Figure 2. RR spectra at 77 K with 413.1-nm excitation for (top) Ni^{II}TPP (0.2 mM) in CH$_2$Cl$_2$ (50-mW incident laser power) and for (bottom) frozen solutions containing [Ni^{III}TPP]$^+$ formed by freezing after electrolysis as in Figure 1 (10 mW).

Figure 3. RR spectra at 77 K with 568.2-nm excitation for (bottom) Ni^{II}TPP (0.4 mM) in CH$_2$Cl$_2$, (middle) [Ni^{III}TPP]$^+$ frozen after electrolysis as in Figure 1 (40 mW), and (top) Ni^{II}TPP$^{\cdot+}$ frozen after Br$_2$ oxidation in CH$_2$Cl$_2$ (20 mW).

tomerism in oxidized metalloporphyrins.

Registry No. Ni^{III}TPP$^+$, 29484-62-6; Ni^{II}TPP, 14172-92-0.

Visible-Light Production of Molecular Hydrogen by Sensitization of a Cobalt Dihydride Complex

Karen J. Brewer, W. Rorer Murphy, Jr., Kathy J. Moore, Eva C. Eberle, and John D. Petersen*

Visible-light-absorbing, transition-metal complexes have been of interest as a potential catalysts for solar energy conversion by the photodissociation of water. Balzani and co-workers,[1] in developing a two-photon catalytic system for water splitting, have proposed a potential cycle as follows:

$$ML_4H_2{}^{n+} \xrightarrow{h\nu} ML_4{}^{n+} + H_2 \qquad (1)$$

$$X + H_2O \xrightarrow{h\nu'} X^{2-} + 2H^+ + {}^1/_2O_2 \qquad (2)$$

$$ML_4{}^{n+} + X^{2-} + 2H^+ \rightarrow ML_4H_2{}^{n+} + X \qquad (3)$$
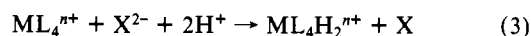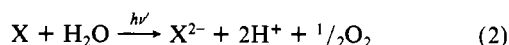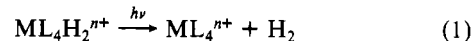
Equation 1, which describes the photoelimination of molecular hydrogen from a metal dihydride, has literature precedence;[2] however, the examples reported require ultraviolet rather than visible light.

Recently, we have been interested in developing photochemical systems in which a bimetallic complex contains a visible-light-absorbing (antenna) fragment covalently coupled to a visible-light-transparent, but photochemically useful reactive metal center. With these systems, absorption of visible light at the antenna fragment can be followed by intramolecular energy (or electron) transfer to the reactive fragment and subsequent reaction. While these bimetallic systems have the advantage that they avoid the inherent inefficiencies of bimolecular sensitization processes, an important criterion in the system is that the energy transfer must be competitive with electronic relaxation at the antenna fragment.

We have studied the bimolecular systems Fe(bpy)$_2$(CN)$_2$ and Co(bpy)(PEt$_2$Ph)$_2$H$_2{}^+$ (where bpy = 2,2′-bipyridine and PEt$_2$Ph = diethylphenylphosphine) to probe the thermodynamic and kinetic constraints of the energy transfer process. The cobalt complex was chosen as a potential metal dihydride complex (eq 1) because of a preliminary report[3] indicating that broad-band irradiation produced a spectral change consistent with H$_2$ loss. The results of this study are reported herein.
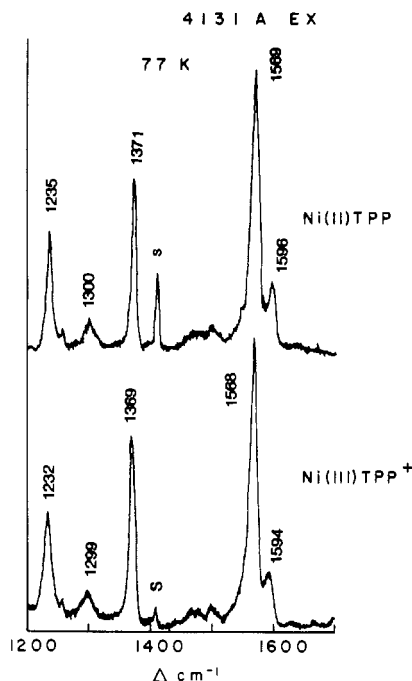
Experimental Section

