

Catalytic Boracarboxylation of Alkynes with Diborane and Carbon Dioxide by an N-Heterocyclic Carbene Copper Catalyst

Liang Zhang, Jianhua Cheng, Béatrice Carry,[†] and Zhaomin Hou*

Organometallic Chemistry Laboratory and Advanced Catalyst Research Team, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

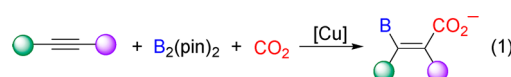
Supporting Information

ABSTRACT: By the use of an N-heterocyclic carbene copper(I) complex as a catalyst, the boracarboxylation of various alkynes (e.g., diaryl alkynes, aryl/alkyl alkynes, and phenylacetylene) with a diborane compound and carbon dioxide has been achieved for the first time, affording the α,β -unsaturated β -boralactone derivatives regio- and stereoselectively via a borylcupration/carboxylation cascade. Some important reaction intermediates were isolated and structurally characterized to clarify the reaction mechanism.

The use of CO₂ as a low-cost and renewable C1 building block for the synthesis of value-added chemicals is of great importance and has attracted increasing interest.¹ The direct carboxylation of carbon nucleophiles with CO₂ as an electrophile is a straightforward protocol for the synthesis of carboxylic acids.^{2,3} It was recently demonstrated that α,β -unsaturated carboxylic acids and their derivatives can be prepared by transition-metal-catalyzed carboxylations (e.g., hydrocarboxylation, alkylative/arylativative carboxylation, and double carboxylation) of alkynes with CO₂.^{4–7} In principle, the heterocarboxylation of alkynes (such as boracarboxylation) with CO₂, which would lead to the addition of both a heteroatom unit (e.g., boryl) and a carboxylate group to the C–C triple bond could serve as a useful method for the synthesis of multifunctionalized alkenes, which are potentially versatile building blocks for various synthetic applications. However, there have been only a few reports on stoichiometric heterocarboxylation of highly reactive substrates. Previously, aminative carboxylation^{8a} and hydroxycarboxylation^{8b} of allenes were achieved by the use of a stoichiometric amount of a Ni complex. The insertion of CO₂ into copper intermediates formed by silylcupration of dienes was reported to give the corresponding silacarboxylation products.^{8c} Three-component coupling reactions of alkynes, imines, and CO₂ were reported to afford benzoxazinone derivatives.^{8d} In contrast, the catalytic heterocarboxylation of simple unsaturated C–C bonds with CO₂ has remained almost unexplored to date.⁹

Boracarboxylation of alkynes with a boron compound and CO₂ is of particular interest and importance in view of the wide utility of C–B bonds in various chemical transformations.¹⁰ Moreover, the catalytic regio- and stereoselective synthesis of multifunctionalized alkenes remains one of the most difficult tasks in synthetic organic chemistry.¹¹ Herein we report the first catalytic boracarboxylation of alkynes with a diborane

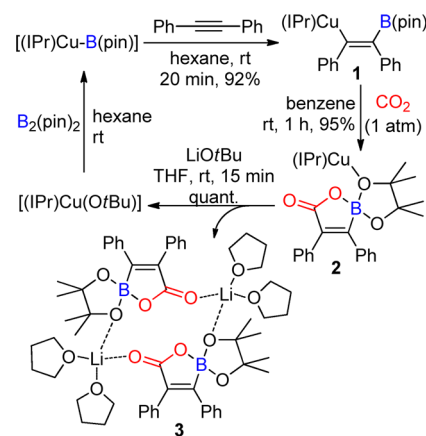
compound and CO₂ using an N-heterocyclic carbene (NHC) copper catalyst (eq 1). Both a boryl moiety and a carboxylate



group are added regio- and stereoselectively to the C–C triple bond via a borylcupration/carboxylation sequence to afford α,β -unsaturated β -boralactone derivatives. Several reaction intermediates were isolated and structurally characterized, thus providing important insight into the mechanistic aspects of the catalytic cycle.

