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***Photogeneration of Hydride Donors and Their Use
Toward CO₂ Reduction***

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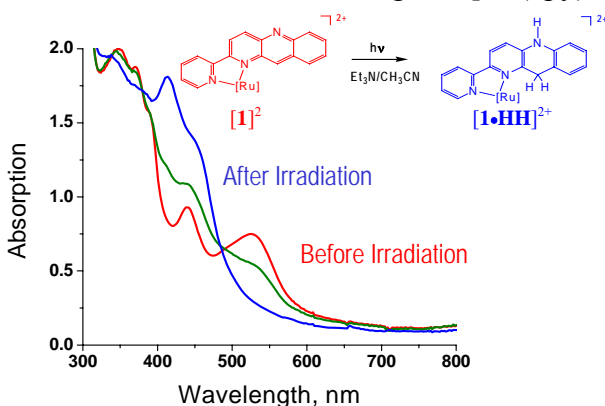
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PHOTOGENERATION OF HYDRIDE DONORS AND THEIR USE TOWARD CO₂ REDUCTION

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Despite substantial effort, no one has succeeded in efficiently producing methanol from CO₂ using homogeneous photocatalytic systems. We are pursuing reaction schemes based on a sequence of hydride-ion transfers to carry out stepwise reduction of CO₂ to methanol. We are using hydride-ion transfer from photoproducted C–H bonds in metal complexes with bio-inspired ligands (*i.e.*, NADH-like ligands) that are known to store one proton and two electrons.

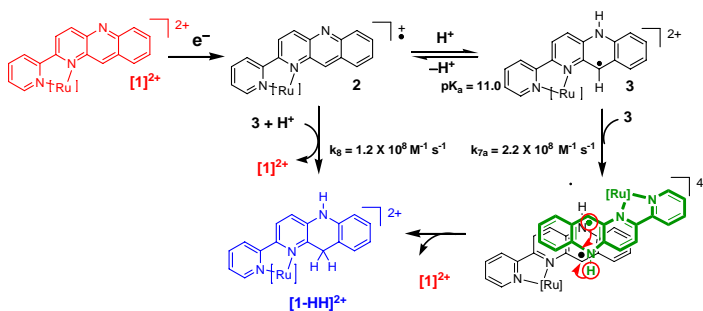
1. Photogeneration of Hydride Donors: We have shown that a polypyridylruthenium complex with an NAD⁺/NADH model ligand, [Ru(bpy)₂(pbn)]²⁺ (**[1]**²⁺, bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) in a wet CH₃CN/amine solution, undergoes



proton-coupled two-electron reduction to give [Ru(bpy)₂(pbnHH)]²⁺ (**[1•HH]**²⁺, pbnHH = 5,10-dihydro-2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) upon irradiation of visible light (300-600 nm). When triethylamine was used as a sacrificial electron donor, the quantum yield for **[1•HH]**²⁺ formation is 0.21 at 355 nm. This result opens a new door to *photoinduced catalytic hydride-transfer reactions* !

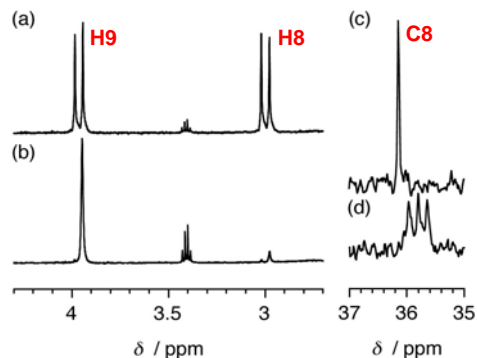
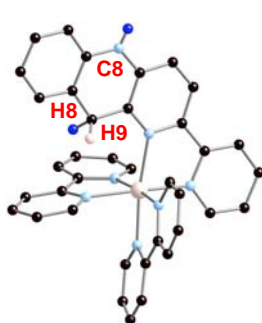
2. Kinetic and Mechanistic Investigation of Hydride Donor Generation by Pulse Radiolysis: Using the pulse radiolysis technique, we determined the mechanism of formation of **[1•HH]**²⁺ in water.

Protonation of the one-electron-reduced species **[2]** takes place below pH 11 to form **[3]** (*pK_a* ~11). Species **[3]** disproportionates through a π -stacked dimer at low pH (see below), and the dimer dissociates to yield **[1]**²⁺ and **[1•HH]**²⁺. The cross reaction between **[2]** and **[3]** yields the same final products at high pH, probably by forming a N–H \cdots N hydrogen bonding interaction between the two species, the transfer of an electron to **[3]**, which subsequently acquires a proton.



