Synthesis of Stereodefined 1,1-Diborylalkenes *via* Copper-Catalyzed Diboration of Terminal Alkynes

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Supporting Information Placeholder

ABSTRACT: A copper-catalyzed method for the *E*-selective 1,1-diboration of terminal alkynes is described. The tandem process involves sequential dehydrogenative borylation of the alkyne substrate with HBdan (HBdan = 1,8-diaminonaphthalatoborane), followed by hydroboration with HBpin (HBpin = pinacolborane). This method proceeds efficiently under mild conditions, furnishing 1,1-diborylalkenes with excellent stereoselectivity and broad functional-group tolerance. Taking advantage of the different reactivities of the two boryl moieties, the products can then be employed in stepwise cross-couplings with aryl halides for the stereocontrolled construction of trisubstituted alkenes.
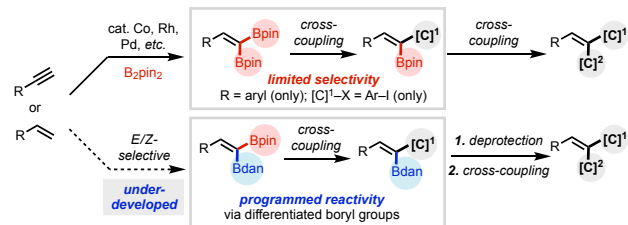
Alkenyl boronic acids and their derivatives are non-toxic, shelf-stable organometallic compounds that react with high fidelity in a range of C–C and C–heteroatom couplings, making them useful reagents in organic synthesis.[1] 1,1-Diborylalkenes are an emerging subclass that offer exciting potential for accessing multisubstituted olefins in a stereocontrolled manner through sequential reaction at each of the two C–B bonds.[2] To this end, many approaches to synthesize 1,1-diboryl alkenes bearing two -Bpin groups (Bpin = pinacolatoboryl) have been developed from alkene[2c,3] and alkyne starting materials.[4] When such compounds are then employed in cross-coupling, the inherently similar reactivity of the two C–Bpin bonds makes it challenging to achieve high selectivity for a mono-functionalized product. Indeed, successful mono-selectivity at the less hindered position has only been demonstrated when the 1,1-diborylalkene contains an aryl group at the 2-position and when an aryl iodide is employed as the electrophile (Scheme 1 A).[2c,4b]

We reasoned that the scope of substrates and coupling partners could be expanded if the two boron centers were differentially protected with one –(pin) (pin = pinacolate) and one –(dan) (dan = 1,8-diaminonaphthalenyl) group (Scheme 1 A). The Bdan group is well known to possess diminished Lewis acidity, and to be generally inactive toward transmetalation, a key step of cross-coupling.[5] This so-called protected boron moiety can be reactivated by either deprotection under acidic condition,[5] or interaction with KOtBu or Ba(OH)₂.[6] The sequential masking/unmasking strategy enabled by the Bdan group has been successfully applied to iterative cross-coupling, providing efficient and concise approaches to functional organic molecules including complex oligorenes,[5a-c,6c] and optoelectronic materials.[5d] Moreover, these isomerically pure 1,1-diborylalkenes represent a promising class of prochiral substrates to generate enantioenriched 1,1-diborylalkanes,[7] that are valuable versatile building blocks to access enantioenriched functionalized alkanes.[8]
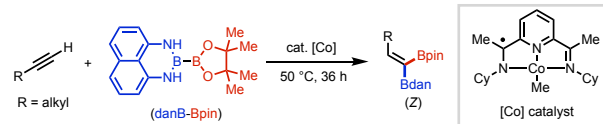
In view of the unique synthetic value of differentially protected 1,1-diborylalkenes, practical synthetic methods to access such complexes in a stereodefined manner are desirable. However, few methods are currently available. In 2017, Chirik and colleagues described a Co-catalyzed 1,1-diboration of aliphatic alkynes to synthesize (*Z*)-1,1-diborylalkenes with use of the mixed diboron reagent pinB–Bdan (Scheme 1 B).[4b] Later, Marder reported a base-catalyzed stereoselective diboration of alkynyl esters and amides with pinB–Bdan (Scheme 1 C).[9] Both methods,

though highly enabling in their own right, have limited substrate scope and only provide access to the *Z*-configured products.
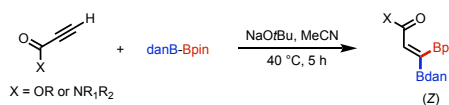

Scheme 1. (A) Synthesis and reactivity of 1,1-diborylalkenes. (B), (C) Prior art to access Z-configured 1,1-diborylalkenes. (D) This work.

