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Hydrogenation

An Alkene-Promoted Borane-Catalyzed Highly Stereoselective Hydrogenation of Alkynes to Give *Z*- and *E*-Alkenes

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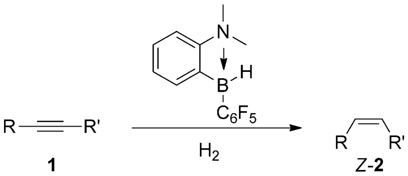
Abstract: The stereoselective hydrogenation of alkynes to alkenes is an extremely useful transformation in synthetic chemistry. Despite numerous reports for the synthesis of *Z*-alkenes, the hydrogenation of alkynes to give *E*-alkenes is still not well resolved. In particular, selective preparation of both *Z*- and *E*-alkenes by the same catalytic hydrogenation system using molecular H_2 has rarely been reported. In this paper, a novel strategy of using simple alkenes as promoters for the $HB(C_6F_5)_2$-catalyzed metal-free hydrogenation of alkynes was adopted. Significantly, both *Z*- and *E*-alkenes can be furnished by hydrogenation with molecular H_2 in high yields with excellent stereoselectivities. Further experimental and theoretical mechanistic studies suggest that interactions between H and F atoms of the alkene promoter, borane intermediate, and H_2 play an essential role in promoting the hydrogenolysis reaction.

Introduction

The stereoselective hydrogenation of alkynes to alkenes is an extremely useful tool in synthetic chemistry.[1] Various heterogeneous and homogeneous metal catalysts have been developed for this transformation, which provide efficient routes for the synthesis of *Z*-alkenes.[2] However, the preparation of *E*-alkenes by the hydrogenation of alkynes has been less developed.[3] For example, McQuillin and Muetterties both independently reported the *E*-selective hydrogenation of alkynes by using homogeneous rhodium catalysts.[3a,b] Similarly, Bargon and co-workers employed a ruthenium complex for this transformation.[3c] Very recently, Fürstner and co-workers described a practical and functional-group-tolerant *E*-selective hydrogenation of alkynes by using ruthenium catalysts.[3d] Milstein and co-workers reported a highly *E*-selective hydrogenation, catalyzed by an iron pincer complex, in which *E*-alkenes were produced by an in situ isomerization of *Z*-alkenes; but pure *Z*-alkenes could not be obtained in this catalytic system.[3e] It should be noted that accessing both *Z*- and *E*-alkenes by the same catalytic hydrogenation system with molecular H_2 is of great interest but it is a significant challenge.[4]

In contrast to transition-metal catalysis, the metal-free catalytic hydrogenation of alkynes has seldom been reported.[5] The chemistry of frustrated Lewis pairs (FLPs) provides a promising approach for metal-free hydrogenation;[6,7] recently, some important progress has been made for the hydrogenation of unactivated multiple C–C bonds.[5b,8–10] For example, Paradies and Grimme reported a low-temperature hydrogenation of alkenes by using phosphine and $B(C_6F_5)_3$.[9a,e] Later, Stephan and Grimme realized a similar transformation that combines ethers and $B(C_6F_5)_3$ as the hydrogenation catalysts.[9b] In addition, Wang and Li described a single Lewis acid $HB(C_6F_5)_2$-catalyzed hydrogenation of alkenes.[9c,11,12] Very recently, Repo and Pápai accomplished the first metal-free hydrogenation of unactivated alkynes **1** to give *Z*-alkenes **2** by using *ansa*-aminohydroborane, which involves a hydroboration process (Scheme 1).[5b] However, their attempts to use $HB(C_6F_5)_2$ in combination with bases as the catalyst proved to be unsuccessful.



Scheme 1. Metal-free hydrogenation of alkynes.

Our initial study indicated that the $HB(C_6F_5)_2$-catalyzed hydrogenation of alkyne **1 a** occurred with quite a low conversion (Scheme 2).[13] In 2007, Stephan described an interesting three-component reaction of $PtBu_3$, $B(C_6F_5)_3$, and an alkene, which attracted intensive mechanistic studies to investigate the alkene–borane interactions.[14] Subsequently, Li reported a theo-

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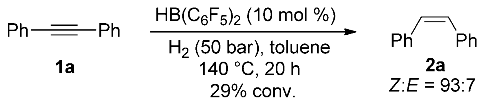
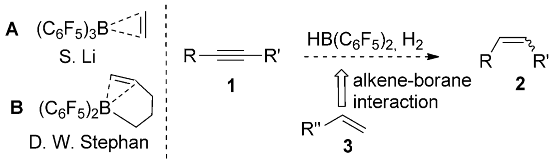


Scheme 2. Initial study on $HB(C_6F_5)_2$-catalyzed hydrogenation of alkyne **1a**.



