Transforming carbon dioxide gas into valuable building block for organic synthesis

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Figure 1: Copper catalysts are at the heart of an environmentally sustainable process that converts carbon dioxide gas into useful organic materials. Copyright : 2010 Zhaomin Hou

Chemists are helping to reduce heat-trapping carbon dioxide (CO_2) emissions, which are a global concern. For example, they are devising new catalytic systems that would enable waste CO_2 to be recycled as a non-toxic and practically free source of carbon for organic synthetic reactions. However, current CO_2 conversion techniques require expensive metal catalysts or drawn-out procedures.

Now, Zhaomin Hou and colleagues from the RIKEN Advanced Science Institute in Wako have found a way to insert CO_2 directly into the framework of aromatic molecules, turning them into carboxylic acid derivatives that are widely used as pharmaceuticals, agrichemicals, and

dyes[1]. Importantly, this transformation can be achieved economically and with negligible environmental impact, thanks to a low cost copper complex bearing an organic ligand.

N-heterocyclic carbenes (NHCs) are molecules with near metal-like reactivity because of an electron-deficient carbon center. For the past two decades, scientists have used NHCs as organic replacements for metal catalysts and as 'spectator' ligands that attach to metal centers and influence their catalytic behavior. Hou and colleagues recently discovered that adding NHCs to copper, one of the most abundant metals in nature, created a complex that catalyzed CO_2 addition to boron esters[2]—a trick the team hoped to repeat with aromatic hydrocarbons.

The most efficient way to incorporate CO_2 into benzene-like molecules is by replacing one of the carbon–hydrogen (C–H) bonds on the outer ring; unfortunately, these bonds are notoriously unreactive. To overcome this problem, the researchers turned to benzoxazole: this double-ringed aromatic compound has a C–H bond situated between nitrogen and oxygen atoms, making it easier to chemically activate this position.

With just a pinch of the NHC–copper catalyst complex, the team found they could convert a mixture of CO_2 and several different benzoxazole-based molecules into solid carboxylic acids and esters in excellent yields (Fig. 1). Carefully characterizing the crystal structures of several intermediate compounds revealed that CO_2 inserted in between a copper–carbon bond formed at the benzoxazole C–H site, followed by a dissociation step that regenerated the catalyst.

According to Hou, the NHC ligand was essential in enabling CO_2 capture. "The electron-donating ability of NHC could make the C–H activation and CO_2 insertion steps easier, while its steric bulk brings stability to the active catalyst species," he notes. The researchers now hope to extend this technique to less reactive C–H bonds by fine-tuning

the catalyst complex and optimizing reaction conditions.

More information: 1. Zhang, L., et al. Copper-catalyzed direct carboxylation of C–H bonds with carbon dioxide. *Angewandte Chemie International Edition* 49, 8670–8673 (2010).
2. Ohishi, T., et al. Carboxylation of organoboronic esters catalyzed by N-heterocyclic carbene copper(I) complexes. *Angewandte Chemie International Edition* 47, 5792–5795 (2008).

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