BH_3 forms from further reduction of BH_2F by HBpin and subsequently acts as the catalyst.^[16] The catalytic cycle for the hydroboration of alkyne catalyzed by BHF_2 is shown in Figure S4 in the computational ESI. The overall activation barrier for this catalytic cycle is calculated to be 30.4 kcal/mol, which is indeed much less favorable than the same process with BH_2F (Figure 3b) and unlikely to happen. The reaction mechanism for the hydroboration catalyzed by BH_3 is shown in Figure S5 in the computational ESI. It is obvious that BH_3 can also efficiently catalyze the conversion of **2a** to **4a**. However, because of the high reactivity of BH_3 species, the reaction is unlikely to stop there. Intrinsic reaction coordinate (IRC) calculation and BOMD

simulations indicate that at around 271 fs after the transborylation giving BH_3 and **4a**, BH_3 species can quickly react to C–C double bond of **4a** without crossing any barrier giving an alkane intermediate (see Figure S6 and S7 in the computational ESI). This is followed by a transborylation with HBpin giving *gem*-diboron alkane as the favorable product. This is inconsistent with our experimental findings in that we can only observe the semi-hydroboration adduct **4a** with our tropylium catalysts. A control studies using BH_3 (commercially available in complexes with Me_2S or THF) as catalyst indeed led to the formation of *gem*-diboron alkane product. Moreover, the activation barrier for the transborylation between BH_2F and HBpin giving BH_3 is calculated to be 8.1 kcal/mol higher than that of the 1,2-*syn*-addition between BH_2F and alkyne **2a** (see Figure S1 in the computational ESI for detail), which indicates that BH_3 is unlikely to be the catalyst for our hydroboration reaction.

Our mechanism, therefore, can be considered a hybridization of the hidden catalysis by borane^[16] and the counterion-activated catalysis by Fe/Co tetrafluoroborate salts.^[22] Both of these were recently reported by the Thomas group as game-changing factors in hydroboration catalysis. While our mechanistic proposal still needs further validations in future work, the fact that a simple species such as tropylium tetrafluoroborate **1a** could potentially trigger hydroboration in several different ways is intriguing. As the hydroboration reaction can also work with tropylium bromide **1b** as catalyst, it has to activate the system through a different pathway since there is no BF₄ anion. Experiment finding suggests that 5 mol% tropylium bromide can promote the hydroboration with similar kinetics and efficiency as 10 mol% tropylium tetrafluoroborate (see Figure 1). Our DFT calculations suggest that HBpin can react with tropylium bromide via **TS-11** to

form BrBpin with the calculated barrier of 21.7 kcal/mol (Figure 4a). From BrBpin, two transborylation steps between BrBpin and two HBpin molecules then take place giving BH₂Br, and B₂pin₃ as the by-product, which will act as a catalyst for the hydroboration of alkyne (Figure 4a). The catalytic cycle for the hydroboration of alkyne **2a** by BH₂Br is shown in Figure 4b and the reaction mechanism is found to be similar to the hydroboration with BH₂F. The reaction starts with a 1,2-*syn*-addition via **TS-14** between BH₂Br and alkyne, which is followed by a stepwise transborylation via **TS-15** and **TS-16** giving alkenylboron product **4a**. The hydroboration catalytic cycle by BH₂Br in Figure 4b has lower energy barriers than the one by BH₂F in Figure 3b, which is consistent with our experimental data that Trop.Br **1b** led to faster reaction than the same catalyst loading of Trop.BF₄ **1a** (see Figure 1a).^[26]