Scheme 3. Strategy for the alkene-promoted hydrogenation of alkynes.

Table 1. Optimization of reaction conditions.[a]

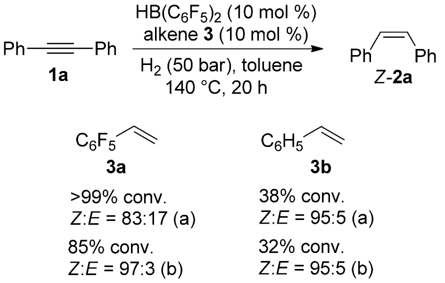
Entry	$HB(C_6F_5)_2$ [mol %]	**3a** [mol %]	Time [h]	Conv. [%][b]	Z:E[b]
1	10	10	20	>99	83:17
2	10	20	10	>99	76:24
3	10	20	6	>99	95:5
4[c]	10	20	20	61	98:2
5[d]	10	20	20	82	97:3
6	10	20	24	>99	25:75
7	12.5	20	24	>99	<1:99

[a] All reactions were carried out with alkyne **1a** (0.25 mmol), H_2 (50 bar), toluene (2.0 mL), at 140 °C. [b] Determined by ^1H NMR analysis of the crude reaction mixture. [c] 120 °C. [d] H_2 (20 bar).

retical study that suggested the formation of a weakly bound alkene–$B(C_6F_5)_3$ complex **A** (Scheme 3).[14c] Stephan's investigation into the interaction between the vinyl group and the boron atom of an alkene-tethered borane compound supported the formation of a van der Waals borane–alkene complex **B**.[14d] The reported borane–alkene interaction is expected to activate the alkene. Conversely, this interaction is also likely to activate the borane. Inspired by these results, and based on our previous work on the development of borane catalysts from alkenes,[15–17] we propose to take advantage of the activation that arises from this alkene–borane interaction to promote the $HB(C_6F_5)_2$-catalyzed hydrogenation of alkynes (Scheme 3). Herein we report our efforts on this subject.

Results and Discussion

Pentafluorostyrene (**3a**) was used in the hydrogenation of alkyne **1a** to test the feasibility of our proposal. To our pleasure, we found that alkene **3a** could indeed promote this hydrogenation reaction efficiently to give the desired alkene **2a** in a quantitative conversion and with good *Z*-selectivity (Scheme 4). In contrast, styrene (**3b**) had very little beneficial influence on this transformation. The charging sequence of the alkene **3**, $HB(C_6F_5)_2$, and alkyne **1a** was found to have a significant impact on the reactivity. Treating alkyne **1a** with $HB(C_6F_5)_2$ for 5 min before the addition of alkene **3a** or **3b** led to a higher conversion to the product (Scheme 4, Conditions a vs. b). In addition, a variety of commercially available alkenes were tested, but none of them were effective for promoting this reaction (see Supporting Information, Figure S1).



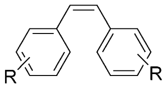
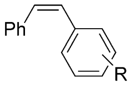
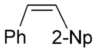
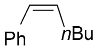
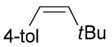
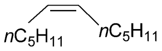
Scheme 4. Alkene-promoted hydrogenation of alkynes: a) treating alkyne **1a** with $HB(C_6F_5)_2$ for 5 min before addition of alkene **3**, b) treating alkene **3** with $HB(C_6F_5)_2$ for 5 min before addition of alkyne **1a**.

Next, the reaction conditions were optimized. It was found that the reactivity was improved when the amount of alkene **3a** was increased to 20 mol % (Table 1, entries 1 vs. 2). Restricting the reaction time to 6 h led to >99 % conversion of the alkyne **1a** to *Z*-alkene **2a** selectively (entry 3). However, a lower reaction temperature or H_2 pressure both resulted in reduced levels of conversions (entries 4 and 5). Significantly, *E*-alkene **2a** can also be obtained as a single isomer by using more $HB(C_6F_5)_2$ over a longer reaction time (entry 7). Thus, both *Z*- and *E*-alkenes can be furnished through a simple adjustment of the reaction conditions.

