

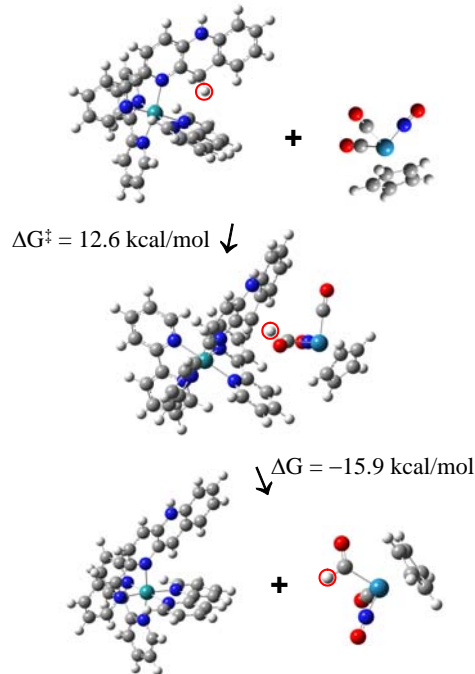
TRANSITION METAL COMPLEXES AS ARTIFICIAL NADPH ANALOGS: TOWARD PHOTOCHEMICAL REDUCTION OF CARBON DIOXIDE

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Artificial photosynthetic systems have received increased attention in the last several years in light of the global problems of rapid depletion of fossil fuels and increased greenhouse gas emissions. Nature elegantly utilizes photocatalytic reactions to store solar energy in the form of chemical equivalents as well as converting carbon dioxide into hydrocarbons. One of the key components of Photosystem I that is responsible for CO₂ reduction is the NADPH co-enzyme, which serves as a hydride donor. Previous work reported the production of [Ru(bpy)₂(pbnHH)]²⁺



(pbnHH = 1,5-dihydro-2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) electrochemically and its use as an electrocatalyst to reduce acetone to isopropanol.¹ We have demonstrated that the same species can be produced photochemically.² The detailed mechanism of the photochemical formation of [Ru(bpy)₂(pbnHH)]²⁺ in water was recently described based on a combination of experimental and theoretical investigations including radiation chemistry and photochemical techniques.³

The theoretical prediction of the hydricity, i.e., the free energy change for the hydride-ion transfer reaction from a hydride donor to the acetonitrile solvent, was carried out for [Ru(bpy)₂(pbnHH)]²⁺ and other reported or proposed hydride donors. Possible ways of increasing the hydricity of [Ru(bpy)₂(pbnHH)]²⁺ based on the theoretical results were proposed. The most promising of these is the photoexcitation and reductive quenching of [Ru(bpy)₂(pbnHH)]²⁺ to [Ru(bpy)₂(pbnHH[•])]⁺, which is predicted to transfer a hydride ion to a carbonyl ligand of CpRe(NO)(CO)₂ as shown in the figure. It was found

experimentally that [Ru(bpy)₂(pbnHH[•])]⁺ can indeed be generated as predicted. The reaction rate of [Ru(bpy)₂(pbnHH)]²⁺ with the strong hydride acceptor (Ph₃C⁺) was rather slow, possibly due to bulky environment of surrounding both donor and acceptor active sites. The photo-chemical generation of the [Ru(bpy)₂(pbnHH[•])]⁺ species and its reactivity with different hydride acceptors will be discussed in this poster.

¹ Koizumi, T.; Tanaka, K., *Angew. Chem. Int. Ed.* **2005**, *44*, 5891-5894.

² Polyansky, D.; Cabelli, D.; Muckerman, J. T.; Fujita, E.; Koizumi, T.; Fukushima, T.; Wada, T.; Tanaka, K., *Angew. Chem. Int. Ed.* **2007**, *46*, 4169-4172.

³ Polyansky, D.; Cabelli, D.; Muckerman, J. T.; Koizumi, T.; Fukushima, T.; Tanaka, K.; Fujita, E. *Inorg. Chem.* **2008**, *47*, 3958-3968.