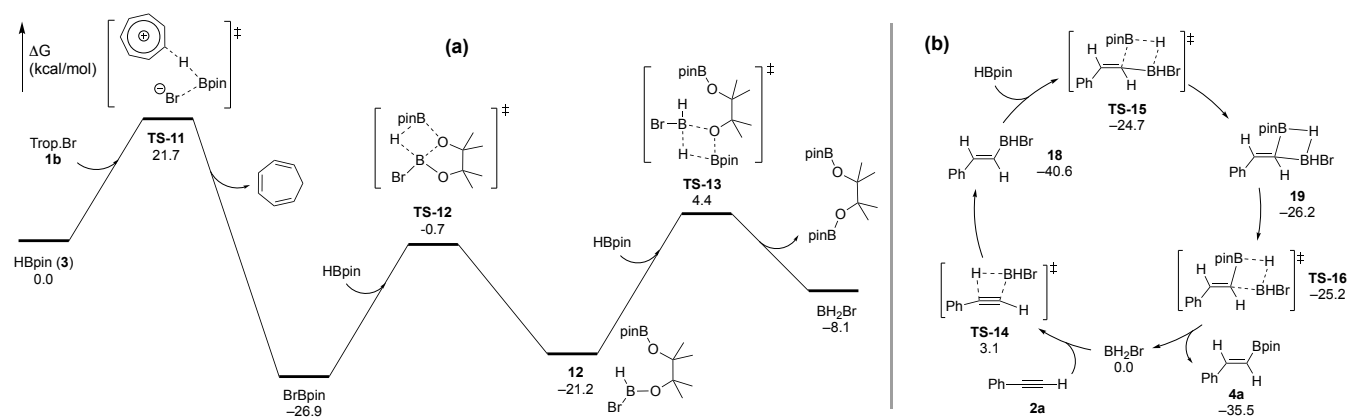
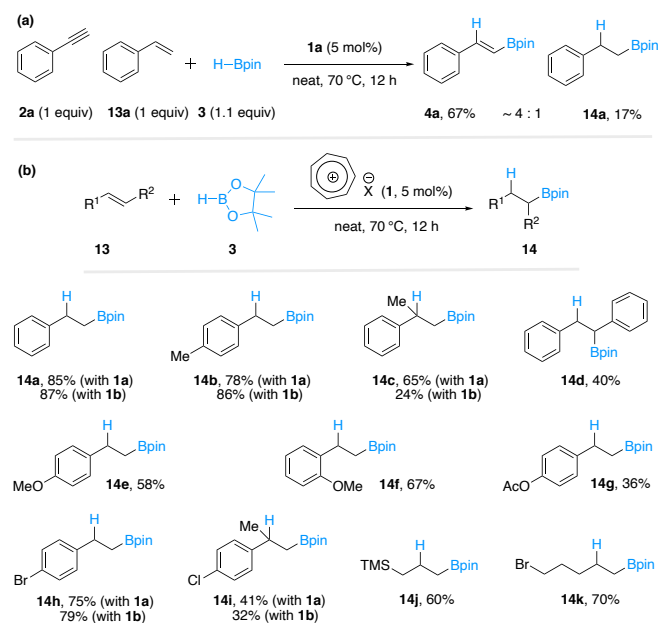


Figure 4. (a) Free energy profile (kcal/mol) for the formation of BH₂Br from HBpin and tropylium bromide and (b) catalytic cycle for the hydroboration of alkyne catalyzed by BH₂F (energy values are relative to BH₂Br).

Hydroboration of Alkenes and Epoxides

Thus, a combination of experiments and DFT calculations suggest that HBpin can react with tropylium salts, i.e. tropylium tetrafluoroborate or bromide, to generate *in situ* boron catalysts, i.e. BH₂F and BH₂Br. We were curious to see if their catalytic activity can be amenable to other types of hydroboration reactions. We chose to investigate this on alkenes and epoxides, as they are more challenging substrates than carbonyl or imines compounds.^[1b, 3a, 3c, 6] A competitive reaction between phenylacetylene **2a** and styrene **13a** with limiting amount of HBpin showed that the hydroboration of alkenes is less favorable than that of alkynes (Scheme 5a). However, with the same set of reaction conditions used in Scheme 2, we were able to hydroborylate a range of aromatic as well as aliphatic alkenes to the desired products with moderate to high yields. Tropylium salts **1a** and **1b** promoted the reaction with similar efficiencies on the substrates we selected for comparative studies (Scheme 5b). We have also calculated the reaction mechanism for the hydroboration of alkene catalyzed by BH₂F species. This mechanism of this reaction is indeed similar to the hydroboration of alkyne where the first step is the 1,2-*syn*-addition to alkene **13**, followed by a transborylation giving boron alkane product **14** (see Figure S8 in the computational ESI). Our calculations were also