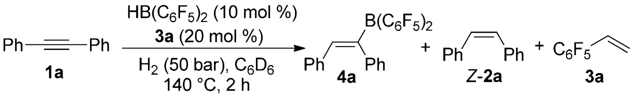
We next examined the substrate scope for the synthesis of the *Z*-alkene. As shown in Table 2, a variety of alkynes **1a–l**, including diaryl, dialkyl, and aryl–alkyl alkynes, were efficiently hydrogenated to furnish the desired *Z*-alkenes **2a–l** in 86–99 % yields with high levels of stereoselectivity (Table 2, entries 1–12). It should be noted that the reaction time for the hydrogenation of alkynes must be strictly controlled to ensure the acquirement of high *Z*-selectivity. The synthesis of *E*-alkenes by the metal-free hydrogenation was also studied. As shown in Table 3, the hydrogenation of alkynes **1a–d**,**f–k**,**m–o** by using $HB(C_6F_5)_2$ (12.5–20 mol %) and alkene **3a** (20 mol %) went smoothly to give the corresponding *E*-alkenes **2** in high yields and excellent levels of stereoselectivity (Table 3, entries 1–13). A small amount of the alkanes that were generated by overhydrogenation were observed in the reactions of alkyne substrates **1c** and **1k** (entries 3 and 13). For alkyne substrates that contained *n*-butyl substituents, substantial C=C bond migration isomers were also formed (entries 11 and 12).

The interesting results that were obtained for the metal-free hydrogenation of alkynes encouraged us to investigate the mechanism of the reaction by both practical experiments and theoretical calculations. Two initial experiments were carried out, as shown in Scheme 5, in which the hydrogenation of alkyne **1a** was terminated after 2 h. Even though different charging sequences were employed, the alkenyl borane **4a** was formed in both reactions, which suggests that this species is an intermediate in the hydrogenation reaction and its hydrogenolysis is likely to be the rate-determining step in the catalytic process. Notably, higher yields of borane **4a** and alkene

Table 2. Hydrogenation of alkynes to *Z*-alkenes.[a]

Entry	Product (**2**)	Time [h]	Conv.[b] (Yield)[c] [%]	*Z*:*E*[b]
				
1	*Z*-**2a**: R=H	6	>99 (96)	95:5
2	*Z*-**2b**: R=4-Me	5.2	97 (93)	97:3
3	*Z*-**2c**: R=4-Cl	10	95 (87)	96:4
4	*Z*-**2d**: R=3,5-Me$_2$	5.5	95 (94)	96:4
5[d]	*Z*-**2e**: R=2-Me	24	92 (86)	97.3
				
6	*Z*-**2f**: R=4-Me	5.5	93 (91)	98:2
7	*Z*-**2g**: R=4-Ph	6	>99 (98)	95:5
8	*Z*-**2h**: R=3,5-Me$_2$	5.5	92 (88)	97:3
				
9	*Z*-**2i**	7	97 (93)	94:6
				
10	*Z*-**2j**	6.5	93 (99)	97:3
				
11	*Z*-**2k**	24	>99 (86)	92:8
				
12	*Z*-**2l**	10	91 (93)	96:4

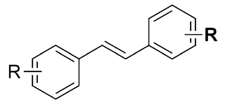
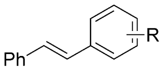
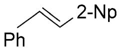
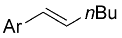
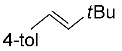
[a] Conditions: alkyne **1** (0.25 mmol), HB(C$_6$F$_5$)$_2$ (0.025 mmol), alkene **3a** (0.05 mmol), H$_2$ (50 bar), toluene (2.0 mL), at 140 °C. [b] Determined by ^{1}H NMR or GC-MS analysis of the crude reaction mixture. [c] Yield of isolated product. [d] HB(C$_6$F$_5$)$_2$ (0.05 mmol) was used.



