Cyclic Boracarbonates

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Synthesis of Lithium Boracarbonate Ion Pairs by Copper-Catalyzed Multi-Component Coupling of Carbon Dioxide, Diboron, and Aldehydes

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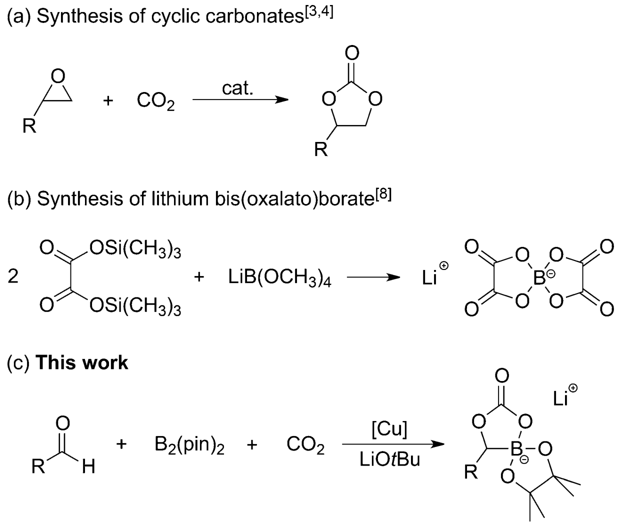
Abstract: *The catalytic selective multi-component coupling of CO_2, bis(pinacolato)diboron, LiOtBu, and a wide range of aldehydes has been achieved for the first time by using an NHC-copper catalyst. This transformation has efficiently afforded a series of novel lithium cyclic boracarbonate ion pair compounds in high yields from readily available starting materials. This protocol has not only provided a new catalytic process for the utilization of CO_2, but it has also constituted a novel route for the efficient synthesis of a new class of lithium borate compounds that might be of interest as potential electrolyte candidates for lithium ion batteries.*

The use of carbon dioxide (CO_2) as a C_1 building block for the synthesis of useful chemicals[1] has received increasing attention from both academia and industry due to its low-cost, easy availability, abundance, nontoxicity, and inherent renewability.[2] However, the chemical transformations of CO_2 for practical applications remained very limited because of its thermodynamic stability and kinetic inertness. The synthesis of cyclic carbonates through cyclic addition of CO_2 to epoxides is among the most successful transformations of CO_2 for chemical synthesis (Figure 1 a).[3] Extensive studies in this area have been carried out in the past a few decades, and cyclic carbonates bearing various exocyclic functional substituents have continuously emerged from this approach.[4] Although incorporation of a heteroatom (e.g., a boron atom) into a cyclic carbonate framework through reaction with CO_2 could be an attractive method for the construction of a new type of heteroatom-implanted cyclic carbonate skeleton, such transformation has not been reported previously, probably because of difficulty in suppressing possible competing side reactions in a multi-component reaction system.



(a) Synthesis of cyclic carbonates[3,4]

(b) Synthesis of lithium bis(oxalato)borate[8]

(c) **This work**

Figure 1. a) Synthesis of cyclic carbonates by coupling of epoxide and CO_2. b) Synthesis of lithium bis(oxalato)borate (LiBOB) from complicated starting materials. c) One-pot synthesis of lithium borate-carbonate ion pairs containing a unique boron-implanted cyclic carbonate structure from easily available starting materials.

Electrolytes[5] play a critically important role in lithium-based rechargeable batteries, which have witnessed great progress and a wide range of applications in the last decades.[6] Recently, functional lithium borate salts,[7] such as lithium bis(oxalato)borate (LiBOB), have attracted intensive interest as electrolytes for high performance lithium batteries, because of their unique properties such as excellent thermal stability, good ionic conductivity, and environmentally benign nature. However, the availability of diversified functional lithium borate salts is quite limited due to the lack of efficient and versatile synthetic methods. For example, the synthesis of a water-free lithium borate such as LiBOB with purity that can meet the requirement of battery grade is tedious as it requires not easily accessible precursors and multi-step operations (Figure 1 b).[8] Therefore, the development of efficient and versatile chemical transformations for the synthesis of diverse functional lithium borate salts from easily available starting materials is highly desirable. On the other hand, cyclic carbonates such as propylene carbonate and ethylene carbonate are among the most commonly used solvents to dissolve electrolyte salts in lithium ion batteries.[5] The combination of lithium borate electrolyte and carbonate solvent is thought essential for solid electrolyte interphase (SEI) formation on electrode surfaces, which has been recognized critically important for high performance lithium

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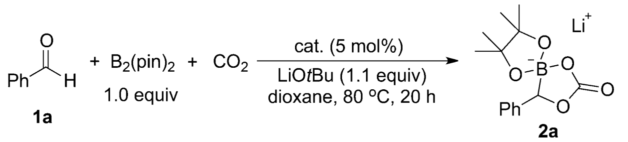
batteries.[5] In view of the importance of lithium borates, cyclic carbonates and their combinations, lithium borate salts containing both a cyclic carbonate structure and a borate unit in one molecule are of much interest. However, the synthesis of such molecular lithium borate-carbonate ion pairs has not been reported previously.

