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# Impact of Ligand Exchange in Hydrogen Production from Cobaloxime-Containing Photocatalytic Systems

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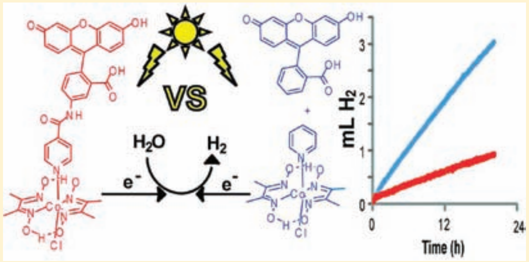
Supporting Information

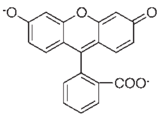
**ABSTRACT:** Ligand exchange on the Co(dmgH)$_2$(py)Cl water reduction catalyst was explored under photocatalytic conditions. The photosensitizer fluorescein was connected to the catalyst through the axially coordinated pyridine. While this two-component complex produces $H_2$ from water under visible light irradiation in the presence of triethanolamine (TEOA), it is less active than a system containing separate fluorescein and [Co$^{III}$(dmgH)$_2$(py)Cl] components. NMR and photolysis experiments show that the Co catalyst undergoes pyridine exchange. Interestingly, glyoximate ligand exchange was also observed photocatalytically and by NMR spectroscopy, thereby showing that integrated systems in which the photosensitizer is linked directly to the Co(dmgH)$_2$(py)Cl catalyst may not remain intact during $H_2$ photogeneration. These studies have also given rise to insights into the catalyst decomposition mechanism.

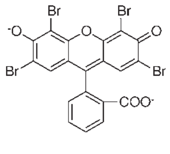


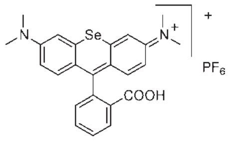
## INTRODUCTION

Artificial photosynthesis to split water into its constituent elements is the most promising approach in the conversion of solar energy into the stored energy of chemical bonds.[1−4] The reductive side of this reaction involves the light-driven generation of hydrogen from aqueous protons. Aspects of this reaction have been studied for more than three decades using molecularly based systems containing a chromophore or photosensitizer for light absorption, a catalyst for $H_2$ generation, an electron source for proton reduction, and a means of electron transfer to the catalyst.[5−10] Advances in the photosensitizer (PS)[10−16] and catalyst[13,15,17,18] components have led to systems having both high turnover frequencies (TOF) and overall turnover numbers (TON), but these systems in general possess limited photostabilities and have rates that may be controlled by diffusion of the components.

In 2009 we reported the first homogeneous system for photoreduction of water that did *not* contain platinum group metals.[7] The system employed the xanthene-based dye Eosin Y as the PS, the Co(III) complex Co(dmgH)$_2$(py)Cl (dmgH = dimethylglyoxime, py = pyridine) as the catalyst, and triethanolamine (TEOA) as the sacrificial electron donor and gave >900 turnovers of $H_2$ with a quantum yield of ~4% for 520−540 nm light. While this system exhibited good rates of $H_2$ production (~70 TON/h, based on photosensitizer), it suffered from photodecomposition, with hydrogen generation ceasing after 12 h. Under the same conditions, the nonhalogenated dye fluorescein (Fl) did not produce $H_2$ but also did not bleach. The dominant electron transfer behavior of the Eosin Y dye was thought to be linked to the heavy atom effect of the bromide substituents, thereby facilitating intersystem crossing (ISC) to the longer-lived $^3\pi\pi^*$ excited state from which electron transfer occurred. Efforts to restart hydrogen generation in this system required addition of both PS *and* catalyst to become active. In 2010, we reported an even more active system in which a Se-containing rhodamine derivative (Rhod-Se) was employed as the photosensitizer along with Co(dmgH)$_2$(py)Cl as the catalyst, but it too suffered from photoinstability.[12] In both sets of studies, it was noted that at higher concentrations of the Co catalyst or with additional free dmgH$_2$ present the systems exhibited increased longevity for $H_2$ generation, suggesting a possible connection between catalyst and PS decomposition.[11,19,20]


**Fl$^{2-}$**


**EY$^{2-}$**


**Rhod-Se**

The present paper describes two different but related studies that were done to address the activity and durability of these $H_2$ photogenerating systems. The first was based on the reported observation that reduction of the Co(dmgH)$_2$(py)Cl catalyst led only to Cl$^-$ dissociation and not dissociation of pyridine.[21,22] This observation stimulated construction of the fluoresein-derivatized pyridine **1** and the resultant integrated system shown as **2** in which the fluorescein dye is linked directly to the catalyst through the pyridyl ligand to facilitate intramolecular electron transfer upon photoexcitation relative to bimolecular reaction

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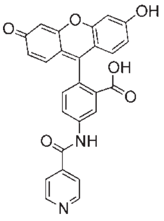
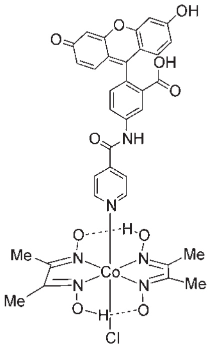
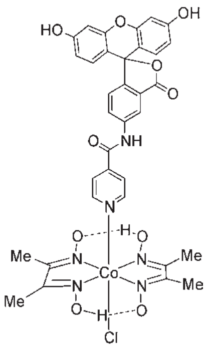
between the indivisual PS and the catalyst molecules.[23−26] The second study arose out of the first in order to rationalize the observation that the newly synthesized linked component system **2** offered no improvement over the corresponding system having separate components. Specifically, as a result of that conclusion, ligand exchange was examined in the Co(dmgH)$_2$(py)Cl complex under catalytic conditions, and the results give insight into the detailed mechanism of operation of the dye + Co(dmgH)$_2$(py)Cl catalyst system.



