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Ligand-Controlled Regiodivergent Copper-Catalyzed Alkylboration of Alkenes

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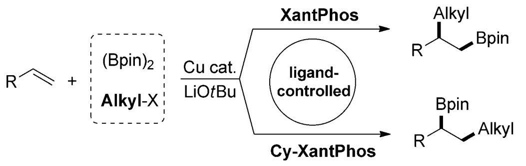
Abstract: *A novel copper-catalyzed regiodivergent alkylboration of alkenes with bis(pinacolato)diboron and alkyl halides has been developed. The regioselectivity of the alkylboration was controlled by subtle differences in the ligand structure. The reaction thus enables the practical, regiodivergent synthesis of two different alkyl boronic esters with complex structures from a single alkene.*

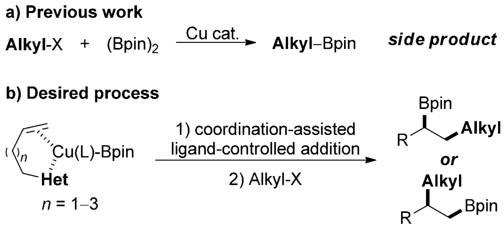
Over the past few decades, transition-metal-catalyzed difunctionalization reactions of C–C multiple bonds have attracted much attention owing to their high efficiency.[1] In particular, carboboration has been established as an important reaction for the expedient synthesis of complex boron-containing compounds from simple starting materials.[2] A large number of carboboration reactions of alkenes, alkynes, and allenes have been achieved by Cu,[3,4] Pd,[5] and Ni[6] catalysis. Among them, the intermolecular carboboration of alkenes can be achieved via carbon(sp^3)–metal intermediates that are obtained by borometalation, which then react in situ with electrophiles, thus providing an efficient strategy for the coupling of sp^3-hybridized carbon centers.[7] For instance, the groups of Brown and Nakao independently reported synergistic Pd/Cu-catalyzed intermolecular arylboration reactions of vinylarenes and methyl crotonate.[7a,b,d] Furthermore, Hoveyda and co-workers realized the copper-catalyzed carboboration of 1,3-enynes with $(Bpin)_2$ and aldehydes.[7c] In all of these pioneering examples, excellent regioselectivities were achieved, but only one regioisomer could be afforded. Considering that regioselectivity is a key factor in the carboboration of alkenes, achieving both regioselectivities concurrently and on demand clearly constitutes a desirable goal and presents an intriguing challenge.[8]

Owing to our interest in copper-catalyzed $C(sp^3)$–$C(sp^3)$ couplings and the synthesis of boron-containing compounds,[9] we hypothesized that the copper-catalyzed intermolecular alkylboration of alkenes would be an efficient strategy for constructing $C(sp^3)$–$C(sp^3)$ bonds.[10,11] In this approach, alkyl copper intermediates are generated in situ by the migratory insertion of CuBpin complexes across alkenes;[12] these then react with alkyl electrophiles. Compared with standard cross-coupling procedures, this strategy avoids the use of air-sensitive organometallic compounds. Moreover, a Bpin group, which can be easily converted into useful functional groups, is introduced. Notably, although an intermolecular alkylboration of alkenes has been reported by Yoshida and co-workers,[13] the scope of this transformation was limited to activated alkenes (e.g., styrene and silyl-substituted alkenes) or activated alkyl halides (e.g., benzyl chloride). The alkylboration of unactivated alkenes with unactivated alkyl electrophiles remains a significant challenge. Herein, we report a regiodivergent, copper-catalyzed alkylboration of alkenes with bis(pinacolato)diboron and alkyl halides. The regioselectivity can be controlled by the judicious choice of ligand, and both of the alkyl boronic ester[14] backbones can be constructed in a regiodivergent manner from a single alkene substrate (Scheme 1).

