Homogeneous Catalysis

International Edition: DOI: 10.1002/anie.201510132
German Edition: DOI: 10.1002/ange.201510132

Catalytic Borylative Opening of Propargyl Cyclopropane, Epoxide, Aziridine, and Oxetane Substrates: Ligand Controlled Synthesis of Allenyl Boronates and Alkenyl Diboronates

*Jian Zhao and Kálmán J. Szabó**

Dedicated to Professor Todd B. Marder on the occasion of his 60th birthday

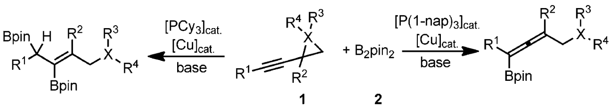
Abstract: *A new copper-catalyzed reaction for the stereo- and regioselective synthesis of alkenyl diboronates and allenyl boronates is presented. In this process propargyl derivatives of strained three/four-membered rings were employed as substrates and B_2pin_2 was used as the boronate source. Selective formation of the alkenyl diboronate versus the allenyl boronate products was controlled by the choice of phosphine ligand.*

Allyl, alkenyl, and allenyl boronates are very useful reagents in stereoselective synthesis, in particular for synthesis of natural products.[1] However, selective synthesis of these organoboron compounds is still a very challenging task in organic synthesis because of the specific properties of the carbon–boron bonds conjugated with carbon–carbon double bonds. Synthesis of functionalized allyl boronates and boronic acids is probably the most developed area in the field of preparation of unsaturated boronates.[2] Recently, the synthesis and application of alkenyl diboronates, in which one of the carbon–boron bonds is in the vinylic position and the other is in the allylic position, has attracted a lot of attention.[3] The reason for the attraction is that the two types of carbon–boron bonds may undergo either orthogonal functionalization or consecutive functionalization, thus creating molecular complexity in a single reaction step with high stereoselectivity. Another emerging area is allenylboration of carbonyl compounds.[4] This powerful synthetic transformation requires a diversity of allenyl boronates. However, synthesis of stereodefined functionalized allenylboronates is still a major challenge in organic synthesis.[3a,5]

The first platinum catalyzed diboration of allenes for the preparation of alkenyl diboronates was reported by Miyaura and co-workers.[6] Subsequently, a series of studies based on palladium-catalyzed reactions was published by the groups of Cheng[7] and Morken.[3e,g] Recently, transition-metal-free diboration of allenes was also reported.[3i] The groups of Hoveyda,[8] Tsuji,[9] Ma,[10] and others[11] published several studies on the efficient synthesis of alkenyl boronates by copper-catalyzed hydroboration of allenes using diboronates. However, copper-catalyzed hydroboration of allenyl boronates is an unexplored area in organic synthesis.

Opening of a strained ring bearing a propargylic moiety is an efficient approach for the synthesis of functionalized allenes.[12] Recently, we reported[3a] a new method for the synthesis of allenyl boronates based on catalytic borylation of propargyl carbonates and related compounds. We also attempted to prepare allenyl boronates by borylative ring opening of propargylic epoxides. These efforts remained fruitless, as the reaction led to formation of bis(borodiene)s, probably via allenyl boronate intermediates.

We have now found that by appropriate choice of the catalytic system, in particular the employed phosphine ligand, the outcome of the borylation reaction can be fully controlled. When the reaction with a propargylic cyclopropane (**1**; or other strained rings) and B_2pin_2 (**2**) was carried out with a copper catalyst in the presence of PCy_3 (Cy = cyclohexyl) the reaction resulted in alkenyl diboronates [Eq. (1)]. However, when the same reaction conditions were used in the presence of the bulky $P(1\text{-nap})_3$ (1-nap = 1-naphthyl) ligand, the reaction led to an allenyl boronate product.



