

# Mechanistic and Kinetic Studies of Cobalt Macrocycles in a Photochemical CO<sub>2</sub> Reduction System: Evidence of Co–CO<sub>2</sub> Adducts as Intermediates

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**Abstract:** Cobalt macrocycles mediate electron transfer in the photoreduction of CO<sub>2</sub> with *p*-terphenyl as a photosensitizer and a tertiary amine as a sacrificial electron donor in a 5:1 acetonitrile/methanol mixture. The mechanism and kinetics of this system have been studied by continuous and flash photolysis techniques. Transient spectra provide evidence for the sequential formation of the *p*-terphenyl radical anion, the Co<sup>I</sup>L<sup>+</sup> complex, the [Co<sup>I</sup>L–CO<sub>2</sub>]<sup>+</sup> complex, and the [S–Co<sup>III</sup>L–(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> complex (L = HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; S = solvent) in the catalytic system. The electron-transfer rate constant for the reaction of *p*-terphenyl radical anion with Co<sup>II</sup>L<sup>2+</sup> is  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and probably diffusion controlled because of the large driving force ( $\sim +1.1 \text{ V}$ ). Flash photolysis studies yield a rate constant  $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and an equilibrium constant  $1.1 \times 10^4 \text{ M}^{-1}$  for the binding of CO<sub>2</sub> to Co<sup>I</sup>L<sup>+</sup> in the catalytic system. These are consistent with those previously obtained by conventional methods in acetonitrile. Studies of catalytic systems with varying cobalt macrocycles highlight some of the factors controlling the kinetics of the photoreduction of CO<sub>2</sub>. Steric hindrance and reduction potentials are important factors in the catalytic activity for photochemical CO<sub>2</sub> reduction.

## Introduction

In recent years photochemical and electrochemical reductions of CO<sub>2</sub> have been studied extensively in light of the twin problems of global warming and depletion of fossil fuels.<sup>1</sup> The use of transition-metal macrocycles as electrocatalysts in CO<sub>2</sub> reduction was first reported by Fisher and Eisenberg.<sup>2</sup> They used cobalt(II) and nickel(II) macrocycles to electrochemically reduce CO<sub>2</sub> and H<sub>2</sub>O to CO and H<sub>2</sub>, respectively, in acetonitrile/water mixtures. Since their report much interest has focused on the use of 14-membered transition-metal macrocycles in CO<sub>2</sub> reduction.<sup>2–26</sup> Beley et al.<sup>4,6</sup> reported that [Nicyclam]<sup>2+</sup> (cyclam = 1,4,8,11-tetraazacyclotetradecane) is remarkably efficient and

selective for the electrochemical reduction of CO<sub>2</sub> to CO, even in H<sub>2</sub>O. The importance of adsorbed [Ni<sup>I</sup>cyclam]<sup>+</sup> as an active catalyst in the system was reported by the authors and was further studied by two groups.<sup>12,17,20</sup> Although the [Nicyclam–CO<sub>2</sub>]<sup>+</sup> and [Nicyclam–COOH]<sup>2+</sup> complexes have received extensive attention as intermediates in electrochemical CO<sub>2</sub> reduction, they have not yet been characterized.

Photochemical CO<sub>2</sub> reduction has been reported in a catalytic system using Ru(bpy)<sub>3</sub><sup>2+</sup> as the sensitizer, cobalt or nickel macrocycles as the electron relay catalysts, and ascorbate as a sacrificial reductive quencher.<sup>3,8,13</sup> These systems also produce H<sub>2</sub> via reduction of water.<sup>27</sup> In the case of [Nicyclam]<sup>2+</sup>, the quantum yield of CO production is  $\sim 10^{-4}$  at pH = 4 and the yields of both CO and H<sub>2</sub> are pH dependent. In order to improve the yield, complexes that covalently link the sensitizer to the catalysts have been prepared. Complexes made up of Ru-

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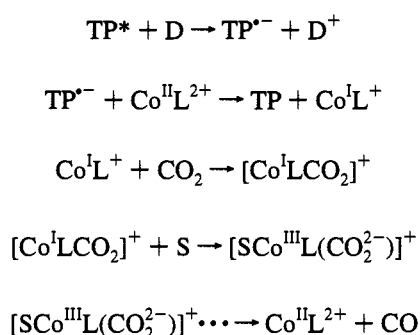
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(bpy)<sub>3</sub><sup>2+</sup> or Ru(phen)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) bound to Nicyclam<sup>2+</sup> have been prepared, and their photophysical and catalytic properties have been studied.<sup>23,28,29</sup> However, both the multimolecular and supramolecular photochemical systems studied show low yields of CO production due to competing processes in the quenching of the photoexcited complexes.

Recently, Matsuoka et al. reported that oligo(*p*-phenylene)s ranging from *p*-terphenyl (TP) to *p*-sexiphenyl sensitize the photoreduction of CO<sub>2</sub> to formic acid. The systems use triethylamine (TEA) as a sacrificial electron donor in aprotic polar solvents such as *N,N*-dimethylformamide (DMF) and acetonitrile (MeCN).<sup>14,30</sup> The photoreduction of CO<sub>2</sub> proceeds via electron transfer from the photogenerated anion of the *p*-phenylene directly to the CO<sub>2</sub> molecule. In the case of TP, the quantum yield of HCO<sub>2</sub><sup>-</sup> formation is 7.2% at 313 nm. Unfortunately, a competitive photo-Birch reduction of the TP producing dihydroterphenyl derivatives occurs in parallel with the photoreduction process and the photoactivity is quickly lost. This is the result of the reactivity of the TP radical anion ( $E^\circ \sim -2.2$  V vs NHE) and the unreactivity of the CO<sub>2</sub> toward one-electron reduction ( $E^\circ \sim -1.9$  V vs NHE).<sup>30</sup> Because of the reported catalytic activity of metal macrocycles for CO<sub>2</sub> reduction and the well-characterized properties<sup>9,10,15,16,31</sup> of the CO<sub>2</sub> adducts, we added metal macrocycles as electron mediators in order to stabilize the TP via fast electron transfer from the radical anion to the metal macrocycles. The cobalt macrocycles were found to mediate electron transfer in the photoreduction of CO<sub>2</sub> with TP as photosensitizer and a tertiary amine (including the  $\beta$ -hydroxylated tertiary amine) as sacrificial electron donor in acetonitrile/methanol mixtures.<sup>19,32</sup> The system enhances the activity of the TP by suppressing the formation of dihydroterphenyl derivatives and produces CO and formate efficiently with only small amounts of H<sub>2</sub>. The total quantum yield of CO and formate is 25% at 313 nm in the presence of triethanolamine (TEOA) and Co(cyclam)<sup>3+</sup> complex. The proposed mechanism for CO production<sup>19</sup> is shown in Scheme 1:

Scheme 1



(1) Quenching of the photoexcited state of *p*-terphenyl by the sacrificial electron donor to form the radical anion, (2) reduction of the Co(II) complex by the radical anion of TP forming the

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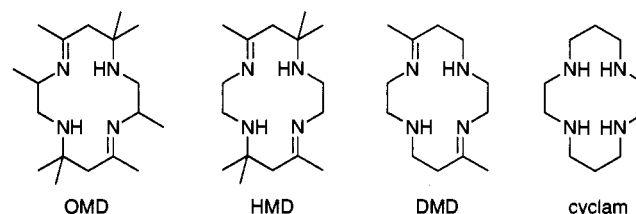
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Co(I) complex, (3) coordination of the Co(I) complex by CO<sub>2</sub> to give [Co<sup>I</sup>L(CO<sub>2</sub>)]<sup>+</sup>, and (4) reaction of [Co<sup>I</sup>L(CO<sub>2</sub>)]<sup>+</sup> with solvent to form the d<sup>6</sup> metal complex [S-Co<sup>III</sup>L-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> which then is reduced to form CO, OH<sup>-</sup>, and a Co(II) species. The formate is thought<sup>19</sup> to result from the insertion of CO<sub>2</sub> into a d<sup>6</sup> hydride complex, [H-Co<sup>III</sup>L-S]<sup>2+</sup> (S = solvent or TEA), derived from the reaction of [Co<sup>I</sup>L]<sup>+</sup> with H<sup>+</sup>. To determine the mechanism and the kinetics in the catalytic system, we have carried out flash photolysis experiments on TP, TEA, a cobalt macrocyclic, and CO<sub>2</sub> in a 5:1 acetonitrile/methanol mixture. Here we report spectroscopic evidence for the formation of the TP radical anion, the Co<sup>I</sup>L<sup>+</sup> complex, the [Co<sup>I</sup>L-CO<sub>2</sub>]<sup>+</sup> complex and the [S-Co<sup>III</sup>L-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> complex. The effect of changes in the metal macrocycle on the kinetics and the production of CO in the catalytic cycle are considered.

