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$ZnBr_2$-Catalyzed Dehydrogenative Borylation of Terminal Alkynes

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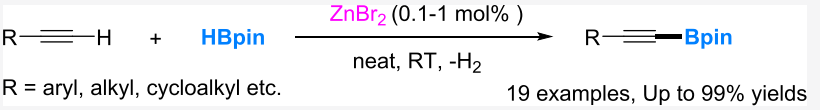

ABSTRACT: The simple, commercially available $ZnBr_2$ has been successfully employed as a highly efficient and chemoselective catalyst for the dehydrogenative borylation of terminal alkynes with HBpin under mild conditions. It shows a good tolerance toward various functional groups such as aryl, alkyl, heteroaryl, etc. The plausible reaction mechanism has been investigated based on the corresponding stoichiometric experiments and DFT calculations.

INTRODUCTION

The development of convenient, practical, and economic synthetic approaches has always been one of the priorities of modern organic chemistry. Because much attention is paid to the environmental and economic aspects, a number of significant and efficient synthetic methods were improved based on some conventional synthetic transformations.[1,2] This is the reason why more and more synthetic procedures are developed by employing common and earth-abundant metals.[3−6] These synthetic strategies provide new perspectives that attract an increasing number of organic chemists.

Organoboron compounds play vital roles in the construction of many functional molecular skeletons because of the ubiquitous applications in several carbon−carbon and carbon−heteroatom coupling reactions.[7−18] In the traditional methods, these organoboron compounds were synthesized by employing stoichiometric amounts of Grignard or organolithium reagents, which are inconvenient to handle during the reaction. In addition, many functional groups could not be tolerated under these reaction conditions. For those reasons, it is essential to develop novel synthetic strategies to obtain the organoboron compounds. Among these reported methods for the preparation of organoboron compounds, hydroboration reactions employing HBpin as the boron source are one of the most common methods. Hydroboration of internal or terminal alkynes is already one of the well-established strategies for the construction of alkenyl boron compounds.[19−25] Meanwhile, dehydrogenative borylation of terminal alkynes is also an attractive coupling route that furnishes a variety of alkynyl boron compounds.[26]

Compared to the widely studied alkyne hydroboration, however, there are few examples of catalytic dehydrogenative borylation of terminal alkynes (Scheme 1). In 2013, Ozerov et al. first reported the dehydrogenative borylation of terminal alkynes catalyzed by an ancillary SiNN pincer iridium complex.[27] Four years later, a copper-catalyzed dehydrogenative borylation of terminal alkynes with HBpin was developed by Bertrand and co-authors. Cyclic (alkyl)(amino)carbenes (CAACs) or *N*-heterocyclic carbenes (NHCs) were essential for this C(sp)−B coupling.[28] Recently, Ingleson et al. synthesized a low-coordinate NHC−zinc hydride complex, which works as an effective catalyst for the preparation of alkynyl boron compounds employing terminal alkynes and HBpin at 60 °C.[29] In 2018, a dehydrogenative borylation of terminal alkynes was realized by the group of Darcel in the presence of iron salt ($Fe(OTf)_2$) and 1,4-diazabicyclo[2.2.2]-octane (DABCO) at high temperature (100 °C) for three days.[30] However, some hydroboration side products (alkenylboranes) were also generated irrepressibly during the reaction. Additionally, the C(sp)−H borylation of terminal alkynes catalyzed by silver, zinc, and magnesium salts and the corresponding bases using other borylating agents such as ^{i}PrOBpin, 1,8-naphthalenediaminato borane (HBdan), and diisopropylamine borane (DIPAB) have been reported as well.[31−33] However, in the above-mentioned examples, multiple steps are required to prepare the corresponding bulky pincer or NHC metal catalysts or additional bases as additives. In some cases, the competing hydroboration or hydrogenation of the triple bond, which affords alkenyl boronic esters or olefinic products, was also observed during the dehydrogenative borylation of terminal alkynes. Hence, it is highly desirable to develop a practical, simple, and mild strategy to obtain these remarkable alkynyl boron products. Driven by our previous work on earth-abundant metal-catalyzed hydroboration reactions,[12,13,25] we herein successfully developed a simple zinc-catalyzed dehydrogenative borylation of terminal alkynes only using 0.1−1 mol % amount of inexpensive

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Scheme 1. Metal-Catalyzed Hydroboration and Dehydrogenative Borylation of Alkynes

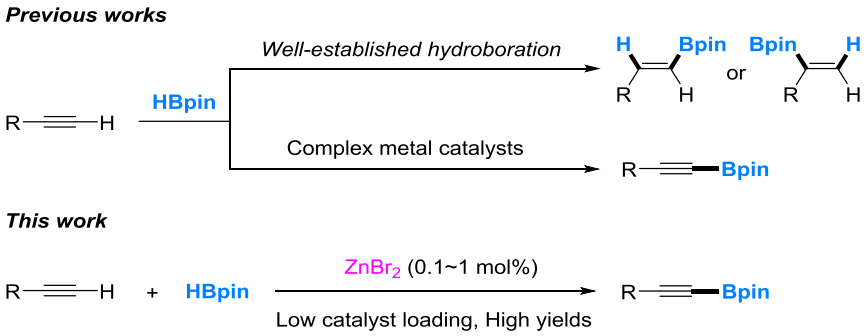
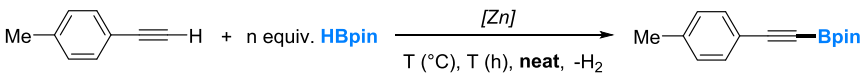


Table 1. Optimization of the Dehydrogenative Borylation of 4-Ethynyltoluene



1b 2 3b

entry	*n*	catalyst (mol %)	time (h)	temp (°C)	conversion (%)[a]
1	1.5	none	6	rt	0
2	1.5	none	6	90	10
3	1.5	ZnI_2 (5)	6	90	99
4	1.5	ZnI_2 (5)	6	rt	99
5	1.5	ZnI_2 (1)	6	rt	99
6	1.1	ZnI_2 (1)	6	rt	99
7	1.1	$ZnBr_2$ (1)	3	rt	99
8	1.1	$ZnCl_2$ (1)	20	rt	94
9	1.1	$ZnBr_2$ (0.1)	3	rt	28
10	1.1	$ZnBr_2$ (0.1)	3	60	66
11	1.5	$ZnBr_2$ (0.1)	3	60	86
12	1.5	$ZnBr_2$ (0.1)	6	60	99

[a]Conversion was determined by ^{1}H NMR spectroscopy.

commercially available zinc halide without extra chemicals under mild conditions to efficiently afford a large panel of alkynyl boron compounds.

