

Photocatalytic CO₂ reduction to CO using osmium complexes bearing PNNP-type tetradentate ligands

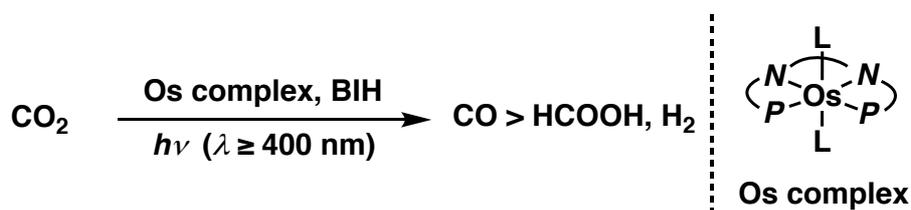
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Photocatalytic reduction of carbon dioxide (CO₂) is recognized as an important research area owing to problems related to the depletion of fossil fuels and environmental issues. Two electron reduction of CO₂ gives carbon monoxide (CO) and formic acid (HCOOH), which are useful and more energy-rich compounds than CO₂. CO₂ photoreduction by transition metal complexes in many cases has been achieved with the combination of photosensitizer (PS) and reduction catalyst (Cat). On the other hand, photocatalysts which act as both PS and Cat enable the mononuclear photocatalytic systems.

In our previous work, an iridium complex bearing a PNNP-type tetradentate ligand was developed as an efficient photocatalyst to reduce CO₂ to formic acid selectively with a turnover number (TON) of 2560.¹ We report here that osmium (Os) photocatalysts bearing PNNP-type tetradentate ligands reduce CO₂ to CO instead of the formic acid in the presence of a sacrificial reagent, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) under visible light irradiation (Scheme 1). The Os photocatalysts can utilize a wider wavelength range of the solar radiation as a photosensitizer of Os(II) tris-diimine complex.² A high TON and long photocatalyst lifespan were achieved owing to the structural robustness of PNNP-type tetradentate ligands. Mechanistic insights were provided by cyclic voltammetry, UV-Vis absorption spectroscopy, EPR measurements and laser flash photolysis measurements.

Scheme 1. Photocatalytic reduction of CO₂ with an Os complex as a photocatalyst under visible light irradiation



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