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## Cu-catalyzed carboboration of acetylene with Michael acceptors†

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A copper-catalyzed three-component carboboration of acetylene with  $B_2Pin_2$  and Michael acceptors is reported. In this reaction, a cheap and abundant C2 chemical feedstock, acetylene, was used as a starting material to afford *cis*-alkenyl boronates bearing a homoallylic carbonyl group. The reaction was robust and could be reliably performed on the molar scale. Furthermore, the resulting *cis*-alkenyl boronates could be converted to diverse functionalized molecules with ease.

Copper-catalyzed *syn*-1,2-borofunctionalization of alkynes has become a powerful and practical strategy for the installation of both boron and other functional groups across the  $C\equiv C$  bond in excellent regio- and stereoselectivity.<sup>1</sup> The general mechanism is that the borofunctionalization is initiated by the *syn*-addition of nucleophilic Cu-Bpin across the  $C\equiv C$  bond to generate the key intermediate species borylated alkenyl copper, followed by the interception of electrophiles to produce multi-substituted alkenyl boronates (Scheme 1a). So far, different electrophiles, such as  $H^+$ , halides (including alkyl, allyl, aryl and alkenyl halides) and  $CO_2$ , have been successfully and efficiently employed to intercept the putative borylated alkenyl copper.<sup>2–4</sup> In sharp contrast, as excellent electrophiles, Michael acceptors (acrylate, vinyl ketone, acrylonitrile *etc.*) have rarely been employed to capture the *in situ* generated borylated alkenyl copper intermediate. This is not because Michael acceptors are not capable of reacting with the nucleophilic alkenyl copper, but because the electron-deficient Michael acceptors are typically more reactive than the electron-rich alkynes toward the borylcupration of Cu-Bpin species<sup>5</sup> (Scheme 1b). To circumvent this challenge, Lin and Tian reported a Cu-catalyzed asymmetric borylative cyclization of cyclohexadienone-containing 1,6-enynes through an intramolecular Michael addition.<sup>6</sup> In this reaction, the authors smartly leveraged the steric hindrance from the quaternary carbon of C1 to suppress the undesired borylcupration of cyclohexadienone (Scheme 1c). Recently, by using the same strategy, Carretero and Mauleón also reported an intramolecular borylative cyclization of 1,6-enynes with a  $\beta,\beta$ -disubstituted acrylate fragment to provide densely functionalized pyrrolidines.<sup>7</sup> Despite these elegant studies, due to

the competition between two different borylcupration pathways, copper-catalyzed carboboration of alkynes through intermolecular Michael addition is still challenging and remains unknown.



Scheme 1 Cu-catalyzed borofunctionalization of alkynes.

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† Electronic supplementary information (ESI) available: Experimental details and characterization of all compounds, and copies of  $^1H$  and  $^{13}C$  NMR spectra. CCDC 2165502 (2t). For ESI and crystallographic data in CIF or other electronic format see <https://doi.org/10.1039/d2sc02306g>



Acetylene, with the molecular formula  $C_2H_2$ , is the simplest and smallest alkyne.<sup>8</sup> Due to its structural simplicity and high reactivity, acetylene represents a unique C2 alkenyl building block for organic synthesis through addition of its triple bond.<sup>9</sup> Highly industrially important vinyl-containing monomers, such as vinyl ether,<sup>10</sup> vinyl amine,<sup>11</sup> vinyl chloride,<sup>12</sup> acrylic acid and its derivatives,<sup>13</sup> are being synthesized in millions of tons per year globally. However, in fine chemistry, catalytic protocols directly incorporating acetylene into high value-added chemicals are limited. In fact, while phenylacetylene acts as a model substrate in many state-of-the-art catalytic systems concerning alkyne transformations, acetylene is usually neglected in the substrate scope studies due to its gaseous nature and explosive hazard.<sup>9a,h</sup> This obscures the true reactivity of acetylene and makes the acetylene chemistry lag behind in the progress of modern catalytic alkyne chemistry.

