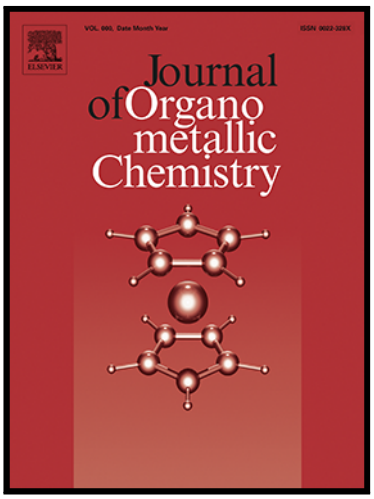

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Dehydrogenative Diboration of Alkynes Catalyzed by Ir/CO/^{t}BuNC System

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ABSTRACT. Catalytic dehydrogenative diboration (DHDB) of alkyne with HBpin was achieved using $[Ir(COD)Cl]_2$ and other related Ir precursors under CO atmosphere. The selectivity for DHDB over hydroboration was higher in less polar solvent and under increasing CO pressure. It was further improved when catalytic amount of ^{t}BuNC was added to the reaction. It was possible to achieve DHDB of both terminal and internal alkynes with selectivity for DHDB of up to 9:1 under the best conditions. Some DHDB products were isolated on the preparative scale.

KEYWORDS. Iridium, catalysis, alkynes, diboration, hydroboration.

1. Introduction

1,2-Diboration of alkynes is a reaction that produces 1,2-diborylalkenes [1],which are useful building blocks for the syntheses of polysubstituted alkenes [2-6]. It is typically conceived stoichiometrically as a formal addition of the B-B bond in a diborane across a triple bond of an alkyne [7,8]. The diborane usually carries heteroatom substituents on the borons, with the B_2pin_2 and B_2cat_2 being the most common reagents. This reaction has been catalyzed by a transition metal complexes such as Pt [9-16] or Cu [17-19], by strong bases for certain substrates [20],via organocatalysis [21,22],and has even been shown to proceed without a catalyst for some diboranes [23]. An Ir catalyst for diboration using a B-B reagent has also been reported [24].

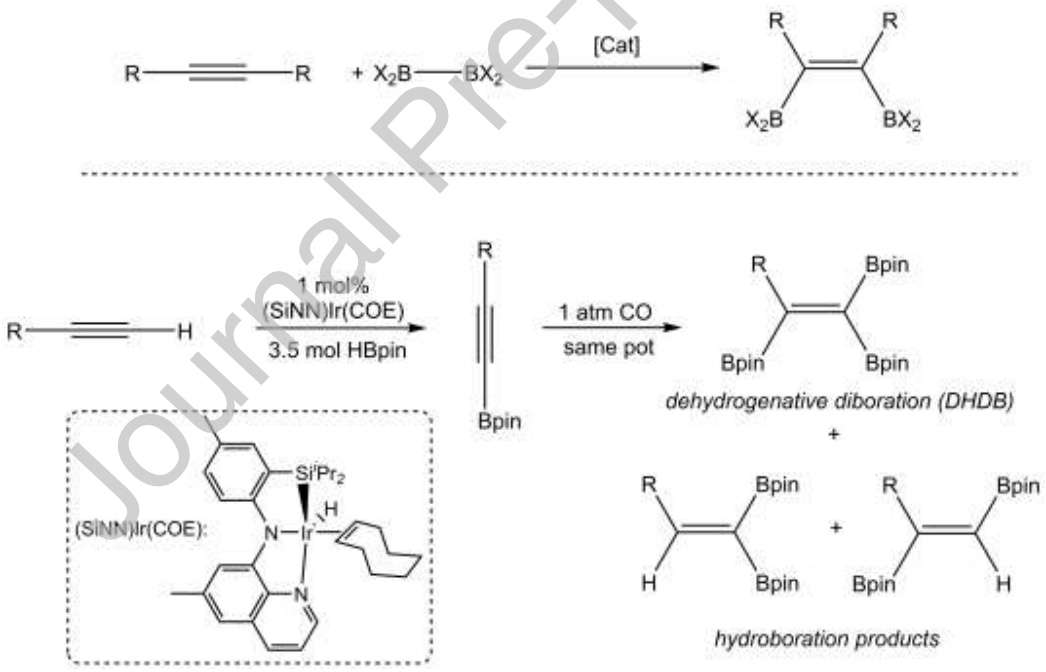


Figure 1. Top: conventional diboration of alkynes with a B-B reagent. Bottom: dehydrogenative diboration of alkynylboronates with HBpin using a (SiNN)Ir catalyst.

In 2015, we reported on tandem catalysis of the conversion of terminal alkynes into triborylalkenes by the Ir complexes supported by the SiNN ligand [25]. The first step of the transformation is the dehydrogenative borylation of terminal alkynes (DHBTA), on which we and others extensively reported separately [26-36]. DHBTA results in the formation of alkynylboronates which are diborated in the second step to yield triborylalkenes by a (SiNN)Ir catalysts modified by the addition of CO. The unusual part of this reaction was that the diboration was not of a kind depicted at the top of Figure 1 but instead used HBpin as the boron substrate and thus was net dehydrogenative. This is potentially an attractive alternative to the diboration with diboranes because it relies on a simpler boron starting material. We were not able to establish the mechanism by which this dehydrogenative diboration (DHDB) happens, but did isolate a (SiNN)Ir(CO) complex which was itself a competent catalyst. The selectivity for the diboration was not perfect and competitive hydroboration also took place to some extent. Fortuitously, alkenes with three -Bpin substituents proved to be less soluble and were easily isolated by recrystallization out of mixtures containing tri- and diboryl alkenes.