We previously demonstrated that NHC–copper(I) complexes such as [(IPr)Cu(OtBu)], where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, can serve as excellent catalysts for the carboxylation of various nucleophiles.^{3f,g,i,q} To see whether an NHC–Cu catalyst is suitable for the boracarboxylation of alkynes, we examined first the sequential reactions of [(IPr)Cu(OtBu)] with bis(pinacolato)diboron [B₂(pin)₂], diphenylacetylene, and CO₂ (Scheme 1). As reported previously,¹² the reaction of [(IPr)Cu(OtBu)] with B₂(pin)₂ at room temperature instantly gave the borylcopper complex [(IPr)CuB(pin)]. The subsequent reaction of [(IPr)CuB(pin)] with diphenylacetylene afforded β -boryl alkenyl-

Scheme 1. Sequential Reactions of a Copper Alkoxide with a Diboron Compound, an Alkyne, CO₂, and a Lithium Alkoxide



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copper complex **1** in 92% isolated yield through insertion of the C–C triple bond into the Cu–B bond in a syn fashion (Scheme 1 and Figure 1). Exposure of **1** to a CO₂ atmosphere

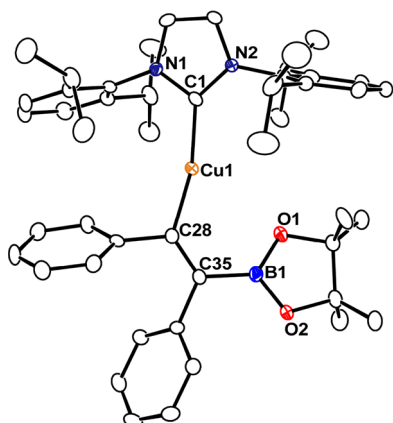


Figure 1. ORTEP drawing of **1** with thermal ellipsoids set at 30% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu1–C1, 1.910(3); Cu1–C28, 1.924(4); C28–C35, 1.356(5); C35–B1, 1.557(5); C1–Cu1–C28, 166.4(1); Cu1–C28–C35, 130.2(3).

gave carboxylation product **2** in 95% isolated yield. X-ray crystallographic analysis revealed that complex **2** adopts a cyclic structure through a bonding interaction between the boron atom and the carboxylate unit, and the NHC–copper moiety is bonded to an O atom of the boronic ester group (Figure 2).

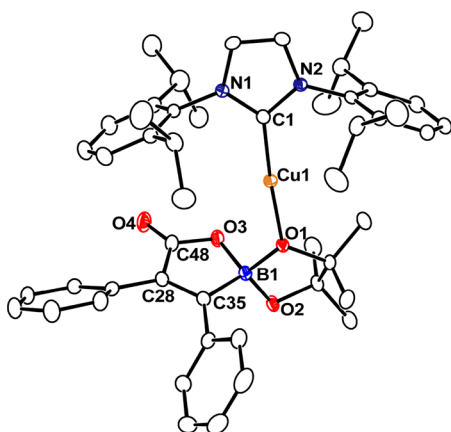


Figure 2. ORTEP drawing of **2** with thermal ellipsoids set at 30% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu1–C1, 1.862(2); Cu1–O1, 1.872(2); O4–C48, 1.206(3); O3–C48, 1.336(3); O3–B1, 1.504(3); O1–B1, 1.509(3); O2–B1, 1.443(3); C35–B1, 1.619(4); C1–Cu1–O1, 173.3(1); O3–C48–O4, 122.6(2).

Treatment of **2** with 1 equiv of LiOtBu in tetrahydrofuran (THF) quantitatively yielded the copper alkoxide complex [(IPr)Cu(OtBu)] and lithium borolactone derivative **3** through a transmetalation reaction. An X-ray crystallographic study showed that **3** possesses a dimeric structure resulting from an “intermolecular” interaction between the Li atom and the carbonyl group (Scheme 1 and Figure 3). To the best of our knowledge, complexes **2** and **3** represent the first examples of structurally characterized α,β -unsaturated borolactone compounds.