**1**



**2**



**2b**

## ■ EXPERIMENTAL SECTION

**Materials.** The complexes [Co$^{III}$(dmgH)$_2$(py)Cl],[27] [Co$^{III}$(dpgH)$_2$(py)Cl],[28] and [Co$^{III}$(dmgH)$_2$(py)$_2$]PF$_6$[29] were synthesized by previously reported methods and recrystallized from methylene chloride. All solvents were used without further purification unless otherwise stated. Dimethylglyoxime (dmgH$_2$) and diphenylglyoxime (dpgH$_2$) were purchased from Aldrich and used without further purification. $^1$H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer; data are reported in ppm.

**Syntheses.** *Pyridine-4-amido-aminofluorescein (**1**).* Aminofluorescein (1.5 g, 4.3 mmol) and isonicotinoyl chloride hydrochloride (0.92 g, 6.5 mmol) were stirred in 100 mL of anhydrous pyridine for 24 h under a nitrogen atmosphere. The yellow precipitate was collected by vacuum filtration. The product was purified on a silica column with an ethyl acetate:methanol:hexanes 3:2:1 eluent. The collected product was dissolved in a 0.1 M NaOH in MeOH solution and precipitated by adding acetic acid dropwise. The orange precipitate was collected by vacuum filtration and washed three times each with water, ethanol, and diethyl ether (1.05 g, 53.7%). Anal. Calcd for $C_{26}H_{16}N_2O_6 \cdot CH_3OH$: C, 67.08; H, 3.96; N, 5.79. Found: C. 67.27; H. 3.62; N. 5.93. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.91 (s, 1H), 10.15 (br, 2H), 8.81 (d, $J$ = 6.0 Hz, 2H), 8.45 (d, $J$ = 1.2 Hz, 1H), 8.06 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.88 (d, $J$ = 5.6 Hz, 2H), 7.27 (d, $J$ = 8.4 Hz, 1H), 6.65 (d, $J$ = 2.0 Hz, 2H), 6.60 (d, $J$ = 8.4 Hz, 2H), 6.54 (d, $J$ = 2.0 Hz, 2H) ppm.

*Co(dmgH)$_2$(py-aminofluorescein)Cl (**2**).* Co(dmgH)$_2$Cl$_2$ (158 mg, 0.442 mmol) was mixed in 20 mL of methanol, resulting in a green suspension. Sodium hydroxide (17.7 mg, 0.442 mmol) was added, and after 3 min, **1** (200 mg, 0.442 mmol) was added with the mixture left to stir for 24 h. The orange-brown mixture was filtered, and 67 mg of **2** was collected. By slow evaporation of the solvent from the filtrate, red-brown crystals were obtained (130 mg, 40%). HRMS-EI $C_{34}H_{30}O_{10}N_6Co_1$: calcd 741.1350, found, 741.13245, $\Delta = -3.4$ ppm. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.97 (s, 1H) 10.11 (s, 2H), 8.34 (d, $J$ = 1.6 Hz, 1 H), 8.22 (d, $J$ = 6.8 Hz, 2H), 7. 92 (dd, 1H), 7.86 (d, $J$ = 6.8 Hz, 2H), 7.24 (d, $J$ = 8.4 Hz, 1 H), 6.64 (d, $J$ = 2.4 Hz, 2 H), 6.57−6.52 (m, 4H), 2.26 (s, 12H) ppm.

**Hydrogen Evolution Studies.** A $1 \times 10^{-4}$ M solution of Eosin Y in 9:1 H$_2$O/TEOA (adjusted to pH 7 using concentrated HCl) was prepared and protected from light before use. A $5 \times 10^{-4}$ M solution of cobaloxime complex (either [Co$^{III}$(dmgH)$_2$(py)Cl] or [Co$^{III}$(dpgH)$_2$(py)Cl]) in acetonitrile was prepared. Equal volumes of the dye and cobaloxime solutions were added to total 5 mL in 40 mL scintillation vials. Varying amounts of dmgH$_2$ and dpgH$_2$ were added as solids. The samples were placed into a temperature-controlled block at 15 °C and sealed with airtight caps fitted with a pressure transducer and septa. The samples were degassed by bubbling with a 20% mixture of CH$_4$ in N$_2$, in which CH$_4$ was later used as the internal standard for GC analysis of evolved H$_2$. The cells were irradiated from below with high-power Philips LumiLEDs Luxeon Star Hex, green (520 nm) 700 mA, LEDs. The light power of each LED was set to 0.15 W, measured with a L30 A Thermal sensor and Nova II Power meter (Ophir-Spiricon LLC). The samples were mixed by placing the apparatus on an orbital shaker. The pressure changes in the vials were recorded using a Labview program read from a Freesale semiconductor pressure sensor (MPX4250A series). At the end of the irradiation, the headspace of the vials was sampled by gas chromatography to ensure that the measured pressure changes were caused by H$_2$ generation and to double check that the amount of generated hydrogen calculated by the change in pressure corresponded to the amount determined by the GC. The amounts of hydrogen evolved were determined using a Shimadzu GC-17A gas chromatograph with a 5 Å molecular sieve column (30 m, 0.53 mm) and a TCD detector by injecting 100 $\mu$L of headspace into the GC and were quantified by a calibration plot to the internal CH$_4$ standard. The LED photolysis setup was built with guidance and help from Profs. Stefan Bernhard and Karen Brewer.[15,30]

**UV−vis Absorption Spectra.** A $1 \times 10^{-5}$ M solution of **1**, **2**, and fluorescein in 0.1 M NaOH$_{aq}$ was analyzed on a Hitachi U2000 spectrometer in a 1 cm path length quartz cuvette.

**Fluorescence Quantum Yield.** The absorbance of dilute solutions of **1**, **2**, and fluorescein in 0.1 M NaOH$_{aq}$ solutions at 491 nm were set to 0.1 recorded on a Hitachi U2000 spectrometer. The area under the emission spectra was recorded on a Spex Fluoromax-P fluorimeter with a photomultiplier tube detector. The quantum yields were calculated using the ratio of the numerical integration of the emission spectra of **1** and **2** to the fluorescein standard.