We desired to explore whether an analogous DHDB can be applicable to alkynes other than alkynylboronates and also if the selectivity towards diboration could be improved. Although we intended to focus on the Ir complexes of the SiNN ligand, this report describes how it was discovered that the SiNN ligand was not necessary and that a simpler catalyst formulation was possible.

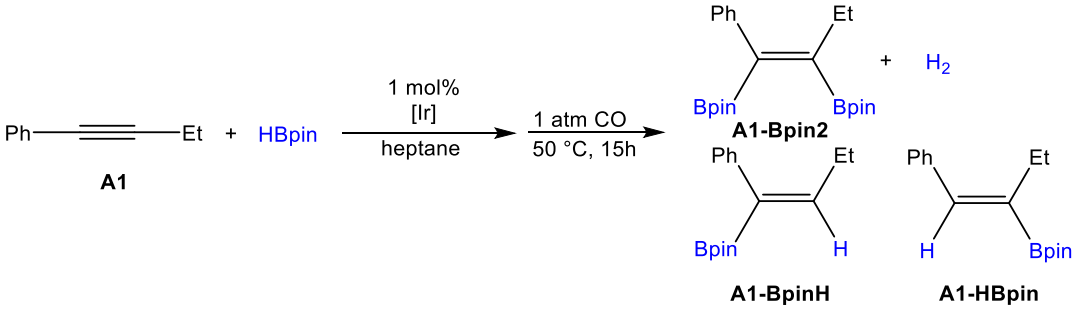
2. Results and Discussion

2.1. *Optimization of DHDB of 1-phenyl-1-butyne.*

We selected 1-phenyl-1-butyne as the test substrate to examine whether DHDB can be extended to internal, carbon-substituted alkynes. Application of 1% (SiNN)Ir(COE) as the catalyst under conditions similar to those we reported in 2015 resulted in the formation of the predominantly DHDB product along with two isomeric hydroboration products. Performing a control experiment with 1 mol% $[Ir(COD)Cl]_2$ as the catalyst (all molar percentages refer to the Ir content, not the molar amount of the dimeric precursor), we found that it furnished essentially the same product distribution. This was surprising because our control experiment with 5 mol% $[Ir(COE)_2Cl]_2$ in the 2015 paper led primarily to hydroboration and to little or no diboration products. The culprit in this instance was that 5 mol% Ir is a high catalyst loading and the introduction of CO via freeze-pump-thaw cycles takes some time (that the 2015 experiment did not control for) after the mixing the alkyne, HBpin, and the Ir catalyst. Thus, it is possible to consume the reagents (primarily via hydroboration) before CO is properly introduced.

Having realized this, we examined a series of simple Ir precursors (Table 1) at 1 mol% Ir loading and taking care to minimize the exposure time prior to the introduction of CO. Except for $[Ir(COD)\ Br]_2$ and $[Ir(COD)I]_2$, all the entries in Table 1 resulted in approximately the same distribution of DHDB/hydroboration products. This suggests that the same active species was generated in entries 1, 2, and 5-7 and that implies that the anionic ligand attached to Ir in the precursor (Cl, OH, or OMe) was replaced with another. We hypothesize that the HBpin reagent undergoes metathesis with the Ir-O and Ir-Cl bonds to replace them with Ir-H, which may further react with H-Bpin to give rise to Ir-B and H_2 (as byproduct of DHDB was shown in Figure S18), but that such metathesis is ineffective with Ir-Br or Ir-I.

Table 1. Alkyne diboration with different iridium precursors[a]



entry	[Ir]	Yield of A1-Bpin2	Yield of A1-BpinH	Yield of A1-HBpin
1	(SiNN)IrCOE	77%	14%	7%
2	$[Ir(COD)Cl]_2$	74%	17%	7%
3	$[Ir(COD)Br]_2$	5%	85%	8%
4	$[Ir(COD)I]_2$	10%	75%	14%
5	$[Ir(COD)OH]_2$	71%	17%	10%
6	$[Ir(COD)OMe]_2$	72%	16%	10%
7	$[Ir(COE)_2Cl]_2$	76%	14%	8%

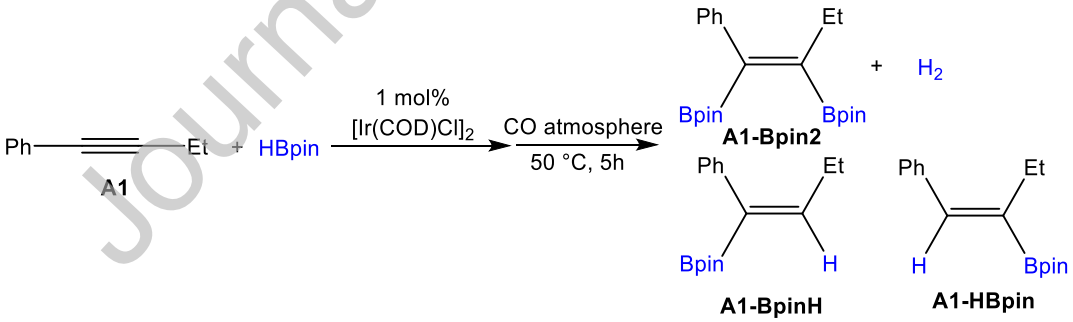
a. All reactions performed at 50 °C in heptane with 0.08 mmol 1-phenyl-1-butyne, 0.28 mmol HBpin, and 1 mol% catalyst loading under 1 atm CO. b. Yields were determined by ^{1}H NMR integration versus 1,4-dioxane as an internal standard.

