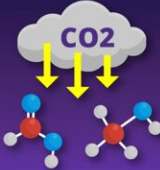


# Fighting climate change: Photoinduced reduction of carbon dioxide to formic acid with ruthenium complexes


February 9 2023

## Photoinduced Reduction of Carbon Dioxide to Formic Acid with Ruthenium Complexes



CO<sub>2</sub>

Chemically converting carbon dioxide (CO<sub>2</sub>) into value-added chemicals is a promising route to mitigating global warming



Direct one-electron reduction of CO<sub>2</sub> requires a lot of energy

### Photoinduced hydride transfer to CO<sub>2</sub> catalyzed by ruthenium (Ru) complexes

**Active catalyst**  
[Ru(bpy)(bpy•)(pbnHH)]<sup>+</sup>

**Two-electron reduction**  
[Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup>


bpy: 2,2'-bipyridine  
 pbn: 2-(pyridin-2-yl)benzo[*b*]-1,5-naphthyridine  
 BIH: 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole  
 CH<sub>3</sub>CN: acetonitrile

- ✓ First catalytic organic hybrid transfer to CO<sub>2</sub>
- ✓ Two-electron reduction in presence of visible light
- ✓ Transfer not affected by excess proton source

**63 moles of CO<sub>2</sub> converted by a mole of catalyst**

The proposed CO<sub>2</sub> conversion method can help realize valuable chemicals and renewable materials

Photoinduced Catalytic Organic-Hydride Transfer to CO<sub>2</sub> Mediated with Ruthenium Complexes as NAD<sup>+</sup>/NADH Redox Couple Models  
 Kinoshita et al. (2023) | *ChemSusChem* | DOI: 10.1002/cssc.202300032



Researchers have recently developed a chemical method that utilizes ruthenium complexes for catalyzing the reduction of CO<sub>2</sub> to formic acid, a value-added chemical. The novel technology will help maintain the carbon cycle and develop renewable materials. Credit: Hitoshi Tamiaki from Ritsumeikan University, Japan

Climate change is a global environmental concern. A major contribution to climate change comes from excessive burning of fossil fuels. They produce carbon dioxide (CO<sub>2</sub>), a greenhouse gas responsible for global warming. In this light, governments globally are framing policies to curb such carbon emissions. However, merely curbing carbon emissions may not be enough. Managing the generated carbon dioxide is also necessary.

On this front, scientists have suggested chemically converting CO<sub>2</sub> into value-added compounds, such as methanol and formic acid (HCOOH). Producing the latter requires a source of hydride ion (H<sup>-</sup>), which is equivalent to one proton and two electrons. For instance, the [nicotinamide adenine dinucleotide](#) (NAD<sup>+</sup>/NADH) reduction-oxidation couple is a hydride (H<sup>-</sup>) generator and reservoir in biological systems.

Against this backdrop, a group of researchers led by Professor Hitoshi Tamiaki from Ritsumeikan University, Japan, have now developed a novel chemical method that reduces CO<sub>2</sub> to HCOOH using NAD<sup>+</sup>/NADH-like ruthenium complexes. Their work was published in the journal *ChemSusChem* on January 13, 2023.

Prof. Tamiaki explains the motivation behind their research. "Recently, a ruthenium complex with an NAD<sup>+</sup> model—[Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub>—was shown to undergo photochemical

two-electron reduction. It produced the corresponding NADH-type complex  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  under visible light irradiation in the presence of triethanolamine in acetonitrile ( $\text{CH}_3\text{CN}$ )," he says.

"Further, the bubbling of  $\text{CO}_2$  into the  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  solution regenerated  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  and produced formate ion ( $\text{HCOO}^-$ ). However, its yield was quite low. Therefore, transferring  $\text{H}^-$  to  $\text{CO}_2$  required an improved catalytic system."

Consequently, the researchers explored various reagents and [reaction conditions](#) to facilitate  $\text{CO}_2$  reduction. Based on those experiments, they proposed a photoinduced two-electron reduction of the  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}/[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  redox couple in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole (BIH). Moreover, water ( $\text{H}_2\text{O}$ ), instead of triethanolamine, in  $\text{CH}_3\text{CN}$  further improved the yield.

In addition, the researchers explored the underlying reaction mechanism using techniques like nuclear magnetic resonance, cyclic voltammetry, and UV-Vis spectrophotometry. Based on this, they proposed the following: First, the photo-excitation of  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  produces  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{pbn}\cdot^-)]^{2+*}$  radical, which undergoes reduction by BIH to give  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{pbn}\cdot^-)]^{2+}$  and  $\text{BIH}\cdot^+$ . Following this,  $\text{H}_2\text{O}$  protonates the ruthenium complex, generating  $[\text{Ru}(\text{bpy})_2(\text{pbnH}\cdot)]^{2+}$  and  $\text{BI}\cdot$ . The obtained product undergoes disproportionation to generate  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  and gives back  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ . Then, the former is reduced by  $\text{BI}\cdot$  to produce  $[\text{Ru}(\text{bpy})(\text{bpy}\cdot^-)(\text{pbnHH})]^+$ . This complex is an active catalyst and transfers  $\text{H}^-$  to  $\text{CO}_2$ , producing  $\text{HCOO}^-$  and formic acid.

The researchers showed that the proposed reaction demonstrated a high turnover number—moles of  $\text{CO}_2$  converted by a mole of catalyst—of 63.

Excited by these findings, the researchers hope to develop a new methodology of energy conversion (sunlight to [chemical energy](#)) for the production of novel renewable materials.

"Our method would also decrease the total amount of CO<sub>2</sub> gas on Earth and help maintain the carbon cycle. Thus, it could reduce [global warming](#) in the future," adds Prof. Tamiaki. "Further, the novel organic hydride transfer technology will provide us with invaluable chemical compounds."

**More information:** Yusuke Kinoshita et al, Photoinduced Catalytic Organic-Hydride Transfer to CO<sub>2</sub> Mediated with Ruthenium Complexes as NAD<sup>+</sup>/NADH Redox Couple Models\*\*, *ChemSusChem* (2023). [DOI: 10.1002/cssc.202300032](https://doi.org/10.1002/cssc.202300032)

Provided by Ritsumeikan University

Citation: Fighting climate change: Photoinduced reduction of carbon dioxide to formic acid with ruthenium complexes (2023, February 9) retrieved 28 July 2024 from <https://phys.org/news/2023-02-climate-photoinduced-reduction-carbon-dioxide.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.