Inspired by the elegant studies of Lin, Tian, Carretero and Mauleón, in which a steric hindered Michael acceptor was used to suppress the undesired conjugate borylation of Cu-Bpin, we envisioned that the small size of acetylene might also enable the borylcupration of the  $C\equiv C$  bond to outcompete the borylcupration of the Michael acceptor, thus allowing the Cu-catalyzed carboboration of acetylene through the challenging intermolecular Michael addition (Scheme 1d). However, the application of acetylene in the copper-catalyzed carboboration reaction through intermolecular Michael addition might encounter the following potential challenges: (1) competition between two different borylcupration processes; (2) suppression of the undesired hydroborylation side reaction; (3) safety issues related to the manipulation of acetylene gas and formation of the potentially explosive copper acetylide.

With this above design in mind, we initially investigated the competition of the borylcupration reaction among different types of alkynes. As shown in Scheme 2, when equal amounts of acetylene, phenylacetylene and 1-pentyne were subjected to the typical borylcupration catalytic system with 1.0 equivalent of  $B_2pin_2$  as the limiting reagent and IMesCuCl as the catalyst, an unexpected reaction selectivity was observed. The hydroborylation product of acetylene (**A1**) was observed in 62% yield, which is about 8 times higher than that of phenylacetylene (**A2**). In addition, no corresponding hydroborylation product of 1-pentyne (**A3**) was detected by NMR. The competition results obviously indicated that the borylcupration of acetylene is much faster than that of both aryl alkynes and alkyl alkynes. More importantly, by comparison of the hydroborylation of acetylene

and 1-pentyne, we can draw the conclusion that the steric hindrance of the substituent does have a significant impact on the borylcupration of the  $C\equiv C$  bond by taking into account that both of them are unactivated alkynes.

Encouraged by the above results, we further investigated Cu-catalyzed three-component carboboration of different alkynes in the presence of  $B_2pin_2$  and butyl acrylate **1a** with IMesCuCl as the catalyst and NaO<sup>t</sup>Bu as the base. As shown in Table 1, when the substituted alkynes, phenylacetylene and 1-pentyne, were used as substrates, the desired three-component carboboration product **2** could not be detected (entries 1–4), even with a large excess of alkynes (12.5 equivalents, entries 2 and 4). The hydroborylation reactions of alkynes and butyl acrylate always dominated, giving the corresponding products **A** and **B**. However, the distribution of **A** and **B** clearly indicated that the hydroborylation of electron-deficient butyl acrylate (Michael acceptor) is much faster than that of substituted alkynes, which echoes their borylcupration reactivities (Scheme 1b). In sharp contrast, the desired three-component carboboration product **2a** could be successfully generated when acetylene was applied as the alkyne component (entries 5 and 6). The carboboration product **2a** could be produced in 38% yield even with 1.0 equivalent of acetylene, which is equal to the yield of hydroborylation product **B** (entry 5). When the amount of acetylene was further increased up to 12.5 equivalents (the gaseous acetylene was supplied with a balloon), the hydroborylation of butyl acrylate was completely suppressed with no byproduct **B** detected, furnishing the desired carboboration product **2a** in 62% yield (entry 6). Taken together, the application of acetylene, due to its small size, could enable the realization of the *syn*-1,2-carboboration of the  $C\equiv C$  bond through an intermolecular Michael addition, producing the highly useful alkenyl boronates.

With the initial success achieved, we then systematically screened the reaction conditions and the optimal reaction

Table 1 Cu-catalyzed carboboration of different alkynes



Entry	R	x	A	B	2
1	Ph	1.0	14%	72%	n.d.
2		12.5	34%	40%	n.d.
3	Pr	1.0	n.d.	65%	n.d.
4		12.5	8%	65%	n.d.
5	H	1.0	9%	38%	<b>2a</b> (38%)
6 <sup>a</sup>		12.5	22%	n.d.	<b>2a</b> (62%)

<sup>a</sup> The reaction was conducted with a balloon containing acetylene; the saturated solution of acetylene in 1,4-dioxane was about 0.50 M (about 12.5 eq.).