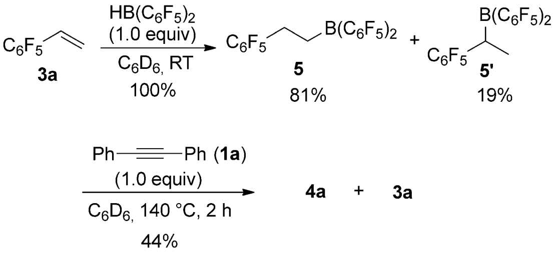
	4a	***Z*-2a**	**3a**
3a + HB(C$_6$F$_5$)$_2$ before addition of **1a**:	3%	16%	11%
1a + HB(C$_6$F$_5$)$_2$ before addition of **3a**:	7%	40%	18%

Scheme 5. Controlled experiments to investigate the reaction outcome with different charging sequences.

Table 3. Hydrogenation of alkynes to *E*-alkenes.[a]

Entry	HB(C$_6$F$_5$)$_2$ [mol %]	Product (**2**)	Yield [%][b]	*Z*:*E*[c]
				
1	12.5	*E*-**2a**: R=H	97	<1:99
2	12.5	*E*-**2b**: R=4-Me	98	<1:99
3	20.0	*E*-**2c**: R=4-Cl	98[d]	<1:99
4	12.5	*E*-**2d**: R=3,5-Me$_2$	99	<1:99
5	20.0	*E*-**2m**: R=4-MeO	95	<1:99
				
6	12.5	*E*-**2f**: R=4-Me	99	1:99
7	15.0	*E*-**2g**: R=4-Ph	99	<1:99
8	12.5	*E*-**2h**: R=3,5-Me$_2$	99	3:97
9	20.0	*E*-**2n**: R=4-MeO	91	<1:99
				
10	15.0	*E*-**2i**	98	<1:99
				
11	12.5	*E*-**2j**: Ar=Ph	89[e]	5:95
12	15.0	*E*-**2o**: Ar=2-Np	96[e]	4:96
				
13	17.5	*E*-**2k**	96[d]	<1:99

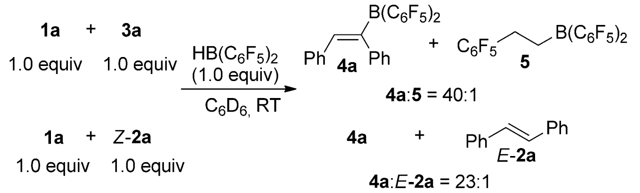
[a] Conditions: alkyne **1** (0.25 mmol), alkene **3a** (0.05 mmol), H$_2$ (50 bar), toluene (2.0 mL), at 140 °C for 24 h. [b] Yield of isolated product. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Including 5–8% alkane. [e] Including 24–30% C=C bond migration isomers.



Scheme 6. Experiments on hydroboration and retrohydroboration from alkene **3a**.

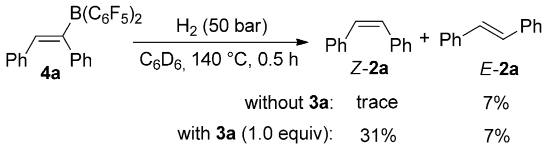
3a were observed for the reaction with the more productive charging sequence. However, boranes derived from alkene **3a** and HB(C$_6$F$_5$)$_2$ were not formed in these reactions (Scheme 5). In fact, boranes **5** and **5′** can be formed very quickly by the hydroboration of alkene **3a** with HB(C$_6$F$_5$)$_2$ at room temperature. These boranes can be further converted into borane **4a** and alkene **3a** by a retrohydroboration process at high temperature (Scheme 6).[17] However, significant amounts of unidentified side products were also observed by ^{1}H NMR analysis, which most likely resulted from the decomposition of boranes **5** and **5′**. Therefore, the relatively low reactivity observed when the alkene **3a** and HB(C$_6$F$_5$)$_2$ were combined prior to the addition of the alkyne is attributed to an additional retrohydroboration process followed by decomposition.

Because various unsaturated compounds, including the alkyne substrate, the alkene product, and alkene **3a**, were all involved in the catalytic reaction, competition experiments to compare their rates of hydroboration with HB(C$_6$F$_5$)$_2$ were carried out. As shown in Scheme 7, the hydroboration of alkyne **1a**, to furnish alkenyl borane **4a**, was much faster than that of alkenes **3a** and *Z*-**2a**. This demonstrates that the hydroboration of alkynes is the predominant process, unless alkynes are exhausted, and it further supports the proposal that **4a** is an intermediate in the catalytic reaction.