## Experimental Section

**Materials.** The complexes [CoOMD(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (OMD = 3,5,7,7-,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene),<sup>33,34</sup> *N-rac*-[CoHMD(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>,<sup>35,36</sup> [CoDMDCl<sub>2</sub>]ClO<sub>4</sub> (DMD = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene),<sup>37</sup> and [Co(cyclam)Cl<sub>2</sub>]ClO<sub>4</sub><sup>38</sup> were prepared as previously described and characterized by UV-vis and IR spectroscopies. Analyses for cobalt and anions of these complexes were satisfactory. (**Warning:** The perchlorate salts used in this study may be explosive and potentially hazardous.) TP was purified by recrystallization from methanol. Tetraethylammonium perchlorate (TEAP) was used after three recrystallizations from a water/ethanol mixture. Acetonitrile (MeCN), methanol (MeOH), and TEA were purified in the published manner<sup>39</sup> and stored under vacuum over activated molecular sieves (3A), magnesium methoxide, and sodium-potassium alloy (NaK), respectively. Research grade CO<sub>2</sub> (CO<sub>2</sub> > 99.998%) was used without further purification.



**Solubility of CO<sub>2</sub> in the Reaction Mixture.** The solubility of CO<sub>2</sub> in the MeCN/MeOH (v/v = 5) solution containing 0.1 M TEAP at 1 atm of CO<sub>2</sub> was determined by adding an aliquot of a CO<sub>2</sub> saturated solution to a known excess of aqueous Ba(OH)<sub>2</sub>.<sup>15</sup> The resultant solution was back-titrated with standardized HCl. The saturated CO<sub>2</sub> solution was prepared by bubbling CO<sub>2</sub> through the solvent. In order to avoid evaporation of the mixed solvent, the CO<sub>2</sub> was passed through three MeCN/MeOH (v/v = 5) solutions before bubbling into the test solution containing TEAP at 25 °C. The solubility of the mixed solvent was found to be 0.25 M at 25 °C, which is similar to the 0.28 M value in pure MeCN.<sup>15</sup> Dalton's law of partial pressure was assumed to hold within experimental error in the mixed solvent as was found in pure MeCN.<sup>15</sup>

**Spectroscopic Measurements.** Degassed and CO<sub>2</sub>-containing solutions for UV-vis and transient-absorption measurements were prepared using high-vacuum techniques to avoid contamination by H<sub>2</sub>O and air.

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Mixed solvent, MeCN/MeOH ( $v/v = 5$ ), was used as previously reported for the TP-catalyzed photoreduction of  $\text{CO}_2$ .<sup>19</sup> TEAP was added to the sample solution to maintain a constant ionic strength of 0.1 M. A typical sample preparation is the following: (1) A solution containing the required amount of TP, TEAP, and cobalt complex was placed in a vacuum sample holder of known volume equipped with a 10 mm path length quartz spectrofluorimeter cell; (2) the sample was evaporated to dryness under high-vacuum overnight; (3) 2.5 mL of MeCN, 0.5 mL of MeOH, and 0.2 mL of TEA were transferred to the cell through a vacuum line; (4) for measurement under  $\text{CO}_2$  atmosphere, a known amount of  $\text{CO}_2$  was transferred into the sample through the vacuum line using liquid  $\text{N}_2$ ; (5) the concentration of  $\text{CO}_2$  in the solution at 25 °C was calculated assuming ideal gas behavior from the amount of  $\text{CO}_2$ , the solubility of  $\text{CO}_2$ , and the gas and solution volumes. The  $\text{CO}_2$  concentration ranged from 0 to 0.26 M.

UV-vis spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer before and after flash photolysis experiments. While  $\text{Co}^{\text{II}}\text{HMD}^{2+}$  decomposes slowly in a solution containing TEA and air, under our conditions of vacuum or  $\text{CO}_2$  atmosphere the cobalt(II) complex is indefinitely stable. The  $\text{Co}^{\text{I}}\text{HMD}^+$  produced by flash photolysis is a stable species and its concentration increases with multiple excitation pulses. For rate measurements involving  $\text{Co}^{\text{I}}\text{HMD}^+$ , vigorous stirring and a limited number of laser shots are required to avoid artifacts.

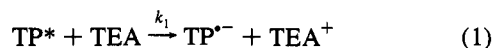
Transient-absorption spectra and lifetimes of various intermediates were measured on a previously described apparatus.<sup>40</sup> Excitation was with the fourth harmonic of a Nd:YAG laser (30 ps pulse). Transient absorption spectra were obtained with an intensified photodiode array (PDA) system with a 20-ns gate. Transient spectra are the average of multiple laser pulses. The solution was vigorously stirred between laser shots. Data were signal averaged and corrected for the dark current of the PDA. Changes in absorption spectra were obtained at specified times after laser excitation of the sample. Absorbance changes were calculated by taking the log of the ratio of the transmitted light intensity with and without laser excitation of the sample. For kinetics measurements, the monochromatic light was detected by a photomultiplier whose output was amplified and digitized. The intensity of the excitation light was monitored and only laser shots within  $\pm 15\%$  of the average reading were used. The kinetics of the signal-averaged data was analyzed using Levenberg-Marquardt nonlinear least-squares routines written in MATLAB.

Measurements of the effect of laser intensity on the kinetics and yields were made by using a 3 mM aqueous solution of  $\text{CuSO}_4$  to absorb the actinic light. Path lengths of 2, 5, and 10 cm were used with transmittances at 266 nm of 0.64, 0.42, and 0.16, respectively.

**Continuous Photolysis.** Solutions were irradiated using light from a 100 W high-pressure Hg-Xe lamp. The light passes through a 1/4 M monochromator to isolate the 313 nm line. The instrument has a 16 nm band-pass.

## Results

**Formation of the TP Radical Anion.** Figure 1a shows the transient-absorption spectrum observed after excitation of a degassed sample containing 0.1 mM TP, 0.5 M TEA, and 0.1 M TEAP in MeCN/MeOH and no cobalt macrocycle or  $\text{CO}_2$ . The spectrum forms promptly after excitation and decays only slowly. The transient absorption spectrum is consistent with the reported spectrum<sup>41,42</sup> of the TP radical anion,  $\text{TP}^{\bullet-}$ , within the resolution of our spectrometer. The rate constant for the radical formation,  $k_1$  in eq 1, has been reported to be  $3 \times 10^9$

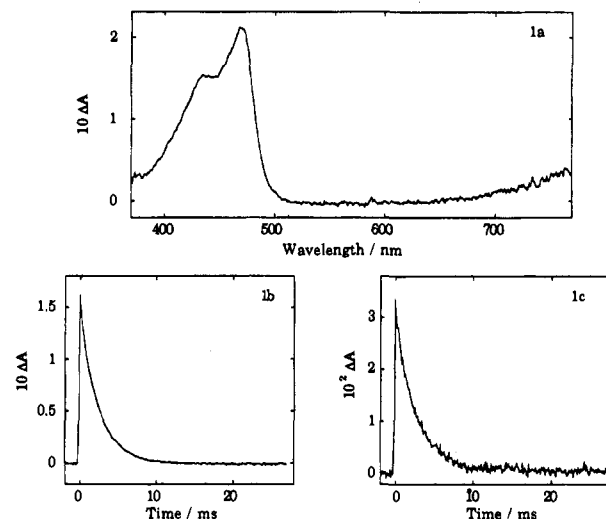


$\text{M}^{-1} \text{s}^{-1}$  in THF.<sup>30</sup> We did not determine the rate in MeCN/MeOH but it is also very fast ( $t_{1/2} < 2$  ns in our solutions).