Materials. Water used for synthesis and photochemical studies was deionized and then distilled from alkaline permanganate in an all-glass apparatus. Argon for deoxygenating solutions was purified by passing through two gas-washing bottles equipped with coarse air stones containing a Cr(II) solution over amalgamated Zn to remove O$_2$, one gas-washing bottle filled with unactivated R3-11 catalyst (Chemalog) to remove any residual H$_2$, and one gas-washing bottle filled with methanol to saturate the gas. All other materials were of reagent grade and used without further purification.
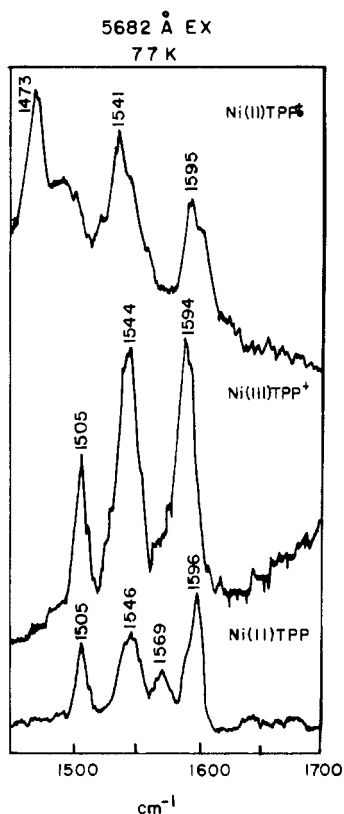
Syntheses. [Co(bpy)(PEt$_2$Ph)$_2$(H$_2$)](ClO$_4$) was prepared by the method of Camus et al.[3] Recrystallization was achieved in a minimum volume of acetone by adding water until the first evidence of precipitation was observed. The mixture was allowed to stand in the dark for 1 h while some of the acetone evaporated. The resulting crystals were collected by filtration and dried by washing with anhydrous diethyl ether. The complex was stored in a desiccator in the dark, but slow decomposition occurred over a period of months.

Fe(bpy)$_2$(CN)$_2$ was prepared by a previously published procedure.[4]

Instrumentation. The electronic spectra of the complexes and the spectroscopic changes observed during the photochemical reaction were measured on a Bausch & Lomb Spectronic 2000 spectrophotometer using

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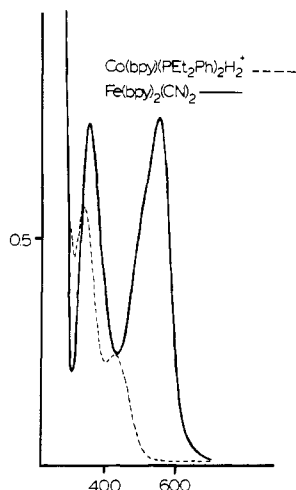
Figure 1. Superposition of the absorption spectra of $Fe(bpy)_2(CN)_2$ and $Co(bpy)(PEt_2Ph)_2H_2^+$ at the same concentration $(1.1 \times 10^{-4}$ M) in methanol.

1-cm or 5-cm quartz cuvettes. Chromatographic measurement of photochemically evolved H_2 utilized a Gow-Mac Series 550 gas chromatograph, a Spherocarb (Analabs) column and high-purity argon (Linde) as a carrier gas. The procedure used for quantitative measurement of hydrogen has been reported elsewhere.[5]

Photochemistry. The solutions were irradiated using a continuous wave apparatus consisting of a 200-W high-pressure mercury-arc source lamp (Oriel), mercury line interference filters, collimating lens, and a hollow-brass, thermostated cell compartment all mounted on an optical bench. Usable light intensities from this configuration were measured by ferrioxalate $(\lambda_{irr} \leq 436$ nm)[6] or Reineckate $(\lambda_{irr} > 436$ nm)[7] actinometry.

The photolysis solutions of $Co(bpy)(PEt_2Ph)_2H_2^+$ were prepared by washing the solid, perchlorate salt with water to remove any decomposition products, washing with ether to dry the solid, and dissolving a weighted amount of material in methanol. These solutions were deoxygenated for 20 min with argon before being transferred into two, 5-cm, quartz, cylindrical cells. For experiments involving chromatographic determination of hydrogen, one of the necks of the cuvette was fitted with a septum and, after the cell was filled, 500 μL of solution was displaced by argon to establish a known dead volume for sampling.

