Cu-catalyzed carboboration of acetylene with Michael acceptors†

Tairan Cheng, Boxiang Liu, Rui Wu and Shifa Zhu *

A copper-catalyzed three-component carboboration of acetylene with B₂Pin₂ 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≡C bond in excellent regio- and stereoselectivity.¹ The general mechanism is that the borofunctionalization is initiated by the syn-addition of nucleophilic Cu-Bpin across the C≡C bond to generate the key intermediate species borylated alkenyl copper, followed by the interception of electrophiles to produce multi-substituted alkynyl boronates (Scheme 1a). So far, different electrophiles, such as H⁺, halides (including alkyl, allyl, aryl and alkynyl halides) and CO₂, have been successfully and efficiently employed to intercept the putative borylated alkenyl copper.²⁻⁴ 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 species⁵ (Scheme 1b). To circumvent this challenge, Lin and Tian reported a Cu-catalyzed asymmetric borocyclosylation of cyclohexadienone-containing 1,6-enynes through an intramolecular Michael addition.⁶ 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 borocyclosylation of 1,6-enynes with a β,β-disubstituted acrylate fragment to provide densely functionalized pyrrolidines.⁷ 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.
Acetylene, with the molecular formula C₂H₂, is the simplest and smallest alkyne. Due to its structural simplicity and high reactivity, acetylene represents a unique C₂ alkynyl building block for organic synthesis through addition of its triple bond. Highly industrially important vinyl-containing monomers, such as vinyl ether, vinyl amine, vinyl chloride, acrylic acid and its derivatives, 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 alkynyl transformations, acetylene is usually neglected in the substrate scope studies due to its gaseous nature and explosive hazard. 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 sterically 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≡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 B₂pin₂ 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≡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 B₂pin₂ and butyl acrylate 1a with IMesCuCl as the catalyst and NaO'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 2 could be successfully generated when acetylene was applied as the alkynyl component (entries 5 and 6). The carboboration product 2 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 2 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≡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 conditions were obtained (Table 1).

**Table 1** Cu-catalyzed carboboration of different alkynes

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

*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\textsubscript{t}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).†

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\textsubscript{t}Bu has usually been considered to cause poor functional group tolerance. However, the introduction of \(\text{S}^2\text{N}_2\)-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% yield.

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

| Acrylates | Vinyl ketone | Vinyl sulphone | Polymer |
|-----------|-------------|---------------|---------|
| 2a, 72%   | Bpin        | Bpin          | from PEGDA 2an, 79% |
| 2b, 67%   | Bpin        | Bpin          | 2am, 79% |
| 2c, 99%   | Bpin        | Bpin          | 2al, 86% |
| 2d, 75%\textsuperscript{e} | Bpin | Bpin | 2a, 96%\textsuperscript{e} (9 min) |
| 2e, 88%   | Bpin        | Bpin          | 2b, 68% |
| 2f, 89%   | Bpin        | Bpin          | 2r, 60% (53 min) |
| 2g, 91% (39 min) | Bpin | Bpin | 2a, 53% (13 min) |
| 2h, 91% (42 min) | Bpin | Bpin | 2a, 86% |
| 2i, 82% (2.1 g, 64%) | Bpin | Bpin | 2a, 76% |
| 2j, 76% (22 h) | Bpin | Bpin | 2a, 74% |
| 2k, 61% (23 h) | Bpin | Bpin | 2v, 90%\textsuperscript{h} (14 min) |
| 2l, 88% (40 min) | Bpin | Bpin | 2w, 99% (14 min) |

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yields. The most unexpected thing was that even after a delib-
erate 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$_2$-2-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 ef-
ficient substrate to capture the
β-boryl alkynyl 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
bulker 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
bulker 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. A variety of substituents 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$_3$ and
NO$_2$) also succeeded through system acidity increase,7 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 alkylvinyl ketone and
divinyl ketone served as substrates, the reactions only select-
ively transformed the unsubstituted vinyl groups, while leaving
the substituted alkynyl group intact (2ah and 2ai). An interest-
ing feature of the transformation of aryl and alkynyl 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 accep-
tors, 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, polyethylene glycol 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. 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 2/1E 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 trans-
formations of cis-alkenyl boronates 2b and 2t were then per-
formed (Scheme 5). First the pinacolatoborin 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
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 alkylation 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_3PÎn_2 and Michael acceptors. In this reaction, the cheap and abundant C_2 chemical feedstock acetylene was used as the starting material to afford the homoallylic carbonyl group-containing cis-alkenyl boronates in a regiospecific 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. 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 C_2 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 ESL†

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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When the steric hindrance of the aryl group in vinyl ketones increases, tandem Michael additions forming byproduct C were suppressed and the yields of 2 increased correspondingly.

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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.