We selected $[Ir(COD)Cl]_2$ for the next set of experiments aimed at improving the selectivity of the reaction towards DHDB. The results are summarized in Table 2. The selectivity for DHDB increased modestly but steadily as the polarity of the solvent decreased (entries 1-4, 9, 10). It was also noted that the selectivity increased with increased pressure of CO (entries 4, 18, 19). We surmise that these two facts are related. CO is more soluble in less polar solvents [37] and thus the effective concentration of CO is influenced by both the nature of the solvent and by the CO pressure introduced into the reaction vessel. Increasing the reaction temperature (entries 4-6) decreased the selectivity for DHDB. Although CO solubility may increase with temperature [38,39], it is possible that the binding of CO to Ir is less favorable at higher temperatures.

Although we have not established the identity of the Ir species in the catalytic mixture, it seems reasonable to propose that DHDB requires binding of one or more CO ligands to Ir, and that the "last" CO binding to Ir is not bound very strongly, such that its concentration is affected by temperature, solvent polarity and CO pressure. Hydroboration does proceed without CO, and it may also proceed via species with CO bound to Ir, but with fewer CO ligands than may be required for DHDB.

The effect of other additives was also explored. Adding tricyclohexylphosphine or pyridine had a negligible effect on the outcome of the reaction (entries 12 and 13). The use of ^{t}BuNC *instead* of CO did not lead to any DHDB products (entry 18); however, the use of ^{t}BuNC *in addition to* CO resulted in the improvement of selectivity. Finally, it should be noted that performing the reaction in the presence of liquid mercury did not affect the outcome (entry 11), suggesting that the catalysis proceeds homogeneously.

Table 2. Summary of the optimization of alkyne diboration



entry	Solvent	**A1-Bpin2**/(**A1-BpinH**+**A1-HBpin**)[b]	Additive	CO pressure
1	THF	42/58	none	1 atm
2	PhF	52/48	none	1 atm
3	toluene	57/43	none	1 atm

4	C_6D_6	59/41	none	1 atm
5	C_6D_6	70/16[e]	none	1 atm
6	C_6D_6	17/83[f]	none	1 atm
7	C_6D_6	N/A[g]	none	1 atm Ar
8	C_6D_6	0/0[h]	none	1atm
9	isooctane	69/31	none	1 atm
10	heptane	78/22	none	1 atm
11	C_6D_6	58/42	Hg drop	1 atm
12	C_6D_6	55/42	4 mol% P(*c*-C_6H_{11})$_3$	1 atm
13	C_6D_6	57/43	4 mol% pyridine	1 atm
14	C_6D_6	65/35	1.1 mol% ^{t}BuNC	1 atm
15	C_6D_6	73/27	2.1 mol% ^{t}BuNC	1 atm
16	C_6D_6	75/25	4.1 mol% ^{t}BuNC	1 atm
17	heptane	86/14	3 mol% ^{t}BuNC	1 atm
18	C_6D_6	0/50	4.1 mol% ^{t}BuNC	1 atm Ar[c]
19	heptane	86/14	none	2 atm[d]
20	heptane	91/9	none	3 atm[d]
21	C_6D_6	59/41[i]	none	1 atm

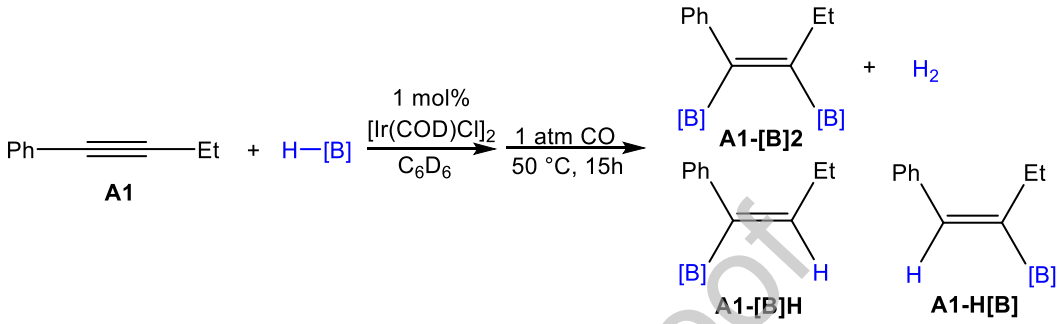
a. All reactions performed at 50 °C with 0.08 mmol 1-phenyl-1-butyne, 0.28 mmol HBpin, and 1 mol% catalyst loading in a J. Y tube for 5 h. b. Yields were determined by ^{1}H NMR integration versus 1,4-dioxane as an internal standard. c. The reaction was conducted under 1 atm Ar instead of CO. d. The reaction was conducted in a top-screw capped schlenk flask. e. The reaction was performed at room temperature (25 °C) for 3 d. f. The reaction was performed at 80 °C. g. All of the alkyne was converted into a mixture of hydroboration, hydrogenation and other unidentified products. h. B_2Pin_2 was used as boron source. i. After all the **A1** was consumed, 1 mol % [Ir(COD)Cl] was loaded to the reaction mixture. Then the resulting mixture was degassed and back-filled with CO, then heated at 50 °C for 15 h.