Scheme 2 The competition of borylcupration among different alkynes.



conditions were established by using 5 mol% IMesCuCl as the catalyst, 0.5 equivalents of NaO<sup>t</sup>Bu as the base and 2.5 equivalents of EtOH as the proton source in a solution of 1,4-dioxane (0.04 M) under a 1 atm acetylene atmosphere at room temperature. The desired alkenyl boronate **2a** could be obtained in 90% NMR yield and 72% isolated yield (see the ESI for details).<sup>†</sup>

With the optimized reaction conditions in hand, we then explored the generality of this Cu-catalyzed carboboration of acetylene. As shown in Scheme 3, this reaction has a very broad substrate scope and excellent functional group tolerance. Different acrylates, thioacrylates, vinyl ketones, 1,3-dienyl

ketone, acrylonitrile and vinyl sulphones with rich functional groups could be applied as effective substrates for this carboboration reaction. The carboboration of acetylene with acrylates was first demonstrated (**2a–2m**). Simple butyl, ethyl and phenyl acrylate could be transformed to target boronates **2a**, **2b** and **2c** in 72%, 67% and 99% yields, respectively. As a base stronger than NaOH, NaO<sup>t</sup>Bu has usually been considered to cause poor functional group tolerance. However, the introduction of S<sub>N</sub>2-sensitive functional groups such as methylsulfonyloxy, epoxy and alkyl bromide caused no deleterious effect on the reaction efficiency giving the desired products **2e**, **2f**, and **2i** in >82%



Scheme 3 Cu-catalyzed carboboration of acetylene with B<sub>2</sub>Pin<sub>2</sub> and Michael acceptors. <sup>a</sup>0.4 mmol of Michael acceptor in 10 mL 1,4-dioxane; <sup>b</sup>the purity of the product was 93% by weight and the reported yield is based on the pure product; <sup>c</sup>with 2.0 eq. EtOH; <sup>d</sup>with 10 mol% IMesCuCl; <sup>e</sup>substrate diluted with 1,4-dioxane or toluene and added dropwise for about 2 min; <sup>f</sup>with 15 mol% IMesCuCl; <sup>g</sup>with 2.5 eq. MeOH instead of EtOH; <sup>h</sup>substrate (1.0 mol L<sup>-1</sup> in pentane) was added dropwise.



yields. The most unexpected thing was that even after a deliberately lengthened reaction time (22 hours), product **2j** which contains an iodoalkyl group could still be isolated in 76% yield. In addition, no protodeborylation byproduct was observed. Markedly, besides the  $S_N2$ -sensitive functional groups, the carbon-carbon triple bond was also found to be compatible, furnishing the desired products containing terminal alkynes in excellent yields (**2g–2h**). This was consistent with the results observed in Table 1 that the borylcupration process prefers acetylene substantially to other substituted alkynes. Free hydroxy and nitrile groups have no obvious negative effects on the reaction efficiency (**2d** and **2l**). The carbon-silicon bond was also tolerable leading to the desired product **2k** in 61% yield. Though acrylamide was not an efficient substrate to capture the  $\beta$ -boryl alkenyl copper intermediate, thioacrylate could be used to furnish the product **2m** in 44% yield.

In addition to acrylate derivatives, vinyl ketones were also suitable substrates for this transformation. Simple ethyl and phenyl vinyl ketones gave **2n** and **2t** in 55% and 61% yields, respectively. Replacing the ethyl group in **2n** with sterically bulkier triethylmethyl (**2o**) made no significant difference in yield. The functional groups of imide (**2p**), tertiary amine (**2q**), and internal alkyne (**2s**) were all well-tolerated, leading to the products in good yields. Besides alkyl vinyl ketones, aryl vinyl ketones were also suitable for this reaction (**2t–2ag**). The steric hindrance of the aryl group was found to have a beneficial effect on the reaction results. For example, the simple phenyl vinyl ketone gave the product **2t** only in 61% yield, but the yields for bulkier 2,6-dimethyl phenyl, 2-naphthalenyl and 9-anthracenyl vinyl ketones increased substantially to 74%, 90% and 99% for **2u**, **2v** and **2w**, respectively. The abnormal steric effects on products' yields were at least partially due to the suppression of the undesired multi-Michael addition byproduct C by the steric hindrance of the aryl ring.<sup>14</sup> A variety of substitutions on the aryl ring are compatible. Both the electron-donating methoxyl group and weakly withdrawing halogen atoms did not affect the reaction (**2x–2z**). Strongly withdrawing groups (COOMe, CF<sub>3</sub> and NO<sub>2</sub>) also succeeded through system acidity increase,<sup>7</sup> reaction time control and slow addition (**2aa**, **2ab** and **2ac**). Michael acceptors derived from heteroaromatic rings such as furan thiophene, benzofuran and indole performed equally well (**2ad**, **2ae**, **2af**, and **2ag**). Interestingly, when alkenyl vinyl ketone and divinyl ketone served as substrates, the reactions only selectively transformed the unsubstituted vinyl groups, while leaving the substituted alkenyl group intact (**2ah** and **2ai**). An interesting feature of the transformation of aryl and alkenyl substituted vinyl ketones was the high reaction rate. Except **1ag** whose carbonyl group was deactivated by indole nitrogen, from **1v** to **1aj**, all reactions were typically completed in less than 30 minutes.

