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Access to Cyclic Borates by Cu-Catalyzed Borylation of Unactivated Vinylcyclopropanes

Cheng Zhang and Clément Mazet*

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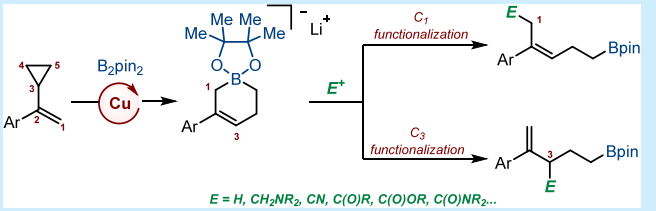
ABSTRACT: We report the copper-catalyzed borylation of unactivated vinylcyclopropanes to form six-membered cyclic borate salts. A copper complex bearing an N-heterocyclic ligand in combination with bis(pinacolato)diboron and LiO*t*Bu catalyzes the ring-opening of the substrate under mild reaction conditions. The protocol can be applied to aryl- and heteroaryl-substituted vinylcyclopropanes and can be conducted on a gram scale. The synthetic utility of the lithium salts of the cyclic borate has been demonstrated through regioselective ring-opening functionalizations.



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The Cu-catalyzed borofunctionalization of π systems has emerged as an enabling approach for installing a C−B bond and simultaneously a vicinal C−H, C−C, or C−heteroatom bond across readily accessible unsaturated systems.[1] Because of the central role of organoboron compounds, the growing interest observed for this strategy stems from the rapid access it offers to polyfunctional frameworks containing contiguous sp^2- or sp^3-hybridized carbon atoms using a nontoxic earth-abundant metal.[1,2] The commonly admitted mechanism for these reactions involves migratory insertion of a Cu−boryl species across the π system followed by trapping of the alkyl−copper intermediate by an electrophile and subsequent demetalation.[3,4] To date, diversely substituted cyclic and linear alkenes, 1,3-dienes, allenes, alkynes, enynes, and even dendralenes have been engaged in Cu-catalyzed borofunctionalization reactions.[1,3,5] These have been combined with more than 20 different electrophiles, including alkyl halides, aryl halides, aldehydes, ketones, imines, carbon dioxide, amines, or isocyanates, to name just a few (Figure 1A).

Vinylcyclopropanes (VCPs) are often described as homologues of conjugated 1,3-dienes because of the overlap of the p orbitals of the cyclopropane with the adjacent C=C bond (Figure 1B).[6] This structural feature is evidenced by the partial double-bond character of the σ bond between the cyclopropyl and ethylene units. In the presence of transition metal complexes, coordination to the alkene combined with the high ring-strain energy of the cyclopropane (28 kcal/mol) renders VCPs susceptible to ring-opening to generate allyl−metal intermediates. From a reactivity standpoint, a distinction is usually drawn between activated VCPs (**B**), which possess strong electron-withdrawing groups, and unactivated VCPs (**A**), which lack acceptor substituents. The chemistry of activated VCPs has aroused considerable interest, in particular for the development of addition reactions, allylic substitutions, or cycloadditions in the presence of a π system (intra- or

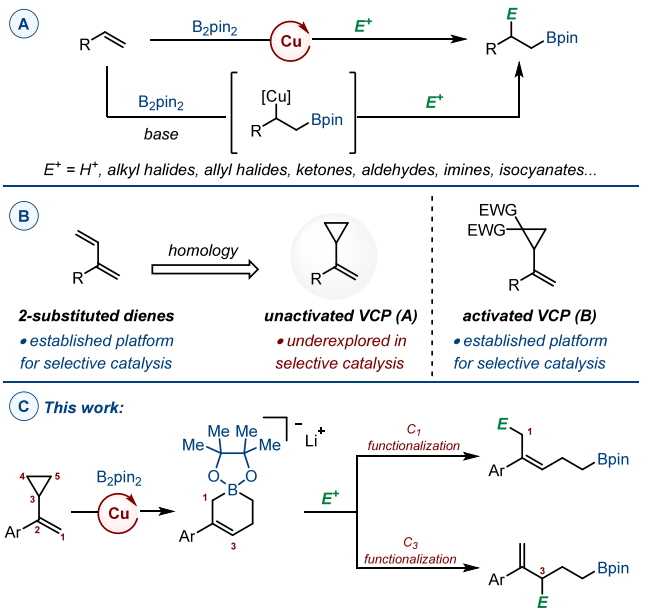

Figure 1. (A) General equation for the Cu-catalyzed borofunctionalization of terminal alkenes. (B) Homology between 1,3-dienes and vinylcyclopropanes (VCPs). (C) Cu-catalyzed borylative cyclization of unactivated VCPs and regioselective postcatalytic functionalizations.