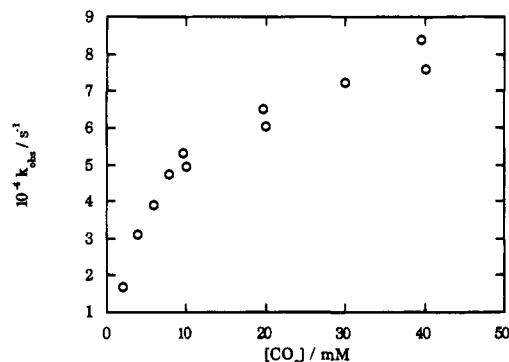
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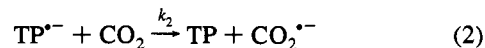
**Figure 1.** (a) Transient absorption spectrum of the TP radical anion observed 6  $\mu\text{s}$  after the excitation for the degassed sample containing 0.1 mM TP, 0.5 M TEA, and 0.1 M TEAP in MeCN/MeOH. (b) Decay of  $\text{TP}^{\bullet-}$  monitored at 470 nm. (c) Decay of  $\text{TP}^{\bullet-}$  monitored at 750 nm. The first-order fitting of both curves gives the lifetime of 2.5 ms.



**Figure 2.** Kinetic behavior of the TP radical anion in the presence of  $\text{CO}_2$ , as shown by a plot of the observed first-order rate constant vs  $\text{CO}_2$  concentration.

Decay of  $\text{TP}^{\bullet-}$  in MeCN/MeOH solution was monitored at 470 and 750 nm as shown in Figure 1, parts b and c, respectively. Both decays follow first-order kinetics and give a rate constant  $k_{\text{obsd}} = 400 \text{ s}^{-1}$ .

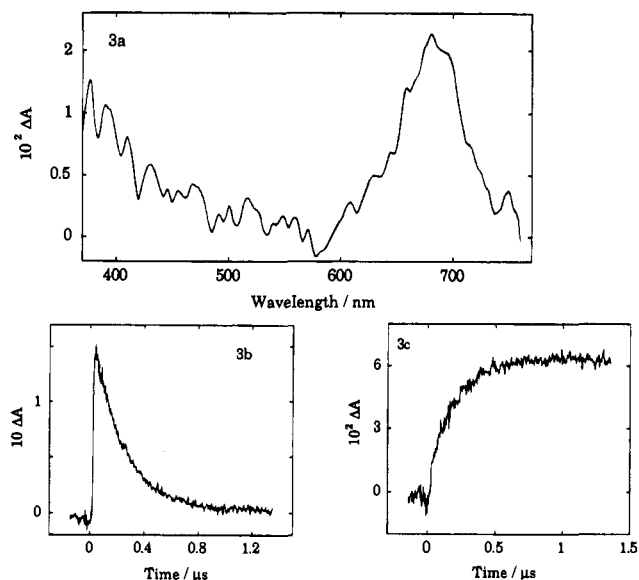
**Electron Transfer from  $\text{TP}^{\bullet-}$  to  $\text{CO}_2$ .** The decay of the absorption of  $\text{TP}^{\bullet-}$  was observed for solutions containing  $\text{CO}_2$  with no cobalt macrocycle (0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, and  $\text{CO}_2$  (1.0–40 mM)) in MeCN/MeOH. The fit of the decay to a single exponential shows systematic deviations at low  $\text{CO}_2$  concentrations. As shown in Figure 2, a plot of the decay rate constant vs  $\text{CO}_2$  concentration is not linear.



**Electron Transfer from  $\text{TP}^{\bullet-}$  to  $\text{CoHMD}^{2+}$ .** Figure 3a shows the transient-absorption spectrum observed after the excitation of the sample with added  $\text{Co}^{\text{II}}\text{HMD}^{2+}$  (1 mM  $\text{Co}^{\text{II}}\text{HMD}^{2+}$ , 0.1 mM TP, 0.5 M TEA, and 0.1 M TEAP in MeCN/MeOH). The spectrum is that expected for the  $\text{Co}^{\text{I}}\text{HMD}^+$  with the peak at 685 nm due to an MLCT transition of the square-planar complex.<sup>9,15,43</sup> The  $\text{Co}^{\text{I}}\text{HMD}^+$  species formed under these conditions is quite stable with a lifetime of  $> 1$  s.

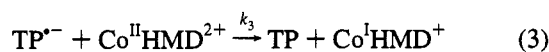
The decay of the  $\text{TP}^{\bullet-}$  absorption and the growth of the  $\text{Co}^{\text{I}}\text{HMD}^+$  absorption are shown in Figure 3, parts b and c,

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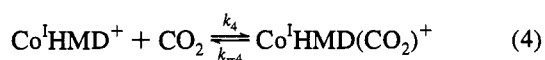
**Figure 3.** (a) Transient absorption spectrum of Co<sup>I</sup>HMD<sup>+</sup> observed 6 μs after the excitation for a degassed sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, and 1 mM Co<sup>II</sup>HMD<sup>2+</sup> in MeCN/MeOH. (b) Decay of TP<sup>\*-</sup> monitored at 470 nm. (c) Growth of Co<sup>I</sup>HMD<sup>+</sup> monitored at 670 nm.

respectively. The magnitudes of the changes in absorbance at 470 and 685 nm establish that the stoichiometry of the formation of Co(I) from TP<sup>\*-</sup> is 1:1 ± 0.2. Both decays are well fit by a first-order decay/growth function. The plot of the observed first-order rate constant ( $k_{\text{obsd}}$ ) for the decay of TP<sup>\*-</sup> vs Co<sup>II</sup>-HMD<sup>2+</sup> concentration is linear and gives a second-order rate constant  $k_3 = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  as shown in Figure S1 (supplementary material).

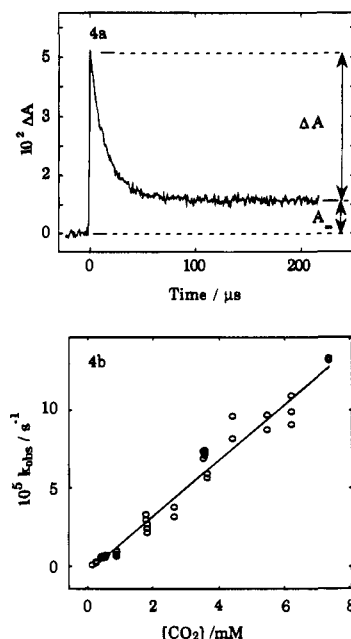


The observed first-order rates for the decay of TP<sup>\*-</sup> and growth of Co<sup>I</sup>HMD<sup>+</sup> are similar; however, the formation of the Co(I) is slightly faster than the decay of the TP<sup>\*-</sup> anion. For example,  $1.1 \times 10^6$  vs  $1.5 \times 10^6$ ,  $2.2 \times 10^6$  vs  $2.4 \times 10^6$ ,  $3.3 \times 10^6$  vs  $4.0 \times 10^6$ , and  $4.5 \times 10^6$  vs  $5.1 \times 10^6 \text{ s}^{-1}$  for 0.1, 0.2, 0.3, and 0.4 mM Co<sup>II</sup>HMD<sup>2+</sup>, respectively. Larger differences in rates between the formation of Co(I) and disappearance of TP<sup>\*-</sup> were observed in pure MeCN:  $4.2 \times 10^5$  vs  $7.7 \times 10^5$ ,  $1.5 \times 10^5$  vs  $2.5 \times 10^5$ ,  $2.2 \times 10^6$  vs  $6.0 \times 10^6$ , and  $2.6 \times 10^6$  vs  $1.0 \times 10^7 \text{ s}^{-1}$ , for 0.1, 0.2, 0.3, and 0.4 mM Co<sup>II</sup>-HMD<sup>2+</sup>, respectively.

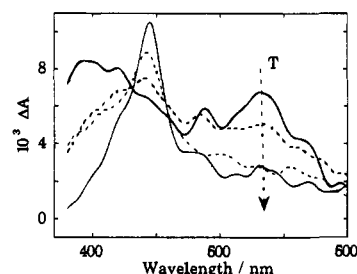
**Reaction of Co<sup>I</sup>HMD<sup>+</sup> by CO<sub>2</sub>.** When CO<sub>2</sub> is introduced into the photosystem, the lifetime of Co<sup>I</sup>HMD<sup>+</sup> changes dramatically. Figure 4a shows the decay of Co<sup>I</sup>HMD<sup>+</sup> monitored at 670 nm for a sample containing 0.1 mM TP, 0.5 M TEA, 1 mM Co<sup>II</sup>HMD<sup>2+</sup>, 0.1 M TEAP, and 0.53 mM CO<sub>2</sub> in MeCN/MeOH. The curve is well fit as a first-order decay process with a rate constant of  $6.5 \times 10^4 \text{ s}^{-1}$ . The variation of the observed rate constants for Co<sup>I</sup>HMD<sup>+</sup> decay with CO<sub>2</sub> concentrations (0.53 to 7.2 mM) is shown in Figure 4b.



