CO_2 photoreduction using a tungsten complex bearing a PNNP-type tetradentate ligand

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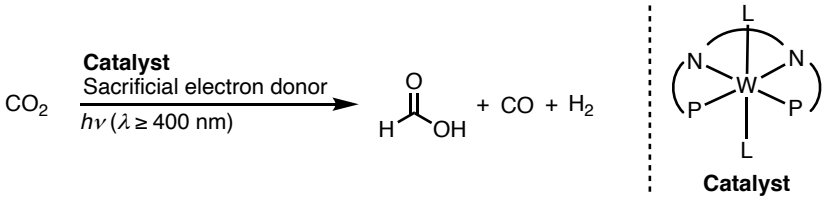
Carbon dioxide (CO_2) is widely considered as the main cause of global warming. In contrast, it is an attractive carbon resource because it is low toxic, cheap, and abundantly present in the atmosphere. Photocatalytic CO_2 reduction is one of the most promising methodologies to convert CO_2 into value-added chemicals, which can offer a sustainable solution to energy and climate problems. In our laboratory, iridium[1] and ruthenium[2] complexes bearing PNNP-type tetradentate ligands have been developed to exhibit efficient photocatalytic abilities towards CO_2 reduction under visible light irradiation. Although these photocatalysts kept high reactivities for a long time due to the robust PNNP ligands, the use of precious metals remains a challenge. To solve this issue, we focused on the tungsten (W) as a promising candidate. Even though a W is relatively abundant and cheap in 5d transition metals, to our knowledge, no W complex has been reported for photocatalytic CO_2 reduction so far.

Herein, we report the synthesis of a new W complex bearing a PNNP-type tetradentate ligand and its catalytic ability towards photocatalytic CO_2 reduction. Under visible light irradiation of a CO_2-saturated DMA solution containing the W complex and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as a sacrificial electron donor, photocatalytic reduction of CO_2 occurred to give HCOOH selectively without an additional photosensitizer (Scheme 1). The amount of HCOOH increased as the reaction solution was irradiated for a longer time and addition of a small amount of water enhanced the reactivity. UV-vis measurements and cyclic voltammetry measurements were conducted to interrogate its catalytic ability.



Scheme 1. CO_2 photoreduction using a W complex

1) K. Kamada, J. Jung, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *J. Am. Chem. Soc.* **2020**, *142*, 10261. 2) K. Kamada, H. Okuwa, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, J. Jung, S. Saito, *Synlett* (Invited Cluster, honoring Prof. Shunichi Fukuzumi's 70th birthday) **2022**, DOI: 10.1055/a-1709-0280 (accessed 2022-1-11).