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研究課題名(和文) 銅触媒による二酸化炭素を用いるアルケン及びアルキンのポリル化/カルボキシル化

研究課題名(英文) Copper-Catalyzed Borylation/Carboxylation of Alkenes and Alkynes with Carbon Dioxide

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研究成果の概要(和文)：N-ヘテロ環カルベン銅触媒と塩基であるLiOtBuを使うことによって、ビスピナコレートジボランと二酸化炭素を不飽和基質に導入し、温和な条件下で選択的に新規 β -ボラクトン誘導体を合成することに成功した。これはアルキンやアルケン類に簡易に二酸化炭素を導入する、ボラカルボキシル化反応の初めての例である。また今回の反応は、多官能基化された有機化合物の合成に対し、広い基質適応範囲と位置・立体選択性を示した。また、いくつかの反応中間体の単離、構造解析を行うことで反応メカニズムを明らかにした。

研究成果の概要(英文)：We have developed the first example of catalytic boracarboxylation of simple alkynes and alkenes with carbon dioxide (CO₂). In the presence of N-heterocyclic carbene (NHC)-copper complexes as a catalyst and LiOtBu as a base, the reaction of unsaturated substrates with bis(pinacolato)diboron and CO₂ (1 atm) selectively affords a novel family of beta-borolactone derivatives under mild conditions. The current reaction shows broad substrate scope, high regio- and stereoselectivity for the preparation of multifunctionalized hydrocarbons. We have also successfully isolated and structurally characterized some key reaction intermediates from stepwise stoichiometric reactions of related NHC-copper complexes. Based on the experimental results and rational analysis, a possible mechanism of the current reaction is proposed. The work on alkynes has been published in Journal of American Chemical Society and highlighted in SYNFACTS. The manuscript of the results of alkenes is now in preparation.

研究分野：基礎化学

科研費の分科・細目：基礎化学 有機化学

キーワード：二酸化炭素 銅触媒 カルベン配位子 カルボキシル化反応 ポリル化反応 アルケン アルキン

1. 研究開始当初の背景

The use of carbon dioxide (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. The direct carboxylation of carbon nucleophiles with CO₂ as an electrophile is a straightforward protocol for the synthesis of carboxylic acids. It was recently demonstrated that *α*, β -unsaturated carboxylic acids and aliphatic carboxylic acids can be prepared by transition-metal catalyzed hydrocarboxylation of alkynes or alkenes with CO₂. It is of more interest and significance to develop selective transformations generating more diversified organic products from CO₂ for the synthesis of fine chemicals and pharmaceutical agents. However, this kind of reactions remains largely unexplored.

In principle, the heterocarboxylation of alkynes or alkenes with CO₂ would lead to the addition of both a heteroatom unit and a carboxylate group to the C-C multiple bond. This transformation could serve as a useful method for the synthesis of multifunctionalized hydrocarbons, 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. In contrast, the catalytic heterocarboxylation of simple unsaturated C-C bonds with CO₂ has remained almost unexplored.

2. 研究の目的

This research aims to develop the boracarboxylation of simple alkynes or

alkenes with diborane and CO₂ to prepare organoboron groups-containing carboxylic acids. This kind of reaction is of particular interest and importance in view of the wide utility of C-B bonds in various chemical transformations. Further elaboration of the difunctionalized products will provide diversified building blocks for chemical synthesis. Mechanistic study will also be carried out to help us to better understand the catalytic cycle of the proposed reaction.

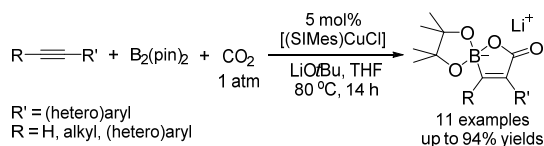
3. 研究の方法

This research starts with the synthesis of *N*-heterocyclic carbene (NHC) ligands, which are used in the following preparation of the corresponding NHC-copper complexes. Then the reaction factors, such as copper catalysts, bases, solvents, temperature, and CO₂ pressure, are systematically screened for a model reaction. The structures of the obtained products are determined by several analytical skills. With the optimized reaction conditions in hand, the substrate scope is investigated in detail. Further elaboration of the obtained products are developed to show the potential synthetic application of this method. Some important reaction intermediates are expected to be isolated from stepwise stoichiometric reactions. The fully structural characterization of these complexes will provide important insight into the reaction mechanism.

4. 研究成果

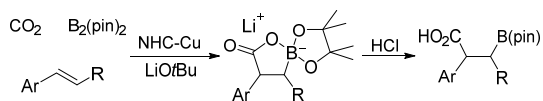
We have developed the first example of copper-catalyzed boracarboxylation of

simple alkynes or alkenes with bis(pinacolato)diboron ($B_2(\text{pin})_2$) and CO_2 . A novel family of α -boralactone derivatives have been synthesized selectively under mild reaction conditions.