(1)

First we optimized the reaction of the borylative opening of the propargylic cyclopropane derivative **1a** (Table 1). When **1a** was reacted with 3 equivalents of B_2pin_2 (**2**) in the presence of *t*BuOK and a catalytic amount of CuCl, the alkenyl diboronate **3a** and allenyl boronate **4a** were formed in 3:97 ratio with 61% yield (entry 1). The reaction could be carried out at room temperature, and is beneficial as the borylated product may undergo protodeborylation or other undesired transformations at elevated temperatures. Use of CuI instead of CuCl led to exclusive formation of **4a**, albeit with a lower yield (entry 2). In this case a large amount of unreacted starting material, **1a**, remained. We found that addition of alcohols substantially improved the yield. By using

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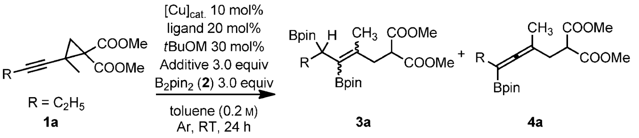
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510132.

Table 1: Development of copper-catalyzed mono- and diboration of **1a**.[a]



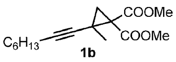
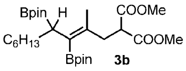
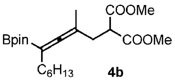
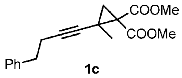
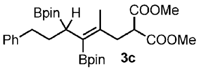
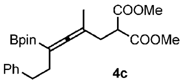
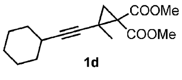
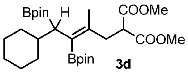
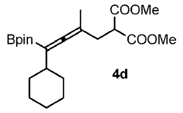
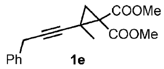
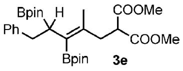
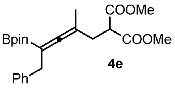
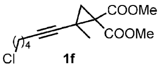
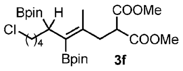
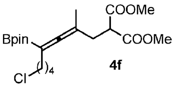
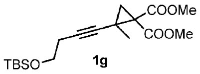
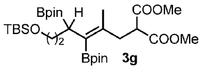
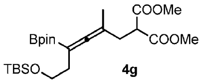
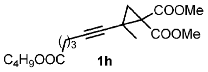
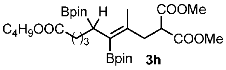
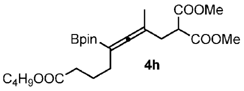
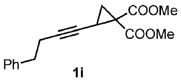
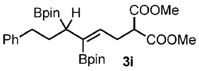
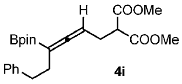
Entry	$[Cu]_{cat.}$	Ligand	M	Additive	(*E*)-**3a**/ (*Z*)-**3a**/**4a**[b]	Yield [%][c]
1	CuCl	PCy_3	K	–[d]	3:0:97	61
2	CuI	PCy_3	K	–[d]	0:0:100	47
3	CuI	PCy_3	K	MeOH	32:3:65	93
4	CuI	PCy_3	K	*t*BuOH	96:4:0	(88)
5	CuI	PPh_3	K	*t*BuOH	80:9:11	94
6	CuI	$P(C_6H_4\text{-}p\text{-}OMe)_3$	K	*t*BuOH	33:3:64	91
7	CuI	P(1-nap)$_3$	K	*t*BuOH	18:0:82	83
8	CuI	P(2,4,6-tri-methylphenyl)$_3$	K	*t*BuOH	5:0:95	67
9	CuI	P(1-nap)$_3$	Li	*t*BuOH	0:0:>99	(76)
10[e]	CuI	P(1-nap)$_3$	Li	*t*BuOH	0:0:>99	(74)
11[f]	CuI	P(1-nap)$_3$	Li	*t*BuOH	0:0:>99	(68)

[a] Reaction conditions: **1a** (0.10 mmol), B_2Pin_2 (**2**; 3.0 equiv), Cu catalyst (10 mol %), ligand (20 mol %), *t*BuOM (30 mol %), and additive (3.0 equiv) in toluene (0.2 M) were reacted at RT for 24 h under Ar. [b] The ratio was determined from ^1H NMR analysis of the crude reaction mixture. [c] Combined yield as determined by ^1H NMR spectroscopy using naphthalene as an internal standard. The yields of the isolated products are shown within parentheses. [d] Without any additive. [e] B_2Pin_2 (1.3 equiv) and *t*BuOH (2.0 equiv) were used. [f] The reaction was carried out for 72 h.