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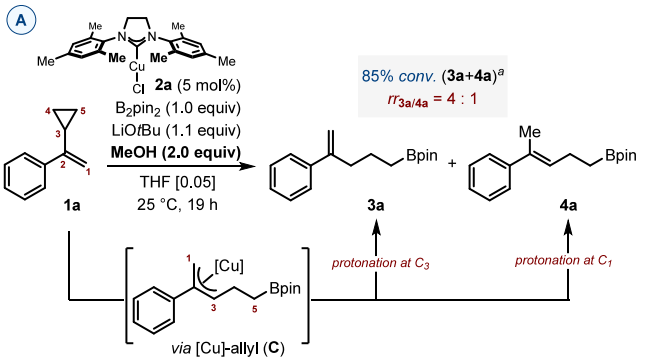
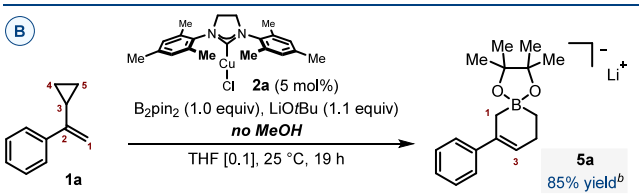
intermolecularly).[6,7] The reactivity of unactivated VCPs has been comparatively much less explored, although they offer the advantage of being employed as either three-carbon or five-carbon synthons.[8] As an extension of our interest in investigating the potential of 2-substituted 1,3-dienes as a platform for the development of selective catalytic processes, we decided to explore the reactivity of the structurally related 2-substituted VCPs (Figure 1C).[9,10] In this report, we describe the serendipitous discovery of a Cu-catalyzed borylation of vinylcyclopropanes that offers access to six-membered cyclic borates. The regioselective ring-opening of these compounds in the presence of various electrophiles is also presented.

We initiated our study by evaluating the reactivity of vinylcyclopropane **1a** under the prototypical conditions employed for the Cu-catalyzed protoboration of π systems (Figure 2A). In the presence of bis(pinacolato)diboron





Entry	Deviation from standard conditions	Conv. (%)[a]
1	*none*	>99 (85)[b]
2	Toluene instead of THF	90 (76)[b]
3	NaO*t*Bu instead of LiO*t*Bu	32
4	KO*t*Bu instead of LiO*t*Bu	<5
5	PCy_3/CuCl instead of **2a**	52
6	**2b** instead of **2a**	<5
7	**D1** instead of B_2pin_2	<5
8	**D2** instead of B_2pin_2	<5

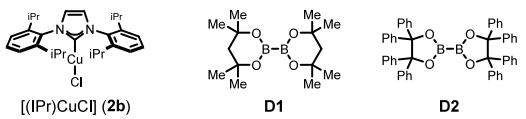


Figure 2. (A) Cu-catalyzed protoboration of an unactivated VCP. (B) Cu-catalyzed borylation of an unactivated VCP (0.5 mmol scale). [a]Conversion was determined by ^{1}H NMR against an internal standard. [b]Yield after purification in parentheses.