RESULTS AND DISCUSSION

We embarked on our investigation by employing 4-ethynyltoluene as a model substrate and HBpin as a reductant under neat conditions at room temperature. Initially, the reaction of 4-ethynyltoluene with 1.5 equiv of HBpin was performed in the absence of any catalyst; no desired hydroboration product was observed at room temperature after 6 h and only the starting material was retained (Table 1, entry 1). The dehydrogenative borylation product was obtained in 10% yield after 6h when the reaction temperature was increased to 90 °C, which was different from the desired hydroboration product (Table 1, entry 2). To our delight, when 5 mol % of readily accessible ZnI_2 was added into the above reaction mixture under the same reaction conditions, the dehydrogenative borylated product was produced selectively in 99% yield concomitant with vigorous H_2 gas evolution (Table 1, entry 3). We further optimized the alkyne dehydrogenative borylation reaction conditions. When the temperature was decreased from 90 °C to room temperature, 99% conversion was observed as well (Table 1, entry 4). Further lowering the catalyst loading of ZnI_2 from 5 to 1 mol % resulted in high yield (Table 1, entry 5). When HBpin was decreased from 1.5 to 1.1 equivalent, the reaction proceeded equally well (Table 1, entry 6). Subsequently, the catalytic performance of other different zinc salts such as $ZnBr_2$ and $ZnCl_2$ was evaluated, which also can be used as efficient catalysts in the dehydrogenative borylation of 4-ethynyltoluene. $ZnBr_2$ shows better catalytic activity than ZnI_2 and $ZnCl_2$, requiring a shorter reaction time (3 h vs 6 h, 20 h) (Table 1, entries 7 and 8). However, similar iron salts such as $FeCl_2$, $FeBr_2$, etc showed less reactivity and lower selectivity.[30] To our surprise, when 0.1 mol % of $ZnBr_2$ and 1.5 equiv of HBpin were employed, conversion of styrene was also completed after 6 h at 60 °C (Table 1, entries 9−12).

With the optimized reaction conditions in hand that there are no ancillary ligands and no base additives, we next explored the substrate scope of the alkyne dehydrogenative borylation. A broad range of aryl- and alkyl-substituted terminal alkynes underwent successful dehydrogenative borylation (Table 2). The aromatic ring with electron-donating and electron-withdrawing groups such as −Me, −OMe, −Cl, −F, $-CF_3$, $-NO_2$, etc were successfully borylated with HBpin to yield the corresponding borylated products in excellent conversion (Table 2, entries 1−8). It is worth noting that halogen-substituted alkyne derivatives only need 5 h at room temperature to deliver solid products (**3e**−**3g**) with complete conversion (Table 2, entries 5−7); however, 4-nitrophenylacetylene requires a relatively longer reaction time to achieve a high yield (**3h**, Table 2, entry 8). This is different from the NHC−Zn catalyst, in which the reduction of the nitro group was preferred over alkyne C−H borylation.[29] Sterically bulky mesityl-substituted alkyne also works very well in our system

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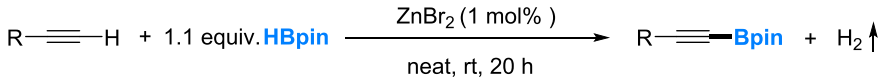
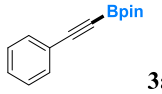
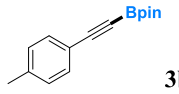
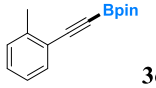
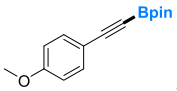
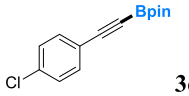
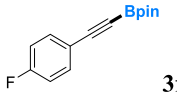
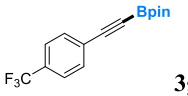
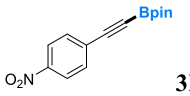
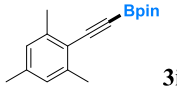
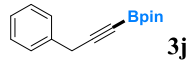
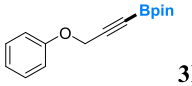
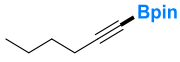
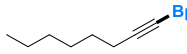
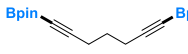
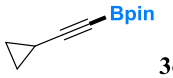
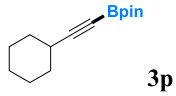
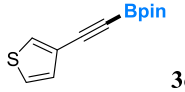
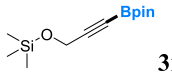
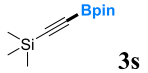
Table 2. $ZnBr_2$-Catalyzed Dehydrogenative Borylation of Alkynes



1 2 3

Entry	Product	Conversion (%)[a]	Entry	Product	Conversion (%)[a]
1	 **3a**	99[c](97[c])	2	 **3b**	99[c](86[l])
3	 **3c**	99	4	 **3d**	91(99)
5	 **3e**	99[bc]	6	 **3f**	99[bc](85[l])
7	 **3g**	99[bc]	8	 **3h**	90[de](95[df])
9	 **3i**	90(93)	10	 **3j**	93(97)
11	 **3k**	97(99)	12	 **3l**	99[g](89[l])
13	 **3m**	99[eg](93[fg])	14	 **3n**	99[ch](83[l])
15	 **3o**	99(99)	16	 **3p**	99[ec](96[c])
17	 **3q**	99[bc](86[l])	18	 **3r**	96(95)
19	 **3s**	98[cgi]			

[a]Conversion was determined by ^{1}H NMR spectroscopy, unless otherwise specified; the reaction conditions are rt, 20 h; 60 °C, 8 h in parentheses. [b]rt, 5 h. [c]Solid product. [d]With a small amount of C_6D_6. [e]rt, 36 h. [f]60 °C, 20 h. [g]2 mol % of $ZnBr_2$. [h]The ratio of alkyne to HBpin is 1:2.1. [i]60 °C, 24 h, alkyne-to-HBpin ratio is 1:1.5. [l]Isolated yield.