MeOH the yield was indeed improved, but lowered the **3a**/**4a** selectivity (entry 3). However, application of *t*BuOH (instead of MeOH) maintained the high yield and gave an excellent **3a**/**4a** selectivity and *E*/*Z* ratio (entry 4). Application of PCy_3 was very important for the selectivity of the reaction. The **3a**/**4a** selectivity decreased when PCy_3 was replaced with either PPh_3 or $P(C_6H_4\text{-}p\text{-}OMe)_3$ (entries 5 and 6). When PCy_3 was replaced with a more bulky ligand, such as P(1-nap)$_3$ or P(2,4,6-trimethylphenyl)$_3$, the **3a**/**4a** selectivity was shifted toward formation of **4a** (entries 7 and 8). Noticeably, by using P(2,4,6-trimethylphenyl)$_3$, **4a** was formed with high selectivity, but the yield was reduced (entry 8). The high yield and high selectivity could also be achieved when P(1-nap)$_3$ was used and *t*BuOK was replaced by *t*BuOLi (see entries 7 and 9). Apparently, a slight change in basicity was beneficial for the allenyl selectivity. In the above optimization studies, we used 3 equivalents of **2** to allow either disubstitution (**3a**) or monosubstitution (**4a**). However, the amount of B_2pin_2 can be reduced to 1.3 equiv without significant change in the yield of **4a** (entry 10). The very high allenyl selectivity could be maintained, even if the reaction time was extended to 72 hours with using 3 equivalents B_2pin_2 (entry 11). In the absence of the copper salt and the ligand, the borylated products **3a**/**4a** were not observed.

With the optimal reaction conditions in hand, we studied the synthetic scope of the reaction. Similar to **1a**, either **1b** or **1c** reacted with **2** in the presence of catalytic amounts of CuI and PCy_3 (Method A) to give the diborylated products **3b** and **3c**, respectively, at room temperature with excellent *E*/*Z* ratios (Table 2, entries 1 and 3). By changing the ligand to

Table 2: Borylative opening of propagyl cyclopropanes.

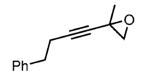
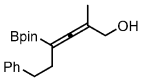
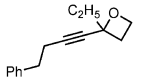
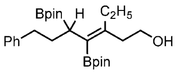
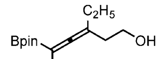
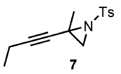
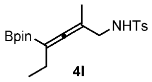
Entry	Substrates	Method[a]	Product	Yield [%][b]
1	 **1b**	A	 **3b**	87 *E*/*Z* 21:1
2	**1b**	B	 **4b**	73
3	 **1c**	A	 **3c**	75 *E*/*Z*19:1
4	**1c**	B	 **4c**	61
5	 **1d**	A[c]	 **3d**	83 *E*/*Z* 25:1
6	**1d**	B[d]	 **4d**	93
7	 **1e**	A[e]	 **3e**	67 *E*/*Z* >20:1
8	**1e**	B[e]	 **4e**	56
9	 **1f**	A	 **3f**	93 *E*/*Z* 22:1
10	**1f**	B[e]	 **4f**	56
11	 **1g**	A	 **3g**	83 *E*/*Z* 29:1
12	**1g**	B	 **4g**	73
13	 **1h**	A	 **3h**	85 *E*/*Z* >20:1
14	**1h**	B	 **4h**	66
15	 **1i**	A[f]	 **3i**	62 *E*/*Z* >20:1
16	**1i**	C[g]	 **4i**	51% mono/di >96:4

[a] Method A: a mixture of **1** (0.10 mmol), **2** (0.30 mmol), CuI (10 mol %), PCy_3 (20 mol %), *t*BuOK (30 mol %),and *t*BuOH (3.0 equiv) in toluene (0.2 M) was reacted at RT for 24–48 h under Ar. Method B: **1** (0.10 mmol), **2** (0.13 mmol), CuI (10 mol %), P(1-nap)$_3$ (20 mol %), *t*BuOLi (30 mol %), and *t*BuOH (2.0 equiv) in toluene (0.2 M) was reacted at RT for 24–48 h under Ar. [b] Yield of isolated product. The *E*/*Z* ratio was determined by ^1H NMR analysis of the crude reaction mixture. [c] The reaction was performed at 35 °C for 48 h. [d] The reaction was performed for 36 h. [e] The reaction was performed for 48 h. [f] The reaction was performed at 15–20 °C for 48 h. [g] CuCl (10 mol %), PCy_3 (20 mol %), *t*BuOK (30 mol %) were used. TBS = *tert*-butyldimethylsilyl.