The bimolecular CO<sub>2</sub> binding rate constant,  $k_4$  in eq 4, obtained from the slope of Figure 4b is  $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The observed decay of the Co<sup>I</sup>HMD<sup>+</sup> in all cases results in a finite absorbance at long times. The absorbance change at short times due to the formation of Co<sup>I</sup>HMD<sup>+</sup> produced by the quenching of the TP<sup>\*-</sup>



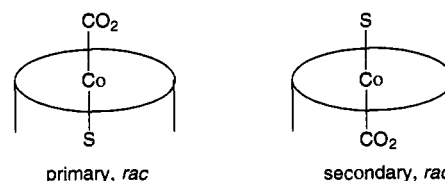
**Figure 4.** (a) Transient decay curve of Co<sup>I</sup>HMD<sup>+</sup> monitored at 670 nm for a sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, 1 mM Co<sup>II</sup>HMD<sup>2+</sup>, and 0.53 mM CO<sub>2</sub> in MeCN/MeOH. (b) Kinetic behavior of the Co<sup>I</sup>HMD<sup>+</sup> in the presence of CO<sub>2</sub>, as shown by a plot of the pseudo-first-order rate constant vs CO<sub>2</sub> concentration.  $k_{\text{obs}} = (1.7 \times 10^8)[\text{CO}_2] - (3 \pm 6) \times 10^4 \text{ (s}^{-1}\text{)}$ .



**Figure 5.** Temperature-dependent transient absorption spectrum of Co<sup>I</sup>HMD(CO<sub>2</sub>)<sup>+</sup> at 50, 25, 0, and -25 °C. The peaks at 530 and 475 nm, due to the 5-coordinate Co<sup>I</sup>HMD(CO<sub>2</sub>)<sup>+</sup>, diminish upon cooling, while the peak at 440 nm, due to the 6-coordinate S-Co<sup>I</sup>HMD(CO<sub>2</sub>)<sup>+</sup>, increases. The spectra were observed 6 μs after the excitation for the sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, 1 mM Co<sup>II</sup>-HMD<sup>2+</sup>, and 0.2 M CO<sub>2</sub> in MeCN/MeOH.

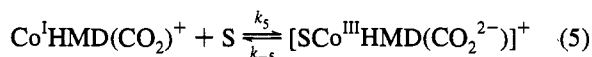
is linear in laser intensity while the rate constant observed for the decay of the Co<sup>I</sup>HMD<sup>+</sup> is independent of laser intensity.

To identify the product of the reaction of CO<sub>2</sub> with Co<sup>I</sup>HMD<sup>+</sup> in the photocatalytic system, the transient spectra were measured 6 μs after the excitation at 50, 25, 0, and -25 °C. The spectra are shown in Figure 5. The transient spectrum at 25 °C is similar to that obtained by pulse radiolysis in H<sub>2</sub>O at 25 °C.<sup>16</sup> The transient spectrum at 50 °C is similar to that for well-characterized 5-coordinate *prim-N-rac*-CoHMD(CO<sub>2</sub>)<sup>+</sup> observed previously in MeCN at 25 °C.<sup>15,31</sup> Both transient spectra at 25 and 50 °C have a small absorption at 480 nm, in addition to the peak at 530 nm. The peak at 480 nm may be due to the



*sec-N-rac*-CoHMD(CO<sub>2</sub>)<sup>+</sup> as found previously in H<sub>2</sub>O by a

pulse radiolysis technique.<sup>16</sup> Here primary ("prim") and secondary ("sec") refer respectively to the face on which the 1,8-NH and axial 7,14-CH<sub>3</sub> groups are found (see diagram above). As the temperature decreases the intensity of the peaks at 530 and 480 nm decreases while the intensity of the peak at 440 nm increases. From equilibrium studies in MeCN it has been shown that the peak at 530 nm is due to the 5-coordinate CoHMD(CO<sub>2</sub>)<sup>+</sup> while the peak at 440 nm is due to a 6-coordinate S-CoHMD(CO<sub>2</sub>)<sup>+</sup> species. In MeCN at long times the two species are in reversible equilibrium with the 6-coordinate species more stable at low temperature and the 5-coordinate one more stable at high temperature.<sup>31</sup>



The kinetic scheme in eqs 4 and 5 suggests that the equilibrium constant for CO<sub>2</sub> binding can be studied by transient methods. If  $k_4[\text{CO}_2] \sim k_{-4}$  then a plot of  $k_{\text{obs}}$  vs  $[\text{CO}_2]$  will have a slope of  $k_4$  and an intercept of  $k_{-4}$ . However, if  $k_4[\text{CO}_2] \gg k_{-4}$ , as is the case here, then the intercept will be small and poorly defined (see Figure 4b). Alternatively, the initial and final absorbances at 670 nm can give the ratio of the total cobalt-CO<sub>2</sub> complex to the unreacted cobalt complex since the CO<sub>2</sub> adducts have no significant absorption.<sup>9,15,31</sup> We can define

$$\begin{aligned} K_{\text{CO}_2} &= \frac{[\text{CoHMD} - \text{CO}_2]}{[\text{Co}^{\text{I}}\text{HMD}^+][\text{CO}_2]} \\ &= \frac{\Delta A}{A_{\infty}[\text{CO}_2]} \end{aligned} \quad (6a)$$

where  $[\text{CoHMD} - \text{CO}_2]$  is the total concentration of the cobalt CO<sub>2</sub> adducts (*i.e.*,  $[\text{CoHMD}(\text{CO}_2)^+] + [\text{S}\text{CoHMD}(\text{CO}_2)^+]$ ). The  $[\text{CoHMD} - \text{CO}_2]$  is given by the  $[\text{Co}^{\text{I}}\text{HMD}^+]$  that has disappeared. The ratio of  $[\text{CoHMD} - \text{CO}_2] / [\text{Co}^{\text{I}}\text{HMD}^+]$  is given by  $\Delta A / A_{\infty}$  where  $\Delta A = A_{\infty} - A_0$  when  $A_{\infty}$  and  $A_0$  are the absorbances at 670 nm at long times and at  $t = 0$ , respectively (see Figure 4a). The above assumes that the Co<sup>I</sup>HMD<sup>+</sup> is rapidly formed, both the Co<sup>I</sup>HMD<sup>+</sup> and the CO<sub>2</sub> adduct are stable on the transient absorption time scale, and only the Co<sup>I</sup>HMD(CO<sub>2</sub>)<sup>+</sup> absorbs.<sup>9,15,31</sup> In fact the final absorbance is quite stable in our solvent mixture and shows no decomposition for times < 1 ms when  $[\text{CO}_2] > 10^{-3}$  M.

The kinetic fits of the Co<sup>I</sup>HMD<sup>+</sup> decay yield values of  $\Delta A$  and  $A_0$ . When the CO<sub>2</sub> concentration is lowered, the  $\Delta A$  value is reduced and  $A_{\infty}$  increases.  $K_{\text{CO}_2}$  is calculated from eq 6a as  $(1.1 \pm 0.2) \times 10^4 \text{ M}^{-1}$  from solutions with  $[\text{CO}_2] = (1.42 - 5.7) \times 10^{-4} \text{ M}$  (0.1 mM TP, 0.5 M TEA, 1 mM Co<sup>II</sup>HMD<sup>2+</sup>, and 0.1 M TEAP) as shown in Table 1. The equilibrium constant  $K_{\text{CO}_2}$  is given by

$$K_{\text{CO}_2} = K_4(1 + K_5[\text{S}]) \quad (6b)$$

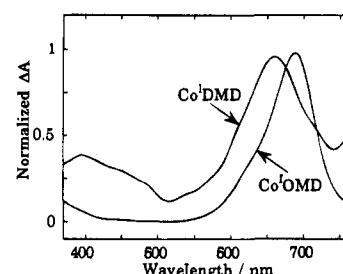
where  $K_4$  and  $K_5$  are the equilibrium constants for eqs 4 and 5, respectively. Our previous study in MeCN indicates that  $K_4$  and  $K_5[\text{S}]$  are  $1.2 \times 10^4 \text{ M}^{-1}$  and 0.17, respectively, for Co<sup>I</sup>HMD<sup>+</sup> at 25 °C.<sup>9,15,31</sup> Therefore, the  $K_{\text{CO}_2}$  by conventional methods is  $1.4 \times 10^4 \text{ M}^{-1}$ , which is consistent with the value obtained in this study.

