



Fixation of CO₂ as a C1 source into organic compounds catalyzed by lanthanide metal complexes

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Abstract

Methylation reaction of amine derivatives has been developed as an organic reaction utilizing carbon dioxide as a carbon source. In this reaction, a catalytic amount of lanthanum complexes and boron compounds, hydrosilanes as reducing agents, and secondary amines as substrates are used under atmospheric pressure of CO₂ to selectively afford *N*-methylated tertiary amines. Computational study on the reaction mechanism clarifies that the ion-pair formation consisting of the lanthanum complex and the hydridoborate anion is active for the initial hydrosilylation reaction of carbon dioxide, and the subsequent reaction with the secondary amine and deoxygenative reduction gives the final products.

Background & Results

Carbon dioxide (CO₂) is a thermodynamically stable molecule, and its partial reduction leads to reactive CO₂-derived molecules such as formic acid and formaldehyde. However, because of the high stability of CO₂, its reduction requires energy, and over-reduction of the initial CO₂-reduced compounds provides chemically inert methane as the final product; it is thus important to quickly use the initially formed reduced molecules for organic synthesis. In this study, we found that by using a lanthanum complex with a large ionic radius as a catalyst, triarylboron and hydrosilane, a lanthanum complex with a hydridoborate anion is generated and the hydrosilylation of CO₂ proceeds under mild conditions. Furthermore, it was found that when a secondary amine is added to the reaction mixture, the initially reduced products from hydrosilylation of CO₂ reacts with secondary amines to give amides, and the deoxygenative reduction of the amides undergoes under the same reaction conditions, leading to the methylation reaction of secondary amines. During the catalyst screening, it was found that the ionic radius of the central metal affects the reactivity; in fact, the catalytic activity of rare earth metals other than lanthanum decreases. The reaction proceeded efficiently, especially when aniline derivatives were used as substrates, and dialkylaniline derivatives with various functional groups were obtained as the final product. In order to clarify the details of this reaction, each reaction steps were investigated using theoretical calculations. The transition state consists of carbon dioxide bound to the lanthanum center with adjacent hydridoborate anion. The transition state energy required for this reaction is greatly influenced by the Lewis acidity of the triarylboron used as a co-catalyst. It was also found that the non-covalent interaction between the cationic lanthanum complex and the anionic hydrido borate is important for lowering the transition state energy of the reaction.

Significance of the research and Future perspective

Reactions using CO₂, a greenhouse gas, as a carbon source in organic synthesis are important research targets from the viewpoint of carbon cycle without relying on fossil fuels. In particular, the development of catalysts for the direct incorporation of CO₂ as a C1 source into organic compounds is one of the scientific technologies that will contribute for lowering carbon dioxide concentration. We are conducting research on improving possible catalysts that can selectively utilize only carbon dioxide under a mixed gas

atmosphere, thereby making it possible to directly utilize carbon dioxide in the atmosphere for organic synthesis in near future.

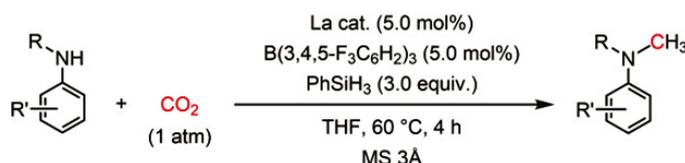
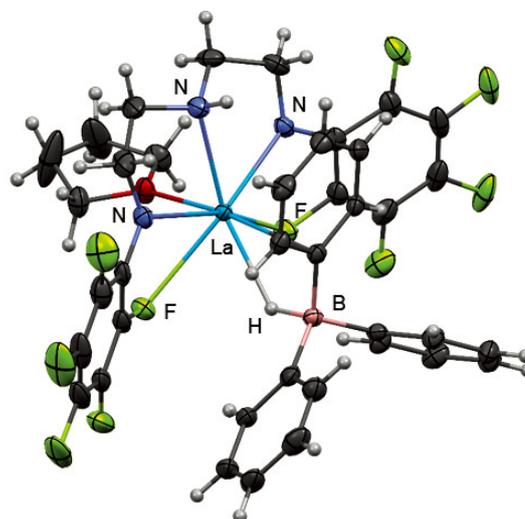
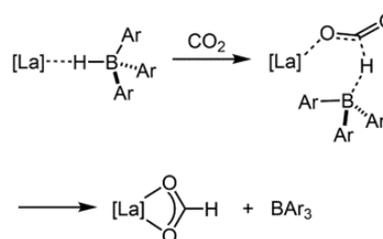
Figure 1 Methylation of *sec*-amines

Figure 2 Molecular structure of catalytically active species

Figure 3 Mechanism of CO₂ hydrogenation

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Keyword

Shinohara, Koichi; Tsurugi, Hayato; Mashima, Kazushi. *N*-methylation of aniline derivatives with CO₂ and phenylsilane catalyzed by lanthanum hydridotriarylborate complexes bearing a nitrogen tridentate ligand. *ACS Catalysis* 2022, 12 (14), 8220-8228. doi: 10.1021/acscatal.2c01658CO₂ fixation, homogeneous catalyst, synthetic organic chemistry