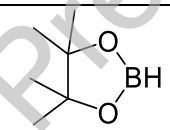
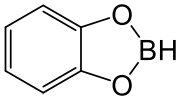
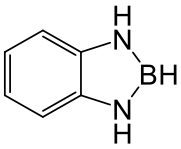
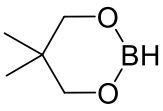
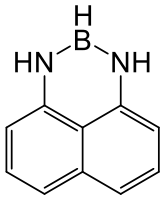
2.2. *Exploration of the scope of DHDB.*

Next, we examined the reaction of 1-phenyl-1-butyne with boranes other than HBpin (Table 3). The use of HBCat (entry 2) resulted in similar selectivity for DHDB, while the use of HBneop

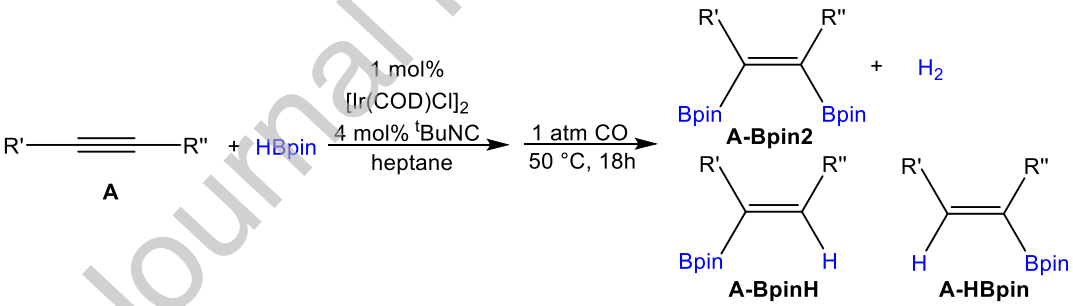
(entry 4) led to predominantly hydroboration, with only 9% of the DHDB product. Reactions with HBdan and HBdaz (entry 3&5) did not lead to any DHDB at all.

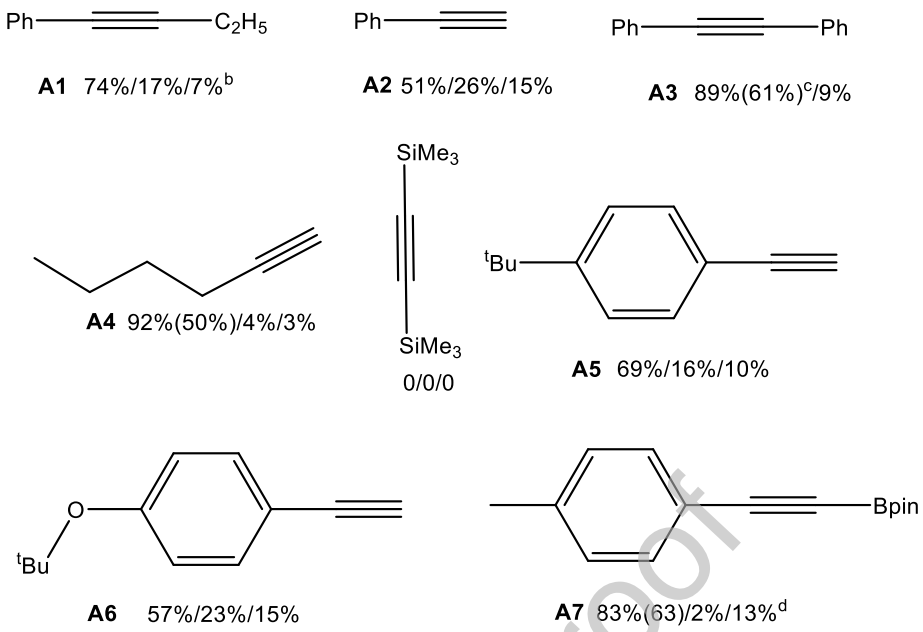
Table 3. DHDB with different boranes.



entry	H-[B] abbreviation	H-[B]	**A1-[B]2**/(**A1-[B]H**+**A1-H[B]**)	Alkyne conversion
1	HBpin		74/26	100%
2	HBcat		72/28	100%
3	HBdaz		0/100	52%
4	HBneop		9/91	100%
5	HBdan		0/100	20%

The alkyne substrate scope of Ir/CO/tBuNC system was briefly examined and is outlined in Figure 3. Although lower temperature increased the DHDB selectivity, the reaction at RT was too slow, requiring days for completion. Because of this, we elected to perform the reactions at 50 °C and with 1 atm of CO for convenience. Heptane was used as solvent to improve CO solubility. It was found that alkyl- and aryl-substituted internal and terminal alkynes can be diborylated with HBpin to yield *cis*-diborylalkenes with modest to high selectivity. Bis(trimethylsilyl)acetylene did not engage in the reaction, possibly owing to the steric hindrance. The diboration products derived from A3 and A7 were easily isolated as pure white solids by removing the volatiles at the end of the reaction, followed by recrystallization from a toluene solution layered with pentane at -35 °C. For terminal alkynes, the diboration products could be isolated by column chromatography.





a. All the reaction performed at 50 °C with 0.08 mmol 1-phenyl-1-butyne, 0.28 mmol HBpin, and 1 mol% catalyst loading in a J. Y tube for 5 h b. b. Yields were determined by ^{1}H NMR integration versus 1,4-dioxane as an internal standard and were given in the following order: **A-Bpin2**/**A-BPinH**/**A-HBpin**. c. isolated yield in 2.0 mmol scale were given in parenthesis. d. without ^{t}BuNC.

