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**Copper-Catalyzed Multi-Component Coupling of
Carbon Dioxide, Diboron and Carbon-Heteroatom
Unsaturated Bonds**

2016

Tokyo Institute of Technology

Béatrice Marie-Pierre Carry

Preface

The study presented in this thesis has been carried out in the organometallic chemistry laboratory of RIKEN during the period 2013-2016. The studies are concerned with the design of multi-component coupling reactions of carbon dioxide, diboron and carbon-heteroatom unsaturated bonds.

I would like to express my sincere gratitude to those who have provided support and encouragement during my doctoral studies. First and foremost, I wish to acknowledge my advisors, Prof. Zhaomin Hou and Prof. Munetaka Akita. I am grateful to Prof. Zhaomin Hou for the opportunity to study in his laboratory and for providing me with an excellent learning environment. I would like also to thank Prof. Munetaka Akita for his assistance and his guidance in my graduate studies.

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Chapter 5. Summary

The author succeeded in the development of the NHC-copper-catalyzed multi-component coupling reaction between a carbon-heteroatom unsaturated bond, carbon dioxide (CO_2), bis(pinacolato)diboron (B_2pin_2) and lithium *tert*-butoxide (LiO^tBu). This protocol afforded efficiently new classes of lithium borate ion pair compounds in a regioselective manner. Various aldehydes and aldimines were suitable for this novel transformation affording lithium boracarbonates and lithium bora-oxazolidinones respectively.

The mechanism of the reaction was also investigated in detail by isolation and structural characterization of some key reaction intermediates. The novel boron-implanted cyclic carbonate and oxazolidinone structures were constructed by the nucleophilic addition of a copper boryl complex to an aldehyde or an aldimine followed by CO_2 insertion into the resulting copper-heteroatom bond and ring closure through the formation of a boron-oxygen bond. These transformations took place sequentially and selectively through competing side reactions like the diboration of the carbon-heteroatom bond, the carbon dioxide reduction to carbon monoxide, the carboxylation of copper *tert*-butoxide and the Brook-rearrangement of the boryl copper alkoxide complex. The author has also characterized by X-ray crystallography the first insertion product formed from a copper boryl complex and an aldimine substrate. Alternative reaction mechanism has also been explored experimentally, such as the carboxylation of the rearrangement product of the boryl copper alkoxide intermediate. However, the outlined mechanism didn't proceed in the catalytic reaction as the carboxylation occurs before the rearrangement.

Summary

The present development not only discloses a new route for the conversion of CO₂ but constitutes also a versatile method for the synthesis of new functionalized lithium borate molecules that are of particular interest as potential electrolyte candidates for lithium ion batteries or as building blocks for organic synthesis.

Scientific production

Papers

CARRY, Beatrice; ZHANG, Liang; NISHIURA Masayoshi; HOU, Zhaomin (2016) Synthesis of Lithium Boracarbonate Ion Pairs by Copper-Catalyzed Multi-Component Coupling of Carbon Dioxide, Diboron, and Aldehydes **Angew. Chem., Int. Ed.** 55, 6257–6260, **Angew. Chem.** 128, 6365-6368

ZHANG, Liang; CHENG, Jianhua; **CARRY, Beatrice**; HOU, Zhaomin (2012) Catalytic Boracarboxylation of Alkynes with Diborane and Carbon Dioxide by an N-Heterocyclic Carbene Copper Catalyst, **J. Am. Chem. Soc.** 134, 14314–14317

CARRY, Beatrice; ZHANG, Liang; NISHIURA Masayoshi; HOU, Zhaomin Copper-Catalyzed Boracarboxylation of Aldimines with Bis(pinacolato)diboron and Carbon Dioxide *In preparation*

ZHANG, Liang; LUO, Yong; CHENG, Jianhua; *CARRY, Beatrice*; HOU, Zhaomin Copper-Catalyzed Boracarboxylation of Styrenes with Bis(pinacolato)diboron and Carbon Dioxide *In preparation*

Poster presentations

CARRY, Beatrice; ZHANG, Liang; HOU, Zhaomin *Copper-Catalyzed Boracarboxylation of Aldehydes with Diborane and Carbon Dioxide*. The 16th International Conference on Organometallic Chemistry. 1P159, Student Poster Prize, Sapporo-Japan (July 2014)

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Oral presentations

CARRY, Beatrice; ZHANG, Liang; HOU, Zhaomin *Copper-Catalyzed Boracarboxylation of Aldehydes with Diborane and Carbon Dioxide.* The 94th Chemical Society of Japan Annual Meeting, 4F4-12, Nagoya-Japan (March 2014)

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