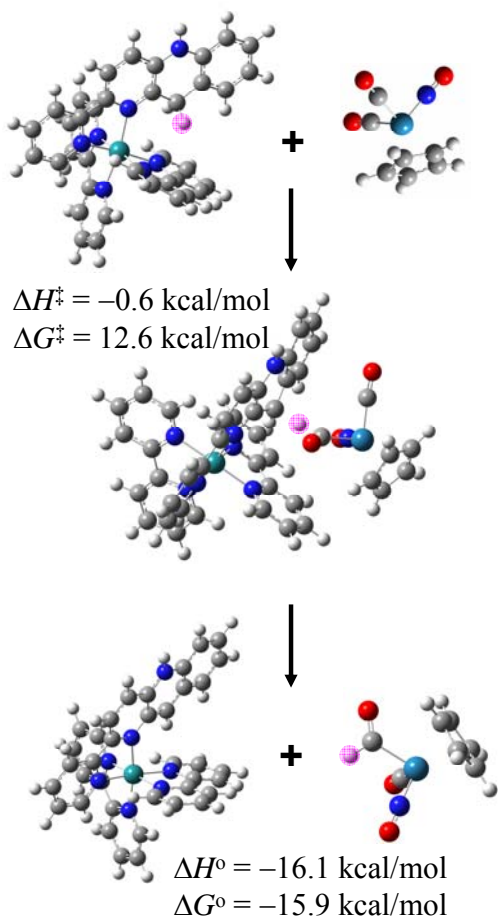
3. Stereo-Specific Photochemical Formation of a C–H Hydride: Our photolysis experiments with D₂O and H₂O solutions containing **[1]**²⁺/CH₃CN/triethanolamine produced **[1•DD]**²⁺ (*m/z* 337.5838) and **[1•HH]**²⁺ (*m/z* 336.5725), respectively. ¹H and ¹³C NMR indicate that stereo-

specific hydrogenation takes place at C8 (see figure at right) in the photochemical reduction of $[1]^{2+}$. The reduction of $[1]^{2+}$ with $\text{Na}_2\text{S}_2\text{O}_4$ in D_2O did not afford any stereospecific products in the deuteration at C8 of pbn. The stereoselective formation of Δ -(S)- $[1\cdot\text{DD}]^{2+}$ and Λ -(R)- $[1\cdot\text{DD}]^{2+}$, which are enantiomers with the same ^1H NMR spectra, clearly indicate that a π -stacked dimer is a key intermediate in the photo-reduction of $[1]^{2+}$. The chiral recognition reaction *via* stereospecific dimerization of a racemic mixture of monomers, followed by disproportionation, may open new directions for photochemical stereospecific hydride-transfer reactions to organic molecules.



Photoproduct of $[1]^{2+}$ in H_2O (a) and (c); in D_2O (b) and (d). H8 is located above the pyridine ring of bpy.

4. Hydricity and Hydride Transfer Reactions: While $[1\cdot\text{HH}]^{2+}$ can transfer a hydride to Ph_3C^+ ($k = 4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$), it cannot transfer a hydride to CO_2 or $\text{M}-\text{CO}$. We have carried out



calculations of the thermodynamic hydricity, or hydride donating power, of this photo-generated catalyst and the hydrided form of possible hydride acceptor molecules for hydride transfer reactions related to CO_2 reduction.

Our theoretical calculations predict that free CO is difficult to convert to the formyl anion by hydride transfer reactions, however, $\text{M}-\text{CO}$ is much easier to convert to $\text{M}-\text{CHO}$. Our calculations also show that the further photoreduction of $[1\cdot\text{HH}]^{2+}$ can create a $[1\cdot\text{HH}]^+$ species with a dramatically increased hydricity that can donate its hydride to $[\text{CpRe}(\text{NO})(\text{CO})_2]^+$ to form $\text{CpRe}(\text{NO})(\text{CO})(\text{CHO})$, the most difficult step in CO_2 reduction to methanol. Our experiments indicate that the excited state of $[1\cdot\text{HH}]^{2+}$ lives 70 ns and can be reductively quenched by amine to form $[1\cdot\text{HH}]^+$, which is a very strong hydride donor that stores the energy of three photons. This suggests that photoinduced hydride transfer reactions to $\text{M}-\text{C}_1$ species are possible. In order to test this scenario we are currently carrying out experiments with $[1\cdot\text{HH}]^+$. [This work was carried out in collaboration with Koji Tanaka, Institute for Molecular Science, Japan.]

DOE Sponsored Publications 2006-2008

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