(**3i**, Table 2, entry 9). The alkyl-substituted substrates bearing benzyl, phenoxy, butyl, and hexyl motif could also afford the dehydroborated products, and the steric parameters of the alkyl substituent had little effect on the catalyst activity (**3j**−**3m**, Table 2, entries 10−13). The double dehydroboration also took place when 1,6-heptadiyne was used as a substrate with 2.1 equiv of HBpin to give the diborylated product **3n** in 99% yield as a solid (Table 2, entry 14). This is quite different from the iron catalyst system in which only the corresponding monoborylated derivative was obtained in 72% yield, even in the presence of 2 equiv of HBpin, no trace of diborylated compound was detected.[30] Remarkably, alkynes bearing cyclic side chains such as cyclopropylacetylene and cyclohexylacetylene could also be easily transformed to the corresponding dehydroborated products, despite their ring strain (**3o**−**3p**, Table 2, entries 15 and 16). The dehydrogenative borylation of heteroaryl 3-ethynylthiophene resulted in the corresponding solid boronic ester **3q** at room temperature in a very high yield (Table 2, entry 17). To our delight, this methodology is readily applicable to silyl-substituted alkynes. Both trimethylsilylacetylene and 3-trimethylsiloxy-1-propyne proceeded smoothly in nearly quantitative yields of the alkynylboronic esters (**3r**−**3s**, Table 2, entries 18 and 19). To demonstrate the practical utility of this method, a gram-scale reaction of **1b** (10 mmol) and HBpin catalyzed by 1 mol % of $ZnBr_2$ at room temperature was carried out to afford an alkynylboronic ester **3b** in 86% isolated yield (2.08 g) after 20 h (Scheme 2). To prove the formation of hydrogen gas, the corresponding trapping experiment was performed (Scheme 3), and 1,2-

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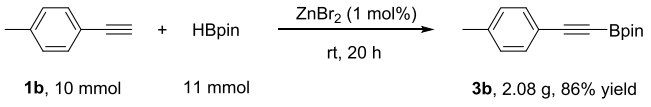
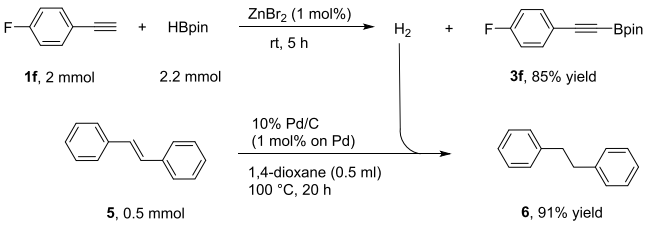
Scheme 2. Scale-up Reaction of 4-Ethynyltoluene with HBpin Catalyzed by $ZnBr_2$



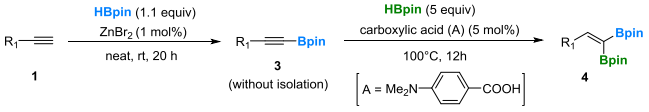
diphenylethane (**6**) was obtained in 91% yield to confirm the generation of H_2.

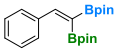
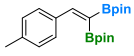
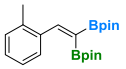
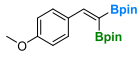
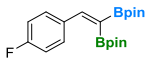
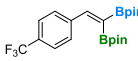
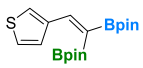
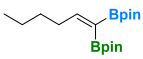
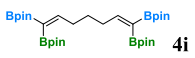
Scheme 3. Trapping Experiment of Hydrogen Gas



Alkenyldiboronates are versatile in organic synthesis because they offer two distinct boron substituents, which could be further converted into various useful functional groups (e.g., anticancer agent tamoxifen, Suzuki-Miyaura crosscoupling, etc).[34] They are usually prepared from the diboration of terminal or internal alkynes and borylated reagents (B_2Pin_2, HBpin, etc) catalyzed by transitional-metal catalysts such as Rh, Pd, Ir, and Co or Lewis acid, base, etc.[35] Compared to the well-explored 1,2-diboration, examples of competitive 1,1-diboration of alkyne are scarce. Although the alkynylboronic esters (**3**) shown in Table 2 are useful, they are extremely sensitive to the protodeborylation reaction. Therefore, we seek to in situ use the same zinc halide as catalysts to generate the corresponding hydroboration product for a subsequent transformation of alkynylboronates. In spite of the observation of alkyne hydroboration as a side product (<2% yield) in some cases of the aforementioned dehydrogenative borylation, increasing catalyst loading of $ZnBr_2$, reaction temperature (up to 120 °C), or excessive HBpin leads to the formation of only the dehydrogenative borylated product and not the diboration product. When the resultant dehydrogenative borylated products **3** were directly treated with carboxylic acid without isolation, the designed hydroboration proceeded smoothly to generate the 1,1-diboration products selectively. The scope of alkynylboronate hydroboration is studied using 5 mol % of 4-(dimethylamino)benzoic acid (A) as a catalyst at 100 °C for 12 h (Table 3).[36] The hydroboration of 2-phenyl-1-ethynylboronic acid pinacol ester (**3a**) proceeds efficiently to produce the desired 1,1-diborylalkene product **4a** with high yield under the above-mentioned optimized reaction conditions reported by Jin et al. (Table 3, entry 1).[36] Substrates with the phenyl ring bearing electron-donating groups such as methyl or methoxyl afford good to high yields regardless of the position of methyl substituent (**4b**–**4d**, Table 3, entries 2–4). The hydroboration of alkynylboronate with electron-withdrawing groups such as fluorine or trifluoromethyl on the benzene ring also took place with exclusive regioselectivity in almost quantitative yields (**4e** and **4f**, Table 3, entries 5 and 6). However, the heteroaryl 2-thienylalkynylboronate can be obtained only in a moderate yield (**4g**, Table 3, entry 7). The aliphatic alkynylboronate substituted with *n*-butyl group is also a suitable substrate to produce the corresponding 1,1-diborylalkene product **4h** in good yield (Table 3, entry 8). When 1,6-diynylboronate is used as a substrate, the

Table 3. Catalytic Hydroboration of Various Alkynylboronates (3) with HBpin[a]



Entry	Product	Conversion (%)[b]	Entry	Product	Conversion (%)[b]
1	 **4a**	98 (93[d])	2	 **4b**	92
3	 **4c**	88	4	 **4d**	80
5	 **4e**	98 (90[d])	6	 **4f**	98
7	 **4g**	60	8	 **4h**	80
9	 **4i**	80[c]			

[a]Reaction conditions: **3** (0.2 mmol), HBpin (1 mmol), 4-(dimethylamino)benzoic acid (5 mol %), octane (0.2 mL), 100 °C, and 12 h. [b]Conversion was determined by ^1H NMR spectroscopy. [c]120 °C, 12 h, 10 equiv of HBpin. [d]Isolated yield.