Spectroscopic determination of the photochemical reaction required irradiation for time intervals ranging from 30 s to 30 min. Five to seven of these time periods were used to monitor the first 20–25% of the photolysis reaction. Initial quantum yields were reported by extrapolating results back to 0% reaction to correct for secondary photolysis and inner-filter effects.[8] Quantum yields for photochemical reactions involving both $Co(bpy)(PEt_2Ph)_2H_2^+$ and $Fe(bpy)_2(CN)_2$ in solution were only determined by direct chromatographic measurement of evolved hydrogen.[9]

Results and Discussion

The electronic absorption spectrum of $Co(bpy)(PEt_2Ph)_2H_2^+$ is illustrated in Figure 1. There are two peaks observed in the spectral region above 300 nm. The peak at 435 nm ($\epsilon = 2.2 \times 10^3$ M^{-1} cm^{-1}) is expected to be the lowest spin-allowed ligand field transition (with a large intensity contribution from the adjacent charge-transfer band) while the peak at 346 nm ($\epsilon = 6 \times 10^3$ M^{-1}cm^{-1}) is presumably a metal-to-ligand charge-transfer (MLCT) transition involving the Co(III) and either the phosphine of the bipyridine ligand. These assignments are consistent with analogous spectra of iridium(III) complexes.[10]

The quantitative photochemistry of $Co(bpy)(PEt_2Ph)_2H_2^+$ is summarized in Table I. Irradiation of the complex at 436 nm

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(8) Figard, J. E.; Petersen, J. D. *Inorg. Chem.* **1978**, *17*, 1059.
(9) Evolved H_2 was measured by a Gow-Mac Series 550 gas chromatograph, equipped with two $^1/_8$ in. $\times$ 6-ft copper columns packed with 100–120 mesh Spherocarb and a thermal conductivity detector, using prepurified argon as a carrier gas.
(10) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.

Table I. Quantum Yields for the Photoelimination of H_2 from $[Co(bpy)(PEt_2Ph)_2H_2]ClO_4$[a]

λ_{irr}, nm	Φ_{H_2},[b] mol/einstein	λ_{irr}, nm	Φ_{H_2},[b] mol/einstein
313	c	436	0.1
366	0.07 ± 0.03[d]		0.12 ± 0.01[e]
405	0.14 ± 0.02[d]		

[a] In methanol, 25 °C. [b] Quantum yields for production of H_2 determined by electronic spectral changes unless otherwise noted. [c] Absorbance change could not be reversed by addition of H_2 after irradiation. [d] Partial regeneration of starting material by addition of H_2 after irradiation. [e] Determined by gas chromatography technique described in ref 5.
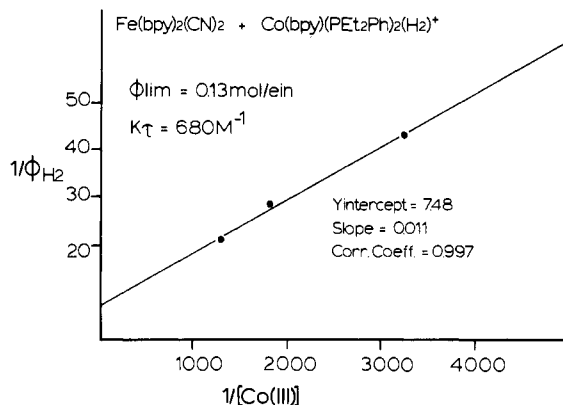
Figure 2. Quenching plot for sensitization of the photoelimination of H_2 from $Co(bpy)(PEt_2Ph)_2H_2$ in the presence of $Fe(bpy)_2(CN)_2$: y axis, $1/\Phi_{H_2}$; x axis, $1/[Co(bpy)(PEt_2Ph)_2H_2^+]$.

results in H_2 production. The quantum yield for H_2 production at 436 nm is 0.1 mol/einstein as measured by spectroscopic change and 0.12 mol/einstein as measured by gas chromatography.[5] Addition of H_2 to a sample that had been irradiated at 436 nm resulted in a regeneration of starting material. As the irradiation wavelength was shifted to higher energy, the photoelimination of molecular hydrogen became less reversible. At irradiation wavelengths of 405 and 366 nm, only partial regeneration of the starting material was observed. At the irradiation wavelength of 313 nm, the photochemistry was irreversible.