Driven by our interest in developing new metal-catalyzed alkyne difunctionalization methods, we recently reported a CuH-catalyzed cascade process to access enantioenriched α-aminoboron compounds via sequential hydroboration and hydroamination of terminal alkynes.[10] Here we report an exclusively *E*-selective Cu-catalyzed three-component reaction to produce 1,1-diborylakenes through a tandem sequence comprised of dehydrogenative C(sp)−H borylation with HBdan and hydroboration of the resulting alkynylBdan intermediate with HBpin (Scheme 1 D).

Our investigation commenced by examining reaction conditions using phenylacetylene (**1a**) as pilot substrate, with HBdan and HBpin as coupling partners. After extensive optimization, we identified an effective protocol in which HBdan is first mixed with **1a** in the presence of 5 mol% Cu(OAc)₂ and 5 mol% (*Rₐ*)-DTBM-SEGPHOS in THF for 15 min. After this period HBpin is added, and the reaction is allowed to stir for an additional 16 h at room temperature, at which point the desired product **2a** is isolated in 69% yield. (Table 1, entry 1) The timing of HBpin addition was found to be important. The yield of **2a** decreased when HBpin added earlier, with larger amount of side products observed (Table 1, entries 2–3).

Another key finding from these studies was that acetate counteranion and (*Ra*)-DTBM-SEGPHOS ligand were both required (Table 1, entries 4–12). CuOAc was slightly less effective than Cu(OAc)$_2$ (Table 1, entry 4), while other copper sources such as CuBr and CuCl, together with NaO*t*Bu, showed no catalytic activity. In terms of other ligands tested, (*Ra*)-DM-SEGPHOS gave slightly lower yield of **2a** than (*Ra*)-DTBM-SEGPHOS (Table 1, entry 12). Other phosphine ligands unfortunately led to either low yield or no reaction. There was no reaction in the absence of a ligand (Table 1, entry 13). The structure and (*E*)-stereochemical configuration of **2a** were unambiguously assigned by X-ray crystallography (Table 2, top left).

Table 1. Optimization of reaction conditions for Cu-catalyzed 1,1-diboration of phenylacetylene.

Entry[a]	variation from standard conditions	Yield[b]	
		2a	**2aa + 2ab**
1	none	69%	17%
2	HBpin added after 8 min	52%	23%
3	HBpin added together with **1a**	31%	20%[c]
4	CuOAc in place of Cu(OAc)$_2$	55%	20%
5	CuBr in place of Cu(OAc)$_2$[d]	0	0
6	CuCl in place of Cu(OAc)$_2$[d]	0	0
7	PPh$_3$ as ligand	23%	5%
8	PCy$_3$ as ligand	0	0
9	dppp as ligand	4%	0
10	dppf as ligand	9%	4%
11	(*Ra*)-SEGPHOS as ligand	23%	5%[e]
12	(*Ra*)-DM-SEGPHOS as ligand	64%	10%[e]
13	No ligand	0	0
14	toluene as solvent	48%	46%

[a]Standard reaction conditions: **1a** (0.10 mmol), HBdan (0.11 mmol), HBpin (0.12 mmol), Cu(OAc)$_2$ (5 mol%), and (*Ra*)-DTBM-SEGPHOS (5 mol%) in THF (0.25 mL). [b]^{1}H NMR yield using CH$_2$Br$_2$ as internal standard. [c]10% of PhCHCH(Bpin) was also observed. [d]Together with NaO*t*Bu (10%). [e]9% of PhCHC(Bpin)$_2$ was observed.