**Fluorescence Quenching.** A solution of fluorescein in a 1:1 mixture of CH$_3$CN:H$_2$O was prepared in a quartz cuvette fitted with a septum cap. Aliquots of 30 $\mu$L of TEOA were added, and the intensity of the fluorescence was monitored by steady state fluorescence exciting at 500 nm on a Spex Fluoromax-P fluorimeter with a photomultiplier tube detector.

**Kinetic NMR Experiments for Pyridine Exchange.** A 0.012 M solution of [Co$^{III}$(dmgH)$_2$(py)$_2$]PF$_6$ in CD$_3$CN was prepared and transferred to a J. Young resealable NMR tube. Immediately before the first NMR measurement, 4 mol equiv of 4-*tert*-butylpyridine (*t*Bupy) was added. NMR spectra were subsequently recorded periodically at room temperature until spectral changes were no longer observed.

**Kinetic NMR Experiments for Dimethyl- or Diphenylglyoxime Exchange.** A 0.012 M solution of [Co$^{III}$(dmgH)$_2$(py)Cl] in 9:1 CD$_3$CN/D$_2$O was prepared and transferred to a J. Young resealable NMR tube. Immediately before the first NMR measurement, 4 mol equiv of dpgH$_2$ was added. NMR spectra were subsequently recorded periodically at room temperature until spectral changes were no longer observed.

**X-ray Crystal Structure Determination of 2.** A crystal of **2** ($0.22 \times 0.16 \times 0.06$ mm$^3$) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[31] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using Mo K$\alpha$ radiation (graphite monochromator) with a frame time of 60 s and a detector distance of 3.97 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50° steps in $\omega$ at four different $\varphi$ settings and a detector position of −38° in $2\theta$. The intensity data were corrected for absorption.[32] Final cell constants were calculated from the *xyz* centroids of 4000 strong reflections from the actual data collection after integration.[33]

The structure was solved using SIR97[34] and refined using SHELXL-97.[35] The space group $P2_1/n$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. When possible hydrogen atoms involved in hydrogen bonding were found from the difference Fourier map, and their positions were refined. Others were placed in reasonable positions to maximize hydrogen bonding. All other hydrogen atoms were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. The final full-matrix least-squares refinement converged to $R1 = 0.0584$ ($F^2, I > 2\sigma(I)$) and $wR2 = 0.1555$ ($F^2$, all data). A table with crystal data and structure refinement for **2** can be found in the Supporting Information (Table S1).

## RESULTS AND DISCUSSION

**Synthesis and Structure.** A version of fluorescein with an appended pyridine was synthesized from the reaction of 4-amino-fluorescein and isonicotinoyl chloride hydrochloride. This reaction yields compound **1**, which in turn displaces $Cl^-$ from $H[Co(dmgH)_2Cl_2]$[27] to give $[Co(dmgH)_2(\mathbf{1})Cl]$ (**2**), as confirmed by NMR spectroscopy and high-resolution mass spectrometry. X-ray crystal structure analysis of **2** verifies the $Co^{III}$ coordination sphere and reveals that the fluorescein of **1** exists as its ring-closed lactone isomer (**2b**, Figure 1). This isomer is known to undergo tautomerization to the ring-opened, anionic form at neutral or basic pH.[36] The molecular structure of **2** reveals little influence on the Co(dmgH) portion of the structure from the attached fluorescein moiety. The bond length to the pyridyl nitrogen is longer (1.952(2) Å, Table 1) than the Co−N bonds to the dmgH ligands (avg. 1.894(5) Å). The geometry around the Co center is a distorted octahedron, with the N−Co−N chelate angles being 81.1(1)° and 81.9(1)° for the two dmgH ligands. These values are similar to those in $[Co(dmgH)_2(4\text{-COOMe-py})Cl]$ (81.90(7)° and 81.30(7)°) and $[Co(dmgH)_2(4\text{-}Me_2N\text{-py})Cl]$ (81.68(4)° and 81.36(4)°).[6] The Co−N bond lengths of **2** are within error the same as those reported for the related complexes $Co(dmgH)_2(4\text{-COOMe-py})Cl$ (1.959(2) Å for Co to pyridyl and ~1.89 Å for Co to dmgH) and $Co(dmgH)_2(4\text{-}Me_2N\text{-py})Cl$ (1.9464(9)Å for Co to pyridyl and avg. 1.894(5) Å for Co to dmgH).[6]

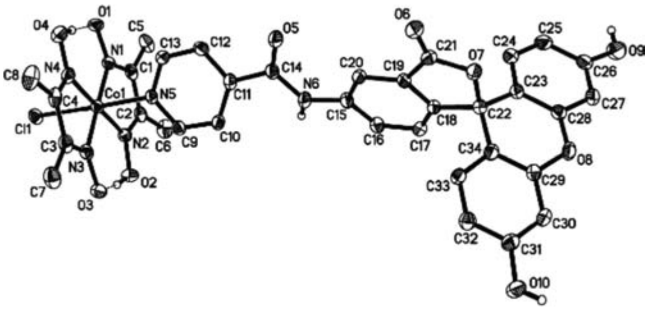


Figure 1. Molecular structure of **2b** with thermal ellipsoids at the 50% probability level. Atom-numbering schemes are shown; the hydrogen atoms are omitted for clarity.

The crystal structure contains one cocrystallized methanol and one and a half cocrystallized water solvent molecules per cobalt complex. There are two major intermolecular hydrogen-bonding motifs present: one between the Co complex and the water and methanol molecules and the other due between the lactone carbonyl oxygen O10 and the neighboring fluorescein O6. Intramolecular hydrogen bonding is also found within the complex between the dimethylglyoximate ligands.