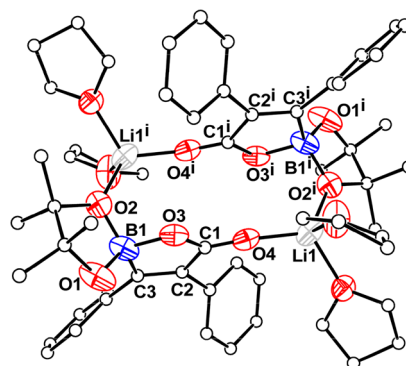


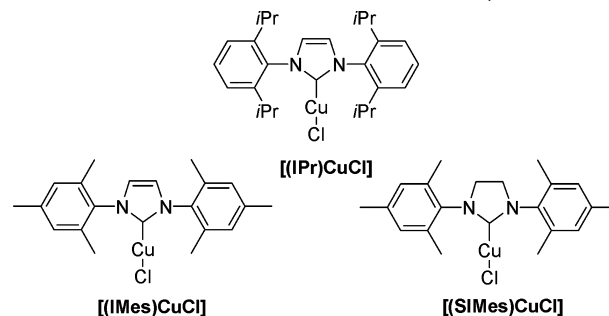
Figure 3. ORTEP drawing of **3** with thermal ellipsoids set at 30% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1–O3, 1.552(6); B1–C3, 1.633(6); O4–Li1, 1.873(8); Li1–O2, 1.949(8); O3–C1–O4, 122.4(3).

With these well-established stoichiometric reactions in mind, we then attempted the catalytic boracarboxylation of diphenylacetylene with B₂(pin)₂ and CO₂. However, when [(IPr)CuCl] (5 mol %) was used as the catalyst in the presence of LiOtBu (1.1 equiv), only a trace amount of the CO₂ insertion product was observed (Table 1, entry 1). To our

Table 1. Catalytic Boracarboxylation of Diphenylacetylene with B₂(pin)₂ and CO₂^a

$\text{Ph}\equiv\text{Ph} + \text{B}_2(\text{pin})_2 + \text{CO}_2 \xrightarrow[\text{THF, 80 } ^\circ\text{C}]{[\text{Cu}] (5 \text{ mol } \%), \text{LiOtBu (1.1 equiv)}} \text{Ph}_2\text{C}(\text{O}^-\text{Li}^+)\text{C}(\text{O}^-\text{Li}^+)\text{B}(\text{pin})_2$				
entry	[Cu]	solvent	T (°C)	yield (%) ^b
1	(IPr)CuCl	THF	80	trace
2	(IMes)CuCl	THF	80	73
3	(SIMes)CuCl	THF	80	81
4	(SIMes)CuCl	THF	80	76 ^c
5	(SIMes)CuCl	dioxane	100	80
6	(SIMes)CuCl	toluene	100	86
7	(SIMes)CuCl	THF	rt	26

^aReaction conditions: [Cu] (5 mol %), diphenylacetylene (0.5 mmol), B₂(pin)₂ (1.0 equiv), CO₂ (1 atm), LiOtBu (1.1 equiv), solvent (3.0 mL), 80 °C, 14 h, unless otherwise noted. ^bIsolated yields. ^c5 h.



delight, replacing the IPr ligand with the less sterically demanding 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) ligand in the copper complex (i.e., using [(IMes)CuCl] instead of [(IPr)CuCl]) resulted in a significant increase of the catalytic activity, giving the boracarboxylation product **4a** in 73% isolated yield (entry 2).¹³ Using the saturated NHC ligand 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes) further increased the product yield to 81% under the same

conditions (entry 3). The catalyst remained similarly active even at 100 °C (entries 5 and 6). At room temperature, the catalyst was not very efficient, and a yield of only 26% was observed (entry 7).

We then used $[(\text{SIMes})\text{CuCl}]$ as a catalyst to examine the boracarboxylation reactions of various alkynes. Some representative results are summarized in Table 2. Diaryl alkynes with

Table 2. Catalytic Boracarboxylation of Various Alkynes with $\text{B}_2(\text{pin})_2$ and CO_2 ^a

$\text{R}-\text{C}\equiv\text{C}-\text{R}' + \text{B}_2(\text{pin})_2 + \text{CO}_2 \xrightarrow[\text{THF, 80 }^\circ\text{C, 14 h}]{[(\text{SIMes})\text{CuCl}] (5 \text{ mol}\%), \text{LiOtBu} (1.1 \text{ equiv})}$		
	4a 81%	
	4b 74%	
	4c 64%	
	4d 77%	
	4e 68%	
	4f 94%	
	4g 94%	
	4h 83%	
	4i 76%	
	4j <5%	
	4k 71% (4k : 4k' , 98:2)	
	4k'	