In the course of our studies on the use of CO_2 as a building block for organic synthesis,[2i,9] we became interested in the synthesis of lithium borate-carbonate ion pair compounds using CO_2 as a starting material. Herein we report the one-pot multi-component coupling reaction of CO_2, bis(pinacolato)-diboron ($B_2(pin)_2$), LiO*t*Bu, and a wide range of aldehydes catalyzed by an NHC-copper complex. This protocol has enabled the efficient and selective synthesis of a series of novel lithium cyclic boracarbonate ion pair compounds which contain a unique cyclic carbonate structure fused with a pinacolatoborate unit (Figure 1c).

We began with examining the reaction of benzaldehyde with 1.0 equiv of $B_2(pin)_2$ and 1.1 equiv of LiO*t*Bu under a CO_2 atmosphere by using various N-heterocyclic carbene (NHC) copper complexes as catalysts (Table 1). When the reaction was carried out under 1 atm of CO_2 with [(IPr)CuCl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as a catalyst, a lithium cyclic boracarbonate ion pair product **2a** was obtained only in a trace amount (entry 1). To our delight, raising the CO_2 pressure to 5 atm led to isolation of **2a** in 35% yield (entry 2). Remarkably, the use of copper catalysts bearing more electron-donating NHC ligands, such as [(ICy)CuCl] (ICy = 1,3-dicyclohexylimidazol-2-ylidene) and [(IMes)CuCl] (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene), afforded the desired product **2a** in much higher yields (entries 3 and 4). When the saturated NHC-ligated catalyst [(SIMes)CuCl] (SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) was used, the yield of **2a** was further improved to 85% (entry 5).

Table 1: Cu-catalyzed coupling of benzaldehyde with $B_2(pin)_2$ and CO_2.[a]



Entry	Catalyst	CO_2 Pressure	Yield [%][b]
1	[(IPr)CuCl]	1 atm	trace
2	[(IPr)CuCl]	5 atm	35
3	[(ICy)CuCl]	5 atm	73
4	[(IMes)CuCl]	5 atm	82
5	[(SIMes)CuCl]	5 atm	85

[a] Reaction conditions: cat. (5 mol%), $B_2(pin)_2$ (0.5 mmol), benzaldehyde (0.5 mmol), LiO*t*Bu (1.1 equiv), dioxane (3.0 mL), CO_2, 80 °C, 20 h. [b] Isolated yields.

Recrystallization of **2a** in DME yielded single crystals of **2a′** suitable for X-ray crystallographic studies. It was revealed that **2a′** adopts a dimeric structure of two novel boracarbonate units (Figure 2). The unique five-membered ring of the boracarbonate is built up by connection of the two oxygen atoms of the carbonate group with a B−C bond. The two boracarbonate units are each bonded to two Li atoms by using the carbonate carbonyl oxygen atom and a pinacolate oxygen atom. The Li atoms are tetrahedral coordinated with two oxygen atoms of the DME ligands, one carbonate carbonyl oxygen atom and one pinacolate oxygen atom. The DME solvent ligands in **2a′** could be removed in vacuo to give the DME-free **2a**, as confirmed by NMR and elemental analyses.