The mechanism of H_2 elimination has been summarized by Geoffroy.[2] In one specific set of experiments on $Mo(\eta^5-C_5H_5)_2H_2)$,[11] the use of deuterated solvents has shown that H_2 photoelimination is concerted. The excited state responsible for concerted H_2 elimination is less certain. Initial studies by Geoffroy[2] on a series of Ir(III) complexes suggested that the MLCT state, owing to an electron-deficient metal center (formally Ir(IV)), would be the driving force for H_2 elimination. However, more recent studies by Geoffroy and Pierantozzi[10] favor an alternate explanation involving population of a ligand field state that is antibonding between the metal and the two hydrogens. The sensitization studies described later in this paper favor this latter interpretation.

Figure 1 also illustrates the electronic absorption spectrum of $Fe(bpy)_2(CN)_2$. This complex has an MLCT absorption band at 580 nm ($\epsilon = 4.8 \times 10^3$ M^{-1} cm^{-1}) and one at 390 nm ($\epsilon = 4.6 \times 10^3$ M^{-1} cm^{-1}).[4] Irradiation of this Fe(II) complex at 577 nm results in no discernible spectral change.

Irradiation of $Fe(bpy)_2(CN)_2$ $(2.3 \times 10^{-5}$ M) in the presence of $Co(bpy)(PEt_2Ph)_2H_2^+$ $((3.08–7.69) \times 10^{-4}$ M) at 577 nm leads to formation of H_2.[12] The quenching plot (Figure 2) shows a limiting quantum yield of 0.13 mol/einstein, which is within the experimental uncertainty of the value obtained for the direct irradiation of the Co(III) complex at 436 nm. These data indicate that the reactivity observed for the direct irradiation of the Co(III) complex results from a partitioning out of the nonspectroscopic

(11) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.
(12) At the irradiation wavelength of 577 nm, the Fe(II) complex accounts for more than 99% of the light absorbed by the system.

reactive state (presumably ^{3}LF) of the Co(III) complex with little or no direct internal conversion to the ground state from the upper excited states in the cobalt complex.

The bimolecular quenching constant (i.e., 680 M^{-1} in Figure 2) represents the product of the lifetime of the donor state of Fe(bpy)$_2$(CN)$_2$ and the bimolecular rate constant for the sensitization process. Assuming diffusion control as the upper limit for the quenching rate constant, a lower limit of 56 ns can be calculated for the lifetime of the Fe(II) donor state.[13] This lifetime estimate is much longer than the 0.81 and 2.54 ns reported for Fe(bpy)$_3$$^{2+}$ and Fe(tpy)$_2$$^{2+}$, respectively.[14] One possible reason for the increase in lifetime is that the LF excited state, which is lowest in energy for Fe(bpy)$_3$$^{2+}$,[15] may be pushed up by CN$^-$ substitution, and an MLCT excited state becomes lowest in energy for Fe(bpy)$_2$(CN)$_2$.[16] While this lifetime is still too short to allow the Fe system to be an efficient sensitizer for intermolecular processes, intramolecular processes should be feasible with the proper bridging ligand system.

Energetically, this study shows that 577-nm light will drive the photoelimination reaction of H$_2$ from Co(bpy)(PEt$_2$Ph)$_2$H$_2$$^+$, thus extending into the visible region the frequency of light required for eq 1. The fact that 577-nm light is energetic enough to populate the reactive excited state of Co(bpy)(PEt$_2$Ph)$_2$H$_2$$^+$ suggests that assignment of a LF excited state proposed by Geoffroy and Pierantozzi[10] is correct since a MLCT reactive state would involve too large a Stokes shift for that type of excited state.[17]

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(13) The lower limit of the lifetime of the iron donor complex was calculated by dividing the experimentally determined quenching constant by the diffusion-controlled rate constant estimated by means of the Stokes–Einstein equation: Porter, G. B. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; p 73.
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(16) Preliminary attempts at measuring a transient absorbance spectrum for Fe(bpy)$_2$(CN)$_2$ have been successful. However, since no change in the absorption spectrum of Fe(bpy)$_2$(CN)$_2$ is observed with the addition of the cobalt complex and no curvature in the quenching plot is apparent, static quenching seems unlikely (see: Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* **1974,** *96,* 3663).
(17) Adamson, A. W., Fleischauer, P. D., Eds. *Photochemistry of Inorganic Compounds*; Wiley: New York, 1965.