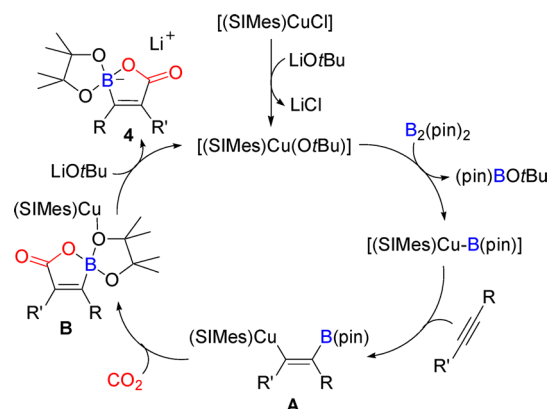
^aReaction conditions: $[(\text{IMes})\text{CuCl}]$ (5 mol %), alkyne (0.5 mmol), $\text{B}_2(\text{pin})_2$ (1.0 equiv), CO_2 (1 atm), LiOtBu (1.1 equiv), THF (3.0 mL), 80 °C, 14 h. Isolated yields are shown.

various substituents on the aromatic ring were generally suitable for this reaction, affording the expected products in good to excellent yields. Aromatic C–Cl bond (**4e**) and ester (**4f**) functional groups could survive the reaction conditions. Dithienylacetylene was also transformed into the corresponding α,β -unsaturated borolactone derivative **4g** in high yield. In the case of 1-phenyl-1-propyne and 1-phenyl-1-butynyl, the carboxylation took place exclusively at the carbon atom having the phenyl substituent, and the borylation occurred at the carbon atom having an alkyl group, selectively giving the α -phenylacrylic acid derivatives **4h** and **4i**, respectively. Remarkably, phenylacetylene could also undergo the boracarboxylation reaction with $\text{B}_2(\text{pin})_2$ and CO_2 to afford α -phenylacrylic acid derivative **4k** with high selectivity.¹⁴ In the case of 2-*tert*-butyl-substituted phenylacetylene, only a trace

amount of the carboxylation product **4j** was obtained, probably because of steric hindrance by the bulky *tert*-butyl group.¹⁵

On the basis of the above experimental observations, a possible mechanism for the current boracarboxylation reactions is shown in Scheme 2. At first, the metathesis reaction between

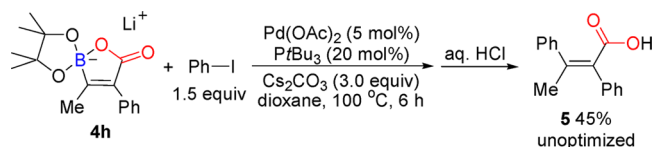
Scheme 2. Possible Mechanism of Catalytic Boracarboxylation



$[(\text{SIMes})\text{CuCl}]$ and LiOtBu would afford $[(\text{SIMes})\text{Cu}(\text{OtBu})]$, which upon reaction with $\text{B}_2(\text{pin})_2$ could generate the borylcopper complex $[(\text{SIMes})\text{CuB}(\text{pin})]$. Subsequent insertion of an alkyne into the Cu–B bond in a syn fashion would give β -boryl alkenylcopper complex **A**. Nucleophilic addition of the alkenylcopper species to CO_2 followed by replacement of the Cu moiety in the resulting carboxylate with the B atom would yield β -borolactone derivative **B**. Finally, the transmetalation reaction between copper complex **B** and LiOtBu should regenerate $[(\text{SIMes})\text{Cu}(\text{OtBu})]$ and release the final product **4**.

In an attempt to check the synthetic utility of the present boracarboxylation products, the Suzuki–Miyaura cross-coupling reaction of **4h** with iodobenzene was carried out under standard conditions (unoptimized), and it afforded tetrasubstituted alkene **5** in 45% isolated yield (Scheme 3).¹⁶

Scheme 3. Suzuki–Miyaura Cross-Coupling Reaction Using **4h**



In summary, we have developed the first catalytic boracarboxylation reaction of alkynes with diborane and CO_2 , which gives a novel family of α,β -unsaturated β -borolactone derivatives with high regio- and stereoselectivity under mild conditions. Some key reaction intermediates have been isolated and structurally characterized, thus offering important insight into the mechanism of the catalytic cycle. The present reaction may serve as an attractive method for the synthesis of multifunctionalized alkenes, as it uses CO_2 and easily available alkynes as building blocks and a relatively cheap copper complex as a catalyst.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, spectroscopic and analytical data for new compounds, and crystallographic data for **1**, **2**, **3**, and **4k** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

houz@riken.jp

Notes

The authors declare no competing financial interest.

[†]B.C. is an intern at RIKEN from Université de Toulouse, INP-ENSIACET, UPS, France.

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