Control of chemoselectivity is essentially important to achieve multicomponent carboboration processes.[4c] Based on our previous work on the borylation of alkyl electrophiles (Scheme 2a),[15] we considered that the ready borylation of alkyl halides may restrain the addition of CuBpin to the alkenes, which would prevent the alkylboration of alkenes. Our work was inspired by Sigman's recent palladium-catalyzed cross-coupling reaction of homoallylic alcohols, which are readily accessible and attractive synthons in organic



Scheme 1. Regiodivergent alkylboration of alkenes.



Scheme 2. a) Previous work on the borylation of alkyl electrophiles. b) The desired alkylboration process.

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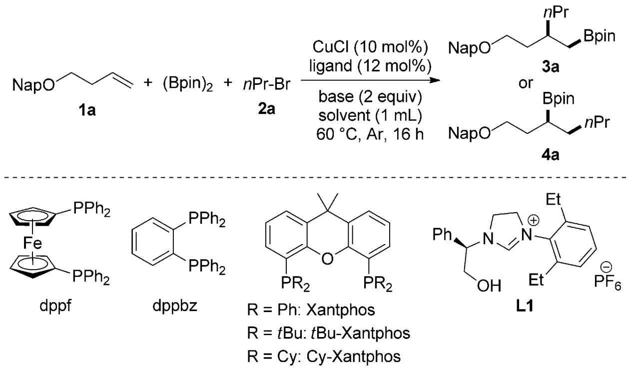
synthesis.[16] We envisioned that the introduction of a heteroatom into the alkene would lead to a weak coordination effect that might accelerate the addition of CuBpin to the alkene;[16c,17] this coordination could suppress the undesired side reaction—the borylation of the alkyl halide coupling partners—and promote alkene alkylboration (Scheme 2b).

Based on the above assumptions, we chose 2-naphthylmethyl (Nap)-protected[18] homoallylic alcohol **1a** as the model substrate. After a preliminary screen, we were delighted to obtain the *anti*-Markovnikov carboboration product **3a** in 57% GC yield with excellent regioselectivity (**3a**/**4a** = 17:1; Table 1, entry 1). We then explored the ligand effect on the reaction. Unfortunately, when dppf, dppbz, 1,10-phen, Ipr·HCl, or **L1**, which are superior in the migratory insertion of CuBpin complexes across alkenes, were used,[4c,19] alkene carboboration was completely suppressed (entries 2–6). However, when *t*Bu-Xantphos was used as the ligand, Markovnikov carboboration product **4a** was obtained as the major product in moderate yield (45%) with inverted regioselectivity (**3a**/**4a** = 1:2.6, entry 7). This result implies that bidentate phosphine ligands with xanthene as the backbone have remarkable effects on the alkylboration of alkenes, and that regiodivergent alkylboration could be realized through tuning of the ligands. We therefore tried other substituted Xantphos ligands. To our delight, when Cy-Xantphos was used, **4a** was obtained in high yield (89%) with good regioselectivity (**3a**/**4a** = 1:5.6, entry 8). Notably, the use of Cy-Xantphos has rarely been reported.[20] Moreover, when [CuCl(Cy-Xantphos)] was used instead of CuCl and Cy-Xantphos, both the yield and the regioselectivity of the reaction improved slightly (92% of **4a**; **3a**/**4a** = 1:5.8; entry 14). Finally, when propyl iodide was used instead of propyl bromide with Xantphos as the ligand, the yield of **3a** improved significantly to 96% (**3a**/**4a** = 18:1; entry 15).

With the optimized reaction conditions in hand, we first synthesized various *anti*-Markovnikov carboboration products (Table 2). A variety of alkenes (**3a**–**3k**) and alkyl iodides (**3l**–**3o**) were tolerated and all gave the corresponding products in satisfactory yields and with excellent regioselectivity. Various primary, secondary, and tertiary homoallylic alcohols with Nap protection (**3a**, **3h**, **3j**, **3k**) reacted smoothly. As an important class of biologically active molecules, various nitrogen-containing moieties, such as indole (**3c**), dibenzylamine (**3e**), and methyl phenyl amine (**3f**), all survived the alkylboration. Notably, bishomoallylic indole **3d** reacted smoothly with moderate yield. Furthermore, a substrate with increased steric hindrance in the allylic position also smoothly underwent the alkylboration reaction to provide the desired product in a diastereomeric ratio of 1:1 (**3i**); this result is consistent with recent work of Ito and coworkers.[11d] Primary alkyl iodides with various side chains or a range of functional groups, such as phenyl, ester, or silyl