Figure 3. DHDB with different alkynes.[a]

3. Conclusion

We have expanded the substrate scope of Ir-catalyzed dehydrogenative diboration (DHDB) to non-alkynylboronate alkynes from an earlier report utilizing (SiNN)Ir complexes. In the present work, we discovered that the SiNN pincer ligand is not required and that a precatalyst as simple as $[Ir(COD)_2Cl]_2$ can be used under the right conditions. The DHDB reaction is in competition with hydroboration which is also catalyzed by Ir. Although hydrogen is presumably produced as a result of DHDB, hydrogenation of the carbon-carbon double or triple bonds was not observed. For some substrates, the selectivity for DHDB was as high as 9:1. A variety of terminal or internal alkynes produced diboration products under optimized conditions and some diboration products were isolated in a pure form. Although we did not pursue the characterization of the Ir compounds present in the catalytic reaction mixture, the experimental data suggest that DHDB is favored by increasing competitive coordination of CO to Ir.

4. Experimental Section.

4.1. General considerations.

Unless otherwise specified, all reactions and manipulations were carried out under an argon atmosphere using glove box or Schlenk line techniques. Solvents were dried and deoxygenated via the solvent purification system and stored over molecular sieves in the glove box filled with argon. Heptane, THF, toluene, C_6H_5F, C_6D_6 were dried over NaK /Ph_2CO/18-crown-6, distilled and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene and C_6D_5Br were dried over CaH_2, distilled and stored over molecular sieves in an Ar-filled glove box. $[Ir(COD)Cl]_2$ [40], $[Ir(COD)Br]_2$ [41], $[Ir(COD)I]_2$ [42], $[Ir(COE)_2Cl]_2$ [43], $[Ir(COD)OH]_2$ [44], $[Ir(COD)OMe]_2$ [45], (SiNN)Ir(COE) [26] were prepared according to previous literature. Alkynes were deoxygenated by three freeze-pump-thaw cycles or dried under vacuum overnight prior transferring into an Ar-filled glove box. All other chemicals were used as received from commercial vendors. Benzodiazaborole (HBdaz) [46], neopentylglycolborane (HBnpg) [47], and 1,8-naphthalenediaminatoborane (HBdan) [48] were prepared according to published procedures. NMR spectra were recorded on a Varian iNova 300 spectrometer (^{1}H NMR, 299.951 MHz, ^{13}C NMR, 75.413 MHz, ^{31}P NMR, and 121.425 MHz), Varian Inova 400 (^{1}H NMR, 399.535 MHz; ^{11}B NMR, 128.185 MHz) and NMRS 500 (^{1}H NMR, 499.703 MHz; ^{13}C NMR, 125.697 MHz) spectrometer. Chemical shifts are given in δ (ppm). ^{1}H NMR and ^{13}C NMR spectra were referenced using the solvent signals.

4.2. Precatalyst screening for DHDB of 1-phenyl-1-butyne with pinacolborane.

A 64 μL stock solution of Ir catalyst (0.0125 M in C_6H_6, 0.00080 mol) was added to a J. Young tube. After removing C_6H_6 under vacuum, 11.3 μL 1-phenyl-1-butyne (0.080 mol), 42 μL pinacolborane (0.28 mol) and 450 μL heptane was loaded via syringe. The J. Young tube was

degased via freeze-pump-thaw 3 cycles, and then refilled with 1 atm CO. the resulting mixture was heated in 50 °C for 15 h. The solvent was removed under vacuum and 500 μL 0.08 M 1,4-dioxane in C_6D_6 was added. The yields of the diboration and hydroboration products were determined via ^{1}H NMR analysis (500 MHz, C_6D_6, Entry 2 is shown as an example in Figure S1). Diboration product **A1-Bpin2** [49]: δ 7.35 – 7.33 (m, Ph*H*, 2H), 7.18 (t, J_{H-H} = 7.7 Hz, Ph*H*, 2H), 7.03 (tt, J_{H-H} = 7.2, 1.4 Hz, Ph*H*, 1H), 2.42 (q, J_{H-H} = 7.5 Hz, C*H*$_2$CH$_3$, 2H), 1.17 (s, Bpin*H*, 12H), 1.13 (t, J_{H-H} = 7.5 Hz, CH$_2$C*H*$_3$, 3H). 1.12 (s, Bpin*H*, 12H). Hydroboration product **A1-BpinH**: δ 7.39 – 7.37 (m, PhH, 2H) 7.24 (t, J_{H-H} = 7.7 Hz, Ph*H*, 2H), 7.12 (t, J_{H-H} = 7.7 Hz, Ph*H*, 1H) 6.96 (t, J_{H-H} = 7.3 Hz, PhCC*H*, 1H), 2.16 (p, J_{H-H} = 7.5 Hz, C*H*$_2$CH$_3$, 2H), 1.06 (s, Bpin*H*, 12H), 0.84 (t, J_{H-H} = 7.5 Hz, CH$_2$C*H*$_3$, 3H); The reason we assigned the resonances to **A1-BpinH** is that for compound **A1-BpinH** the ethyl CH_2 proton would couple to both the CH_3 proton and alkenyl protons, thus giving rise to a quintet instead of quartet resonances for the CH_2 protons, and triplet instead of singlet resonance for the alkenyl proton [50]. The assignment was also consistent with other reactions that afford different **A1-BpinH**/**A1-HBpin** ratios. Hydroboration product **A1-HBpin**: δ 2 Ph*H* resonances are overlapping with product **A1-Bpin2**, 7.72 (s, PhC*H*C, 1H), 7.08 (t, J_{H-H} = 7.4 Hz, 1H), 1.4 Hz, Ph*H*, 1H), 2.65 (q, J_{H-H} = 7.6 Hz, C*H*$_2$CH$_3$, 2H), 1.27 (t, J_{H-H} = 7.5 Hz, CH$_2$C*H*$_3$, 3H), 1.12 (s, Bpin*H*, 12H);