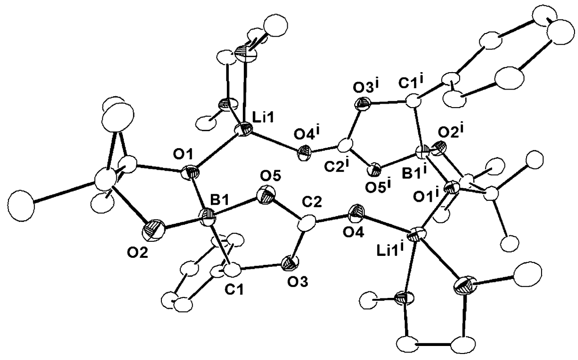


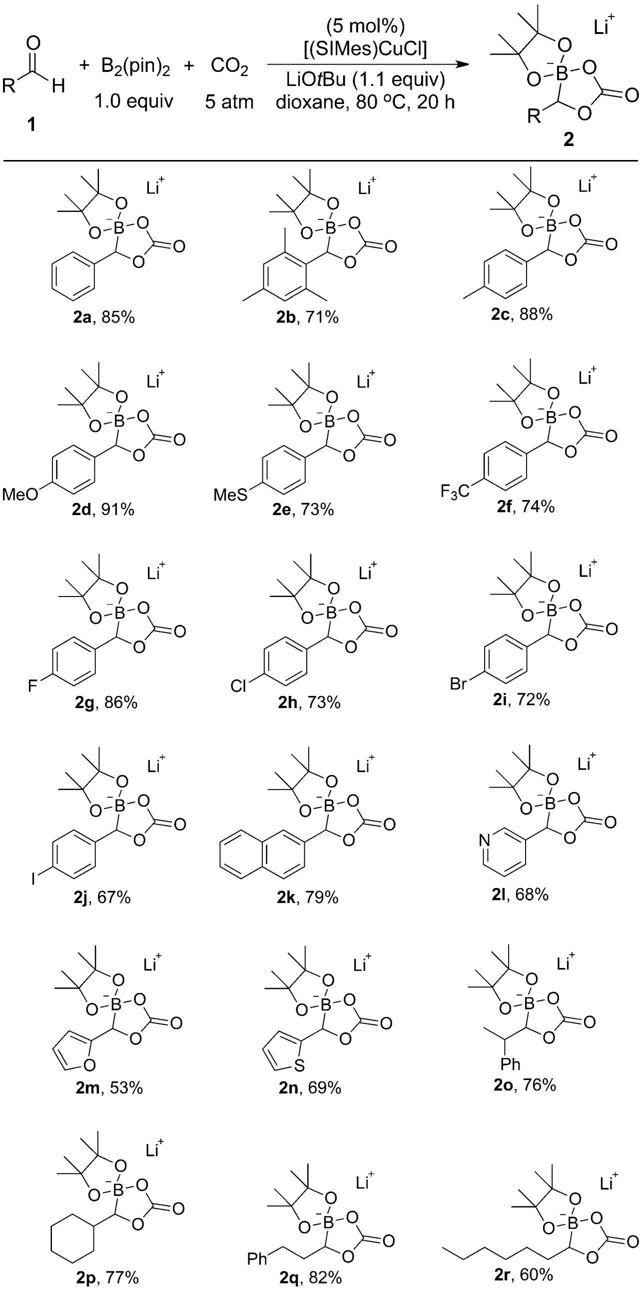
Figure 2. ORTEP drawing of **2a′** with thermal ellipsoids given at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: O1-B1 1.475(5), O2-B1 1.424(5), O5-B1 1.546(4), C1-B1 1.633(5), O5-C2 1.294(4), O3-C2 1.346(4), C2-O4 1.220(4), O1-Li1 1.919(7), Li1-O4^i 1.920(6).

Under the optimized reaction conditions described above, we then investigated the scope of aldehydes for the present coupling reaction with CO_2 and $B_2(pin)_2$ (Table 2). Various aromatic aldehydes bearing either electron-donating or electron-withdrawing groups are suitable for this reaction, affording the desired products in good to excellent yields. For example, the reaction of sterically demanding mesitaldehyde occurred smoothly to give the multi-component cyclic coupling product **2b** in 71% isolated yield. The MeO-, MeS-, and CF_3-substituted benzaldehyde substrates were easily transformed to the desired ion pair products **2d**, **2e**, and **2f**, respectively. Aromatic C−X (X = F, Cl, Br, I) bonds are compatible with the reaction conditions, affording the corresponding halogenated products **2g–j** in good yields. 2-Naphthaldehyde and heteroaromatic aldehydes containing pyridine, furan, and thiophene rings are also applicable, efficiently yielding the desired products **2k–n**. In addition to aromatic aldehydes, various aliphatic aldehydes could also be used as suitable substrates for this reaction, giving the corresponding cyclic boracarbonate products (**2o–r**) in generally high yields.

To gain information on the reaction mechanism of the present catalytic process, we then examined the stoichiometric reaction of a borylcopper complex [(IPr)CuB(pin)], formed by the reaction of [(IPr)Cu(O*t*Bu)] with $B_2(pin)_2$,[10] with mesitaldehyde under 5 atm of CO_2 (Scheme 1). A cyclic boracarbonate complex with a (IPr)Cu unit (**3**) was isolated in 78% yield.[11] The reaction of **3** with 1 equiv of LiO*t*Bu in THF quantitatively afforded the lithium ion pair product **2b** and the copper alkoxide [(IPr)Cu(O*t*Bu)].