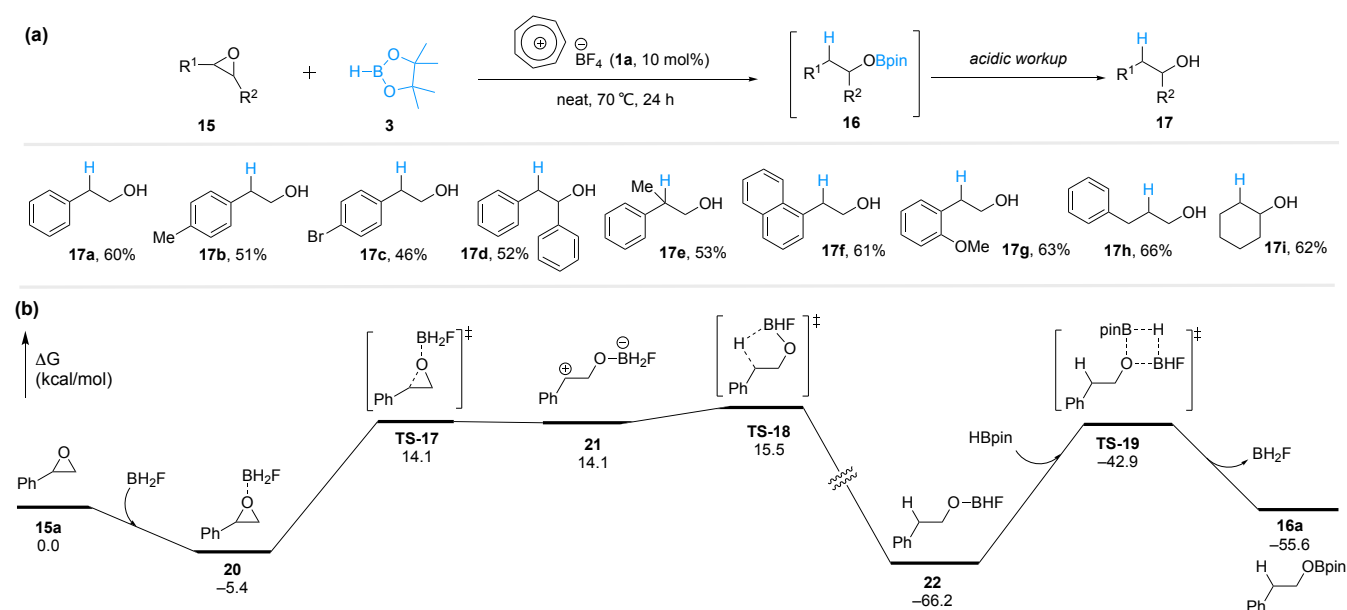
consistent with the fact that hydroboration of alkenes is more challenging than alkynes.



Scheme 5. (a) Competitive reactions between alkyne and alkene; (b) substrate scope of the hydroboration of alkenes.

Similar to alkenes, tropylium-catalyzed hydroboration of epoxides was slightly more challenging than the reaction with alkynes. It required a higher catalyst loading of tropylium catalyst and longer reaction time to achieve complete conversion (Scheme 6a). It should be noted that the boronic ester products **16** were hydrolyzed to alcohols **17** during reaction workup for better purification process.^[27] However, due to this extra step, yields of the isolated alcohol products are not reflective of the reaction efficiency. Indeed, ¹H and ¹¹B NMR analyses of the crude reaction mixtures before workup showed 90%-quantitative conversion of the epoxides to their corresponding boronic esters. We then focused on elucidating the reaction mechanism for the hydroboration of epoxides. The computed free energy profile is

shown in Scheme 6b. It turns out that BH₂F can also act as a catalyst for this reaction. The reaction starts with a ring-opening transition state **TS-17** giving zwitterionic species **21**, followed by a hydride transfer from boron moiety to the carbocationic centre via **TS-18** to form intermediate **22**. To proceed, transborylation (B–O/B–H σ -bond metathesis) between **20** and HBpin in a concerted manner via **TS-19** occurs to give product **16**. We could not locate any transient μ -H bridged species in the transborylation step. The activation barriers of the hydride transfer **TS-18** and the transborylation **TS-19** are calculated to be 20.9 and 23.3 kcal/mol relative to **18** and **20**, respectively.



Scheme 6. (a) Substrate scope of epoxide hydroboration; (b) free energy profile (kcal/mol) for the hydroboration of epoxide **15** catalyzed by BH₂F.

In conclusion, we report a novel hydroboration protocol using tropylium salts as efficient reaction promoters. This method is amenable to alkynes, alkenes and epoxides to produce a broad range of vinyl- and alkylboranes as well as alcohols. Apart from the synthetic value of this metal-free protocol, tropylium salts proved to be attractive and versatile probes to explore mechanistic details of hydroboration reaction. This work offers insights into the controversial topic of hidden or true catalysis for hydroboration reactions. Experimental studies and DFT calculations suggested that the reaction likely follows some interesting pathways, which are triggered by a hydride abstraction of pinacolborane with tropylium ion. This is followed by a series of *in situ* counterion-activated substituent exchanges to generate boron intermediates that promote the hydroboration reaction.

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