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Lewis Basicity of Carbonyl Oxygen in the Presence of a Heteroatom: Reaction of [BiFe$_3$(CO)$_{10}$]$^-$ with CH$_3$SO$_3$CF$_3$

Kenton H. Whitmire,*[1a] Craig B. Lagrone,[1a] and A. L. Rheingold*[1b]

The basicity of μ_2- and μ_3-carbonyl oxygen atoms has been well established.[2] Alkylation, acylation, protonation, or silylation at such sites has been observed for [Fe$_3$(CO)$_{11}$]$^{2-}$,[2] [HFe$_3$(CO)$_{11}$]$^-$,[3] [Fe$_4$(CO)$_{13}$]$^{2-}$,[4,5] [HFe$_4$(CO)$_{13}$]$^-$,[5] [HRu$_3$(CO)$_{11}$]$^-$,[6,7] [HOs$_3$(C-

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(1) (a) Rice University. (b) University of Delaware.
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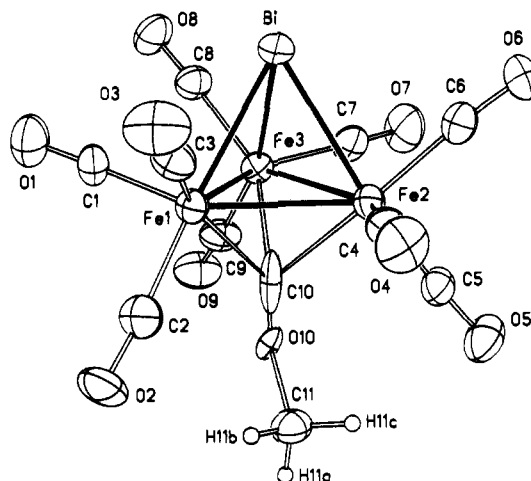
Figure 1. Molecular structure and atom labeling scheme for [Fe$_3$(CO)$_9$](μ_3-COCH$_3$) drawn with 50% probability ellipsoids.

O)$_{11}$]$^-$,[7,8] and [Co$_3$(CO)$_{10}$]$^-$.[9] The low-frequency C–O stretching vibration is used as an indication of basicity and the ability to add R$^+$ reagents to the carbonyl oxygen. To date, however, the alkylation of a bridging carbonyl in a cluster that also contains a main-group heteroatom has not been reported. We were, therefore, prompted to attempt alkylation of [BiFe$_3$(CO)$_{10}$]$^-$, which we recently synthesized. In this molecule, Bi functions as a 3-electron donor, contributing to a total of 12 skeletal electrons for cluster bonding, consistent with localized edge bonding in a tetrahedron. The Bi atom is thus left with a lone pair, which could possibly be alkylated. On the other hand, the μ_3-CO in this molecule appears to be very basic, as judged by IR analysis (ν_{CO} = 1650 cm^{-1}), and the question raised was, "Which site of attack would be preferred?" To answer this question, we have treated [BiFe$_3$(CO)$_{10}$]$^-$ with CH$_3$SO$_3$CF$_3$ and have spectroscopically and structurally characterized the product.

Discussion

The structure of the product BiFe$_3$(CO)$_9$(μ_3-COCH$_3$) (**1**) as shown in Figure 1 consists of a triangle of iron atoms capped by a μ_3-Bi atom on one side and a μ_3-methoxymethyne ligand on the other and shows conclusively that alkylation has occurred at the oxygen of the μ_3-CO. Selected bond distances and angles are given in Table III. The ^{1}H NMR signal for the CH$_3$ group is consistent with values obtained for other methylated carbonyls. The IR spectrum of the terminal carbonyls shows the same pattern as [BiFe$_3$(CO)$_{10}$]$^-$, only shifted to higher energy, as expected for a neutral molecule with the same symmetry as the parent, except that the bridging carbonyl band could no longer be located. The Bi–Fe distances are comparable to those found in Bi$_2$Fe$_3$(CO)$_9$[10] and [BiFe$_3$(CO)$_{10}$]$^-$.[11] The Fe–Fe distances in [BiFe$_3$(CO)$_{10}$]$^-$ are not statistically different from those observed for **1**. Unlike trends observed for [Fe$_4$(CO)$_{13}$]$^{2-}$,[4] the Fe–μ_3-C distances are virtually unchanged upon alkylation. The unusually short μ_3-C–O distance [1.025 (16) Å] is an artifact created by an unresolvable disorder in the position of the μ_3-C.

The presence of the bismuth atom may have a profound influence on the reactivity of this molecule. We carried out the

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