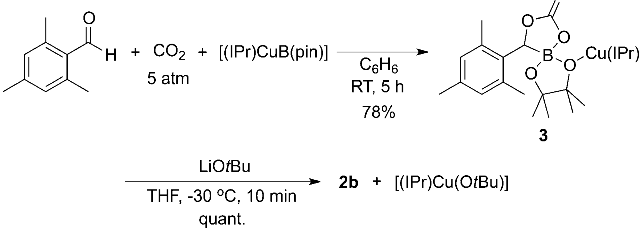
On the basis of the above experimental observations, a possible mechanism for the current catalytic multi-component coupling reaction is proposed in Scheme 2. The initial metathesis reaction between [(NHC)CuCl] and LiO*t*Bu

Table 2: Cu-catalyzed coupling of various aldehydes with $B_2(pin)_2$ and CO_2.[a]

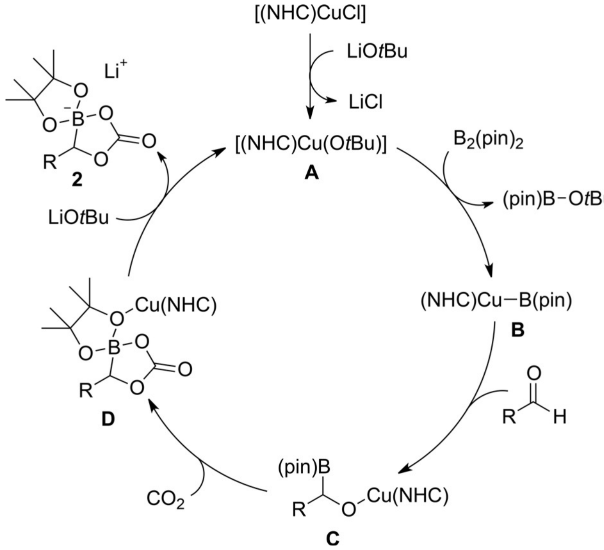


[a] Reaction conditions: [(SIMes)CuCl] (5 mol%), $B_2(pin)_2$ (0.5 mmol), aldehyde (0.5 mmol), LiO*t*Bu (1.1 equiv), dioxane (3.0 mL), CO_2 (5 atm), 80°C, 20 h. Product yields are given in isolated yields.

would afford a copper alkoxide [(NHC)Cu(O*t*Bu)] (**A**), which upon reaction with $B_2(pin)_2$ could generate the boryl copper complex [(NHC)CuB(pin)] (**B**). The subsequent insertion of an aldehyde into the Cu–B bond would give the copper alkoxide **C**. Insertion of CO_2 into the Cu–O bond in **C** followed by migration of the copper unit from the resulting carbonate group to a pinacolate oxygen atom and intramolecular B-O(carbonate) bond formation would generate the cyclic boracarbonate derivative **D**. Transmetallation between the copper complex **D** and LiO*t*Bu should regenerate the copper *tert*-butoxide active species **A** and release the final lithium boracarbonate ion pair product **2**.



Scheme 1. Formation of copper and lithium boracarbonate compounds in stoichiometric reactions.



Scheme 2. A possible reaction mechanism for the coupling of aldehydes with $B_2(pin)_2$ and CO_2.

It is remarkable that the current multi-component coupling reaction took place so selectively and efficiently even though a number of side reactions could be possible, such as the carboxylation of the copper *tert*-butoxide **A** with CO_2, the reduction of CO_2 to CO by the copper boryl species **B**,[10a,b] the rearrangement of the copper alkoxide **C** to an (α-boroxy)-benzylcopper complex,[12] and the metathesis between copper complex **C** with LiO*t*Bu. The present selective formation of **B** from the reaction of **A** with $B_2(pin)_2$ and the selective formation of **C** from the reaction of **B** with an aldehyde demonstrate that the possible competition reactions of the *tert*-butoxide **A** and the boryl species **B** with CO_2 are much slower. Similarly, the selective formation of **D** from the reaction of **C** with CO_2 may suggest that the reaction between the boryl-substituted alkoxide **C** and CO_2 is much faster than that between the *tert*-butoxide **A** and CO_2 and the metathesis reaction of **C** and LiO*t*Bu, and it is even faster than the intramolecular boryl-copper migration reaction in **C**.[12]

In summary, we have developed a new strategy for the synthesis of lithium borate compounds from easily available starting materials. By one-pot coupling of CO_2, $B_2(pin)_2$, aldehydes, and LiO*t*Bu in the presence of an NHC-copper catalyst, we have successfully synthesized a new class of lithium cyclic boracarbonate ion pair compounds, which might be of interest as potential electrolyte candidates for lithium ion batteries in view of their unique structure features. The novel boron-implanted cyclic carbonate structure was constructed by the nucleophilic addition of a copper boryl species to an aldehyde and the subsequent CO_2 insertion into the resulting Cu−O bond followed by ring closing through B−O(carbonate) bond formation. These transformations took place sequentially and selectively by competing against a number of possible side reactions. The present multi-component coupling reaction has not only provided a new class of lithium borate compounds, but it has also constituted a new efficient process for CO_2 utilization. Studies on the electrochemical properties of the lithium boracarbonate compounds obtained in this work and the synthesis of new lithium borate ion pair compounds by reaction of CO_2 with other substrates are in progress.

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[13] CCDC 1453331 (**2a′**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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