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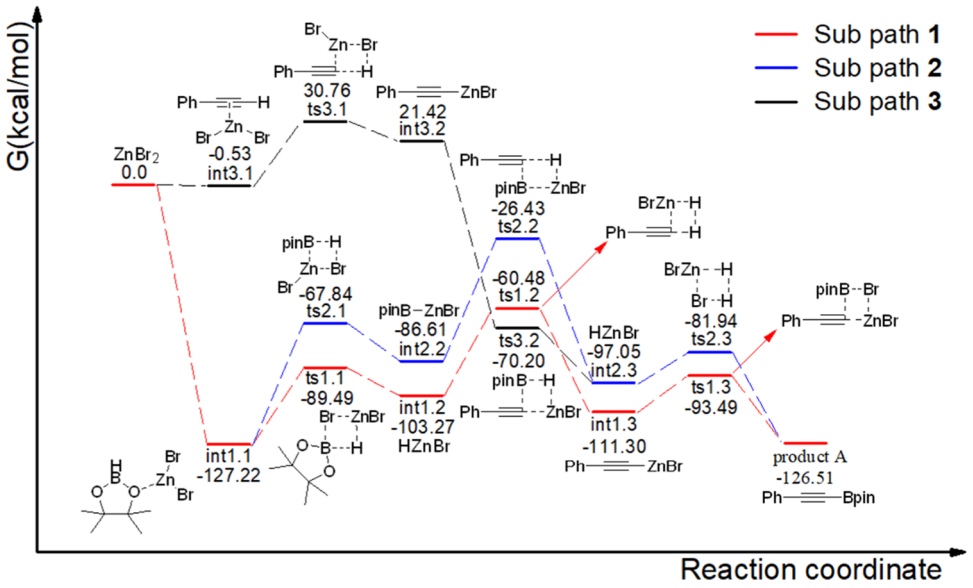

Figure 1. Calculated reaction pathways of $ZnBr_2$-catalyzed dehydrogenative borylation of alkynes at B2PLVP/def2-TZVP//B3LYP/genecp level.

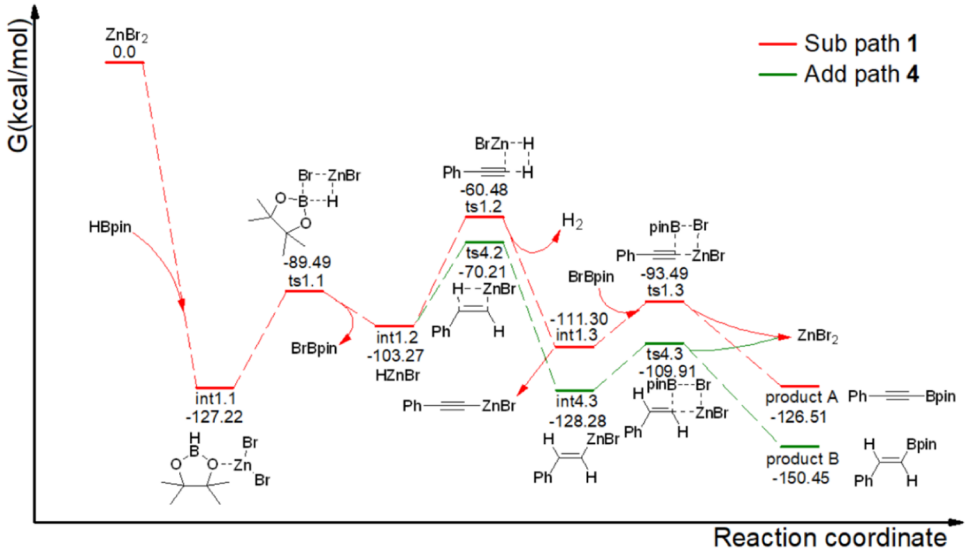

Figure 2. Comparison of the calculated reaction pathways of $ZnBr_2$-catalyzed dehydrogenative borylation and hydroboration of alkynes at B2PLVP/def2-TZVP//B3LYP/genecp level.

dihydroboration reaction also occurs and the corresponding tetraboryldiene **4i** is obtained in one pot with 80% yield (Table 3, entry 9).

In an effort to gain further insight into the catalytic application, a mechanism for the $ZnBr_2$-catalyzed dehydroboration of alkynes was investigated. Some control experiments were attempted. For example, $ZnBr_2$ was first treated with phenylacetylene in a 1:1 stoichiometric ratio; however, only the starting material alkyne was observed in the crude ^1H NMR spectroscopy. This indicates that $ZnBr_2$ has no ability to activate the C−H bond of terminal alkynes to directly produce the corresponding zinc alkynyl intermediate. Therefore, the present alkyne dehydroboration seems likely to start with the activation of the B−H bond of HBpin. The reaction of $ZnBr_2$ and HBpin was also performed in a 1:1 stoichiometric ratio; unfortunately, no new peak was generated in the crude ^1H NMR spectroscopy and HBpin decomposed slowly as time went on. The reason could be that the corresponding zinc hydride was too reactive to stabilize in the solution at room temperature. Hence, the corresponding density functional theory (DFT) calculations were taken to explore their thermodynamic properties and three possible substitution reaction processes were proposed on the basis of the previous reports. As shown in Figure 1, the obtained Gibbs free energy shows that the substitution path **1** (red line) should be the optimal reaction process based on the basic thermodynamics knowledge. At first, $ZnBr_2$ prefer to coordinate to HBpin not phenylacetylene because the intermediate 1.1 is much more stable than the intermediate 3.1 (−127.22 vs −0.53 kcal/mol). This is consistent with the above experiment result of $ZnBr_2$ and phenylacetylene, which cannot form the corresponding zinc alkynyl complex *via* the binding of zinc metal to the C−C triple bond of phenylacetylene. $ZnBr_2$ should be first coordinated to the oxygen atom of HBpin and then the highly reactive zinc hydride BrZnH released *via* the Zn−H−B−Br four-member ring transition state (ts1.1, substitution path **1**).