**Ligand Variations on the Cobalt Complex.** In order to investigate the factors governing the selectivity and the rate of CO<sub>2</sub> reduction, we extended our work to other 14-membered cobalt complexes Co<sup>II</sup>DMD<sup>2+</sup> and Co<sup>II</sup>OMD<sup>2+</sup>. Co<sup>II</sup>DMD<sup>2+</sup> is air oxidizable in solution and was isolated as the Co(III) salt,  $[\text{Co}^{\text{III}}\text{DMDBr}_2]\text{ClO}_4$ . The photolysis solutions were prepared

**Table 1.** Determination of  $K_{\text{CO}_2}$  for Co<sup>I</sup>HMD<sup>+</sup> and Co<sup>I</sup>OMD<sup>+</sup> in MeCN/MeOH (with 0.1 mM TP, 0.5 M TEA, 1 mM Co<sup>II</sup>HMD<sup>2+</sup> or Co<sup>II</sup>OMD<sup>2+</sup>, and 0.1 M TEAP) at 25 °C by Laser Flash Photolysis<sup>a</sup>

| complex                           | [CO <sub>2</sub> ]/M    | A <sub>0</sub>      | A <sub>∞</sub> | K <sub>CO<sub>2</sub></sub> |
|-----------------------------------|-------------------------|---------------------|----------------|-----------------------------|
| Co <sup>I</sup> HMD <sup>2+</sup> | 1.42 × 10 <sup>-4</sup> | 0.0669              | 0.0277         | 1.00 × 10 <sup>4</sup>      |
|                                   |                         | 0.0595              | 0.0192         | 1.47 × 10 <sup>4</sup>      |
|                                   | 2.84 × 10 <sup>-4</sup> | 0.0611              | 0.0141         | 1.17 × 10 <sup>4</sup>      |
|                                   |                         | 0.0707              | 0.0164         | 1.17 × 10 <sup>4</sup>      |
|                                   | 4.26 × 10 <sup>-4</sup> | 0.0517 <sup>a</sup> | 0.00895        | 1.12 × 10 <sup>4</sup>      |
| Co <sup>I</sup> OMD <sup>2+</sup> |                         | 0.0527              | 0.0101         | 0.99 × 10 <sup>4</sup>      |
|                                   | 5.68 × 10 <sup>-4</sup> | 0.0583              | 0.00946        | 0.93 × 10 <sup>4</sup>      |
|                                   |                         | 0.0588              | 0.00959        | 0.90 × 10 <sup>4</sup>      |
|                                   | 9.8 × 10 <sup>-2</sup>  | 0.0578              | 0.0377         | 5.4                         |
|                                   | 1.48 × 10 <sup>-1</sup> | 0.0824              | 0.0408         | 6.9                         |
|                                   | 0.0823                  | 0.0427              | 6.3            |                             |
|                                   | 1.98 × 10 <sup>-1</sup> | 0.0466              | 0.0189         | 7.4                         |
|                                   |                         | 0.0492              | 0.0187         | 8.2                         |
|                                   | 2.48 × 10 <sup>-1</sup> | 0.0456              | 0.0144         | 8.7                         |
|                                   |                         | 0.0363              | 0.0177         | 8.5                         |

<sup>a</sup> Values of  $\Delta A$  and  $A_0$  were obtained from the kinetic fits of the Co<sup>I</sup>HMD<sup>+</sup> decay.



**Figure 6.** Transient absorption spectra of Co<sup>I</sup>DMD<sup>+</sup> and Co<sup>I</sup>OMD<sup>+</sup>. The spectrum of Co<sup>I</sup>OMD<sup>+</sup> was observed 6 μs after the excitation for the degassed sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, and 1 mM Co<sup>II</sup>OMD<sup>2+</sup> in MeCN/MeOH. The spectrum of Co<sup>I</sup>OMD<sup>+</sup> was observed 6 μs after the excitation for the pre-irradiated (at 313 nm, for 30 min to change from Co<sup>III</sup>DMD<sup>3+</sup> to Co<sup>II</sup>DMD<sup>2+</sup>) sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, and 1 mM Co<sup>III</sup>DMD<sup>3+</sup> in MeCN/MeOH.

using Co<sup>III</sup>DMD<sup>3+</sup> (together with 0.1 mM TP, 0.5 M TEA, and 0.1 M TEAP in MeCN/MeOH under vacuum). The solutions were irradiated at 313 nm (continuous photolysis instrument) to convert Co<sup>III</sup>DMD<sup>3+</sup> to Co<sup>II</sup>DMD<sup>2+</sup> before flash photolysis experiments. The end point of the photoreduction was determined by monitoring the UV-vis spectrum. Typically the irradiation time was less than 1 h. Such a photochemical reduction of Co<sup>III</sup> macrocycles has been studied previously.<sup>44-46</sup> The resulting Co<sup>II</sup>DMD<sup>2+</sup> spectrum was consistent with the spectrum determined previously by the electroreduction of Co<sup>III</sup>DMD<sup>3+</sup>.<sup>15</sup> In the presence of Co<sup>II</sup>DMD<sup>2+</sup> or Co<sup>II</sup>OMD<sup>2+</sup>, the lifetime of TP<sup>•-</sup> decreases dramatically and its decay monitored at 470 nm follows first-order kinetics. Plots of the observed decay rate constant vs the Co<sup>II</sup>DMD<sup>2+</sup> or Co<sup>II</sup>OMD<sup>2+</sup> concentration are linear as shown in Figures S2 and S3 (supplementary material), respectively. The bimolecular electron-transfer rate constants are  $8.8 \times 10^9$  and  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

Transient absorption spectra of Co<sup>I</sup>DMD<sup>+</sup> and Co<sup>I</sup>OMD<sup>+</sup> observed in the absence of CO<sub>2</sub> are shown in Figure 6. The spectra were determined 6 μs after excitation for degassed samples containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, and 1 mM Co(II) complex in MeCN/MeOH. The transient-absorption spectra of Co<sup>I</sup>DMD<sup>+</sup> and Co<sup>I</sup>OMD<sup>+</sup> in MeCN/

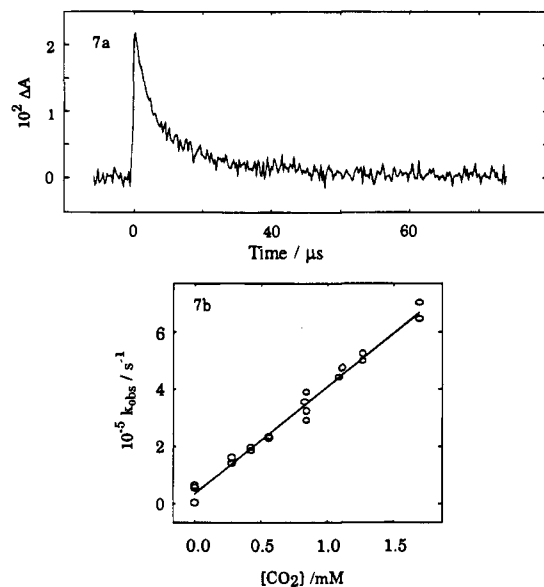
(44) Lampeka, Y. D.; Krasnova, V. A.; Lapshin, V. G. *Russ. J. Inorg. Chem.* **1986**, *31*, 525.

(45) Lampeka, Y. D.; Rosokha, S. V. *Russ. J. Inorg. Chem.* **1988**, *33*, 526.

(46) Yatsimirskii, K. B.; Rosokha, S. V.; Lampeka, Y. D.; Krasnova, V. A. *Russ. J. Inorg. Chem.* **1986**, *31*, 527.