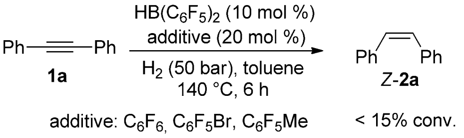


Scheme 7. Competition experiments to determine the relative rates of the hydroboration of alkyne **1 a** and alkenes **3 a** and *Z*-**2 a**.

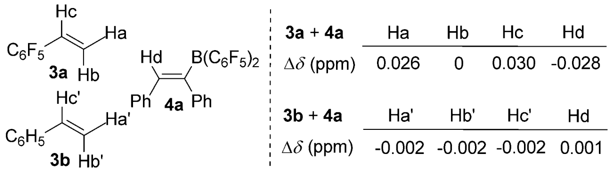
A controlled experiment was next conducted to understand the effect that alkene **3 a** has on the hydrogenolysis of borane **4 a**. Indeed, this process was shown to be promoted by alkene **3 a**, whereas, in the absence of **3 a**, only a trace amount of the desired product *Z*-**2 a** was observed (Scheme 8). Furthermore, various additives that contained the pentafluorophenyl moiety but which lacked the vinyl group were subjected to the hydrogenation reaction (Scheme 9). However, none of them proved to be effective in promoting this reaction. These results and the different activation abilities of alkenes **3 a** and **3 b** suggest that both pentafluorophenyl and vinyl groups are essential for the high productivity of the reaction.



Scheme 8. Hydrogenolysis of borane **4 a**.



Scheme 9. Hydrogenation of alkyne **1 a** with different additives.



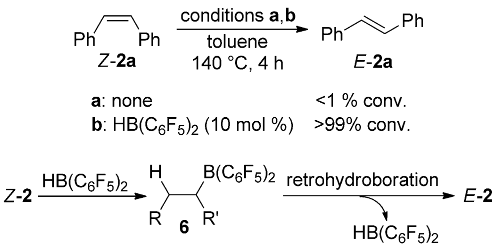
3a + 4a	Ha	Hb	Hc	Hd
Δδ (ppm)	0.026	0	0.030	-0.028

3b + 4a	Ha'	Hb'	Hc'	Hd
Δδ (ppm)	-0.002	-0.002	-0.002	0.001

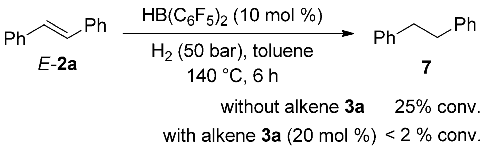
Figure 1. ^1H NMR spectroscopy (500 MHz) study at −80 °C.

The interaction between borane **4 a** and alkene **3 a** was further investigated by ^1H NMR analysis. When a 1:1 mixture of borane **4 a** and alkene **3 a** in [D$_8$]toluene was cooled to −80 °C, the resonances for Ha and Hc in alkene **3 a** were shifted downfield slightly and the resonance for Hd in borane **4 a** was shifted upfield, but the signal of Hb was unchanged (Figure 1). In comparison, a 1:1 mixture of borane **4 a** and styrene (**3 b**), under the same conditions, did not exhibit any changes in the ^1H NMR spectra. These observations suggest that an encounter complex of alkene **3 a** and borane **4 a** is most likely formed through the interactions of H and F atoms,[18] which are distinct from the interactions of the C=C bond and the boron atom proposed by Li and Stephan.[14c,d] A possible explanation for this difference is that the alkene **3 a** is electron-deficient, relative to ethylene and the borane tethered olefin, but it possesses more acidic protons. Unfortunately, analysis by $^1H\{^{19}F\}$ HOESY did not provide any useful information with which to verify the proposed H–F interactions.

The reason for the production of *E*-alkenes was also investigated. As shown in Scheme 10, *Z*-alkene **2 a** is stable at 140 °C; but isomerization of *Z*-alkene **2 a** to give *E*-alkene **2 a** was observed at this temperature in the presence of 10 mol % of HB(C_6F_5)$_2$. The isomerization is proposed to proceed through the hydroboration of alkene *Z*-**2** with HB(C_6F_5)$_2$ to form borane **6**, followed by a retrohydroboration to generate the more stable alkene *E*-**2**.[17] Therefore, it can be deduced that *Z*-alkenes are generated directly by hydrogenation and *E*-alkenes are formed by a subsequent isomerization of the *Z*-alkenes. Owing to the high reactivity of alkynes with HB(C_6F_5)$_2$, the isomerization process is restricted when unreacted alkyne is still present in the reaction mixture, which ensures that the *Z*-alkene is the predominant product. Only after exhaustion of the alkyne substrate can *E*-alkenes be obtained through the isomerization of *Z*-alkenes. Moreover, alkene **3 a** was found to effectively inhibit the over-hydrogenation of alkene *E*-**2 a**, which would produce alkane **7** (Scheme 11). A possible explanation is that the hydrogenation of alkenes to alkanes is a relatively slow transformation, and the competition reaction of alkene **3 a** with HB(C_6F_5)$_2$ is likely to inhibit the reaction of alkene **2 a** with HB(C_6F_5)$_2$ so as to restrict the production of alkane **7**.



