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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Carbon dioxide (CO_2) is an abundant, cheap, non-flammable and renewable carbon source. The use of CO_2 as a building block in straightforward processes to access functionalized compounds is highly desirable but remains challenging. In recent years, heterocarboxylation reactions with CO_2 emerged as a novel tool to synthesize multifunctionalized molecules with the construction of carbon-carbon bonds and carbon-heteroatom bonds (where the heteroatom is a boron or a silicon atom) from simple starting material in a one-step reaction. The reactions were limited to olefinic substrates and the boracarboxylation of an aldehyde or an imine with CO_2 has not been reported to date. With the aim of widening the range of CO_2 conversion possibilities and opening new accesses to attractive chemical compounds, the copper-catalyzed three component coupling reactions between carbon-heteroatom unsaturated bonds, CO_2 and bis(pinacolato)diboron (B_2pin_2) have been investigated.

Chapter 1 describes the background and purpose of this dissertation.

In Chapter 2, experimental studies on the reaction of 2,4,6-trimethylbenzaldehyde with CO_2 and B_2pin_2 were examined by stoichiometric reactions with the copper complex [(IPr)CuCl], where IPr = 1,3-Bis(2,6-diisopropylphenyl)imidazol-2- ylidene]. The reaction of the copper(I) pinacolatoboryl complex [(IPr)CuBpin] with 2,4,6-trimethylbenzaldehyde gave a copper boryloxyalkyl complex with a [Cu–C–O–B] linkage through the rearrangement from a copper(I) alkoxide complex with a [Cu–O–C–B] linkage formed by the insertion of C=O bond of aldehyde into the copper-boryl bond. Further reaction with CO_2 afforded a cyclic boradioxolanone copper complex which was isolated and clearly characterized by X-ray crystallography. This complex is formed via the carboxylation of the carbonyl carbon atom of the aldehyde followed by intramolecular B–O(dioxolanone) bond formation. However, when the borylcupration of the aldehyde was carried out under a CO_2 atmosphere, a boracarbonate copper complex was isolated in good yield and characterized by NMR analysis. The formation of the boracarbonate moiety is thought to proceed via CO_2 insertion into the Cu–O bond of the copper alkoxide intermediate with a [Cu–O–C–B] linkage followed by B–O(boracarbonate)

bond formation. On the basis of above experimental observations, two possible mechanisms are proposed for the catalytic multi-component coupling of CO_2, B_2pin_2 with aldehyde derivatives.

In Chapter 3, the catalytic boracarboxylation of aldehydes with CO_2 with B_2pin_2 was studied. The *N*-heterocyclic carbene-copper(I) catalyzed boracarboxylation of various aldehydes has been achieved for the first time and lead selectively to the formation of boracarbonates derivatives. A new family of lithium boracarbonates ion pairs was obtained in high yields via a borylation/carboxylation sequence from readily available starting materials. The boracarboxylation reaction demonstrated a wide substrate scope for aromatic, heteroaromatic and aliphatic aldehydes. Based on the isolated compounds from stoichiometric reactions, a possible reaction mechanism is proposed. 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 copper-oxygen bond followed by ring closing through the formation of a carbonate. These transformations took place sequentially and selectively by competing against the aldehyde diboration reaction, the carbon dioxide reduction to carbon monoxide, the carboxylation of copper *tert*-butoxide and the carboxylation of the complex resulting from the Brook-rearrangement of the boryl copper alkoxide complex. 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 new lithium borate derivatives that might be of interest as potential electrolyte candidates for lithium-ion batteries.

In Chapter 4, the copper catalyzed multicomponent coupling of CO_2, B_2pin_2 and aldimines substrates was studied. As for their aldehydes counterparts, the reaction proceeds selectively to the formation of lithium boraoxazolidinones ion pair compounds and proceeds without rearrangement of the insertion product of an aldimine into the copper-boron bond. The lithium boraoxazolidinones ion pair compound may be further functionalized to carbamate esters. More remarkably the unprecedented isolation and characterization of key reaction intermediate of the insertion products of aldimines into a copper-boron bond as well as the copper boraoxazolidinones intermediate were isolated giving out more insight into the reaction mechanism.

Chapter 5 includes the general summary of the present dissertation.