(B_2pin_2), LiO*t*Bu, and [(SIMes)CuCl] (**2a**) as a precatalyst, a 4:1 mixture of homoallylboronates **3a** and **4a** was obtained with excellent conversion in THF at room temperature. A plausible scenario to account for the formation of these isomeric products would invoke the formation of a [Cu]−allyl complex (**C**) followed by protonation at either C_1 or C_3 to generate **4a** or **3a**, respectively. While conducting optimizations of this reaction, we found that in a control experiment performed in the absence of methanol, six-membered cyclic borate **5a** could be generated nearly quantitatively and isolated in excellent yield as a hygroscopic off-white powder (Figure 2B). It must be underscored that such borate salts have often been invoked as transient intermediates in several Cu-catalyzed borylation processes developed in recent years.[1] Nonetheless, their isolation and characterization remain rare. Compound **5a** is structurally related to the five-membered cyclic borates obtained by Fujihara and co-workers starting from conjugated 1,3-dienes under comparable catalytic reaction conditions.[11] It also shares similarities with the α,β-unsaturated β-boralactones and the cyclic boracarbonates reported by the Hou group.[12] Quite noticeably, Popp and co-workers isolated and characterized spiroboralactonate Cu(I) complexes that are catalytically competent in the boracarboxylation of vinyl arenes.[13] We found that our system is highly sensitive to subtle variations in the reaction conditions. While appreciable catalytic activity was maintained in toluene, the use of NaO*t*Bu or KO*t*Bu instead of LiO*t*Bu led to little or virtually no conversion in the product. With the exception of the [Cy_3P/CuCl] combination, which delivered **5a** in 52% conversion, other catalytic systems did not generate the borate salt, as exemplified with copper complex **2b**. Other diboron reagents did not prove to be competent either (see the Supporting Information for details).

Given the narrow reactivity window providing access to this unusual cyclic borate salt, we wondered whether other VCPs might be competent substrates. Consequently, the generality of the Cu-catalyzed borylative cyclization was explored using the optimal conditions identified for **1a** (Figure 3A). Beforehand, we established that the model reaction could be conducted on a gram scale (4.0 mmol) with a slight decrease in yield, reflecting more the difficulty associated with product isolation than the catalytic efficiency. Next, we found that a broad range of aryl and heteroaryl rings were compatible with the optimized protocol. High to very high yields were obtained for substrates bearing one or more donor substituents (**1a**−**e**), as was the case for those with weakly electron-withdrawing substituents (**1f** and **1g**). Even though **1h** (R = 4-CN) and **1i** (R = 4-CF_3) both underwent efficient borylation (>90% conversion), the former proved to be more difficult to isolate in practical yields than the latter (40% vs 68%). While a dibenzofuran and a pyridine derivative were well tolerated by the method (**1j**, 51% yield; **1k**, 53% yield), the presence of a ferrocenyl unit led to a markedly decreased yield (**1l**, 23% yield). When *trans*-**1m** was subjected to the catalytic conditions using precatalyst **2b** instead of **2a**, a 6:1 regioisomeric mixture of **5m** and **5m′** was obtained with excellent conversion (85% for **5m** and **5m′**). The major stereoisomer (**5m**), which is formally generated by the ring-opening of the least substituted C−C bond of the cyclopropyl ring, could be isolated in 21% yield by selective precipitation of the borate salt (Figure 3B). Vinylcyclopropanes with alkyl (**1n** and **1o**) or alkynyl (**1p**) substituents did not prove to be competent substrates for the Cu-catalyzed borylative cyclization, as was the case of a VCP with a 1,2-disubstituted alkene (**1q**) instead of a geminal substitution pattern. In these four cases, the substrate was recovered unreacted even after prolonged heating (Figure 3C).[14]

To assess the potential of the borate salts to be used as versatile reagents for organic synthesis, the reactivity of **5a** toward a series of electrophiles was explored next (Figure 4). Treatment of **5a** with 1.2 equivalents of HCl generated homoallyl boronate **3a** in 88% yield with excellent selectivity (*rr* > 25:1). This result is to be compared with that obtained