4.3. Solvent screening for DHDB of 1-phenyl-1-butyne with pinacolborane.

A 64 μL stock solution of [Ir(COD)Cl]$_2$ (0.0125 M in C_6H_6, 0.00080 mol) was added to a J. Young tube. After the benzene was removed under vacuum, 11.3 μL 1-phenyl-1-butyne (0.080 mol), 42 μL pinacolborane (0.28 mol) and 450 μL solvent was loaded via syringe. The J. Young tube was degased through freeze-pump-thaw 3 cycles, and then refilled with 1 atm CO. the resulting mixture was heated in 50 °C for 15 h. The solvent was removed under vacuum and 500

μL 0.08 M 1,4-dioxane in C_6D_6 was added. The yields of the diboration and hydroboration products were determined via ^1H NMR analysis.

4.4. Control experiments.

4.4.1. Reaction of 1-phenyl-1-butyne with bis(pinacolato)diboron catalyzed by [Ir(COD)Cl]$_2$ at 1 atm CO.

To a J. Young tube, 32 μL stock solution of $[Ir(COD)Cl]_2$ (0.0125 M in C_6D_6, 0.00040 mol), 140 μL stock solution of B_2Pin_2 (1.0 M in C_6D_6, 0.28 mol), and 160 μL stock solution of 1-phenyl-1-butyne/1,4-dioxane ([alkyne]: 0.5 M in C_6D_6, 0.080 mol; 1,4-dioxane: 0.25 M in C_6D_6 as internal standard) were loaded via syringe. The J. Young tube was degassed by 3 cycles of freeze-pump-thaw, and then back filled with 1 atm CO. No reaction between alkyne and boron reagents after the tube was heated in 50 °C for 15 h.

4.4.2. Reaction of 1-phenyl-1-butyne with pinacolborane catalyzed by [Ir(COD)Cl]$_2$ at 1 atm Ar.

To a J. Young tube, 32 μL stock solution of $[Ir(COD)Cl]_2$ (0.0125 M in C_6D_6, 0.00040 mol), 280 μL stock solution of borane (1.0 M in C_6D_6, 0.28 mol), and 160 μL stock solution of 1-phenyl-1-butyne/1,4-dioxane ([alkyne]: 0.5 M in C_6D_6, 0.080 mol; 1,4-dioxane: 0.25 M in C_6D_6 as internal standard) were loaded via syringe. The resulting mixture was heated in 50 °C for 18 h. No diboration product A2-$Bpin_2$ was detected by ^1H NMR spectroscopy.

4.4.3. Reaction of 1-phenyl-1-butyne with pinacolborane catalyzed by [Ir(COD)Cl]$_2$ at 1 atm CO, where additional 0.5% [Ir(COD)Cl]$_2$ was added after all the alkyne was converted into diboration and hydroboration products.

A 32 μL stock solution of $[Ir(COD)Cl]_2$ (0.0125 M in C_6D_6, 0.00040 mol) was added to a J. Young tube. Then 240 μL 0.50 M stock solution of 1-phenyl-1-butyne (0.080 mol) in C_6D_6 and 280 μL 1.0 M stock solution of pinacolborane (0.28 mol) in C_6D_6 was loaded via syringe. The J. Young tube was degased via freeze-pump-thaw 3 cycles, and then refilled with 1 atm CO. the resulting mixture was heated in 50 °C for 15 h. 32 μL (0.00040 mol) of iridium catalyst stock solution was added to the resulting mixture followed by the same CO refilling process. The reaction mixture was heated at the same oil bath for another 15 h before the solvent was removed under vacuum and 500 μL 0.08 M 1,4-dioxane in C_6D_6 was added, the ratio of diboration product to hydroboration products remained unchanged.

4.5. ^{t}BuNC-assisted DHDB of 1-phenyl-1-butyne.

To a J. Young tube, 32 μL stock solution of $[Ir(COD)Cl]_2$ (0.0125 M in C_6D_6, 0.00040 mol), 32 μL stock solution of ^{t}BuNC (0.0500 M in C_6D_6, 0.0016 mol), 240 μL stock solution of borane (1.0 M in C_6D_6, 0.24 mol), and 160 μL stock solution of 1-phenyl-1-butyne/1,4-dioxane ([alkyne]: 0.5 M in C_6D_6, 0.080 mol; 1,4-dioxane: 0.25 M in C_6D_6 as internal standard) were loaded via syringe. The J. Young tube was degased via freeze-pump-thaw 3 times, and then refilled with 1 atm CO. The resulting mixture was heated in 50 °C for 15 h. The yields of the diboration and hydroboration products were determined via ^{1}H NMR analysis.