Next, we evaluated the scope and functional group compatibility of this stereoselective process (Table 2). The reactions with aryl-substituted alkynes were found sensitive to both electronic and steric effects. Aryl acetylenes with electron-donating groups normally performed better than those with electron-withdrawing groups. For example, *p*-MeO-substituted phenylacetylene gave product **2c** in 70% yield, while *p*-CF$_3$-substituted phenylacetylene gave product **2f** in 47% yield. Diboration of *para*-substituted phenylacetylenes generally occurred smoothly while *meta*- and *ortho*-substituted phenylacetylenes gave relatively low yield. A range of functional groups, such as halides (**2e, 2k, 2l, 2m**), an ester (**2g**), ethers (**2c, 2i**) and amines (**2d, 2j**), were well tolerated. 2-Ethynylnaphthalene and 3-ethynylthiophene underwent diboration as well to give corresponding 1,1-diborylalkenes (**2h, 2n**).
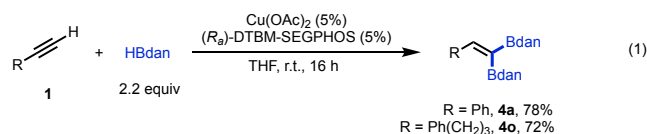
1,1-Diboration was similarly effective with aliphatic alkynes, furnishing the corresponding *E*-configured products as well. The structure of 1,1-diborylalkene **2o** was confirmed by X-ray crystallography (Table 2, bottom left). Remarkably, 1-ethynylcyclohexene underwent 1,1-diboration to furnish product **2s** with C=C double bond intact. Functional groups like carbonate (**2p**), ether (**2q**) and silyl ether (**2t**) were tolerated with products isolated in useful yields.

**Table 2**. Copper-catalyzed stereoselective 1,1-diboration of terminal alkynes.[a]

[a]Conditions: 0.10 mmol scale, THF (0.25 mL). Percentages correspond to isolated yields.

Interestingly, when terminal alkynes **1** were reacted with 2.2 equiv HBdan in the absence of HBpin, 1,1-homodiboration proceeded smoothly, furnishing 1,1-diborylalkenes **4** bearing two -Bdan groups in excellent yields (eq. 1).

To illustrate the practical utility of this procedure, we performed stepwise Suzuki–Miyaura cross-couplings of 1,1-diborylalkenes (Scheme 2). The selective monoarylation of **2a** worked well using 4-iodotoluene as coupling partner under standard cross-coupling conditions, giving 92% **5a** after 12 h at 30 °C. Notably, the reaction with 4-bromotoluene also proceeded, albeit at a higher temperature of 80 °C, giving product **5a** in 85% yield with no diarylation product detected. Next, the Bdan group of **5a** was deprotected, and the resulting boronic acid was carried forward without purification in a second cross-coupling reaction with 4-iodoanisole to produce triarylated alkene **6a** as a single stereoisomer.
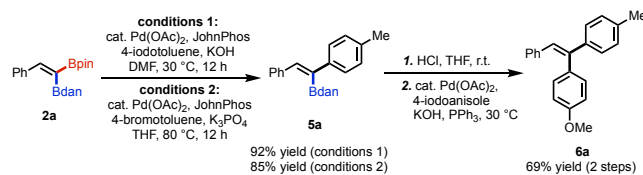
Scheme 2. Stepwise Suzuki–Miyaura coupling reactions of **2a**.

Having established the scope and utility of the (*E*)-selective alkyne 1,1-diboration method, we shifted our attention to investigating the reaction mechanism. Subjecting sterically bulky mesitylacetylene to the standard reaction conditions did not lead to formation of the typical 1,1-diborylated product; instead, alkynylBdan **3u** was isolated in 55% yield (eq. 2). This result suggests that alkynylBdan is the product from first