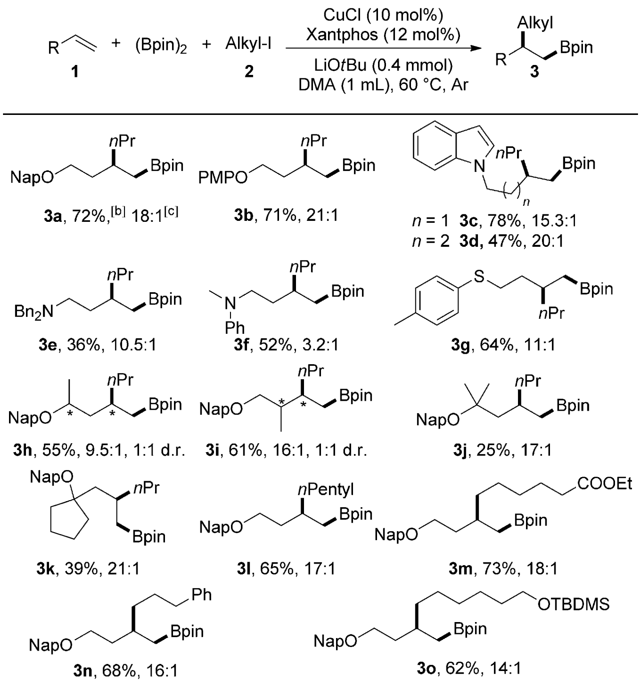
Table 1: Optimization of the reaction conditions.[a]



Entry	Ligand	Base	Solvent	Yield[b] [%]	3a/4a[c]
1	Xantphos	LiO*t*Bu	DMA	57	17:1
2	dppf	LiO*t*Bu	DMA	< 5	–
3	dppbz	LiO*t*Bu	DMA	< 5	–
4	1,10-phen	LiO*t*Bu	DMA	< 5	–
5	IPr·HCl	LiO*t*Bu	DMA	< 5	–
6	**L1**	LiO*t*Bu	DMA	< 5	–
7	*t*Bu-Xantphos	LiO*t*Bu	DMA	45	1:2.6
8	Cy-Xantphos	LiO*t*Bu	DMA	89	1:5.6
9	Cy-Xantphos	NaO*t*Bu	DMA	66	1:5.5
10	Cy-Xantphos	KO*t*Bu	DMA	53	1:5.7
11	Cy-Xantphos	LiO*t*Bu	THF	< 5	–
12	Cy-Xantphos	LiO*t*Bu	toluene	< 5	–
13	Cy-Xantphos	LiO*t*Bu	DMF	84	1:5.7
14[d]	**Cy-Xantphos**	**LiO*t*Bu**	**DMA**	**92 (68)[f]**	**1:5.8**
15[e]	**Cy-Xantphos**	**LiO*t*Bu**	**DMA**	**96 (72)[g]**	**18:1**

[a] Reaction conditions: **1a** (0.2 mmol), $(Bpin)_2$ (0.4 mmol), **2a** (0.6 mmol), CuCl (10 mol%), ligand (12 mol%), base (0.4 mmol), solvent (1 mL) at 60°C for 16 h. DMA = dimethylacetamide, Nap = 2-naphthylmethyl, Pin = pinacolato. [b] Combined yields of **3a** and **4a** as determined by GC analysis. [c] Determined by GC analysis. [d] [CuCl(Cy-Xantphos)] (10 mol%) was used instead of CuCl and Cy-Xantphos. [e] *n*PrI (0.6 mmol) was used instead of **2a**. [f] Yield of isolated **4a**. [g] Yield of isolated **3a**.

