

# Copper-carbene catalysts to help turn waste carbon dioxide into chemical feedstocks

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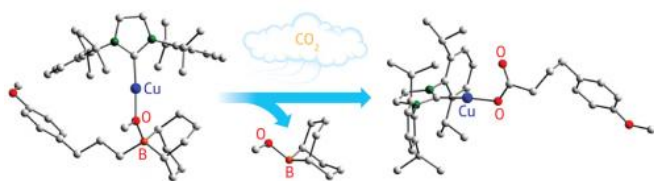


Figure 1: Isolation of a new copper-oxygen-boron complex (left) revealed that carbon dioxide (CO<sub>2</sub>) can insert into its chemical framework (right) by eliminating the organo-boron component (middle panel, lower structure). © 2011 Zhaomin Hou

Using fixation reactions to convert free carbon dioxide (CO<sub>2</sub>) into different organic molecules is an attractive strategy to cut industrial greenhouse gas levels with marginal waste. Now, broadening the scope of CO<sub>2</sub> fixation is possible using a method developed by a research team in Japan led by Zhaomin Hou from the RIKEN Advanced Science Institute in Wako, Japan. The method uses a 'green' catalyst system that transforms alkyl-boron molecules into carboxylic acids-an important ingredient for pharmaceutical production.

Organic boron compounds are attractive [fixation](#) substrates because they readily participate in carbon-carbon bond-forming reactions. Recently, chemists have used transition metal catalysts to activate hydrocarbons bonded to oxygenated boron esters; addition of [CO<sub>2</sub>](#) then splits off the activated group and generates a carboxylic acid derivative. However, attempts to reproduce this chemistry with alkylboranes-a widespread class of important synthetic reagents-have had limited success because the so-called 'catalytic transition metal alkyl' intermediates are usually unstable and decompose before reacting with CO<sub>2</sub>.

Hou and colleagues turned to an innovative chemical system to resolve this instability. By

combining electron-donating, bulky molecules called N-heterocyclic carbenes (NHCs) with copper atoms, they made metal alkyl complexes that can promote carbon-carbon bond formation with CO<sub>2</sub> under mild conditions and at lower cost than most precious metal catalysts-ideal characteristics for sustainably recycling CO<sub>2</sub> emissions.

First, the researchers produced an easily activated alkylborane by connecting borabicyclononane (BBN)-a highly strained set of boron-hydrocarbon rings-to the terminal atom of a carbon-carbon double bond. In this approach, the target hydrocarbon for CO<sub>2</sub> addition is physically and electronically quite different from the two carbon-boron bonds of the BBN rings.

Hou and colleagues then mixed the alkylborane with the copper-NHC catalyst, a base, and CO<sub>2</sub> in a pressurized chamber. After one day at 70 °C, they found that the target had transformed into a new carboxylic acid with near-quantitative yields. Diverse molecules bearing aromatic, halogenated, and bulky functional groups could all act as CO<sub>2</sub> fixation substrates using this technique.

The copper-NHC catalyst offered another advantage to the team: a unique chemical environment that enabled isolation of several catalytic intermediates as solid crystals. X-ray measurements of these structures provided the first hard evidence that bonding interactions between alkoxide base molecules, copper atoms, and alkylboranes are critical to enabling CO<sub>2</sub> addition (Fig. 1). "Fine-tuning the combination of central metals, bases, and supporting ligands will eventually lead to more efficient and selective catalysts," notes Hou.

**More information:** Ohishi, T., Zhang, L., Nishiura, M. & Hou, Z. Carboxylation of alkylboranes by N-heterocyclic carbene copper catalysts: Synthesis of carboxylic acids from terminal alkenes and carbon dioxide. *Angewandte Chemie International Edition*

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