step of the tandem process and that the second hydroboration step is sensitive to steric hindrance. Consistent with this notion, the reaction between **2a** and HBdan before addition of HBpin was monitored by ^{1}H NMR spectroscopy (eq. 3), and 16% alkynylBdan **3a** and H_2 were both observed after 30 min (SI, Figure S1). To further support our hypothesis, the proposed intermediate **3a** was independently synthesized and submitted to the reaction with HBpin under the standard conditions. Hydroboration of **3a** proceeded smoothly to furnish **2a** in 60% yield (eq. 4).
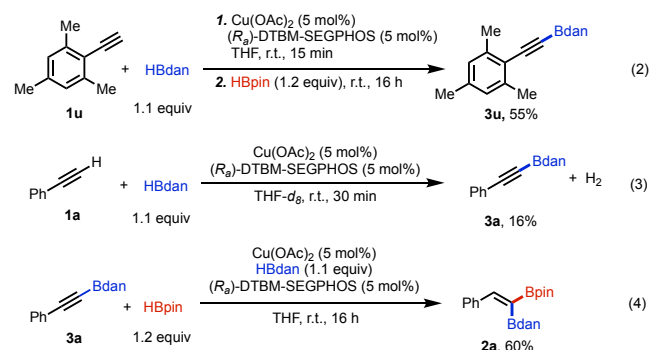
Based on our experimental observations and previous reports,[11-13] a Cu-catalyzed tandem process comprised of dehydrogenative borylation of terminal alkynes and following hydroboration is proposed (Scheme 3). [LCuOAc] **a1**, generated by reduction of $Cu(OAc)_2$ in the presence of phosphine,[14] reacts with terminal alkynes to give the alkynylcopper intermediate **a2** and HOAc.[13b,15] Following σ-bond metathesis between **a2** and HBdan gives alkynylBdan **3** and [LCuH] **a3**.[11,16] *syn*-Insertion of **a3** to intermediate **3** generates alkenyl copper species **a4**,[12,13,17] which then undergoes σ-bond metathesis with HBpin to furnish the (*E*)-1,1-diborylalkenes and regenerate [LCuH] **a3**.

Under the optimal conditions, prior to addition of HBpin, the right cycle alone proceeds through several turnovers to build up **3a**, and upon addition of HBpin the left cycle turns on. This strategy limits the formation of side products caused by the high reactivity of HBpin. In the 1,1-homodiboration system with HBdan only, both cycles presumably proceed in parallel.[18]

In conclusion, we have reported the first (*E*)-selective synthesis of 1,1-diborylalkenes bearing one -Bpin group and one -Bdan group from terminal alkynes *via* a Cu-catalyzed tandem process. A wide range of aryl- and alkyl-substituted alkynes underwent this transformation, giving the corresponding 1,1-diborylalkenes with broad functional group tolerance. We have also demonstrated that differentially protected 1,1-diborylalkenes are useful synthetic intermediates for the construction of multi-substituted alkenes with stereocontrol. Further applications of 1,1-diborylalkenes for the synthesis of more complex compounds are being pursued in our laboratory.
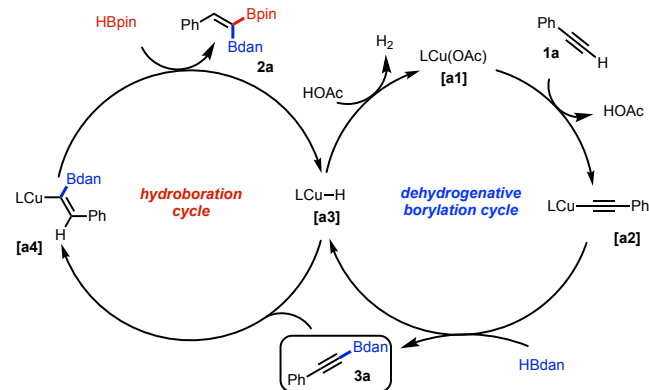
Scheme 3. Proposed mechanism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at DOI: [filled later].

Detailed experimental procedures and compound characterization (PDF)
Crystallographic data for **2a** (CIF)
Crystallographic data for **2o** (CIF)

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Notes

The authors declare no competing financial interests.

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(18) In the 1,1-homodiboration reaction of phenylacetylene with HBdan, the dehydrogenative borylation cycle was found much faster than the hydroboration cycle. After 2 h, 50% of **3a** and less than 5% of **4a** were observed by ¹H NMR spectroscopy.

TOC graphic
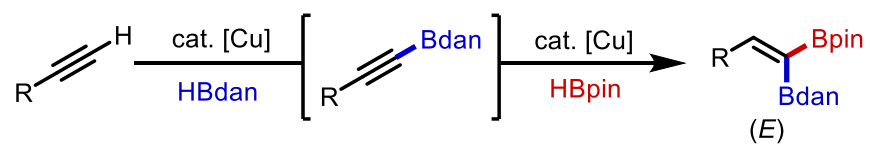
- *exclusive E-selectivity* • *broad scope* • *mild conditions*
- *sequential cross-couplings of the two C–B bonds*