**Photogeneration of Hydrogen.** Using **2** as both PS and catalyst, photogeneration of $H_2$ occurs under irradiation with visible light ($5 \times 10^{-4}$ M **2**, 5% v/v TEOA in 1:1 $CH_3CN$:$H_2O$, pH 7). During 24 h of irradiation with 520 nm light a total 1.0 mL of $H_2$ is produced at a constant rate (TON = 20). Addition of 10 equiv of $dmgH_2$ prolongs this constant rate of $H_2$ generation for 72 h. The $Co(dmgH)_2(py)Cl$ catalyst is minimally soluble in water, but complex **2** is soluble in 5% TEOA/water (v:v with pH adjusted to ~7 with HCl). When this solution is used as the solvent without any additional organic solvent, $H_2$ generation is observed. However, when using water as the solvent under otherwise identical conditions, the rate of $H_2$ generation is ca. one-third of that seen in the water/MeCN system (11 vs 32 TON over 28 h). Hydrogen generation from systems with molecular catalysts in water only has been reported a few times.[37]

To assess the benefit of the attached PS−catalyst complex, a $H_2$-generating system composed of the derivatized fluorescein **1** ($5 \times 10^{-4}$ M) as the PS and $[Co^{III}(dmgH)_2(py)Cl]$ ($5 \times 10^{-4}$ M) as the catalyst in 1:1 $CH_3CN$:$H_2O$ with TEOA was prepared. Photogeneration of $H_2$ from this system resulted in 31 TON over 24 h (1.3 mL/day), which was slightly greater in rate and TON than when **2** was used as both PS and $H_2$-generating catalyst under the same conditions (pH 7, $\lambda$ = 520 nm). A system containing fluorescein as the PS (rather than **1**) and $[Co^{III}(dmgH)_2(py)Cl]$ as the catalyst at the same concentrations as those used for the system containing **2** ($5 \times 10^{-4}$ M each) produced $H_2$ at even higher rates and TON's (63 TON in 24 h, 3.6 mL/day) than for either **2** or **1** + $[Co^{III}(dmgH)_2(py)Cl]$, as shown in Figure 2. These observations indicate that attachment of fluorescein to the catalyst complex via pyridine in **2** offers no benefit in $H_2$ generation and led to the suggestion that despite the earlier assertion that pyridine does not dissociate upon reduction of

**Table 1. Selected Bond lengths [Å] and angles [deg] for 2**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)−N(4) | 1.891(2) | O(7)−C(22) | 1.511(3) | N(3)−Co(1)−N(2) | 98.2(1) |
| Co(1)−N(3) | 1.892(2) | C(22)−C(23) | 1.493(4) | N(2)−Co(1)−N(1) | 81.1(1) |
| Co(1)−N(2) | 1.895(2) | C(22)−C(34) | 1.507(4) | N(2)−Co(1)−N(5) | 89.18(9) |
| Co(1)−N(1) | 1.899(2) | C(26)−O(9) | 1.346(3) | N(1)−Co(1)−N(5) | 88.83(9) |
| Co(1)−N(5) | 1.952(2) | C(28)−O(8) | 1.368(3) | N(2)−Co(1)−Cl(1) | 92.41(7) |
| Co(1)−Cl(1) | 2.2390(7) | O(8)−C(29) | 1.372(3) | N(1)−Co(1)−Cl(1) | 91.11(7) |
| N(1)−C(1) | 1.289(4) | C(31)−O(10) | 1.367(3) | C(23)−C(22)−C(34) | 111.6(2) |
| N(1)−O(1) | 1.348(3) | N(4)−Co(1)−N(3) | 81.9(1) | C(23)−C(22)−O(7) | 108.4(2) |
| C(18)−C(22) | 1.505(4) | N(4)−Co(1)−N(2) | 179.56(10) | C(34)−C(22)−O(7) | 107.4(2) |

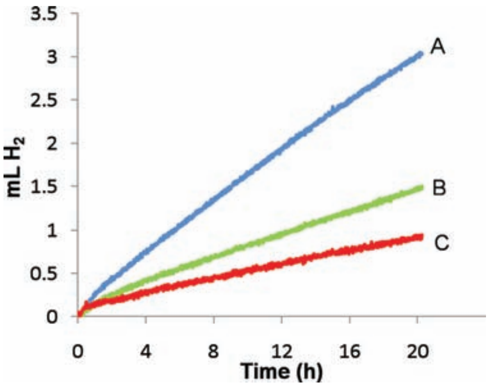


**Figure 2.** Hydrogen generation from $5.0 \times 10^{-4}$ M solutions of (A) fluorescein and $[Co^{III}(dmgH)_2(py)Cl]$, (B) derivatized fluorescein **1** and $[Co^{III}(dmgH)_2(py)Cl]$, and (C) the fluorescein-containing $Co^{III}$-$(dmgH)_2$ complex **2**. All samples are in 5% TEOA in 1:1 $CH_3CN{:}H_2O$, pH 7; irradiated with 520 nm light.

$[Co^{III}(dmgH)_2(py)Cl]$, the py ligand is indeed labile during hydrogen-generating conditions, thereby precluding any value from the PS−catalyst linkage.

Previous reports have stated that Fl itself is not an effective PS for photogeneration of hydrogen,[7] but the present observations indicate otherwise. However, for $H_2$ photogeneration to occur with Fl as the photosensitizer, the PS concentration must be $>1 \times 10^{-4}$ M. At this concentration, the fluorescein emission is red shifted to $\lambda_{max}$ = 545 nm and its emission intensity is diminished relative to dilute solutions ($\lambda_{max}$ = 515 nm). The observed shift is attributed to dye aggregation and a longer lived dimer emission, $\tau \approx 12$ ns, relative to Fl monomer emission from dilute solution with $\tau \approx 5$ ns.[38] When [PS] is decreased from $5 \times 10^{-4}$ to $1.2 \times 10^{-4}$ M while $[Co^{III}(dmgH)_2(py)Cl]$ is maintained at $5 \times 10^{-4}$ M, the system produces 175 TON per mol of PS over 50 h. Decreased PS concentration decreases hydrogen production rates (see Figure S1, Supporting Information). However, a change in catalyst concentration does not affect the rate but rather alters system longevity for $H_2$ generation (see Figure S2, Supporting Information). These observations are consistent with the turnover-limiting step in the light-driven production of $H_2$ involving the photosensitizer only and not the catalyst.