P(1-nap)$_3$ (Method B) the outcome of the reaction was different (entries 2 and 4), and resulted in the allenyl boronates **4b** and **4c**, with no formation of either **3b** or **3c**. A bulky alkynyl substituent, such as in **1d**, led to slower borylation, and therefore the reaction was either conducted at 35 °C (entry 5) or the reaction time was extended (entry 6). By using PCy$_3$ (Method A) **3d** was formed with a high diastereoselectivity ($E/Z = 25{:}1$), while with P(1-nap)$_3$ (Method B) the reaction resulted in a high yields of the allenyl boronate **4d**. The reaction tolerated several functional groups, such as chloro, ether, ester groups (entries 9–14). Gratifyingly, the outcome and the selectivities of the reactions using **1f–h** as substrates were similar to those for **1b–e**. In most cases, we used disubstituted methy-propargyl-type cyclopropane derivatives to obtain tetrasubstituted allenyl boronates. However, trisubstituted allenyl boronates (such as **4i**) or less-substituted alkenyl diboronates (such as **3i**) can also be obtained by using the propargyl cyclopropane **1i** (entries 15 and 16). In the case of the synthesis of **4i** the reaction conditions were slightly changed. By using CuI and P(1-nap)$_3$ (Method B) a protodeborylation of **4i** occurred, therefore we used catalytic amounts of CuCl and PCy$_3$ (Method C) to improve the yield of **4i.**

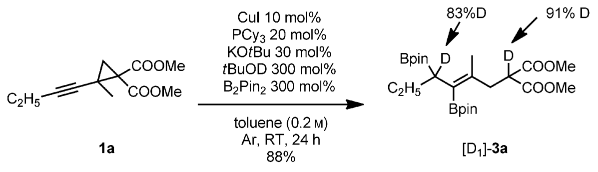
We found that the borylative opening of the propargylic cyclopropanes **1a–i** can be extended to propargylic substrates with other strained rings (Table 3), such as the epoxide **5**, oxetane **6**, and aziridine **7**. The ligand effects on the outcome of the reaction were identical to those of the reactions for **1**. By using bulky P(1-nap)$_3$ (Method B) the reaction resulted in allenyl boronate products, such as **4j** (entry 1), **4k** (entry 3), and **4l** (entry 4). However, by using PCy$_3$ (Method A), the reaction led to formation of the diborylated product **3j** (entry 2). It is interesting to point out that according to our previous studies,[3a] the epoxide **5** gave the diborylated product when PCy$_3$ (or PPh$_3$) was employed under similar reaction conditions. The solution for stopping the reaction at the formation of the allenyl boronate product was to use the bulky P(1-nap)$_3$ ligand (entry 1). In the above reactions (Tables 2 and 3), we observed full ligand control. Except for formation of **4i** (Table 2, entry 16) and **4j** (Table 3, entry 1), the reaction resulted in a single borylated product.

Table 3: Extension of the scope of the reaction to propargylic epoxide, oxetane, and aziridine substrates.