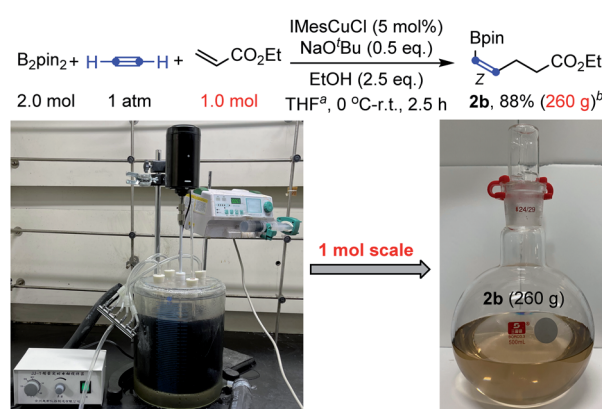
Besides the acrylate and vinyl ketone-based Michael acceptors, 1,3-dien-1-yl ketone could be transformed to skipped diene **2aj** in 57% yield. Acrylonitrile **1ak** and vinyl sulphones **1al** and **1am** were also proved to be competent coupling partners, leading to the corresponding products in up to quantitative yields. Interestingly, polyethyleneglycol diacrylate (PEGDA), a commercially available polyethylene glycol-based material

that is used as a prepolymer solution that can be used in the formation of a cross-linked polymeric system, could also be decorated with borylalkenyl groups on both ends with 79% yield under the standard catalytic conditions (**2an**). The reactions were easily scaled-up to the gram scale and to even more than 10 grams with good yields (**2i**, **2n**, **2t**, **2ak** and **2b**).

Given the high functional group tolerance obtained by this methodology, four acrylates derived from probenecid, estrone, febuxostat and indomethacin were subjected to the standard reaction conditions. To our delight, products **2ao–2ar** were produced in excellent to quantitative yields, which further demonstrated the robustness of this methodology. Pitifully only Michael acceptors with an unsubstituted vinyl group were compatible in this reaction.

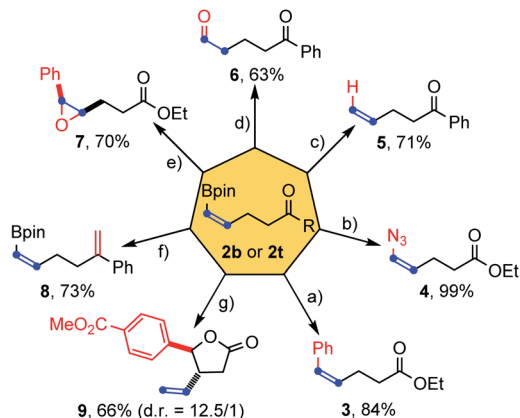
To further showcase the robustness of this carboboration, a large-scale preparation was also tested. Large-scale synthesis has a special meaning for this transformation, because many substrates of this reaction, such as acetylene, acrylates and vinyl ketones, are bulk industrial raw materials and the products, *cis*-alkenyl boronates, are also important and useful synthetic intermediates.<sup>3b,15</sup> As shown in Scheme 4, an efficient molar-scale synthesis of *cis*-alkenyl boronate **2b** using ethyl acrylate as the Michael acceptor has been successfully realized under slightly modified reaction conditions. 260 grams of light brown product boronate **2b** could be distilled from the reaction mixture with 88% yield (based on the pure product) and 86% purity after a simple work-up procedure. The purity could be further improved by a further distillation process. Fortunately, no *Z/E* isomerization was found during the distillation with the temperature up to 200 °C.