Addition of extra py to the system containing the tethered PS−catalyst complex **2** and TEOA results in a higher rate of $H_2$ production. Over 24 h, a $4.8 \times 10^{-4}$ M solution of **2** to which 2 mol equiv of py is added produces 45 TON, as compared to 32 TON when no extra py is added (see Supporting Information, Figure S3). This observation is also consistent with the higher rates found using $Co(dmgH)_2(py)Cl$ as the catalyst with **1** as the PS since py is already coordinated to the catalyst. In contrast, addition of sterically hindered 2,6-dimethylpyridine that is inhibited from coordinating to Co exhibits no effect on $H_2$ generation. The results thus suggest that the effect of py on $H_2$ generation rates is associated solely with coordination.

In order to probe the possibility of py exchange from the catalyst, complexes $[Co^{III}(dmgH)_2(py)Cl]$ and $[Co^{III}(dmgH)_2(py)_2]PF_6$ were examined by $^1H$ NMR spectroscopy. Addition of 4 equiv of 4-*tert*-butylpyridine (*t*Bupy) to a solution of $[Co^{III}(dmgH)_2(py)_2]PF_6$ in $CD_3CN$ at room temperature results in a mixture of 32% $[Co^{III}(dmgH)_2(py)_2]^+$, 53% $[Co(dmgH)_2(py)(tBupy)]^+$, and 15% $Co(dmgH)_2(tBupy)_2{}^+$ after 86 h (Figure 3a), as judged by $^1H$ NMR spectroscopy. After 1 week the system is near equilibrium, with 82% of the initial $[Co^{III}(dmgH)_2(py)_2]PF_6$ complex showing exchange in a mixture of 18% $[Co^{III}(dmgH)_2(py)_2]^+$, 59% $[Co(dmgH)_2(py)(tBupy)]^+$, and 23% $[Co(dmgH)_2(tBupy)_2]^+$. This indicates that *slow* exchange of the py ligands is occurring at a rate consistent with the inertness of $Co^{III}$. The py exchange reactions were found to proceed more rapidly under other conditions consistent with those produced during hydrogen generation. For example, when 2 equiv of *t*Bupy was added to $[Co^{III}(dmgH)_2(py)Cl]$ in $CD_3CN$ under irradiation by light of $\lambda > 420$ nm for 2 h, a mixture of 40% $[Co^{III}(dmgH)_2(py)Cl]$ and 60% $[Co^{III}(dmgH)_2(tBupy)Cl]$ was observed by $^1H$ NMR spectroscopy. The exchange is accelerated by light, consistent with photosubstitution. It was also anticipated that reduction of Co(III) to Co(II) would result in much faster py exchange because of the lability of $Co^{II}$. In support of this hypothesis, when a mixture of $[Co^{III}(dmgH)_2(py)_2]^+$ and 4 equiv of *t*Bupy in $CD_3CN$ is stirred over Zn amalgam for 10 min, a mixture of 82% $[Co(dmgH)_2(py)(tBupy)]^+$ and 18% $[Co^{III}(dmgH)_2(py)_2]^+$ is obtained.

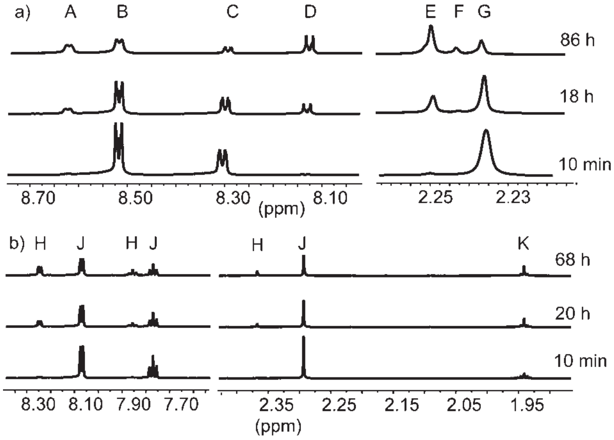


**Figure 3.** $^1H$ NMR spectra for ligand exchange reactions: (a) $[Co(dmgH)_2(py)_2]^+$ with 4 equiv of *t*Bupy and (b) $[Co(dmgH)_2(py)Cl]$ with 4 equiv of $dpgH_2$. Labels for resonances are as follows: (A) free py, (B) free *t*Bupy, (C) py coordinated to Co, (D) *t*Bupy coordinated to Co, (E) dmgH methyl on $[Co(dmgH)_2(py)(tBupy)]^+$, (F) dmgH methyl on $[Co(dmgH)_2(tBupy)_2]^+$, (G) dmgH methyl on $[Co(dmgH)_2(py)_2]^+$, (H) $[Co(dmgH)(dpgH)pyCl]$, (J) $[Co(dmgH)_2(py)Cl]$, and (K) free $dmgH_2$ (intensity of each segment is scaled for clarity).

**Exchange of Glyoximate Ligands.** The observation of pyridine exchange from the Co glyoximate complexes raised the question of whether glyoximate exchange was also occurring during active catalysis of $H_2$ generation. Such exchange was not expected because of the bidentate nature of these ligands and the H bonding between the glyoximate ligands that holds the two monoanionic chelates in the equatorial positions of a tetragonally distorted octahedral complex. However, reports of increased system stability through addition of free $dmgH_2$ ligand suggested the possibility of exchange.[7,12,19,37]

The notion of glyoximate exchange was examined in two different ways. The first was by monitoring NMR spectra of samples containing both complex and additional glyoximate ligand, and the second was by examination of $H_2$ photogeneration using systems with either one or two different glyoximate ligands present. The initial NMR experiments showed that when