4.6. Borane substrate scope for DHDB of 1-phenyl-1-butyne.

4.6.1. General procedure.

To a J. Young tube, 64 μL stock solution of $[Ir(COD)Cl]_2$ (0.0125 M in C_6D_6, 0.00080 mol), 280 μL stock solution of borane (1.0 M in C_6D_6, 0.28 mol), and 160 μL stock solution of 1-phenyl-1-butyne/1,4-dioxane ([alkyne]: 0.5 M in C_6D_6, 0.080 mol; 1,4-dioxane: 0.25 M in C_6D_6 as internal

standard) were loaded via syringe. The J. Young tube was degassed via freeze-pump-thaw 3 times, and then refilled with 1 atm CO. The resulting mixture was heated in 50 °C for 15 h. The yields of the diboration and hydroboration products were determined via ^{1}H NMR analysis.

4.6.2. Selected NMR data for the products and other reaction observations.

HBcat as boron source (Figure S2): **A1-Bcat2**: δ 7.31 – 7.29 (m, aromatic*H*, 2H), 7.19 (t, J_{H-H} = 7.7 Hz, aromatic*H*, 2H), 7.08 (tt, J_{H-H} = 7.2, 1.4 Hz, aromatic*H*, 1H) 6.93 (dd, J_{H-H} = 5.8, 3.3 Hz, Bcat*H*, 2H), 6.85 (dd, J_{H-H} = 5.9, 3.4 Hz, Bcat*H*, 2H), 6.76 (dd, J_{H-H} = 5.9, 3.3 Hz, Bcat*H*, 2H), 6.70 (dd, J_{H-H} = 5.9, 3.2 Hz, Bcat*H*, 2H), 2.49 (q, J_{H-H} = 7.6 Hz, CH_2CH$_3$, 2H), 1.06 (t, J_{H-H} = 7.6 Hz, CH$_2$CH_3, 3H). **A1-BcatH**: δ aromatic resonances (aromatic*H*) of **A1-BcatH** cannot be differentiated from that of **A1-HBcat**, 2.11 (p, J_{H-H} = 7.5 Hz, CH_2CH$_3$, 2H), 0.83 (t, J_{H-H} = 7.5 Hz, CH$_2$CH_3, 3H). **A1-HBcat**: δ aromatic resonances of **A1-HBcat** cannot be differentiated from that of **A1-BcatH**, 7.82 (s, ArC*H*C, 1H), 2.65 (q, J_{H-H} = 7.6 Hz, CH_2CH$_3$, 2H), 1.23 (t, J_{H-H} = 7.5 Hz, CH$_2$CH_3, 3H).

HBdaz as boron source (Figure S3): around 52% alkyne was converted into a mixture of unidentified products.

HBnpg as boron source (Figure S4): **A1-BnpgH**: δ 7.31 – 7.25 (m, aromatic*H*, 2H), 7.29 – 7.15 (m, aromatic*H*, 2H), 7.14 – 7.08 (m, aromatic*H*, 1H), 6.87 (t, *J* = 7.3 Hz, ArCC*H*, 1H), 3.26 (s, BnpgCH_2, 4H), 2.09 (p, *J* = 7.5, CH_2CH$_3$, 2H), 0.84 (t, *J* = 7.5 Hz, CH$_2$CH_3, 3H), 0.52 (s, BnpgCH_3, 6H). **A1-HBnpg**: δ 7.65 (s, ArC*H*C, 1H), 7.39 – 7.30 (m, aromatic*H*, 2H), 7.08 – 7.01 (m, aromatic*H*, 2H), 3.32 (s, BnpgCH_2, 4H), 2.62 (q, *J* = 7.4 Hz, CH_2CH$_3$, 2H), 1.24 (t, *J* = 7.5 Hz, CH$_2$CH_3, 3H), 0.51 (s, BnpgCH_3, 6H). Around 91% of hydroboration products were formed.

Due to the difficulties on purification of HBnpg as well as low diboration yield, no further study was conducted using this boron source.

HBdan as boron source (Figure S5): **A1-BdanH**: 6.75 (t, *J* = 7.3 Hz, ArCC*H*, 1H), 6.01 (dd, *J* = 6.3, 2.0 Hz, Bdan*H*, 2H), 1.99 (p, *J* = 7.4 Hz, C*H*$_2$CH$_3$, 2H), 0.86 (t, *J* = 7.5 Hz, CH$_2$C*H*$_3$, 3H). **A1-HBdan**: δ 6.05 (dd, *J* = 5.9, 2.5 Hz, Bdan*H*, 2H), 2.21 (q, *J* = 8.4 Hz, C*H*$_2$CH$_3$, 2H). With only 20% of the alkyne was converted, alkenyl proton resonances of hydroboration product **A1-HBdan** could be overlapped with aromatic proton resonances, which make it difficult to conclude whether **A1-HBdan** or **A1-Bdan2** is formed. However, based on the ratio of CH_2 resonance to Bdan resonance (1:1), it is more likely the hydroboration product **A1-HBdan** (9%). According to the coupling between alkenyl proton and ethyl CH_2 proton in **A1-BdanH**, it would be reasonable to claim that 11% of **A1-BdanH** was formed. Therefore, for this borane no DHDB product was formed.

4.7. Alkyne substrate scope of DHDB.

4.7.1. General procedure.

To a J. Young tube, 20 μL stock solution of [Ir(COD)Cl]$_2$ (0.010 M in C_6D_6, 0.00020 mol), 40 μL stock solution of ^{t}BuNC (0.040 M in C_6D_6, 0.00160 mol), 44 μL (0.30 mol) HBpin, 0.1 mmol of alkyne and 400 μL isooctane were loaded via syringe in the Glove box. The J. Young tube was degased via freeze-pump-thaw 3 cycles, and then refilled with 1 atm CO. The resulting mixture was heated in 50 °C for 15 h. The yield of diboration and hydroboration was revealed by ^{1}H NMR analysis.