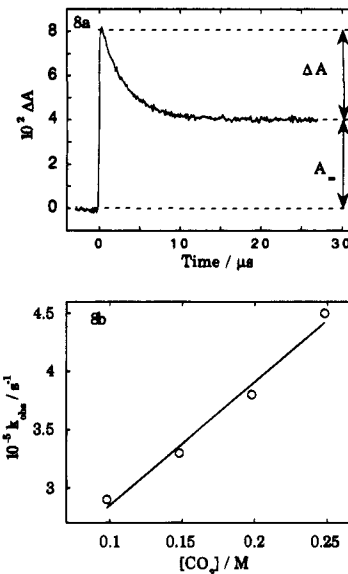
**Table 2.** Comparison of the Rate Constants, Lifetimes, and the CO<sub>2</sub> Binding Constants at 25 °C

|  |                                | CoOMD                | CoHMD                | CoDMD             |
|--|--------------------------------|----------------------|----------------------|-------------------|
| $E^{1/2}$ (in MeCN) <sup>a</sup>   | V vs SCE                       | -1.28                | -1.38                | -1.51             |
| relative CO production <sup>b</sup>  |                                | 1                    | 2.5                  | 6.8               |
| TP <sup>•-</sup> + Co <sup>II</sup> L <sup>2+</sup> → TP + Co <sup>I</sup> L <sup>+</sup>                  | $k_3, M^{-1} s^{-1}$           | $1.1 \times 10^{10}$ | $1.1 \times 10^{10}$ | $8.8 \times 10^9$ |
| lifetime of Co <sup>I</sup> L <sup>+</sup>   |                                | 6 h                  | ~2 s                 | 16 μs             |
| Co <sup>I</sup> L <sup>+</sup> + CO <sub>2</sub> ⇌ Co <sup>I</sup> L(CO <sub>2</sub> ) <sup>+</sup>        | $k_{4f}, M^{-1} s^{-1}$        | $1.1 \times 10^6$    | $1.7 \times 10^8$    | $3.7 \times 10^8$ |
|  | $k_{4r}, s^{-1}$               | $1.8 \times 10^5$    | $1.6 \times 10^4$    |                   |
|  | $K_4 (=k_{4f}/k_{4r}), M^{-1}$ | 6                    | $1.1 \times 10^4$    |                   |
| Co <sup>I</sup> L <sup>+</sup> + CO <sub>2</sub> + S ⇌ SCo <sup>III</sup> L(CO <sub>2</sub> ) <sup>+</sup> | $K_{CO_2}, M^{-1}$             | 7                    | $1.1 \times 10^4$    | $>5 \times 10^4$  |

<sup>a</sup> ref. 15. <sup>b</sup> ref. 19.**Figure 7.** (a) Transient decay curve of Co<sup>I</sup>DMD<sup>+</sup> monitored at 650 nm for the sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, 1 mM Co<sup>II</sup>DMD<sup>2+</sup>, and 0.42 mM CO<sub>2</sub> in MeCN/MeOH. (b) Kinetic behavior of the Co<sup>I</sup>DMD<sup>+</sup> in the presence of CO<sub>2</sub>, as shown by a plot of the pseudo-first-order rate constant vs CO<sub>2</sub> concentration.  $k_{obs} = (3.7 \times 10^8)[CO_2] - (3 \pm 3) \times 10^4 (s^{-1})$ .

MeOH have absorption maxima at 663 and 690 nm, respectively. The spectra are similar to those observed in pure MeCN.<sup>15</sup> Under flash photolysis conditions, the lifetime of Co<sup>I</sup>DMD<sup>+</sup> is only 16 μs, while that of Co<sup>I</sup>OMD<sup>+</sup> is 5.8 h (no CO<sub>2</sub> present). The lifetime of Co<sup>I</sup>OMD<sup>+</sup> was measured by irradiating a solution in the laser flash-photolysis apparatus and then monitoring the concentration of Co<sup>I</sup>OMD<sup>+</sup> on a conventional UV-vis spectrometer at very long times.

Transient decay curves of the Co<sup>I</sup>DMD<sup>+</sup> and Co<sup>I</sup>OMD<sup>+</sup> for the samples containing CO<sub>2</sub> (0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, 1 mM cobalt complex, and 0.42 mM CO<sub>2</sub> (for Co<sup>I</sup>DMD<sup>+</sup>) or 0.1 M CO<sub>2</sub> (for Co<sup>I</sup>OMD<sup>+</sup>)) in MeCN/MeOH are presented in Figures 7a and 8a, respectively. From the slopes of the plots, shown in Figures 7b and 8b, the rate constants for CO<sub>2</sub> binding to Co<sup>I</sup>DMD<sup>+</sup> and Co<sup>I</sup>OMD<sup>+</sup> are determined to be  $3.7 \times 10^8$  and  $1.1 \times 10^6 M^{-1} s^{-1}$ , respectively. The CO<sub>2</sub> binding constant for Co<sup>I</sup>OMD<sup>+</sup> was obtained by two methods: (1) using eq 6a  $K_{CO_2} = 7 M^{-1}$ ; (2) using the ratio of the slope ( $1.1 \times 10^6 M^{-1} s^{-1}$ ) and the intercept ( $1.8 \times 10^5 s^{-1}$ ),  $K_4 = k_4/k_{-4} = 6 M^{-1}$ , from Figure 8b. These results suggest that for Co<sup>I</sup>OMD<sup>+</sup> the six-coordinate complex is not stable,  $K_5[S] \ll 1$ , as expected from the spectra observed.<sup>15</sup> The results are summarized in Table 2 along with  $E_{1/2}$ , relative CO yields, rate constants, and Co(I) lifetime. The CO<sub>2</sub> binding constant for Co<sup>I</sup>DMD<sup>+</sup> was difficult to determine by either method because the Co<sup>I</sup>DMD<sup>+</sup> and [CoDMD-CO<sub>2</sub>]<sup>+</sup> are not stable under low [CO<sub>2</sub>] and the intercept of Figure 7b is small. Therefore only the lower limit is given in Table 2. In this case the stability of

**Figure 8.** (a) Transient decay curve of Co<sup>I</sup>OMD<sup>+</sup> monitored at 680 nm for the sample containing 0.1 mM TP, 0.5 M TEA, 0.1 M TEAP, 1 mM Co<sup>II</sup>OMD<sup>2+</sup>, and 0.1 M CO<sub>2</sub> in MeCN/MeOH. (b) Kinetic behavior of the Co<sup>I</sup>OMD<sup>+</sup> in the presence of CO<sub>2</sub>, as shown by a plot of the pseudo-first-order rate constant vs CO<sub>2</sub> concentration.  $k_{obs} = (1.1 \times 10^6)[CO_2] + 1.8 \times 10^5 (s^{-1})$ .

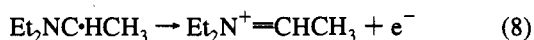
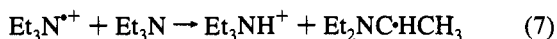
the six-coordinate complex is quite high<sup>15</sup> and the measurement reflects  $K_4K_5[S]$ . (See eq 6b.)

**Continuous Photolysis of Solutions with TEA and Co(II).** When a sample containing 1 mM Co<sup>II</sup>HMD<sup>2+</sup> and 0.5 M TEA but no TP in MeCN is irradiated under vacuum at 313 nm, an absorption due to Co<sup>I</sup>HMD<sup>+</sup> is observed at 680 nm in MeCN. A 3 h photolysis produced  $5.6 \times 10^{-6} M$  Co<sup>I</sup>HMD<sup>+</sup> in MeCN, but none in MeCN/MeOH. The same amount of Co<sup>I</sup>HMD<sup>+</sup> can be produced within 40 s in MeCN solution containing  $1 \times 10^{-4} M$  TP, 0.1 M TEAP, 0.5 M TEA and  $1 \times 10^{-4} M$  Co<sup>II</sup>HMD<sup>2+</sup>.

## Discussion

**The Lifetime of TP<sup>•-</sup>.** The observed lifetime of the TP radical anion in MeCN/MeOH determined in this work is 2.5 ms and the observed decay is first order in TP<sup>•-</sup>. Matsuoka et al. has measured the lifetime as 8.3 μs in THF by pulse radiolysis.<sup>30</sup> The strongly reducing TP<sup>•-</sup> probably decays by reacting with a proton to produce the dihydroterphenyl derivatives.<sup>30</sup> Thus, the lifetime of TP<sup>•-</sup> will depend on the availability of protons in solution. In THF protons could be donated by either trace water or THF. In our MeCN/MeOH mixture a proton could be donated by trace water, the MeOH, or by Et<sub>3</sub>NH<sup>+</sup> which is produced from the radical cation of TEA (see eq 7).<sup>47</sup> Since trace water is suspected to be the primary proton donor we have gone to great lengths to remove water from our solvent. We believe that the water levels are significantly lower in this work than those in the earlier study,<sup>30</sup> resulting in the long lifetime of the TP<sup>•-</sup> observed here.