Table 2: Substrate scope of the *anti*-Markovnikov alkylboration.[a]



3a, 72%,[b] 18:1[c]
3b, 71%, 21:1
n = 1 **3c**, 78%, 15.3:1
n = 2 **3d**, 47%, 20:1
3e, 36%, 10.5:1
3f, 52%, 3.2:1
3g, 64%, 11:1
3h, 55%, 9.5:1, 1:1 d.r.
3i, 61%, 16:1, 1:1 d.r.
3j, 25%, 17:1
3k, 39%, 21:1
3l, 65%, 17:1
3m, 73%, 18:1
3n, 68%, 16:1
3o, 62%, 14:1

[a] Reaction conditions: **1** (0.2 mmol), $(Bpin)_2$ (0.4 mmol), **2** (0.6 mmol), CuCl (10 mol%), Xantphos (12 mol%), LiO*t*Bu (0.4 mmol), DMA (1 mL) at 60°C for 16 h. PMP = 4-methoxyphenyl, TBDMS = *tert*-butyldimethylsilyl. [b] Yield of isolated product. [c] Ratio of **3**/**4**.

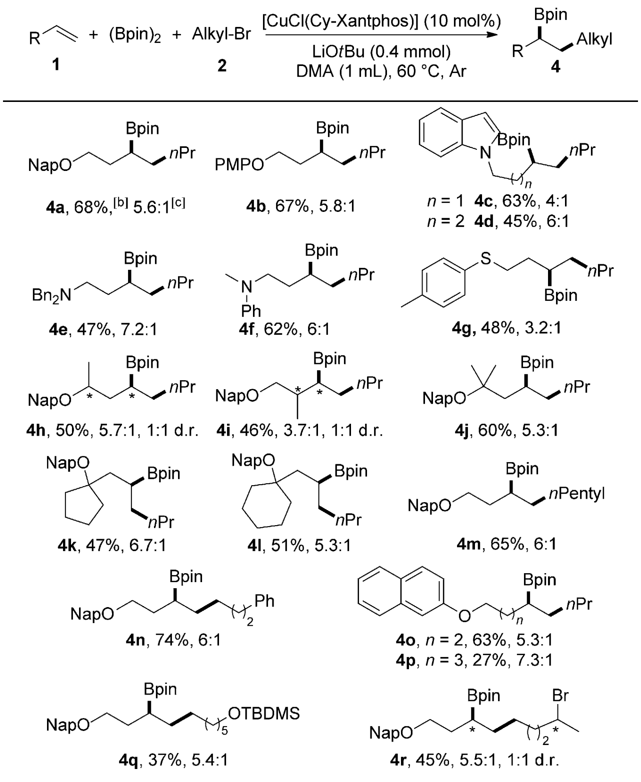
ether moieties (**3l**–**3o**), were also suitable substrates. However, as for most copper-catalyzed reactions, secondary alkyl halides were inert in this reaction.[10a,b]

We then explored the alkylboration reaction with Cy-Xantphos as the ligand (Table 3).[21] The scope of this reaction with respect to variations of the alkene and alkyl halide coupling partners was similar to that of the reaction with Xantphos as the ligand (**4a**–**4n** and **4q**). In fact, the Markovnikov alkylboration was applicable to a broader scope of alkene substrates than the *anti*-Markovnikov alkylboration (**4o**, **4p**).

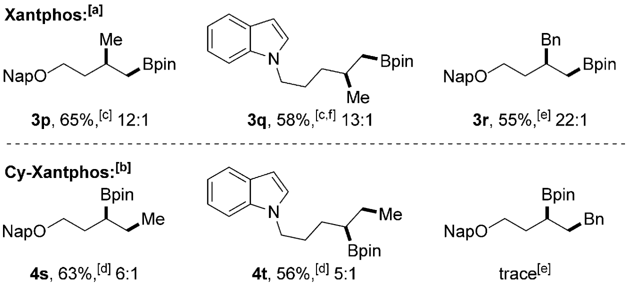
Efforts were then put into further expanding the reaction scope. First, we achieved the methylboration of various alkenes (Scheme 3). When MeOTs and MeOMs were used as the methyl electrophiles for the *anti*-Markovnikov and Markovnikov alkylboration, respectively, these reactions proceeded smoothly (**3p**, **3q**, **4s**, **4t**). When BnCl was used as the electrophile, the *anti*-Markovnikov benzylboration product (**3r**) was obtained in moderate yield, whereas the Markovnikov benzylboration was not observed (Scheme 3).