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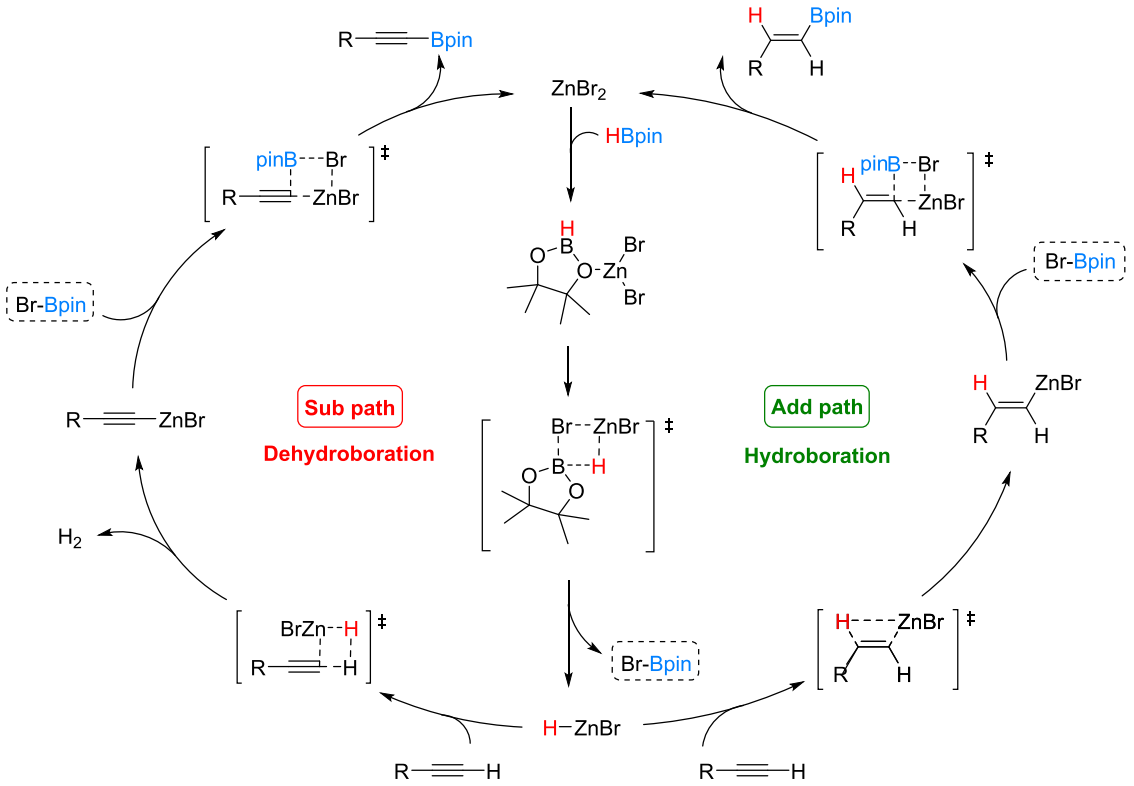
Scheme 4. Plausible Mechanism of $ZnBr_2$-Catalyzed Alkyne Dehydrogenative Borylation



In this step, there are two possible routes. Substitution path **2** (blue line) was excluded because it required high energy compared to substitution path **1**. The resulting two-coordinated extremely reactive zinc hydride BrZnH was subsequently reacted with phenylacetylene to afford the corresponding zinc alkynyl species int1.3. It was further treated with BrBpin to produce the desired dehydroboration product A and regenerate the catalyst $ZnBr_2$.

From the above DFT calculation and experiment results, we infer that the substitution path **1** was the most probable alkyne the dehydrogenative borylation reaction process. Due to the observation of some minor byproduct of hydroboration in some cases, the corresponding DFT calculation of alkyne hydroboration was also carried out (green line, Figure 2). Before the formation of zinc hydride HZnBr, both reaction processes are the same. To our surprise, the transition state energy of the hydroboration intermediate zinc alkenyl complex int4.3 is lower than that of the dehydroboration intermediate zinc alkynyl complex int1.3. This indicated that the addition process has thermodynamic advantages. The computational calculation results seem to be contrary to the obtained experimental data. However, taking into consideration the generation of hydrogen gas during the reaction, the substitution reaction had more dynamic advantages. In addition, we found that the higher the reaction temperature, the more substitution products are formed, which proved that it was an entropy-driven reaction, and the proportion of these two competitive reaction products were greatly affected by the temperature. In other words, the dehydroboration reaction generated the kinetic products (alkynylboronic esters, product A) and the hydroboration reaction generated thermodynamic products (alkenylboranes, product B). The production of hydrogen is favorable for moving the competing chemical equilibrium in the direction of kinetic products.

Based on the experiment results and DFT calculations, one possible mechanism for the $ZnBr_2$-catalyzed dehydroboration of alkynes was proposed (Scheme 4). Initially, the reaction of $ZnBr_2$ with HBpin gives the active zinc hydride species **HZnBr** and **BrBpin**. **HZnBr** was subsequently reacted with alkyne to generate the zinc alkynyl intermediate and release hydrogen gas, which was observed as bubbles during the reaction. This is the key step for the competing dehydrogenative borylation and hydroboration reaction. Finally, the zinc alkynyl intermediate was treated with **BrBpin** to afford the target dehydroboration product and regenerate $ZnBr_2$ to complete the catalytic cycle.

CONCLUSIONS

In summary, we have demonstrated that the commercially available zinc halide ($ZnBr_2$) could be employed as highly efficient catalysts for the dehydrogenative borylation of various terminal alkynes with HBpin at room temperature. A series of alkynylboronates have been successfully synthesized, which were further converted into the 1,1-diborylated alkenes products *via* a one-pot tandem dehydrogenative borylation and hydroboration. The reaction mechanism of catalytic alkyne dehydroboration was also investigated based on the corresponding stoichiometric reactions and DFT calculations. Compared with the previously reported metal catalysts of alkyne dehydrogenative borylation, $ZnBr_2$ is the simplest, cheaper, and more readily available product. This discovery also inspired us to find a simple catalyst to replace complex noble-metal catalysts.

EXPERIMENTAL SECTION

General Information. All air-sensitive compounds were carried out using the standard Schlenk-line or glovebox techniques under high-purity argon. ^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B NMR spectra were recorded at 25 °C on Bruker Avance III 400 MHz spectrometer in deuterated

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solvents and chemical shifts were referenced to $CDCl_3$ (δ = 7.26 for ^1H and δ = 77.16 for $^{13}C\{^1H\}$ NMR) as an internal standard. All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics, and Energy Chemical without further purification.

General Reaction Procedure of Products of 3 and 4. Alkyne (0.20 mmol, 1 equiv), HBpin (0.22 mmol, 1.1 equiv), and $ZnBr_2$ (0.002 mmol, 1 mol %) were added into a 10 mL flask. The reaction temperature and time of the mixture are shown in Table 2. Conversion of product **3** was determined by ^1H NMR. Without isolation, some selected resultant alkynylboronate products **3** were further treated with HBpin (1.00 mmol, 5 equiv), 4-(dimethylamino) benzoic acid (0.01 mmol, 5 mol %), and octane (0.2 mL, 1M). The crude reaction was heated to 100 °C using a heating mantle and stirred for 12 h to achieve 1,1-diborylalkene products **4** by "one-pot" method. Conversion of product **4** was determined by ^1H NMR. **Note**: the carbon signal attached to B was not observed due to low intensity.

Gram-Scale Reaction. In a glovebox, 4-ethynyltoluene (1.27 mL, 10 mmol) and HBpin (1.60 mL, 11 mmol) were added to a 25 mL flask. The catalyst $ZnBr_2$ (22.5 mg, 1 mol %) was then added to the mixture. The reaction mixture was stirred for 20 h at room temperature. The crude product was purified by silica gel column chromatography to give the product **3b** as a white solid in 86% yield (2.08 g).