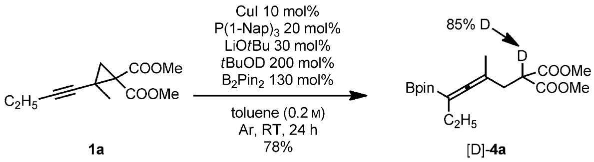
Entry	Substrates	Method[a]	Product	Yield [%][b]
1[c]	 **5**	B[d]	 **4j**	74
2	 **6**	A	 **3j**	64 E/Z >10:1
3	**6**	B[e]	 **4k**	64
4	 **7**	B[f]	 **4l**	56

[a] Method A: a mixture of **1** (0.10 mmol), **2** (0.30 mmol), CuI (10 mol %), PCy$_3$ (20 mol %), *t*BuOK (30 mol %), and *t*BuOH (3.0 equiv) in toluene (0.2 M), was reacted under Ar at RT for 24 h. Method B: **1** (0.10 mmol), **2** (0.13 mmol), CuI (10 mol %), P(1-nap)$_3$ (20 mol %), *t*BuOLi (30 mol %), and *t*BuOH (2.0 equiv) in toluene (0.2 M) was reacted at RT for 24 h under Ar. [b] Yield of isolated product. The E/Z ratio was determined by ^{1}H NMR analysis. [c] In this reaction about 7% of the bis(borodiene) product was also formed. [d] *t*BuOK (30 mol %), MeOH (2.0 equiv) was used instead of *t*BuOLi (30 mol %) with *t*BuOH (2.0 equiv). [e] *t*BuOK (30 mol %) was used instead of *t*BuOLi (30 mol%) and *t*BuOH (2.0 equiv). [f] The reaction was performed for 48 h. Ts = 4-toluenesulfonyl.

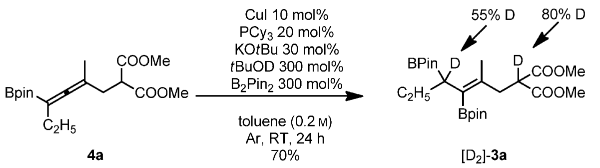
We briefly studied the mechanistic aspects of the process. The reactions proceeded with high yields and selectivities required *t*BuOH as an additive. Our isotope-labelling studies showed that *t*BuOH served as proton source of the process [Eqs. (2)–(4)]. When we added *t*BuOD and PCy$_3$ to the reaction of **1a** and **2** the alkenyl diboronate product [D$_1$]-**3a** was formed [Eq. (2)]. In this compound we observed deuterium uptake at two positions: at the position α to the COOMe groups and at the allylic positions. In case of using P(1-nap)$_3$ as the ligand under similar reaction conditions the allenyl boronate [D]-**4a** was obtained with deuterium uptake only at the position α to the COOMe groups [Eq. (3)]. The isolated **4a** with **2** in the presence of PCy$_3$ resulted in [D$_2$]-**3a** [Eq. (4)]. In this case the deuterium uptake is somewhat lower than for the reaction of **1a** [Eq. (2)]. A possible reason is that **4a** contains an exchangeable proton (α-position to the carbonyls).



(2)



(3)



(4)

Based on the deuterium-labelling studies [Eqs. (2)–(4)] and the above results in Tables 1 and 2, we constructed plausible catalytic cycles, using **1a** an example, and *t*BuOH as the additive (Figure 1). We suggest that CuI in the presence of *t*BuOM (M = K, Li) and either P(1-nap)$_3$ or PCy$_3$ undergoes transmetallation[13] with **2** to give the complex **8**. The complex **8** is selectively inserted[8a,9,14] into the triple bond of **1a** to give