Scheme 1

We have found that the boracarboxylation reaction of various alkynes with $B_2(\text{pin})_2$ and CO_2 proceeded smoothly under mild reaction conditions in the presence of a NHC-copper complex $[(SIMes)CuCl]$ as a catalyst and $LiOtBu$ as a base (Scheme 1). This reaction shows broad substrate scope for different substituted alkynes, efficiently affording a novel family of α -unsaturated α -boralactone derivatives with high regio- and stereoselectivity. The structure of the product was confirmed by X-ray crystallographic analysis. Remarkably, this kind of products can be used as a suitable nucleophile in Pd-catalyzed Suzuki-Miyaura reaction. We also have successfully isolated and structurally characterized some key reaction intermediates from stoichiometric reactions of related NHC-copper complexes. Based on the experimental results and rational analysis, a possible mechanism of the current reaction was proposed. This work has been published in *Journal of American Chemical Society* and highlighted in *SYNFACTS*.



Scheme 2

Based on the development of the first heterocarboxylation of alkynes, we further studied the boracarboxylation of C=C double bonds with CO_2 (Scheme 2). Under the optimized reaction conditions, NHC-copper complex catalyzed reaction of styrene with $B_2(\text{pin})_2$ and CO_2 affords a α -boralactone product in high yield. It was found that the reactions of different substituted styrenes can also generate the corresponding desired products in good to excellent yields. Even β -substituted styrenes are suitable substrates for this reaction, affording *syn*-addition products selectively. The acidification of the obtained α -boralactone products gives the corresponding α -boryl carboxylic acids in high yields. This kind of carboxylic group-containing alkylboranes may serve as useful building block in organic synthesis. We also carried out stepwise stoichiometric reactions of related copper complexes. Several important reaction intermediates were successfully isolated and characterized. A possible mechanism of the current reaction was proposed based on the above mentioned studies. A manuscript for publication of this work is now in preparation.

In summary, we have developed the first catalytic boracarboxylation reaction of unsaturated C=C bonds with $B_2(\text{pin})_2$ and CO_2 . The present reactions may serve as an attractive method for the synthesis of multifunctionalized hydrocarbons from CO_2 .

and easily available substrates.

5. 主な発表論文等

〔雑誌論文〕(計 3 件)

¹ Liang Zhang, Jianhua Cheng, Beatrice Carry, Zhaomin Hou, Catalytic Boracarboxylation of Alkynes with Diborane and Carbon Dioxide by an N-Heterocyclic Carbene Copper Catalyst, Journal of the American Chemical Society, 134, 2012, 14314-14317, DOI: 10.1021/ja3063474.

査読有

² Liang Zhang, Jianhua Cheng, Zhaomin Hou, Highly Efficient Catalytic Hydrosilylation of Carbon Dioxide by an N-Heterocyclic Carbene Copper Catalyst, Chemical Communications, 49, 2013, 4782-4784, DOI: 10.1039/c3cc41838c.

査読有

³ Liang Zhang, Zhaomin Hou, N-Heterocyclic Carbene(NHC)-Copper-Catalysed Transformations of Carbon Dioxide, Chemical Science, 4, 2013, 3395-3403, DOI: 10.1039/c3sc51070k.

査読有

〔学会発表〕(計 3 件)

¹ Liang Zhang, Jianhua Cheng, Beatrice Carry, Zhaomin Hou, Copper-Catalyzed Boracarboxylation of Styrenes with Diborane and Carbon Dioxide, 日本化学会第 93 春季年会, 京都, 立命館大学, 2013 年 03 月 23 日.

² Liang Zhang, Jianhua Cheng, Beatrice Carry, Zhaomin Hou, N-Heterocyclic Carbene-Copper Complexes-Catalyzed Carboxylation Reactions with Carbon Dioxide, The Sixteenth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis,

札幌, 北海道大学, 2013 年 08 月 09 日.

³ Liang Zhang, Jianhua Cheng, Beatrice Carry, Zhaomin Hou, N-Heterocyclic Carbene-Copper Complexes-Catalyzed Boracarboxylation of Alkynes and Alkenes with Diborane and Carbon Dioxide, 錯体化学会第 63 回討論会, 沖縄, 琉球大学, 2013 年 11 月 02 日.

〔図書〕(計 1 件)

Liang Zhang, Zhaomin Hou, Transition-Metal-Catalyzed C-C Bond Forming Reactions with Carbon Dioxide, in New and Future Developments in Catalysis (Steven L. Suib Editor), ELSEVIER, 2013, 253-273.

6. 研究組織

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