The radical cation of TEA, formed in the quenching reaction, reacts by H atom abstraction from TEA producing the reductant,  $\text{Et}_2\text{NC}\cdot\text{HCH}_3$ .<sup>48,49</sup>



The reduction potential of the  $\text{Et}_2\text{N}^+=\text{CHCH}_3$  to give the  $\text{Et}_2\text{NC}\cdot\text{HCH}_3$  free radical has been measured to be  $-1.12$  V vs SCE in MeCN.<sup>50</sup> This neutral radical can reduce the  $\text{SCoL}(\text{CO}_2^{2-})^+$  complex (see below) but not the  $\text{CoL}^{2+}$  complex (see Table 2).

The decay of the  $\text{TP}^{\bullet-}$  is observed to be first order. Neither the radical recombination reaction nor the hydrogenation of the  $\text{TP}^{\bullet-}$  are observed despite the long lifetime of the  $\text{TP}^{\bullet-}$  ( $\sim 2$  ms). Thus, either the rate for these reactions is slow ( $k < 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) or the  $\text{Et}_3\text{N}^{\bullet+}$  decomposes more quickly by reaction with the parent compound.

**Reaction of  $\text{TP}^{\bullet-}$  with  $\text{CO}_2$ .** As shown in Figure 2, the dependence of the decay rate of  $\text{TP}^{\bullet-}$  on  $[\text{CO}_2]$  is not linear. For the electron-transfer reaction between  $\text{TP}^{\bullet-}$  and  $[\text{CO}_2]$ , we estimate a rate constant  $k_3 < 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for the runs with  $[\text{CO}_2] \sim 30$  mM. This rate constant is consistent with the large reorganization of the  $\text{CO}_2/\text{CO}_2^{\bullet-}$  couple (associated the geometry change from a linear to a bent molecule)<sup>51,52</sup> and small driving force for the reaction (0.3 V). Matsuoka et al. have measured the rate constant of reaction 2 to be  $> 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in DMF by pulse radiolysis.<sup>53</sup> In these studies the  $\text{TP}^{\bullet-}$  decays are not well fit by a first-order decay and may involve other species.

**Electron Transfer from  $\text{TP}^{\bullet-}$  to Co(II) Macrocycles.**  $\text{TP}^{\bullet-}$  is a powerful reductant ( $E_{1/2} = -2.45$  V vs SCE in dimethylamine).<sup>54</sup> As can be seen from Table 2, the reduction potentials of the Co(II) complexes studied here range from  $-1.28$  to  $-1.51$  V, thus the driving force for the reaction is about 1 V. The rate constants for the reduction of the Co(II) complexes are probably diffusion controlled, as expected for reactions with this driving force.

Under our photocatalytic conditions (continuous photolysis),  $[\text{CO}_2] = 0.25$  M and  $[\text{CoHMD}^{2+}] = 1.7$  mM, the cobalt reacts with the  $\text{TP}^{\bullet-}$   $> 20$  times faster than does the  $\text{CO}_2$ . Thus the direct reduction of  $\text{CO}_2$  by  $\text{TP}^{\bullet-}$  plays a negligible role under our catalytic conditions and all of the photochemically generated reducing equivalents are captured by the cobalt macrocycle. Under flash photolysis conditions the observed absorbance changes indicate that most ( $> 80\%$ ) of  $\text{TP}^{\bullet-}$  produced react with the  $[\text{CoHMD}^{2+}]$ .

When the electron-transfer rate constant was monitored by observing either the decay of  $\text{TP}^{\bullet-}$  and/or the growth of the

(47) The purification of the THF was less rigorous than that used in the MeCN/MeOH mixture here. The samples in this study were prepared by high-vacuum technique with dried solvents that were stored over drying agents under vacuum. However, in our previous continuous photolysis study<sup>19</sup> the distilled solvents were stored without drying agent and the mixing was done under regular atmosphere. Thus we believe that the THF samples have higher water concentrations than our present samples.

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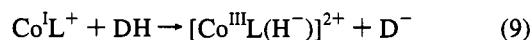
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Co(I) complex, the Co(I) growth rate is slightly greater in the MeCN/MeOH. This difference in rates suggests that two parallel paths produce the Co(I). One path is the direct electron transfer from  $\text{TP}^{\bullet-}$  to the Co(II) complex. The second path would need to be slightly faster than the first and only produce a modest amount of Co(I),  $\sim 10$  to 20%. If more Co(I) were produced the yield of the reaction would not appear to be 1:1 as observed, while if the rate were much faster the two processes would be separable (i.e. on the time scale of the slower process the faster process would appear as a step function).

The reducing free radical  $\text{Et}_2\text{NC}\cdot\text{HCH}_3$  would be expected to be involved in this second pathway. However, as mentioned above the driving force for the reaction is negative.

This second path could involve the direct excitation of an electron from a donor (TP or TEA) to the solvent.<sup>55–58</sup> We would expect this electron to react rapidly with any acceptor including the Co(II) complex.<sup>59</sup> This path would be sensitive to solvent as observed for the reactions studied in pure MeCN. The continuous photolysis of a TEA, Co(II) solution in pure MeCN (0.1 mM  $\text{Co}^{\text{II}}\text{HMD}^{2+}$  and 0.5 M TEA) yields long-lived  $\text{Co}^{\text{I}}\text{HMD}^+$ . The rise time of this Co(I) production is  $< 2$  ns. The Co(I) is not observed in continuous photolysis in the MeCN/MeOH mixture used here. These findings suggest that a second pathway operates in pure MeCN and is suppressed in MeCN/MeOH. In our solutions the importance of this second pathway is unimportant since it produces only a small amount of Co(I) under our conditions.

**Co(I) Complexes and the  $\text{CO}_2$  Binding.** The lifetime of the Co(I) macrocycles in the photocatalytic system is remarkably dependent on reduction potential (see Table 2). The lifetimes and reduction potentials of the  $\text{Co}^{\text{I}}\text{L}$  species are 16  $\mu\text{s}$ ,  $-1.51$  V; 2 s,  $-1.38$  V; and 6 h,  $-1.28$  V for L = DMD, HMD, and OMD, respectively. The Co(I) complex likely decays through reaction with a proton (from MeOH,  $\text{TEAH}^+$ , etc.) as shown in eq 9



where DH is the proton donor. The rate constant,  $k_9$ , has been reported to be  $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{H}_3\text{O}^+$  in  $\text{H}_2\text{O}$  and L = HMD.<sup>16</sup> Since  $\text{Co}^{\text{I}}\text{HMD}^+$  lives  $\sim 2$  s, the protonation is much slower than  $\text{CO}_2$  binding in our catalytic system. The formation of  $\text{H}_2$  and formate proceeds via  $[\text{Co}^{\text{III}}\text{L}(\text{H}^-)]^{2+}$  as shown in eq 9, therefore in the present study only CO is expected to be formed. However, in our previous continuous photolysis study<sup>19</sup> we found both formate and  $\text{H}_2$  production supporting our suspicion that in that work the solutions contain significant amounts of trace water.

The  $\text{CO}_2$  binding rate constant  $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{Co}^{\text{I}}\text{HMD}^+$ , shown in Table 2, is very similar to the rate constant in water,  $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , from pulse radiolysis work<sup>10,16</sup> and in MeCN,  $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , from cyclic voltammogram simulations.<sup>60</sup> The  $\text{CO}_2$  binding constant  $K_{\text{CO}_2}$ ,  $(1.1 \pm 0.2) \times 10^4 \text{ M}^{-1}$ , obtained in this study also shows remarkable agreement with the previous determined value<sup>9</sup> of  $1.4 \times 10^4 \text{ M}^{-1}$

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(59) (a) Typical electron-transfer rate constants from  $\text{e}^-$  to a Co(II) complex are known to be  $4\text{--}6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in water. (b) Ross, A. B.; Mallard, W. G.; Helman, W. P.; Bielski, B. H. J.; Buxton, G. V.; Cabelli, D. E.; Greenstock, C. L.; Huie, R. E.; Neta, P. *NDRL-NIST Solution Kinetic Database: Ver. 1*; National Institute of Standards and Technology, Gaithersburg, MD, 1992.

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(see Results section). These results also indicate that the CO formation proceeds via the binding of CO<sub>2</sub> to the Co<sup>I</sup>HMD<sup>+</sup>.

