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研究課題名(和文) Reductive Incorporation of Carbon Dioxide into Value-Added Chemicals

研究課題名(英文) Reductive Incorporation of Carbon Dioxide into Value-Added Chemicals

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研究成果の概要(和文)：N-ヘテロ環カルベン配位子を有する銅触媒を用いることにより、二酸化炭素、ホウ素化合物、アルデヒド類、リチウムアルコキシドといった複数の入手容易な原料から、1段階で多様なリチウムホウ素化合物を合成する新しい手法の開発に初めて成功した。この手法を用いることで、一連の新規な環状のリチウムボラカーボネートイオン対化合物を高収率で合成することが可能である。今回開発した反応は、新たな触媒的二酸化炭素固定化反応であるだけでなく、リチウムイオン電池の電解質として機能する可能性があるリチウムホウ素化合物の有用な合成法である。

研究成果の概要(英文)：We have achieved the first catalytic selective multi-component coupling of carbon dioxide, bis(pinacolato)diboron, LiOtBu, and a wide range of aldehydes by using an nitrogen heterocyclic carbene-copper catalyst. This reaction 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 carbon dioxide, 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 a potential electrolyte candidates for lithium ion batteries.

研究分野：基礎化学

キーワード：アルデヒド類 ホウ素 二酸化炭素 炭酸エステル 銅触媒

1. 研究開始当初の背景

The use of carbon dioxide (CO₂) as a C1 building block for the synthesis of useful chemicals has received increasing attention from both academia and industry due to its low-cost, easy availability, abundance, nontoxicity, and inherent renewability. However, the chemical transformations of CO₂ for practical applications remained very limited because of its thermodynamic stability and kinetic inertness. The synthesis of cyclic carbonates through cyclic addition of CO₂ to epoxides is among the most successful transformations of CO₂ for chemical synthesis. 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.

Electrolytes 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. Recently, functional lithium borate salts, 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.

2. 研究の目的

Although incorporation of a heteroatom (e.g., a boron atom) into a cyclic carbonate framework through reaction with CO₂ 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.

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.

3. 研究の方法

We began with examining the reaction of benzaldehyde with 1.0 equiv of B₂(pin)₂ and 1.1 equiv of LiOtBu under a CO₂ atmosphere by using various N-heterocyclic carbene(NHC) copper complexes as catalysts. When the reaction was carried out under 1 atm of CO₂ with [(IPr)CuCl] as a catalyst, a lithium cyclic boracarbonate ion pair product was obtained only in a trace amount. To our delight, raising the CO₂ pressure to 5 atm led to isolation of the product in 35% yield. Remarkably, the use of copper catalysts bearing more electron-donating NHC ligands, such as [(ICy)CuCl] and [(IMes)CuCl], afforded the desired product in much higher yields. When the saturated NHC-ligated catalyst [(SIMes)CuCl] was used, the yield of the product was further improved to 85%.

Recrystallization of the product in DME yielded single crystals suitable for X-ray

crystallographic studies. It was revealed that the product adopts a dimeric structure of two novel boracarbonate units. 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 could be removed in vacuo to give the DME-free product, as confirmed by NMR and elemental analyses.

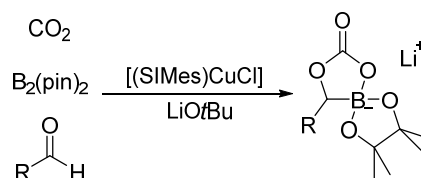
Under the optimized reaction conditions, we then investigated the scope of aldehydes for the present coupling reaction with CO₂ and B₂(pin)₂. Various aromatic aldehydes bearing either electron-donating or electron-withdrawing groups are suitable for this reaction, affording the desired products in good to excellent yields. In addition to aromatic aldehydes, various aliphatic aldehydes could also be used as suitable substrates for this reaction, giving the corresponding cyclic boracarbonate products 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)], with mesitaldehyde under 5 atm of CO₂. A cyclic boracarbonate complex with a (IPr)Cu unit was isolated. Its reaction with 1 equiv of LiOtBu in THF quantitatively afforded the lithium ion

pair product and the copper alkoxide [(IPr)Cu(OtBu)]. On the basis of the above experimental observations, a possible mechanism for the current catalytic multi-component coupling reaction was proposed.

4. 研究成果

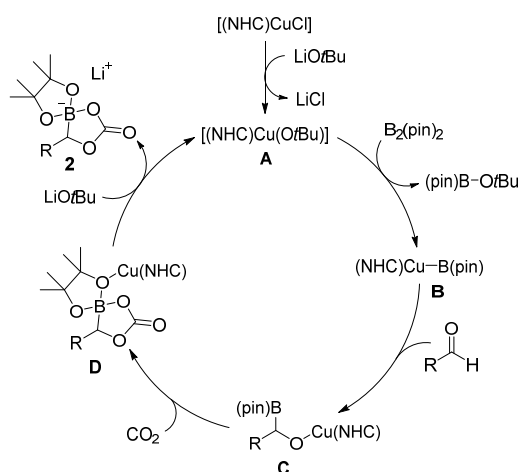
We have developed a new strategy for the synthesis of lithium borate compounds from easily available starting materials (Scheme 1). By one-pot coupling of CO₂, B₂(pin)₂, aldehydes, and LiOtBu in the presence of an NHC-copper catalyst, we have successfully synthesized a new class of lithium cyclic boracarbonate ion pair compounds, which might be of interest as potential electrolyte candidates for lithium ion batteries in view of their unique structure features.



- > 18 examples, up to 91% isolated yields
- > highly selective four-component coupling
- > novel catalytic process for CO₂ fixation
- > new lithium cyclic boracarbonates

Scheme 1

The novel boron-implanted cyclic carbonate structure was constructed by the nucleophilic addition of a copper boryl species to an aldehyde and the subsequent CO₂ insertion into the resulting Cu-O bond followed by ring closing through B-O(carbonate) bond formation (Scheme 2). These transformations took place sequentially and selectively by competing against a number of possible side reactions.



Scheme 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, the rearrangement of the copper alkoxide C to an (α -boryloxy)-benzylcopper complex, and the metathesis between copper complex C with LiOtBu. The present selective formation of B from the reaction of A with $\text{B}_2(\text{pin})_2$ 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 LiOtBu, and it is even faster than the intramolecular boryl-copper migration reaction in C.

The present multicomponent 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.

5. 主な発表論文等

〔雑誌論文〕(計 1 件)

1 Beatrice Carry, Liang Zhang, Masayoshi Nishiura, Zhaomin Hou, Synthesis of Lithium Boracarbonate Ion Pairs by Copper-Catalyzed Multi-Component Coupling of Carbon Dioxide, Diboron, and Aldehydes, *Angewandte Chemie International Edition*, 55, 2016, 6257-6260, DOI: 10.1002/anie.201602278.

査読有

〔学会発表〕(計 1 件)

1 Liang Zhang, Copper-Catalyzed Boracarbonylation Reactions with Diborane and Carbon Dioxide, The 41st International Conference on Coordination Chemistry (ICCC-41), Singapore, Suntec Singapore International Convention & Exhibition Centre, 2014年07月22日.

6. 研究組織

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