Scheme 10. Isomerization of *Z*-alkenes to *E*-alkenes.



Scheme 11. Hydrogenation of *E*-alkene **2 a** to alkane **7**.

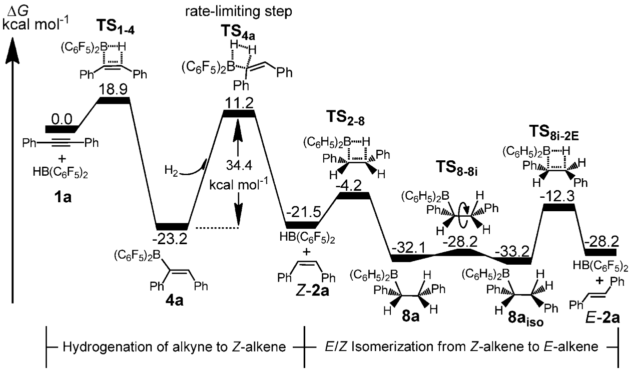


Figure 2. DFT-calculated reaction profile for the hydrogenation of alkyne **1 a** to give *Z*-alkene *Z*-**2 a** without the assistance of **3 a**, and subsequent isomerisation to *E*-alkene *E*-**2 a**. Relative Gibbs free energy (Δ*G*) are reported in kcal mol^{-1}, and all geometries were optimized without DFT dispersion correction.

DFT calculations were then conducted to obtain a mechanistic understanding of the catalytic pathway at the atomic level. Figure 2 depicts the whole reaction profile for the catalytic hydrogenation of alkyne **1 a** based on DFT calculations, without consideration of the effect of alkene **3 a**. The catalytic cycle is initiated by the alkyne hydroboration process to give **4 a**, which needs to overcome an activation energy of 18.9 kcal mol^{-1}. Following this, the hydrogenolysis of **4 a** to give *Z*-**2 a** occurs, which is the rate-limiting step in the catalytic cycle with a substantial reaction barrier of 34.4 kcal mol^{-1}. The formation of *Z*-**2 a** from **1 a** encompasses the catalytic cycle, and $HB(C_6F_5)_2$ is regenerated for hydroboration of another molecule of alkyne **1 a** in the next catalytic cycle. The energy profile from *Z*-**2 a** to *E*-**2 a** in Figure 2 describes the respective isomerization process, which is promoted by $HB(C_6F_5)_2$. It involves the following three steps: a) hydroboration of *Z*-alkene **2 a** to form alkyl borane **8 a**, b) rotation around the $(C_6F_5)_2B(H)(Ph)C{-}CH_2Ph$ single bond to form another conformer **8 a**$_{\mathbf{iso}}$, and c) retrohydroboration of **8 a**$_{\mathbf{iso}}$ to give alkene *E*-**2 a**. The rate-limiting step in this isomerization process is the final retrohydroboration, which has an energy barrier of 20.9 kcal mol^{-1}. This barrier, which is higher than that for alkyne hydroboration (18.9 kcal mol^{-1}), further supports the experimental observation that when the alkyne substrate is present in the reaction mixture, the *E*/*Z* isomerization process is not a kinetically favored process.

