

Photocatalytic CO₂ Reduction to Formate Promoted by the Water-soluble Pentamethylcyclopentadienyl Rhodium Catalysts

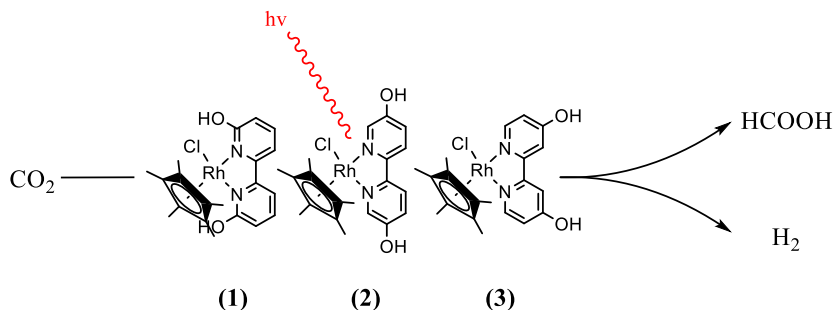
(Department of Chemistry, Kyushu University) ○Dongseob LEE, Yuto SAKAGUCHI, Kosei YAMAUCHI, Ken SAKAI

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Due to the increasing demands to stop global warming, substantial efforts have been made to remove atmospheric CO₂. Photocatalytic CO₂ reduction has attracted considerable attention as one of the promising ways to solve this problem. In particular, it is known that the rhodium complex ligated by pentamethylcyclopentadienyl (Cp*) is one of the efficient catalysts to convert CO₂ into formic acid. Cp* is a strongly electron-donating ligand and increases electron density at the Rh center. Due to this effect, d⁸-Rh(I)Cp* complex can be protonated to give the corresponding rhodium-hydride intermediates, which further promote the activation of CO₂ leading to the formate formation.¹

The RhCp* complex with bpy (bipyridine) ligand was reported to promote the photocatalytic CO₂ reduction into formic acid at 40°C with high activity.¹ However, it is necessary to increase the selectivity of formic acid because the formate and hydrogen generations are often competitively promoted, leading to decrease the overall catalytic efficiency in CO₂ reduction. In this context, comprehension of the intermediate state during CO₂ reduction reaction is necessary to rationally control the selectivity.²

In this study, we focus on the water-soluble catalysts derived from the RhCp* family in order to promote the photocatalytic CO₂ reduction into formic acid under ambient conditions by introducing some hydrophilic ligand such as 4,4'-dihydroxy-2,2'-bpy, 5,5'-dihydroxy-2,2'-bpy and 6,6'-dihydroxy-2,2'-bpy. Moreover, we attempted to clarify the effect of substituents introduced to the bpy moiety in order to improve the selectivity and also to identify the mechanism of CO₂ reduction reaction. Firstly, (1), (2), and (3) RhCp* complexes have been synthesized by introducing the highly hydrophilic bpy ligands. The photocatalytic performance of these complexes together with our DFT results will be discussed in the poster presentation.



1) Y. Himeda, *Eur. J. Inorg. Chem.* **2007**, 3927-3941.

2) T. K. Todorova, T. N. Huan, X. Wang, H. Agarwala, M. Fontecave, *Inorg. Chem.* **2019**, 58, 6893-6903.