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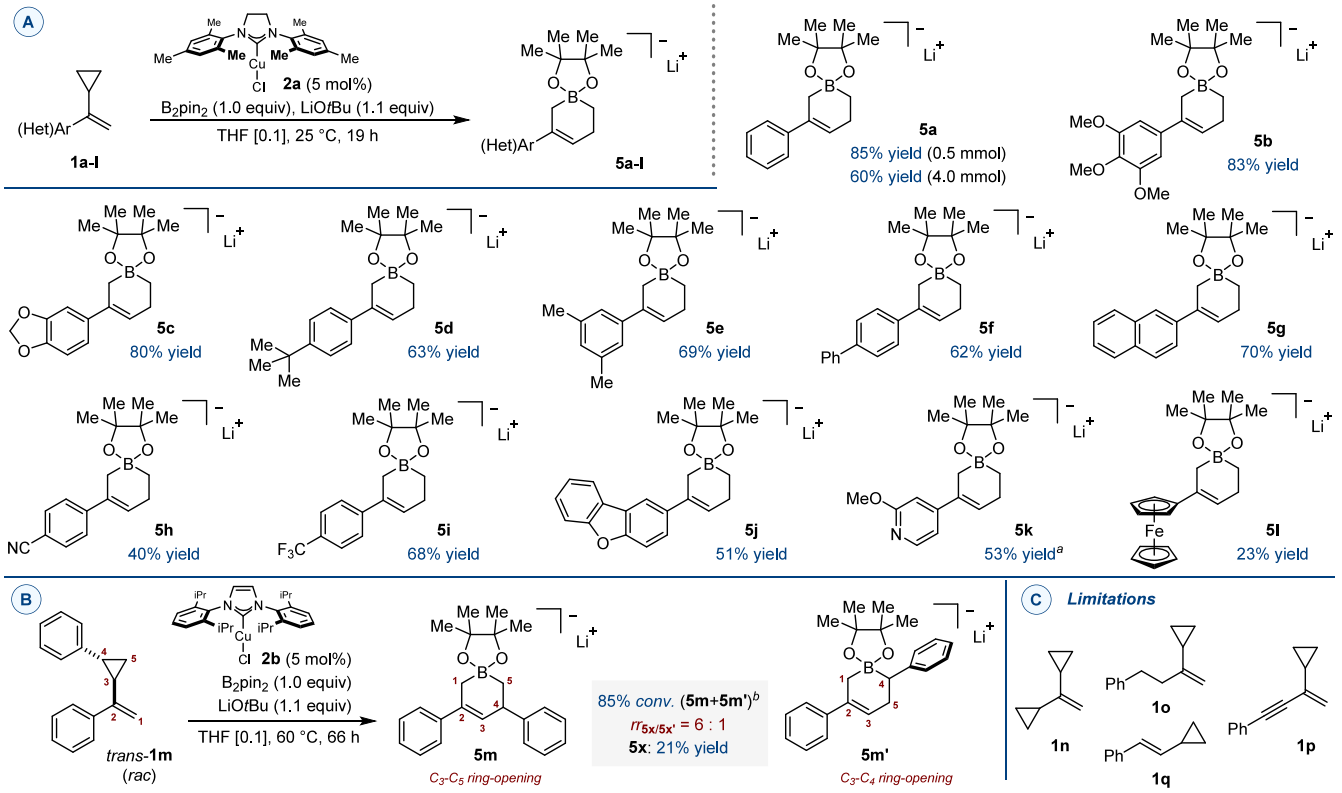

Figure 3. Scope and limitations of the Cu-catalyzed borylative cyclization of vinylcyclopropanes **1a**−**m** (0.5−4.0 mmol). Yields after purification by the precipitation of the borate salt. [a]With 10 mol % **2a**. [b]Determined by ^{1}H NMR of the crude reaction mixture using an internal standard.