Next, the alkylboration of benzyl-protected alkenyl alcohols with different chain lengths was achieved, and similar results were obtained when Nap was used as the protecting group (Scheme 4). Furthermore, the sterically hindered alkyl electrophile *i*Bu–X was also proven to be an effective reagent in both regioselective alkylboration reactions under modified conditions (Scheme 5). Finally, when (bromomethyl)cyclopropane was used, no ring-opening products were detected. **3v** and **4y** were afforded as the sole products, ruling out the involvement of a radical mechanism.

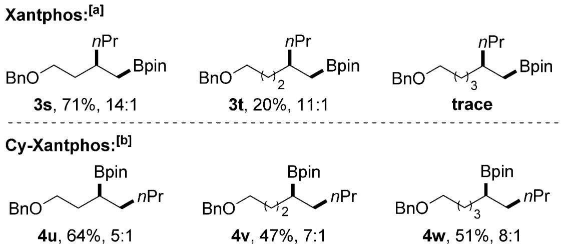
Table 3: Substrate scope of the Markovnikov alkylboration.[a]



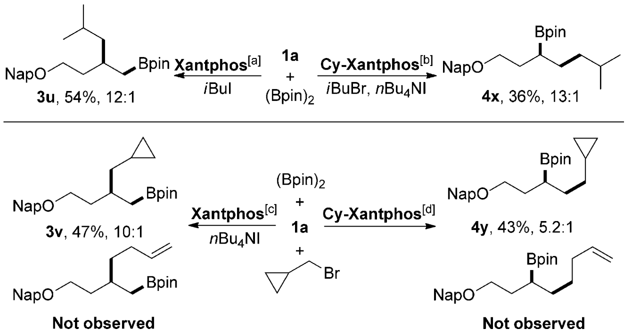
[a] Reaction conditions: **1** (0.2 mmol), (Bpin)$_2$ (0.4 mmol), **2** (0.6 mmol), [CuCl(Cy-Xantphos)] (10 mol%), LiO*t*Bu (0.4 mmol), DMA (1 mL) at 60 °C for 16 h. [b] Yield of isolated product. [c] Ratio of **4**/**3**.



Scheme 3. Methylboration and benzylboration of alkenes. [a] Reaction conditions as in Table 2. [b] Reaction conditions as in Table 3. [c] MeOTs instead of an alkyl iodide. [d] MeOMs instead of an alkyl bromide. [e] BnCl was used as the electrophile. [f] *n*Bu$_4$NI (10 mol%) was added. Ms = methanesulfonyl, Ts = *para*-toluenesulfonyl.

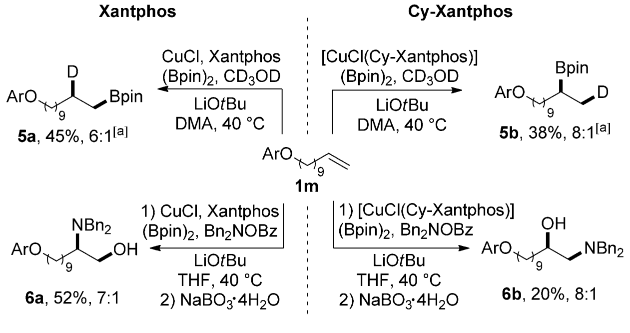


Scheme 4. Alkylboration of benzyl-protected alkenyl alcohols with different chain lengths. [a] Reaction conditions as in Table 2. [b] Reaction conditions as in Table 3.