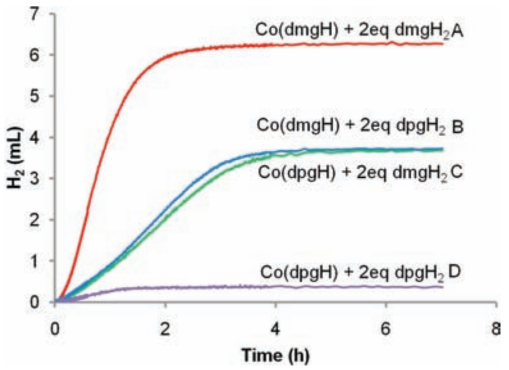


**Figure 4.** Photolyis of Eosin Y 5 × $10^{-5}$ M in 5% TEOA in 1:1 $CH_3CN$:$H_2O$, pH 7; irradiated with 520 nm light, 2.5 × $10^{-4}$ M $[Co^{III}(dmgH)_2(py)Cl]$ or $[Co^{III}(dpgH)_2(py)Cl]$ with 5 × $10^{-4}$ M $dmgH_2$ or $dpgH_2$.

4 equiv of free diphenylglyoxime ($dpgH_2$) was added to a solution of $[Co^{III}(dmgH)_2(py)Cl]$ in $CD_3CN$, no exchange occurred over 2 days. However, by changing the solvent to a mixed $CD_3CN-D_2O$ solvent system (9:1 v/v), exchange did occur to form $[Co^{III}(dpgH)(dmgH)(py)Cl]$ with 35% conversion in 68 h (Figure 3b). To verify if reduction to Co(II) facilitates dmgH ligand exchange, a mixture of $[Co^{III}(dmgH)_2(py)Cl]$ and 4 equiv of free $dpgH_2$ in a $CD_3CN-D_2O$ solvent mixture (9:1 v/v) was stirred over Zn amalgam for 1 min, resulting in a fast exchange of glyoximate ligands with 38% conversion to $[Co^{III}(dpgH)(dmgH)(py)Cl]$. The rate of dmgH ligand exchange can also be catalyzed by addition of 3 mol % $Co^{II}(BF_4)_2\cdot 6H_2O$ under $N_2$. After mixing for 10 min, followed by subsequent exposure to air to oxidize all Co to the +3 state, more than 50% of the $[Co^{III}(dmgH)_2(py)Cl]$ complex was converted to $[Co^{III}(dpgH)(dmgH)(py)Cl]$. While the $Co^{III}$ complex $[Co^{III}(dmgH)_2(py)Cl]$ is substitutionally inert, the exchange process is accelerated significantly by Co(II), possibly via inner-sphere electron transfer through the chloride ligand of the Co(III) dmgH complex.

**Ligand Exchange During $H_2$ Generation.** Both the rate of hydrogen generation and the total amount of hydrogen generated are substantially less when using the diphenylgloximate complex $Co^{III}(dpgH)_2(py)Cl$ as catalyst as compared to those obtained with the dimethylglyoximate catalyst $Co^{III}(dmgH)_2(py)Cl$. On the basis of this observation, it was possible to probe diglyoxime ligand exchange during $H_2$ photogeneration experiments. For these experiments, Eosin Y was used as the PS because of its greater TOF relative to the fluoroscein system. In Figure 4, the amounts of hydrogen evolved as a function of time are plotted for these runs. Curve A shows the results for a system composed of $Co^{III}(dmgH)_2(py)Cl$ + 2 equiv of $dmgH_2$, while curve D exhibits the corresponding results for $Co^{III}(dpgH)_2(py)Cl$ + 2 equiv of $dpgH_2$. The difference in activity between these two catalysts in otherwise identical systems is striking. When the two mixed systems, $[Co^{III}(dmgH)_2(py)Cl]$ + 2 equiv of $dpgH_2$ and $[Co^{III}(dpgH)_2(py)Cl]$ + 2 equiv of $dmgH_2$, are similarly employed, the rates and overall $H_2$ production amounts are identical (see curves B and C in Figure 4) and approximately intermediate between those of $[Co^{III}(dmgH)_2(py)Cl]$ + 2 equiv of $dmgH_2$ and $[Co^{III}(dpgH)_2(py)Cl]$ + 2 equiv of $dpgH_2$ (Figure 4). The results are clear evidence of glyoxime exchange.

If the cobaloxime catalyst remained intact during photolysis, the two experiments would have yielded different rates, consistent with the starting Co complex in each case. Instead, the rate depends on the sum and types of bound and unbound diglyoxime ligands present in the system. It can thus be concluded that during photolysis with water present the chelating ligands are labile. These results help to explain the finding that with $[Co^{III}(dmgH)_2(py)Cl]$ as the catalyst extra $dmgH_2$ in solution increases system longevity through exchange.[7,20,37]

We previously found that to restart hydrogen generation after the system has stopped producing $H_2$ upon irradiation both photosensitizer and catalyst must be added to the system. In the present case, hydrogen generation can also be revived with addition of Eosin and dimethylglyoxime, with the subsequent rate of hydrogen production being slightly less than that observed before photodecomposition. The facts that dimethylglyoxime ligands are being exchanged during $H_2$ generation and that addition of $dmgH_2$ + Eosin reconstitutes activity indicates that the dimethylglyoxime ligand, whether coordinated or free, is being converted into an inactive form for hydrogen generation. One possibility is that the dimethylglyoxime ligand is hydrogenated.[39] While the hydrogenated or otherwise decomposed dimethylglyoximate could act as a ligand for Co, it may exist in a form that does not allow reduction to $Co^{I}$ at a potential accessible by either the excited state of Eosin directly or the reduced Eosin produced by reductive quenching with the sacrificial donor. We suggested previously that the path that leads to photodecomposition of the dye is also the path that leads to $H_2$ generation.[12]