Procedure for Trapping Experiment of Hydrogen Gas. In a glovebox, 4-fluorophenylacetylene (0.23 mL, 2 mmol), HBpin (0.32 mL, 2.2 mmol), and $ZnBr_2$ (4.5 mg, 0.02 mmol) were added to a 10 mL flask of **A**, and the reaction mixture was stirred for 5 h at room temperature. On the other hand, the 10 mL flask of **B** was charged with 10% Pd/C (5.32 mg, 5 μmol), **5** (90.13 mg, 0.5 mmol), and 1,4-dioxane (0.50 mL), and the hydrogen gas generated in flask **A** was transferred to flask **B**. After stirring at 100 °C for 20 h, the resulting solution was filtered through a pad of Celite and then the solvent was evaporated, followed by silica gel column chromatography to give 1,2-diphenylethane (**6**) in 91% yield (83.0 mg).

Spectroscopic Data for Products of 3 and 4. *4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-ioxaborolane (**3a**).*[27a] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51−7.53 (m, 2H), 7.28−7.37 (m, 3H), 1.31 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 132.5, 129.4, 128.3, 121.9, 101.8, 84.4, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.16.

*4,4,5,5-Tetramethyl-2-(p-tolylethynyl)-1,3,2-dioxaborolane (**3b**).*[27a] White solid (37.5 mg, 86%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.42 (m, 2H), 7.10−7.12 (m, 2H), 2.33 (s, 3H), 1.31 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 139.7, 132.5, 129.1, 118.8, 102.2, 84.4, 24.7, 21.6. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.15.

*4,4,5,5-Tetramethyl-2-(o-tolylethynyl)-1,3,2-dioxaborolane (**3c**).*[28] Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47−7.49 (m, 2H), 7.17−7.19 (m, 2H), 2.40 (s, 3H), 1.33 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 141.3, 133.0, 129.4, 129.3, 125.5, 121.7, 100.7, 84.4, 24.7, 20.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.27.

*2-((4-Methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**).*[30] Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.45−7.47 (m, 2H), 6.81−6.83 (m, 2H), 3.79 (s, 3H), 1.31 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 160.5, 134.2, 114.0, 113.8, 102.1, 84.3, 55.2, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.93.

*2-((4-Chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**).*[28] Brown solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.01−7.05 (m, 2H), 6.73−6.76 (m, 2H), 1.02 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 135.2, 133.5, 128.5, 120.6, 100.2, 83.8, 24.3. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.78.

*2-((4-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**).*[28] Yellow solid (41.8 mg, 85%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50−7.53 (m, 2H), 6.99−7.03 (m, 2H), 1.32 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 163.1 (d, J = 251.3 Hz), 134.6 (d, J = 9.1 Hz), 118.0 (d, J = 3.0 Hz), 115.7 (d, J = 22.1 Hz), 100.7, 84.5, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.07.

*4,4,5,5-Tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (**3g**).*[30] Yellow solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.12−7.14 (m, 2H), 6.99−7.01 (m, 2H), 1.03 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 132.4, 130.4 (q, J = 32.2 Hz), 125.7 (m), 125.0 (q, J = 4.0 Hz), 122.7, 99.5, 84.0, 24.3. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.66.

*4,4,5,5-Tetramethyl-2-((4-nitrophenyl)ethynyl)-1,3,2-dioxaborolane (**3h**).*[31] Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50−7.48 (m, 2H), 6.93−6.95 (m, 2H), 1.03 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 147.5, 132.6, 132.4, 123.1, 98.8, 84.2, 24.3. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.70.

*2-(Mesitylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**).*[29] Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.84 (m, 2H), 2.43 (s, 6H), 2.27 (s, 3H), 1.33 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 141.6, 138.8, 127.6, 118.8, 99.5, 84.2, 24.7, 21.4, 21.0. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.43.

*4,4,5,5-Tetramethyl-2-(3-phenylprop-1-yn-1-yl)-1,3,2-dioxaborolane (**3j**).*[28] Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.17−7.34 (m, 5H), 3.67 (s, 2H), 1.27 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 135.3, 128.6, 128.1, 126.7, 101.8, 84.2, 25.9, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.93.

*4,4,5,5-Tetramethyl-2-(3-phenoxyprop-1-yn-1-yl)-1,3,2-dioxaborolane (**3k**).*[31] Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25−7.29 (m, 2H), 6.93−6.98 (m, 3H), 4.68 (s, 2H), 1.25 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 157.6, 129.5, 121.5, 114.8, 97.4, 84.5, 56.0, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.71.

*2-(Hex-1-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**).*[27a] Colorless oil (37.1 mg, 89%). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.96 (t, J = 6.6 Hz, 2H), 1.16−1.29 (m, 2H), 1.01 (s, 16H), 0.65 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 104.0, 83.2, 30.1, 24.6, 24.4, 21.7, 19.0, 13.2. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.27.

*4,4,5,5-Tetramethyl-2-(oct-1-yn-1-yl)-1,3,2-dioxaborolane (**3m**).*[29] Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.15−2.18 (t, 2H, J = 7.2 Hz), 1.41−1.49 (m, 2H), 1.27−1.34 (m, 2H), 1.19 (s, 16H), 0.80 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 105.0, 83.9, 31.3, 28.4, 28.0, 24.8, 24.6, 22.4, 19.5, 13.9. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.58.

*1,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-diyne (**3n**).*[31] White solid (57.1 mg, 83%). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.31 (t, J = 4.7 Hz, 4H), 1.68 (quint, J = 4.7 Hz, 2H), 1.18 (s, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 103.3, 84.0, 24.6, 18.5. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.54.

*2-(Cyclopropylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3o**).*[30] Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.19 (s, 12H), 0.75 (s, 1H), 0.73−0.74 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 108.1, 83.9, 24.6, 8.7, 0.1. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.64.

*2-(Cyclohexylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**).*[28] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.27−2.33 (m, 1H), 1.57−1.71 (m, 4H), 1.31−1.39 (m, 4H), 1.31 (s, 14H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 108.5, 83.8, 32.0, 29.6, 25.7, 24.7, 24.6. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.64.

*4,4,5,5-Tetramethyl-2-(thiophen-3-ylethynyl)-1,3,2-dioxaborolane (**3q**).*[29] Brown solid (40.3 mg, 86%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.59−7.60 (m, 1H), 7.23−7.25 (m, 1H), 7.16−7.17 (m, 1H), 1.31 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 131.7, 130.2, 125.4, 121.2, 96.8, 84.0, 84.4, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 24.24.

*Trimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-yn-1-yl)oxy)silane (**3r**).*[27a] Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 4.27 (s, 2H), 1.23 (s, 12), 0.12−0.14 (tr, J = 3.5 Hz, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 101.2, 84.2, 51.2, 24.6, −0.43. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 23.56.

*Trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)-silane (**3s**).*[27a] Yellow solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.19 (s, 12), 0.10 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 111.1, 84.3, 24.6, −0.59. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 22.93.

*2,2′-(2-Phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4a**).*[36] Colorless oil (66.3 mg, 93%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.70 (s, 1H), 7.47−7.49 (m, 2H), 7.25−7.29 (m, 3H), 1.31 (s, 12H), 1.28 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 155.1, 139.6, 128.4, 128.1, 128.0, 83.6, 83.1, 24.9, 24.6. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.59.

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*2,2′-(2-(p-Tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4b**).*[36] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (s, 1H), 7.38 (d, *J* =8 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.32 (s, 12H), 1.27 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 155.1, 138.4, 136.8, 128.8, 128.2, 83.5, 83.1, 24.9, 24.7, 21.3. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.91.

*2,2′-(2-(o-Tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4c**).*[36] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.05−7.15 (m, 3H), 2.35 (s, 3H), 1.27 (s, 12H), 1.23 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 154.1, 139.2, 136.2, 129.8, 129.5, 128.2, 127.6, 125.4, 83.4, 83.1, 24.9, 24.5, 19.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.95.

*2,2′-(2-(4-Methoxyphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4d**).*[36] Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 1.32 (s, 12H), 1.25 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 159.9, 154.7, 132.4, 129.7, 129.5, 113.4, 83.5, 83.1, 55.2, 24.8, 24.6. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.65.

*2,2′-(2-(4-Fluorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4e**).*[36] Light yellow oil (67.4 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (s, 1H), 7.45−7.47 (m, 2H), 6.96−6.99 (m, 2H), 1.31 (s, 12H), 1.27 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 153.7, 129.9, 129.8, 115.1, 114.9, 83.6, 83.2, 24.8, 24.6. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.62.

*2,2′-(2-(4-(Trifluoromethyl)phenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4f**).*[36] Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (s, 1H), 7.51−7.61 (m, 4H), 1.31 (s, 12H), 1.28 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 153.0, 142.9, 129.9, 128.6, 125.4, 125.1, 83.8, 83.4, 24.8, 24.6. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.62.

*2,2′-(2-(Thiophen-3-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4g**).*[36] Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (s, 1H), 7.43−7.44 (m, 1H), 7.30−7.32 (m, 1H), 7.20−7.22 (m, 1H), 1.33 (s, 12H), 1.27 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 148.1, 142.5, 127.2, 125.6, 125.3, 83.6, 83.1, 24.8, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.85.

*2,2′-(Hex-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4h**).*[36] Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.93 (t, *J* = 4.8 Hz, 1H), 2.26 (dt, *J* = 7.6, 7.6 Hz, 2H), 1.38−1.41 (m, 4H), 1.29 (s, 12H), 1.23 (s, 12H), 0.87 (t, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 162.4, 139.4, 129.5, 83.0, 81.8, 35.1, 31.9, 24.8, 24.7, 22.6, 14.1. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.72.

*1,1,7,7-Tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-hepta-1,6-diene (**4i**).*[36] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.92 (t, *J* = 4.8 Hz, 2H), 2.25−2.29 (m, 4H), 1.53−1.57 (m, 2H), 1.23 (s, 24H), 1.22 (s, 24H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 162.0, 83.0, 81.8, 35.0, 29.2, 24.8, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 27.49, 28.88.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01936.

^{1}H, $^{13}C\{^{1}H\}$, and ^{11}B NMR spectra of products **3** and **4**, and computational studies (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chirik, P.; Morris, R. Getting Down to Earth: The Renaissance of Catalysis with Abundant Metals. *Acc. Chem. Res.* **2015**, *48*, 2495.

(2) Suzuki, A. Cross-Coupling Reactions of Organoboranes: An Easy Way to Construct C−C Bonds (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6722−6737.

(3) Kuciński, K.; Hreczycho, G. Hydrosilylation and Hydroboration in a Sustainable Manner: from Earth-abundant Catalysts to Catalyst-free Solutions. *Green Chem.* **2020**, *22*, 5210−5224.

(4) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and Discovery of Earth-abundant Metal Catalysts using Sodium *tert*-Butoxide. *Nat. Chem.* **2017**, *9*, 595−600.

(5) Bose, S. K.; Deißenberger, A.; Eichhorn, A.; Steel, P. G.; Lin, Z.; Marder, T. B. Zinc-Catalyzed Dual C−X and C−H Borylation of Aryl Halides. *Angew. Chem., Int. Ed.* **2015**, *54*, 11843−11847.

(6) Roscales, S.; Csákÿ, A. G. Transition-Metal-Free C−C Bond Forming Reactions of Aryl, Alkenyl and Alkynylboronic Acids and Their Derivatives. *Chem. Soc. Rev.* **2014**, *43*, 8215−8225.

(7) Li, C.; Song, S.; Li, Y.; Xu, C.; Luo, Q.; Guo, Y.; Wang, X. Selective Hydroboration of Unsaturated Bonds by an Easily Accessible Heterotopic Cobalt Catalyst. *Nat. Commun.* **2021**, *12*, No. 3813.

(8) Manna, S.; Kanti Das, K.; Aich, D.; Panda, S. Synthesis and Reactivity of Allenylboron Compounds. *Adv. Synth. Catal.* **2021**, *363*, 2444−2463.

(9) Wang, R.; Park, S. Recent Advances in Metal-Catalyzed Asymmetric Hydroboration of Ketones. *ChemCatChem.* **2021**, *13*, 1898−1919.

(10) Kostera, S.; Peruzzini, M.; Gonsalvi, L. Recent Advances in Metal Catalyst Design for CO_2 Hydroboration to C1 Derivatives. *Catalysts* **2021**, *11*, 58−83.

(11) Luo, M.; Zang, S.; Yao, W.; Zheng, J.; Ma, M. Recent Advances in Alkaline Earth Metal Catalyzed Hydroboration Reactions. *Sci. Sin. Chim.* **2020**, *50*, 639−654.

(12) Cao, X.; Li, J.; Zhu, A.; Su, F.; Yao, W.; Xue, F.; Ma, M. Syntheses of Asymmetrical Magnesium(I) Complexes and Their Catalytic Application in Epoxide Hydroboration. *Org. Chem. Front.* **2020**, *7*, 3625−3632.