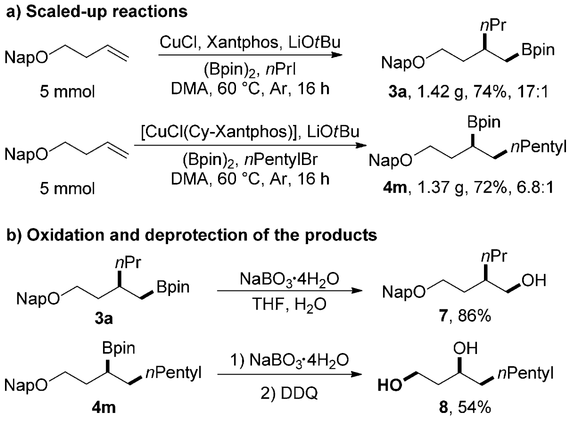
Scheme 5. Alkylboration with sterically hindered primary alkyl halides as the alkyl electrophiles. [a] Reaction conditions as in Table 2. [b] Reaction conditions as Table 3; *n*Bu$_4$NI (50 mol%) was used as an additive. [c] Reaction conditions as in Table 2; *n*Bu$_4$NI (10 mol%) was used as an additive. [d] Reaction conditions as in Table 3.

Further mechanistic studies were also conducted. First, when 1-octene or **1m**, which have longer alkyl chains next to the vinyl moiety, were employed in the regiodivergent alkylboration, only trace amounts of the alkylborated products were detected, whereas significant borylation of the alkyl halides was observed as a side reaction in both cases. Second, we conducted the deuterboration and aminoboration of alkene **1m**. Under these conditions, the deuterborated products **5a** and **5b** and the amino alcohols **6a** and **6b**[22] were regioselectively obtained with Xantphos and Cy-Xantphos, respectively (Scheme 6). These results suggest that 1) the ligand pair Xantphos/Cy-Xantphos is a versatile system for the regiodivergent copper-catalyzed borylation of unactivated terminal alkenes, and 2) that without suitable facilitation, alkylboration is a highly challenging process because of competing side reactions, including borylation of the alkyl halides. Apparently, using an alkene with a coordinating heteroatom is an effective strategy to access the alkylboration products, which presumably facilitates the process by accelerating the addition of CuBpin to the alkene. In this regard, we speculate that the regioselectivity is controlled by a ligand effect in the alkene addition step with LCuBpin. Indeed, DFT calculations of the relative Gibbs free energies of the alkene addition transition states clearly shows an inverse trend with these two ligands (see the Supporting Information).



Scheme 6. Regiodivergent deuterboration and aminoboration of alkenes (see the Supporting Information for details). Ar = 2-naphthyl. [a] Determined by GC analysis. Bz = benzoyl.

Potential applications of the new alkene alkylboration reaction were also tested (Scheme 7). Gratifyingly, two regioselective alkylboration reactions could be smoothly conducted on gram scales. Furthermore, 1,3- and 1,4-diols can be obtained by oxidation of Bpin and facile removal of the Nap group by DDQ-mediated oxidation.[18]



Scheme 7. Applications of the alkene alkylboration reaction. a) Scaled-up reactions. b) Oxidation and deprotection of the products (see the Supporting Information for details). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

In summary, we have described the copper-catalyzed, ligand-controlled, regiodivergent alkylboration of alkenes. In this reaction, the regioselectivity was dictated by subtle differences in the ligand structure. The incorporation of a heteroatom in the alkene to facilitate the addition of CuBpin to the alkene was found to be critical for alkylboration. With this user-friendly and synthetically economic strategy, two alkyl boronic esters with complex structures could be synthesized from a single alkene substrate in a regiodivergent manner. Moreover, the two ligands (Xantphos and Cy-Xantphos) that were used in these reactions are also suitable for regiodivergent copper-catalyzed deuterboration and aminoboration reactions, which indicates that the present study may provide a general ligand pattern for the difunctionalization of unactivated terminal alkenes without a heteroatom. Further investigations on the reaction mechanism and the development of an enantioselective version of the reaction are in progress.

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[22] During the preparation of this manuscript, Miura and co-workers reported a regiodivergent aminoboration of unactivated terminal alkenes; see: R. Sakae, K. Hirano, M. Miura, *J. Am. Chem. Soc.* **2015**, *137*, 6460–6463.

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