To clarify the effect that alkene **3 a** has on the rate-limiting step of the catalytic cycle, which involves the formation of *Z*-**2 a** from **4 a**, at the atomic level, we performed further DFT calculations. By considering the non-bonding nature of the interaction (π–π stacking) between **3 a** and **4 a**, DFT dispersion correction (DFT-D3) method was employed in the corresponding geometry optimizations. In the absence of **3 a**, the transition state (TS) for the hydrogenolysis of **4 a** to give *Z*-**2 a** (Figure 3 a, **TS**$_{\mathbf{4a}}$) was calculated to have an activation energy of 35.1 kcal mol^{-1}. Upon addition of **3 a** into the system, the lowest energy TS for the hydrogenolysis of **4 a** was calculated at 33.8 kcal mol^{-1} (Figure 3 b, **TS**$_{\mathbf{4a+3a}}$). Thus, alkene **3 a** exerts a TS stabilization of 1.3 kcal mol^{-1} in the hydrogenolysis process of **4 a**. These calculations support the experimental results that are reported in Scheme 8, which indicate that alkene **3 a** can promote the hydrogenolysis process. It should be noted that, according to transition state theory, a reduction of 1.3 kcal mol^{-1} in the energy barrier of the rate-limiting step is sufficient to speed up the reaction by an order of magnitude.

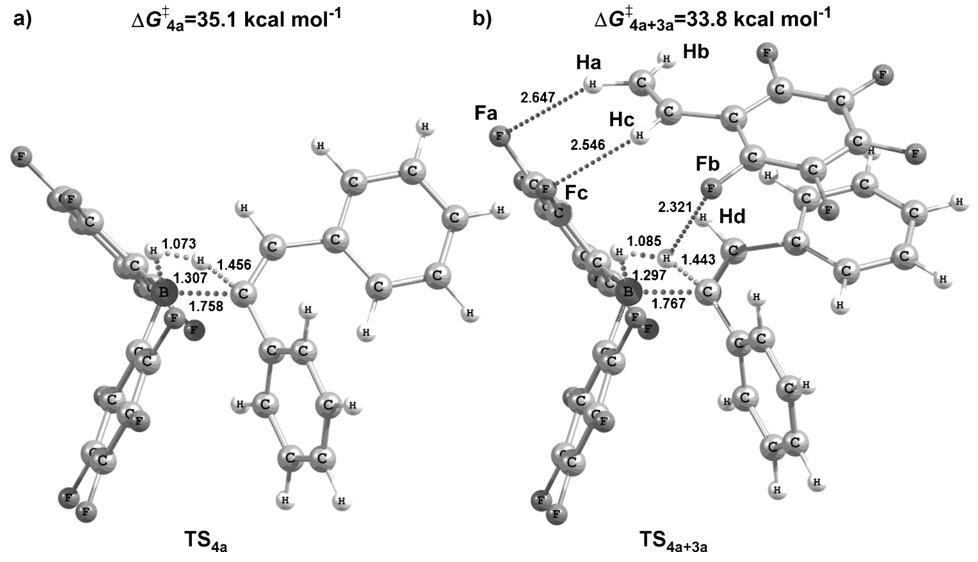
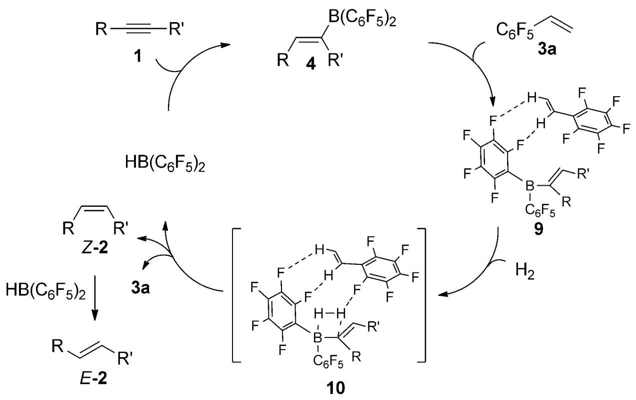


Figure 3. DFT-optimized transition state structures (bond lengths reported in Å) for the hydrogenolysis of **4 a**: a) without **3 a** and b) with **3 a**, both optimized with the DFT dispersion correction method.