(13) Cao, X.; Wang, W.; Lu, K.; Yao, W.; Xue, F.; Ma, M. Magnesium-Catalyzed Hydroboration of Organic Carbonates, Carbon Dioxide and Esters. *Dalton Trans.* **2020**, *49*, 2776−2780.
(14) Shegavi, M. L.; Bose, S. K. Recent Advances in the Catalytic Hydroboration of Carbonyl Compounds. *Catal. Sci. Technol.* **2019**, *9*, 3307−3336.
(15) Wang, W.; Shen, X.; Zhao, F.; Jiang, H.; Yao, W.; Pullarkat, S. A.; Xu, L.; Ma, M. Ytterbium-Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2018**, *83*, 69−74.
(16) Ansell, M. B.; Navarro, O.; Spencer, J. Transition Metal Catalyzed Element-Element' Additions to Alkynes. *Coord. Chem. Rev.* **2017**, *336*, 54−77.
(17) Yoshida, H. Borylation of Alkynes under Base/Coinage Metal Catalysis: Some Recent Developments. *ACS Catal.* **2016**, *6*, 1799−1811.
(18) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*, 9091−9161.
(19) Guo, J.; Cheng, Z.; Chen, J.; Chen, X.; Lu, Z. Iron- and Cobalt-Catalyzed Asymmetric Hydrofunctionalization of Alkenes and Alkynes. *Acc. Chem. Res.* **2021**, *54*, 2701−2716.
(20) Chen, J.; Shen, X.; Lu, Z. Cobalt-Catalyzed Markovnikov-Type Selective Hydroboration of Terminal Alkynes. *Angew. Chem., Int. Ed.* **2021**, *60*, 690−694.
(21) Zhong, M.; Gagne, Y.; Hope, T. O.; Pannecoucke, X.; Frenette, M.; Jubault, P.; Poisson, T. Copper-Photocatalyzed Hydroboration of Alkynes and Alkenes. *Angew. Chem., Int. Ed.* **2021**, *60*, 14498−14503.
(22) Aelterman, M.; Sayes, M.; Jubault, P.; Poisson, T. Electrochemical Hydroboration of Alkynes. *Chem. - Eur. J.* **2021**, *27*, 8277−8282.
(23) Magre, M.; Maity, B.; Falconnet, A.; Cavallo, L.; Rueping, M. Magnesium-Catalyzed Hydroboration of Terminal and Internal Alkynes. *Angew. Chem., Int. Ed.* **2019**, *58*, 7025−7029.
(24) Mandal, S.; Mandal, S.; Geetharani, K. Zinc-Catalysed Hydroboration of Terminal and Internal Alkynes. *Chem. - Asian J.* **2019**, *14*, 4553−4556.
(25) Li, J.; Luo, M.; Sheng, X.; Hua, H.; Yao, W.; Pullarkat, S. A.; Xu, Li.; Ma, M. Unsymmetrical β-Diketiminate Magnesium(I) Complexes: Syntheses and Application in Catalytic Hydroboration of Alkyne, Nitrile and Carbonyl Compounds. *Org. Chem. Front.* **2018**, *5*, 3538−3547.
(26) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C−H Activation for the Construction of C−B Bonds. *Chem. Rev.* **2010**, *110*, 890−931.
(27) (a) Lee, C. I.; Zhou, J.; Ozerov, O. V. Catalytic Dehydrogenative Borylation of Terminal Alkynes by a SiNN Pincer Complex of Iridium. *J. Am. Chem. Soc.* **2013**, *135*, 3560−3566. (b) Lee, C. I.; DeMott, J. C.; Pell, C. J.; Christopher, A.; Zhou, J.; Bhuvanesh, N.; Ozerov, O. V. Ligand Survey Results in Identification of PNP Pincer Complexes of Iridium as Long-lived and Chemoselective Catalysts for Dehydrogenative Borylation of Terminal Alkynes. *Chem. Sci.* **2015**, *6*, 6572−6582. (c) Pell, C. J.; Ozerov, O. V. Catalytic Dehydrogenative Borylation of Terminal Alkynes by POCOP-Supported Palladium Complexes. *Inorg. Chem. Front.* **2015**, *2*, 720−724.
(28) Romero, E. A.; Jazzar, R.; Bertrand, G. Copper-Catalyzed Dehydrogenative Borylation of Terminal Alkynes with Pinacolborane. *Chem. Sci.* **2017**, *8*, 165−168.
(29) Procter, R. J.; Uzelac, M.; Cid, J.; Rushworth, P. J.; Ingleson, M. J. Low-Coordinate NHC−Zinc Hydride Complexes Catalyze Alkyne C−H Borylation and Hydroboration Using Pinacolborane. *ACS Catal.* **2019**, *9*, 5760−5771.
(30) Wei, D.; Carboni, B.; Sortais, J. B.; Darcel, C. Iron-Catalyzed Dehydrogenative Borylation of Terminal Alkynes. *Adv. Synth. Catal.* **2018**, *360*, 3649−3654.
(31) Hu, J. R.; Liu, L. H.; Hu, X.; Ye, H. D. Ag(I)-Catalyzed C−H Borylation of Terminal Alkynes. *Tetrahedron* **2014**, *70*, 5815−5819.
(32) Tsuchimoto, T.; Utsugi, H.; Sugiura, T.; Horio, S. Alkynylboranes: A Practical Approach by Zinc-Catalyzed Dehydrogenative Coupling of Terminal Alkynes with 1,8-Naphthalenediaminatoborane. *Adv. Synth. Catal.* **2015**, *357*, 77−82.
(33) Birepinte, M.; Liautard, V.; Chabaud, L.; Pucheault, M. Magnesium-Catalyzed Tandem Dehydrogenation-Dehydrocoupling: An Atom Economical Access to Alkynylboranes. *Chem. - Eur. J.* **2020**, *26*, 3236−3240.
(34) (a) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457−2483. (b) Lennoxa, A. J. J.; Lloyd-Jones, G. C. Selection of Boron Reagents for Suzuki-Miyaura Coupling. *Chem. Soc. Rev.* **2014**, *43*, 412−443.
(35) Krautwald, S.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed 1,1-Diboration of Terminal Alkynes: Scope, Mechanism, and Synthetic Applications. *J. Am. Chem. Soc.* **2017**, *139*, 3868−3875.
(36) Ho, H. E.; Asao, N.; Yamamoto, Y.; Jin, T. Carboxylic Acid-Catalyzed Highly Efficient and Selective Hydroboration of Alkynes with Pinacolborane. *Org. Lett.* **2014**, *16*, 4670−4673.

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