With regard to the initial photochemical steps in the present systems, electron transfer quenching leading to $H_2$ generation can proceed by PS* oxidation of TEOA to form $PS^-$ that transfers an electron to the Co catalyst or by PS* reduction of the Co catalyst yielding $PS^+$ that is reduced by TEOA. To distinguish between these possibilities, emission quenching studies of fluorescein were carried out separately using $Co^{III}(dmgH)_2(py)Cl$ as the electron acceptor or TEOA as the electron donor. In a test of the former, addition of 50 equiv of $Co^{III}(dmgH)_2(py)Cl$ leads to diminished but still strong Fl emission. Since the Co complex possesses some absorption at an excitation energy of 500 nm, the moderate emission decrease can be attributed, at least in part, to competitive absorption by $Co^{III}(dmgH)_2(py)Cl$. In contrast, when 5% by volume of TEOA is added to a 5 × $10^{-4}$ M solution of Fl, the emission is quenched by 90% (see Figure S4, Supporting Information). These results indicate that for the $Fl/[Co^{III}(dmgH)_2(py)Cl]/TEOA$ system electron transfer leading to $H_2$ generation proceeds by *reductive quenching* of PS* by TEOA.

On the basis of these observations and similar ones obtained using Se-derivatized rhodamine dyes with the $Co^{III}(dmgH)_2(py)Cl$ catalyst,[12] we conclude that $H_2$ production and system decomposition proceed by reductive quenching of PS* to give $PS^-$. In essence, there exists a branchpoint in the reaction scheme following reaction of PS* with TEOA.[19] If the resultant $PS^-$ is able to transfer an $e^-$ to the Co catalyst, $H_2$ production will follow. On the other hand, if the Co species is no longer able to accept an electron from $PS^-$, the latter will decompose by a slow unimolecular path. The exchange of coordinated ligand with free $dmgH_2$ thus accounts for the observed increase in system longevity, since the transformed ligand can exchange with $dmgH_2$ in solution. Further work is underway to better understand the ligand transformation that renders the Co species incapable of hydrogen generation in order to help develop a stable photoreduction catalyst.

**Are Linked Systems Really Better?** In other studies that have been reported, connection of the PS to the catalyst through covalent bonds has yielded at best only modest improvement in overall $H_2$ production relative to systems containing separate PS, catalyst, and a sacrificial electron donor.[10,40] For example, linkage of a polypyridyl ruthenium- or iridium-based PS to a cobaloxime catalyst ($Co(dmgH)_2Cl$ or $Co(dmgBF_2)_2Cl$, where dmg = dimethylglyoxime) has led to relatively small increases in TON relative to the systems of separate components, from 7 to 38 for a Ru photosensitizer[23,25] and from 165 to 210 for an Ir PS.[24]

Several factors may contribute to the slower generation of $H_2$ when Fl is linked to py as in **1**, whether free in solution or incorporated into **2**, relative to the system in which the components are not connected. First is a difference in the photophysical properties of **1**, **2**, and Fl. While the molar absorptivity of the Fl absorption in all three species is very similar (72 000–75 000 $M^{-1}$ $cm^{-1}$), the emissions from **1** and **2** are severely quenched relative to Fl ($\phi_{Fl}$ 6.6% for **1**, 4.8% for **2**, and 93% for Fl).[36] Previously reported amide derivatives of fluorescein have only slightly quenched emission compared to the parent compound ($\phi_{Fl} \approx 80\%$).[41] The fact that emission from **1** is quenched to the same extent as emission for **2** indicates that the observed quenching is not by electron transfer from Fl to the Co catalyst but instead occurs via nonradiative decay, a factor that would lower activity for both **1** and **2** for $H_2$ photogeneration.

Since the Fl emission is quenched by TEOA and not by the Co catalyst in the turnover-limiting step of $H_2$ generation, facilitating electron transfer from Fl to Co is not expected to increase the efficiency of $H_2$ production. The reductive quenching mechanism is thus a second factor contributing to the absence of any benefit from attaching the PS to the catalyst in **2**. Additionally, at lower dye concentrations, quenching of Fl emission is significantly diminished by TEOA (50% quenched by 5% v/v TEOA at [Fl] of $1 \times 10^{-5}$ M), which helps to explain the absence of $H_2$ generation at lower Fl concentrations.

A third factor contributing to the similarity between the tethered and the untethered catalysts is that the PS-containing ligand does not remain attached to the catalyst during the reaction. Under $H_2$-generating conditions, the resting state of the catalyst has been found to be $Co^{II}$.[7] The well-known lability of $Co^{II}$ suggests that ligand exchange occurs readily on the time scale of the catalytic reaction.[42−44] This hypothesis has been supported by both the hydrogen generation and the NMR experiments presented here, which indicate that both pyridine and dmgH ligands exchange readily on the cobalt catalyst during the photogeneration experiments. Recently, using X-ray scattering techniques, a report has indicated that similar cobaloxime–photsensitizer assemblies exist in equilibrium between bound and unbound photosensitizer in acetonitrile solution.[25] The fact that the dmgH ligands exchange under these conditions casts doubt on the feasibility of productive attachment of catalyst and chromophore through any of the supporting ligands on the cobalt center.

## CONCLUSION

In summary, ligand exchange on the $[Co^{III}(dmgH)_2(py)Cl]$ hydrogen production catalyst during the photoreduction of protons accounts for the lack of increase in hydrogen production upon connection of the photosensitizer to the catalyst. It also indicates why system longevity for $H_2$ generation is increased upon addition of free $dmgH_2$ and explains how transformation of the $dmgH_2$ ligand provides the path for system decomposition and cessation of hydrogen generation.

A linked PS–catalyst complex **2** for $H_2$ photogeneration offers no advantages and poorer rates of $H_2$ production than a system consisting of separated PS and catalyst components. We identified three factors which mitigate any potential benefits to attachment. First, the derivatized fluorescein sensitizer increases nonradiative excited state decay pathways for the dye. Second, $H_2$ photogeneration using the system based on fluorescein and $[Co^{III}(dmgH)_2(py)Cl]$ proceeds through reductive quenching, in which the turnover-limiting step is not facilitated by connection of the PS to the catalyst. Third, NMR and $H_2$ photogeneration experiments indicate that there is exchange of both the py and diglyoxime ligands on the catalyst. These studies highlight the importance of analyzing in detail the behavior of system components in the context of system operation so that efforts to design more efficient and active systems for $H_2$ photogeneration are soundly based.

## ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental description, crystal structure data for **2** in CIF format, plots of photolysis experiments, Stern–Volmer plots, and full NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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## REFERENCES

(1) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022–4047.

(2) Nocera, D. G. *Inorg. Chem.* **2009**, *48*, 10001–10017.

(3) Eisenberg, R. *Science* **2009**, *324*, 44–45.

(4) Gray, H. B. *Nat. Chem.* **2009**, *1*, 7.

(5) Du, P.; Knowles, K.; Eisenberg, R. *J. Am. Chem. Soc.* **2008**, *130*, 12576–12577.

(6) Du, P.; Schneider, J.; Luo, G.; Brennessel, W.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 4952–4962.

(7) Lazarides, T.; McCormick, T.; Du, P.; Luo, G.; Lindley, B.; Eisenberg, R. *J. Am. Chem. Soc.* **2009**, *131*, 9192–9194.

(8) Dempsey, J.; Winkler, J.; Gray, H. *J. Am. Chem. Soc.* **2010**, *132*, 16774–16776.

(9) Dempsey, J.; Winkler, J.; Gray, H. *J. Am. Chem. Soc.* **2010**, *132*, 1060–1065.

(10) Tinker, L.; McDaniel, N.; Bernhard, S. *J. Mater. Chem.* **2009**, *19*, 3328–3337.

(11) Probst, B.; Kolano, C.; Hamm, P.; Alberto, R. *Inorg. Chem.* **2009**, *48*, 1836–1843.

(12) McCormick, T.; Calitree, B.; Orchard, A.; Kraut, N.; Bright, F.; Detty, M.; Eisenberg, R. *J. Am. Chem. Soc.* **2010**, *132*, 15480–15483.

(13) Arachchige, S.; Brown, J.; Brewer, K. *J. Photochem. Photobiol., A* **2008**, *197*, 13–17.

(14) Arachchige, S.; Brown, J.; Chang, E.; Jain, A.; Zigler, D.; Rangan, K.; Brewer, K. *Inorg. Chem.* **2009**, *48*, 1989–2000.

(15) Elvington, M.; Brown, J.; Arachchige, S. M.; Brewer, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 10644–10645.

(16) Wang, X.; Goeb, S.; Ji, Z.; Pogulaichenko, N.; Castellano, F. *Inorg. Chem.* **2011**, *50*, 705–707.

(17) Goldsmith, J.; Hudson, W.; Lowry, M.; Anderson, T.; Bernhard, S. *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510.

(18) Cline, E.; Adamson, S.; Bernhard, S. *Inorg. Chem.* **2008**, *47*, 10378–10388.

(19) Probst, B.; Rodenberg, A.; Guttentag, M.; Hamm, P.; Alberto, R. *Inorg. Chem.* **2010**, *49*, 6453–6460.

(20) Zhang, P.; Wang, M.; Dong, J.; Li, X.; Wang, F.; Wu, L.; Sun, L. *J. Phys. Chem. C* **2010**, *114*, 15868–15874.

(21) Connolly, P.; Espenson, J. *Inorg. Chem.* **1986**, *25*, 2684–2688.

(22) Baffert, C.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2007**, *46*, 1817–1824.

(23) Li, C.; Wang, M.; Pan, J.; Zhang, P.; Zhang, R.; Sun, L. *J. Organomet. Chem.* **2009**, *694*, 2814–2819.

(24) Fihri, A.; Artero, V.; Pereira, A.; Fontecave, M. *Dalton Trans.* **2008**, 5567–5569.

(25) Mulfort, K.; Tiede, D. *J. Phys. Chem. B* **2010**, *114*, 14572–14581.

(26) Kobayashi, M.; Masaoka, S.; Sakai, K. *Molecules* **2010**, *15*, 4908–4923.

(27) Schrauzer, G. *Inorg. Synth.* **1968**, *11*, 61.

(28) López, C.; Alvarez, S.; Aguiló, M.; Solans, X.; Font-Altaba, M. *Inorg. Chem. Acta.* **1987**, *127*, 153–159.

(29) Gerli, A.; Marzilli, L. *Inorg. Chem. Acta.* **1992**, *31*, 1152–1160.

(30) Tinker, L.; McDaniel, N.; Curtin, P.; Smith, C.; Ireland, M.; Bernhard, S. *Chem.—Eur. J.* **2007**, *13*, 8726–8732.

(31) *APEX2*, version 2009.9-0; Bruker AXS: Madison, WI, 2009.

(32) Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

(33) *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.

(34) Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *SIR97*; CNR: Bari, Italy, 1999.

(35) Sheldrick, G. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(36) Sjöback, R.; Nygren, J.; Kubista, M. *Spectrochim. Acta, Part A* **1995**, *51*, L7–L21.

(37) Probst, B.; Guttentag, M.; Rodenberg, A.; Hamm, P.; Alberto, R. *Inorg. Chem.* **2011**, *50*, 3404–3412.

(38) Math, N.; Naik, L.; Suresh, H.; Inamdar, S. *J. Lumin.* **2006**, *121*, 475–487.

(39) Simándi, L. I.; Szeverényi, Z.; Budó-Záhony, E. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 773.

(40) Wang, M.; Na, Y.; Gorlov, M.; Sun, L. *Dalton Trans.* **2009**, 6458–6467.

(41) Munkholm, C.; Parkinson, D.; Walt, D. *J. Am. Chem. Soc.* **1990**, *112*, 2608–2612.

(42) Ma, H.; Wan, C.; Zewail, A. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12754–12757.

(43) Parker, W.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. *Inorg. Chem.* **1986**, *25*, 1303–1309.

(44) Parker, W.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. *Inorg. Chem.* **1985**, *24*, 3908–3913.