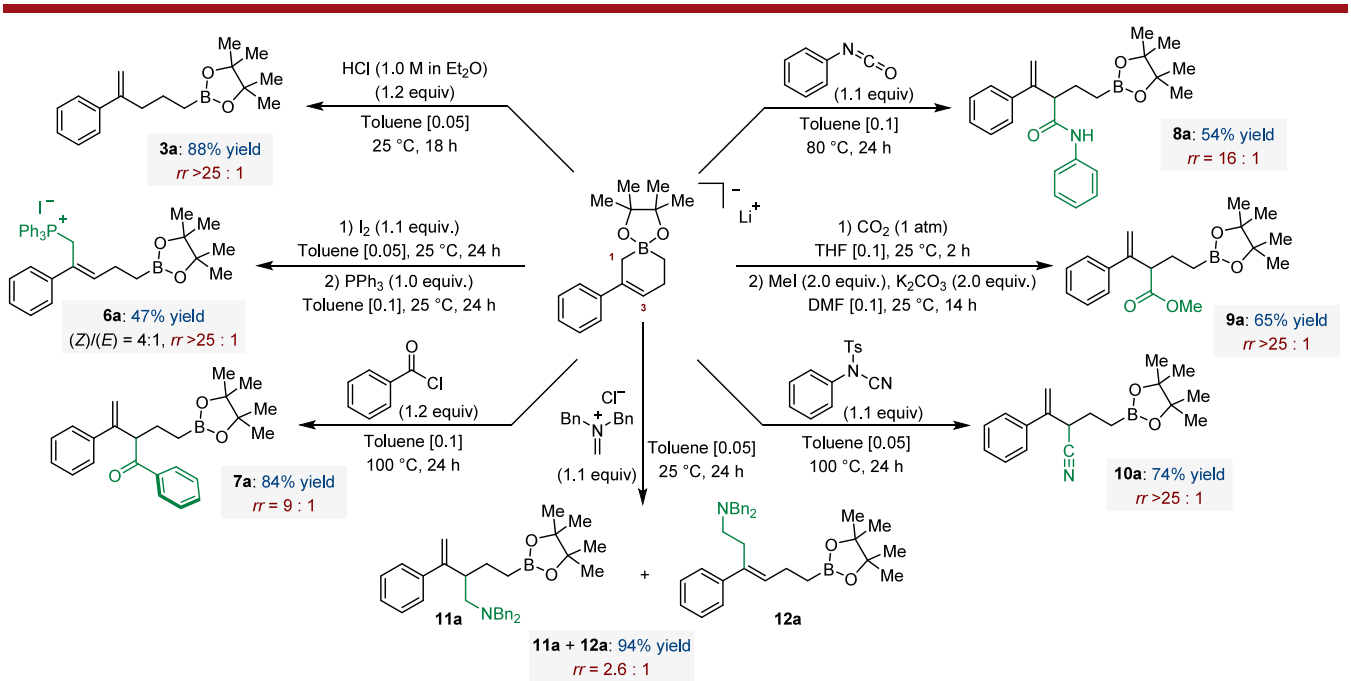

Figure 4. Regioselective postcatalytic derivatizations of the six-membered borate salts. Reaction scale of 0.1−0.3 mmol. Yield after purification. The regioisomeric ratio and stereoselectivity were determined by ^{1}H NMR of the crude reaction mixture using an internal standard.

during our preliminary investigations, as described in Figure 2A. Attempts to obtain **4a** exclusively were not successful (see the Supporting Information). Iodo-phosphonium salt **6a** was formed with excellent C_1 selectivity (*rr* > 25:1) by sequential reaction of the substrate with iodine and triphenylphosphine in toluene at room temperature. A β,γ-unsaturated ketone (**7a**) was obtained in excellent yield and high selectivity (84%; *rr* = 9:1) by reaction with an equimolar amount of benzoyl chloride in refluxing toluene. An amide (**8a**), a methyl ester (**9a**), and a nitrile functionality (**10a**) could be introduced in practical yields and with consistently high C_3 selectivity by reacting **5a** with phenyl isocyanate, carbon dioxide (followed by methylation

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under basic conditions), and *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide, a particularly mild electrophilic cyanating agent, respectively.[15] Dimethylaminomethylation was accomplished in nearly quantitative yield using Echenmoser's salt, $[(Bn)_2N{=}CH_2]Cl$ (94% for **11a** and **12a**), albeit with modest C_3/C_1 selectivity (*rr* = 2.6:1).[16]

In summary, we have developed a Cu-catalyzed borylative cyclization of unactivated VCPs that produces lithium slats of unusual six-membered cyclic borates. The methods operate under mild reaction conditions, are scalable, and were found to be compatible with an array of aryl and heteroaryl substituents. Using a broad set of electrophilic reagents, the synthetic utility of these borate salts has been demonstrated through a variety of highly regioselective functionalizations, leading to the formation of polyfunctional small molecules that hold potential for further orthogonal derivatizations. Current work in our laboratory is being conducted to use these borate salts for the development of enantioselective processes.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.4c01938.

Experimental procedures, characterization of all new compounds, and spectroscopic and spectrometric data (PDF)

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Notes

The authors declare no competing financial interest.

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