4.7.2. Selected product data.

A2-Bpin2 (Figure S6): ^{1}H NMR (500 MHz, C_6D_6): δ 7.65-7.63 (m, Ar*H*, 2H), 7.13 (t, J_{H-H} = 7.6 Hz, Ar*H*, 2H), 7.00 (m, Ar*H*, 1H), 6.63 (s, ArCC*H*, 1H), 1.23 (s, Bpin*H*, 12H), 1.12 (s, Bpin*H*, 12H). **A5-Bpin2** (Figure S9): ^{1}H NMR (500 MHz, C_6D_6): δ 7.65-7.64 (m, Ar*H*, 2H), 7.23-7.22 (m, Ar*H*, 2H), 6.69 (s, ArCC*H*, 1H), 1.27 (s, Bpin*H*, 12H), 1.17 (s, ^{t}Bu*H*, 9H), 1.13 (s, Bpin*H*, 12H). **A6-Bpin2** (Figure S10): ^{1}H NMR (500 MHz, C_6D_6): δ 7.60-7.59 (m, Ar*H*, 2H), 6.93-6.91 (m, Ar*H*, 2H), 6.61 (s, ArCC*H*, 1H), 1.26 (s, Bpin*H*, 12H), 1.16 (s, ^{t}Bu*H*, 9H), 1.13 (s, Bpin*H*, 12H).

4.8 Preparative-scale of DHDB.

4.8.1. General procedure.

To a 25 mL PTFE-valved gas-tight flask, 6.7 mg (0.01 mmol) $[Ir(COD)Cl]_2$, 11 μL (0.08 mmol) ^{t}BuNC, 2.0 mmol alkyne and 871 μL (6.0 mmol) HBpin was loaded in an Argon-filled glove box. The flask was taken out of the box and degassed via freeze-pump-thaw 3 times, and then refilled with 1 atm CO. The resulting mixture was heated in 50 °C for 15 h. The flask was transferred to the box, and the volatile was removed under vacuum. The diboration product was then isolated by the following methods. For **A3** and **A7**: the residue was dissolved with toluene and filtered through a short pad of Celite. Toluene solution was concentrated and then layered with pentane. Crystalline solid **A3-Bpin2** and **A7-Bpin2** were collected after slow diffusion overnight at -35 °C freezer. For **A4**: **A4-Bpin2** was purified by chromatography on silica gel with 2:1 hexane:acetone.

4.8.2. Product yields and NMR data.

A3-Bpin2: white solid, isolated yield: 528 mg (61%) ^{1}H NMR (500 MHz, $CDCl_3$, Figure S12) δ 7.01-7.08 (m, 6H, Ar*H*), 6.95-6.96 (m, 4H, Ar*H*), 1.32 (s, 24H, Bpin CH_3). ^{13}C NMR (125 Hz,

$CDCl_3$, Figure S13) δ 141.38, 129.43, 127.53, 125.90, 84.17, 25.00. HR-MS (EI) calcd for $C_{26}H_{35}B_2O_4$: 433.2716; found 433.2709. The NMR data were consistent with literature values [9].

A7-Bpin2: white solid, isolated yield: 622 mg (63%) ^{1}H NMR (500 MHz, $CDCl_3$, Figure S16) δ 7.18 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, Ar*H*), 7.03 (d, *J* = 7.8 Hz, 2H, Ar*H*) 2.29 (s, 3H, ArCH_3), 1.30 (s, 12H, BpinCH_3), 1.27 (s, 12H, BpinCH_3), 1.10 (s, 12H, BpinCH_3). ^{13}C NMR (125 Hz, $CDCl_3$, Figure S17) δ 142.41, 136.36, 128.44, 127.75, 83.90, 83.47, 83.22, 25.02, 24.94, 24.64, 21.31. HR-MS (EI) calcd for $C_{27}H_{44}B_3O_6$: 496.3448; found 496.3405.The NMR data were consistent with literature values [25].

A4-Bpin2: colorless oil, yield: 340 mg (50%); ^{1}H NMR (500 Hz, $CDCl_3$, Figure S14) δ 0.87 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 3H), 1.26 (s, 12H, BpinCH_3), 1.31 (s, 12H, BpinCH_3), 1.19-1.31 (m, 6H), 1.34-1.45 (m, 2H), 2.21 (t, $^3J_{H\text{-}H}$ = 7.1Hz, 2H), 5.85 (s, 1H). ^{13}C NMR (125 Hz, $CDCl_3$, Figure S15) δ 83.72, 83.35, 39.67, 30.91, 25.03, 25.00, 22.56, 14.10. HR-MS (EI) calcd for $C_{18}H_{35}B_2O_4$: 337.2716; found 337.2708. The NMR data were consistent with literature values [**Error! Bookmark not defined.**].

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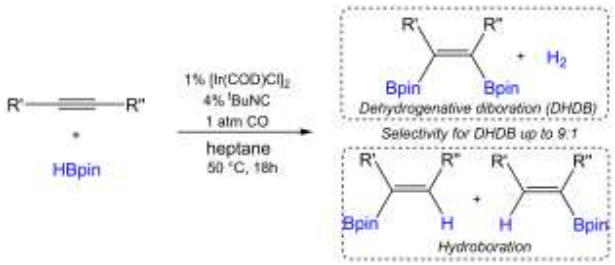
Appendix A. Supplementary data.

Supplementary data to this article can be found online.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



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