To illustrate the synthetic potential of these structurally simple but functional group-rich molecules, a series of transformations of *cis*-alkenyl boronates **2b** and **2t** were then performed (Scheme 5). First the pinacolatoboron group could transform into the phenyl group by Suzuki coupling (product **3**) and the azide group by copper catalysis (product **4**) with full retention of the *cis* double bond configuration. The boron group could be removed by copper catalyzed protodemetalation (product **5**) and a formyl group was introduced successfully by



Scheme 4 Large-scale synthesis. <sup>a</sup>THF (3.0 L). <sup>b</sup>The purity of the product **2a** is 86% after simple distillation and the reported yield is based on the pure product.





a) PhBr, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, THF, reflux, overnight; b) NaN<sub>3</sub>, CuSO<sub>4</sub>, MeOH, r.t., 3 h; c) Cu(OTf)<sub>2</sub>, dioxane/H<sub>2</sub>O, 80 °C, overnight; d) NaBO<sub>3</sub>·4H<sub>2</sub>O, THF/H<sub>2</sub>O, r.t., 3 h; e) PhBr, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, THF, reflux, overnight; then *m*-CPBA, DCM, r.t., 6 h; f) PPh<sub>3</sub>CH<sub>2</sub>Br, KO<sup>t</sup>Bu, THF, 0° C to r.t., 5 h; g) 4-MeO<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>CHO, [Rh(nbd)(CH<sub>3</sub>CN)]SbF<sub>6</sub>, dppm, DCE, 90 °C, 21 h.

Scheme 5 Synthetic applications of products.<sup>16</sup>

direct oxidation of sodium peroxyborate (product 6). Epoxidation of the double bond could be achieved (product 7) once the boron atom is transferred to other oxidation insensitive groups, such as phenyl. Wittig reaction was found to be compatible with the existence of pinacol boron (product 8). Finally, a rhodium-catalyzed allylation tandem intramolecular transesterification reaction with aldehyde forming a five-membered lactone structure was also achieved with good diastereoselectivity and yield (product 9). In general, the three functional groups in the products (pinacol boronate, carbon-carbon double bond and ketone/ester group) could transform individually or synergistically to form other useful structures.

## Conclusions

In conclusion, we have developed a copper-catalyzed three-component carboboration of acetylene with B<sub>2</sub>Pin<sub>2</sub> and Michael acceptors. In this reaction, the cheap and abundant C2 chemical feedstock acetylene was used as the starting material to afford the homoallylic carbonyl group-containing *cis*-alkenyl boronates in a regioselective manner. The reaction has high robustness and can be easily and reliably performed on the molar scale. In this reaction, acetylene does not solve the problems encountered with other alkynes, but in turn, the general problems of substituted alkynes may not definitely confine acetylene.<sup>17</sup> Acetylene is acetylene and it is unique in nature. The small size of the acetylene molecule accelerates the rate of borylcupration and also facilitates the following C-C bond formation process through intermolecular Michael addition, which is typically challenging for substituted alkynes. Moreover, the resulting homoallylic carbonyl group-containing *cis*-alkenyl boronates could be converted to diverse functionalized molecules with ease. It is expected that this unique protocol may inspire and prompt chemists to further explore novel catalytic systems using acetylene as the C2 building block toward the synthesis of valuable chemicals.

## Data availability

Experimental procedures, NMR, IR, HRMS spectra, crystallographic data of 2t and some unsuccessful trials are provided in the ESI.†

## Author contributions

Conceptualization, funding acquisition, resources and supervision were done or provided by S. Z.; project administration, data curation, investigation and formal analysis were done by T. C.; validation was done by B. L.; writing was done by all authors.

## Conflicts of interest

There are no conflicts to declare.

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- 17 No new ligands, new additives or new reagents were developed to expand the reaction scope of substituted alkynes in this work. However, by exploring acetylene's unique properties, traditionally unachievable reactions of substituted alkynes can be achieved with acetylene.