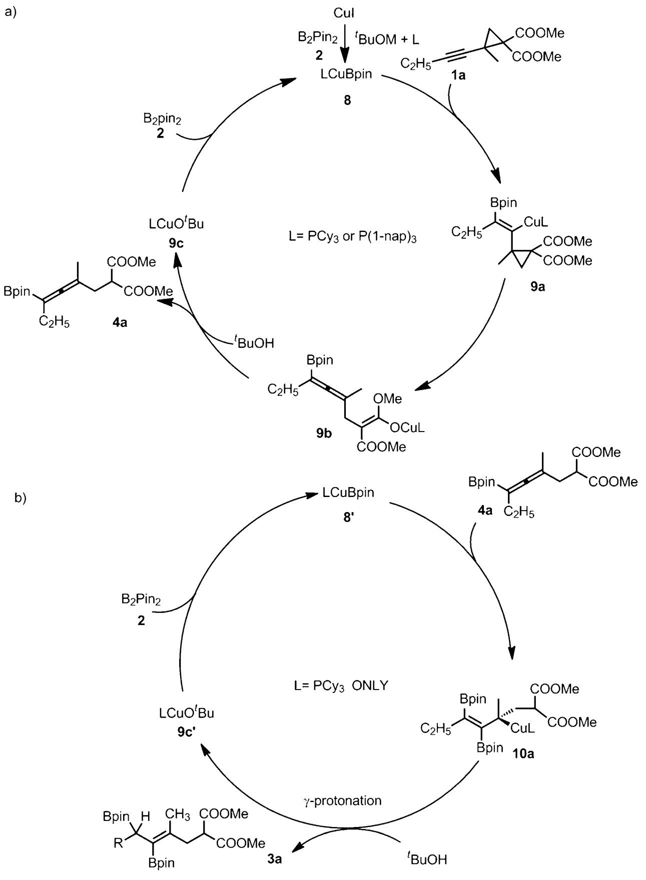


Figure 1. Suggested catalytic cycles for the borylative opening of the propargyl cylopropane **1a**.

9a. The copper opens the strained cyclopropane ring[12b] to give the allenyl boronate **9b**. The proton arising from *t*BuOH replaces the copper in **9b** and after tautomerization the product **4a** is formed together with **9c**. Transmetallation of **9c** with **2** regenerates the catalyst. When the ligand is P(1-nap)$_3$ the reaction stops at the formation of the allenyl boronate product (such as **4a**). The probable reason is that the LCuBpin complex with the bulky L = P(1-nap)$_3$ ligand is not able to undergo insertion of the double bond of the allenyl boronate **4a**. However, in case of PCy_3 this insertion is possible (Figure 1b) and gives the alkenyl diboronate complex **10a**. Subsequently, γ-protonation of copper[8a,b,10b] in **10a** provides **3a.** According to the deuterium-labelling experiments this γ-proton also arises from *t*BuOH [Eqs. (2) and (4)].

In summary, we have presented new catalytic reactions for borylative opening of propargyl cyclopropane, oxirane, oxetane, and aziridine substrates. In this process B_2pin_2 was employed as the boronate source together with the inexpensive copper catalyst CuI and *t*BuOH additive. The reaction displays synthetically useful ligand control. In the presence of PCy_3 alkenyl diboronates form with high regio- and stereoselectivities, while with the bulky P(1-nap)$_3$ ligand the product is the allenyl boronate. This process provides a large variety of allyl/alkenyl- and allenyl boronates, which are useful reagents in functionalization of carbonyl compounds for stereoselective synthesis of homoallyl and homopropargylic alcohols,[1a,3b,c,f,4,15] and useful precursors for allenyl derivatives by Suzuki–Miyaura coupling.[16]

Experimental Section

In a typical procedure (Method A): Boronate source B_2pin_2 (**2**; 0.30 mmol), CuI (10 mol %), PCy_3 (20 mol %), *t*BuOK (30 mol %) were mixed in toluene (0.4 mL) and the resulting slurry was stirred for 10 minutes at room temperature under Ar. Then a toluene solution (0.1 mL) of the mixture of the propargylic cyclopropane **1a** (0.1 mmol) and *t*BuOH (300 mol%) was added by syringe. The reaction mixture was stirred at room temperature for 24 hours, and then diluted by *n*-pentane (1.5 mL). The precipitate was filtered off by a silica pad using and washed with EtOAc/*n*-hexane (1:2 v/v) as an eluent. The solvent was removed and the alkenyl diboronate product **3a** was purified by silica chromatography. The synthesis of the allenyl boronate **4a** was performed in a similar way (Method B), except that P(1-nap)$_3$ (20 mol %), *t*BuOLi (30 mol %), and *t*BuOH (200 mol %) were used.

Acknowledgments

Support from the Swedish Research Council and the Knut and Alice Wallenbergs Foundation is gratefully acknowledged. J.Z. thanks the Wenner-Gren Foundations for funding a postdoctoral fellowship. The generous gift of B_2Pin_2 from Allychem is appreciated.

Keywords: allenes · boron · copper · homogeneous catalysis · strained rings

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 1502–1506
Angew. Chem. **2016**, *128*, 1524–1528

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Received: October 30, 2015