By inspection of the structure **TS**$_{\mathbf{4a+3a}}$ in Figure 3 b, we could identify three hydrogen bonding interactions. Two of them are between protons Ha/Hc of **3 a** and fluorine atoms Fa/Fc of the pentafluorophenyl group in **4 a**. Interestingly, these results are consistent with the NMR spectroscopic data reported in Figure 1, which showed the downfield shifts of the resonances that corresponded to Ha and Hc in **3 a** and the resonance for Hb was not affected. These two hydrogen bonding interactions facilitate the hydrogenolysis of **4 a** by anchoring alkene **3 a** in an appropriate orientation relative to **4 a**. The other hydrogen bond in **TS**$_{\mathbf{4a+3a}}$ is between a proton of H_2, which is being transferred to the vinyl group of **4 a**, and the fluorine atom Fb of **3 a**. This interaction can assist the H–H bond cleavage of H_2 in the hydrogenolysis process, which helps to stabilize **TS**$_{\mathbf{4a+3a}}$ relative to **TS**$_{\mathbf{4a}}$ and thus accelerates the reaction. These three interactions indicate that both pentafluorophenyl and vinyl groups are necessary in alkene **3 a** to make it effective in promoting the hydrogenolysis reaction, which has been further corroborated in the experiments above (Schemes 4 and 9. Another significant structural feature is that the pentafluorophenyl group of **3a** lies closely above Hd. This close proximity may lead to shielding of Hd by the pentafluorophenyl ring, which could explain why the NMR resonance of proton Hd in alkene **4a** was shifted upfield. To further explore the interaction of **3a** with **4a**, we also calculated the Gibbs free binding energy of **3a** to **4a** without H_2 in system. The slightly exergonic binding energy of 0.5 $kcal\,mol^{-1}$ was calculated at $-80\,^{\circ}C$. As a result, the binding of **3a** to **4a** should be disturbed upon an increase in temperature due to the entropy effect and, consequently, this interaction would become undetectable, which is consistent with the NMR experimental observation. In addition, the π–π stacking between **4a** and **3a** is apparent from the geometry of $\mathbf{TS_{4a+3a}}$, as well as in the complex of **3a** and **4a**.

According to the mechanistic study, a plausible catalytic cycle is shown in Scheme 12. The initial hydroboration of alkyne **1** with $HB(C_6F_5)_2$ generates the intermediate borane **4**. Then, an encounter complex **9** of borane **4** and alkene **3a** is formed through H–F interactions. This is followed by hydrogenolysis via transition state **10**, which produces alkene *Z*-**2** and regenerates both the catalyst and alkene **3a**. Finally, after the exhaustion of the alkyne **1**, a $HB(C_6F_5)_2$-promoted isomerization of the alkene *Z*-**2** gives *E*-**2**.



Scheme 12. A plausible catalytic pathway.

All experimental details can be found in the Supporting Information.

Conclusion

An alkene-promoted borane-catalyzed hydrogenation of alkynes has been realized to give both *Z*- and *E*-alkenes in high yields with excellent stereoselectivities. This reaction belongs to the very rare class of catalytic hydrogenation systems that use molecular H_2 to access both alkene isomers selectively just by a simple adjustment of the reaction conditions. *Z*-Alkenes were produced directly by metal-free hydrogenation, and *E*-alkenes were proposed to be generated through an isomerization of the *Z*-alkenes, which was facilitated by $HB(C_6F_5)_2$ once the alkyne substrate was exhausted. Mechanistic studies by both practical experiments and theoretical calculations indicated that the alkenyl borane, which is formed by the hydroboration of the alkyne substrate with $HB(C_6F_5)_2$, is a key intermediate, and its subsequent hydrogenolysis is likely to be the rate-determining step in the catalytic process. Significantly, the newly identified H–F interactions between alkene **3a**, the alkenyl borane intermediate, and H_2, are suggested to play a key role in accelerating this hydrogenation reaction, which might have other interesting applications in FLP chemistry.

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Keywords: alkene · alkyne · hydrogenation · metal-free catalysis · stereoselectivity

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FULL PAPER

Hydrogenation

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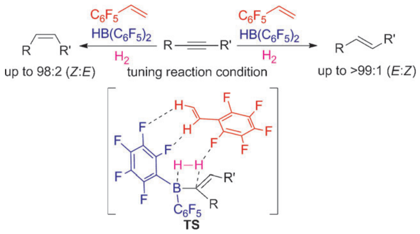
An Alkene-Promoted Borane-Catalyzed Highly Stereoselective Hydrogenation of Alkynes to Give *Z*- and *E*-Alkenes



With a little help from an alkene! A $HB(C_6F_5)_2$-catalyzed metal-free hydrogenation of alkynes, promoted by an alkene through H–F interactions, was successfully achieved. Z- and *E*-alkenes can be accessed respectively in high yields with excellent stereoselectivities (see scheme).