The Co<sup>I</sup>HMD(CO<sub>2</sub>)<sup>+</sup> produced by CO<sub>2</sub> binding has been studied in several media. The metal can coordinate another ligand to give a six-coordinate species. Usually the added ligand is a solvent molecule. In MeCN/MeOH at 25 °C, more 6-coordinate S-CoHMD(CO<sub>2</sub>)<sup>+</sup> is expected to exist than in pure MeCN due to the presence of the strongly coordinating MeOH. (The methyl groups of TEA probably prevent coordination of the TEA due to steric hindrance.) The spectrum of CoHMD(CO<sub>2</sub>)<sup>+</sup> at 25 °C in the flash photolysis system is quite similar to that observed in water measured by pulse radiolysis<sup>16</sup> except for a small peak at 480 nm.

The peak at 480 nm is small considering the noise on the spectra. The peak may be caused by the small steady-state concentration of TP<sup>•-</sup> produced by the probe light. The molar absorptivity of TP<sup>•-</sup> is >60 times that of *prim-N-rac*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup>. Alternatively, the pulse radiolysis study reported that both *sec-N-rac*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup> and *N-meso*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup> show peaks at 475 nm<sup>16</sup> while the *prim-N-rac*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup> absorbs at 530 nm. The *sec-N-rac*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup> is formed by reductive addition of CO<sub>2</sub><sup>2-</sup> to *N-rac*-Co<sup>II</sup>HMD<sup>2+</sup> while *prim-N-rac*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup> forms by CO<sub>2</sub> addition to *N-rac*-Co<sup>I</sup>-HMD<sup>+</sup>. Our sample of Co<sup>II</sup>HMD(ClO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) is more than 90% pure racemic isomer and isomerization of *N-rac*-Co<sup>II</sup>-HMD<sup>2+</sup> to *N-meso*-Co<sup>II</sup>HMD<sup>2+</sup> was not observed in our mixed solvent (MeCN/MeOH/TEA). The CO<sub>2</sub> addition to *N-rac*-Co<sup>I</sup>-HMD<sup>+</sup> may produce some *sec-N-rac*-[CoHMD(CO<sub>2</sub>)]<sup>+</sup> under our conditions.

The CO<sub>2</sub> binding constants (*K*<sub>CO<sub>2</sub></sub>), 6 and > 5 × 10<sup>4</sup> M<sup>-1</sup> for Co<sup>I</sup>OMD<sup>+</sup> and Co<sup>I</sup>DMD<sup>+</sup>, respectively, are determined in the catalytic systems by flash photolysis techniques. Since Co<sup>I</sup>-DMD<sup>+</sup> is unstable, the electrochemical method was used in an earlier study to determine *K*<sub>CO<sub>2</sub></sub> = 7 × 10<sup>5</sup> M<sup>-1</sup>.<sup>15</sup> For Co<sup>I</sup>-OMD<sup>+</sup>, the spectroscopic method provided *K*<sub>4</sub> = 4.0 M<sup>-1</sup> and the electrochemical method provided *K*<sub>CO<sub>2</sub></sub> = 1.7 M<sup>-1</sup>, previously.<sup>15</sup> Although Co<sup>I</sup>DMD<sup>+</sup> (which has no axial methyl groups) prefers the 6-coordinate CO<sub>2</sub> adduct at room temperature, the 6-coordinate S-Co<sup>I</sup>OMD-CO<sub>2</sub> adduct is unfavorable due to the steric hindrance of the four axial methyl groups, as seen in the crystal structure of the Co<sup>I</sup>OMD<sup>+</sup>.<sup>15</sup> Therefore for Co<sup>I</sup>OMD<sup>+</sup>, *K*<sub>CO<sub>2</sub></sub> = *K*<sub>4</sub>. The values obtained in the present study are in reasonable agreement with the values obtained previously.

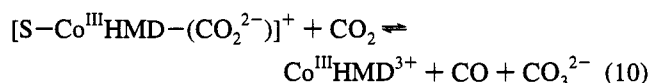
The CO<sub>2</sub> binding rate constant 1.1 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> for Co<sup>I</sup>-OMD<sup>+</sup> is much smaller than the binding rate constants for Co<sup>I</sup>-DMD<sup>+</sup> and Co<sup>I</sup>HMD<sup>+</sup>. The more positive *E*<sub>1/2</sub> of the cobalt complex and greater steric hindrance of the axial methyl groups at the 3 and 10 positions may be responsible for the smaller affinity for CO<sub>2</sub> and the slower binding rate constant for Co<sup>I</sup>-OMD<sup>+</sup>. The amount of CO produced in the photocatalytic system correlates with both the *E*<sub>1/2</sub> and the CO<sub>2</sub> binding constant of the Co(I) complex.<sup>19</sup>

**Reaction of CoL(CO<sub>2</sub>)<sup>+</sup>.** We monitored the decay of CoL(CO<sub>2</sub>)<sup>+</sup> at 530 nm. The signal is very weak and no significant decomposition takes place for times <1 ms when [CO<sub>2</sub>] > 10<sup>-3</sup> M.

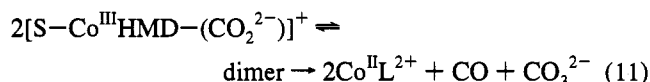
The production of CO from CoL(CO<sub>2</sub>)<sup>+</sup> requires a second reducing equivalent. The source of this equivalent is of interest. Under flash photolysis conditions the TP<sup>•-</sup> has completely reacted before the CoL(CO<sub>2</sub>)<sup>+</sup> is formed while under continuous photolysis it can react with the Co<sup>II</sup>L<sup>2+</sup> or the CoL(CO<sub>2</sub>)<sup>+</sup> complexes. Under flash photolysis conditions, where only Et<sub>2</sub>NC<sup>•</sup>HCH<sub>3</sub> and/or Co<sup>I</sup>L<sup>+</sup> may act as electron donor, the decomposition of CoLCO<sub>2</sub><sup>+</sup> is slow owing to the low concentrations of these two species. In fact, since CoLCO<sub>2</sub><sup>+</sup> decomposes

faster with low [CO<sub>2</sub>] (i.e. higher [CoL<sup>+</sup>]), CoL<sup>+</sup> is the likely electron donor under flash photolysis conditions.

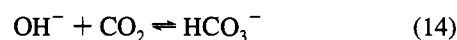
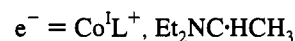
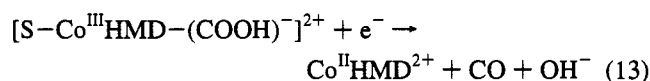
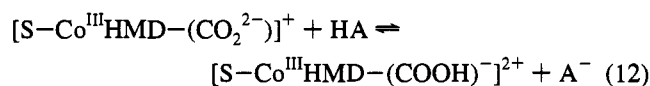
Reaction 10 has been suggested as an alternate route to CO production:



However, [S-Co<sup>III</sup>HMD-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> is stable under high CO<sub>2</sub> concentrations in both the MeCN/MeOH used here and pure MeCN.<sup>31</sup> Further, the equilibrium studies in MeCN show no indication of any interaction between a second CO<sub>2</sub> and the [S-Co<sup>III</sup>HMD-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup>. Another possibility is eq 11:



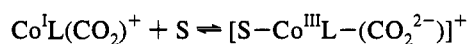
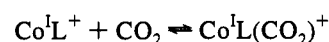
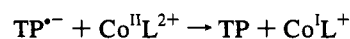
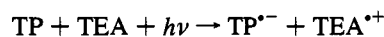
The kinetics of the formation of [S-Co<sup>III</sup>HMD-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> are fast, thus causing eq 11 to be rate controlling and the process to be second order in Co(I). This second-order reaction would be slow due to the low concentration of [S-Co<sup>III</sup>HMD-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup>. In MeCN, [S-Co<sup>III</sup>HMD-(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> shows no decomposition after a day if no proton source is available.<sup>9,15,31</sup> Therefore we suggest that reactions 12–14 are responsible for the production of CO in the photolysis.



The slow step is likely to be the C–O bond breakage of the bound carboxylic acid with either Et<sub>2</sub>NC<sup>•</sup>HCH<sub>3</sub> or Co<sup>I</sup>L<sup>+</sup> acting as electron donor. Unfortunately, the transient spectrum of [S-Co<sup>III</sup>HMD(CO<sub>2</sub><sup>2-</sup>)]<sup>+</sup> is too weak to study the proton dependence of the disappearance.

## Conclusion

The existence of intermediates TP<sup>•-</sup>, Co<sup>I</sup>L<sup>+</sup>, Co<sup>I</sup>L(CO<sub>2</sub>)<sup>+</sup>, and SCo<sup>III</sup>L(CO<sub>2</sub><sup>2-</sup>)<sup>+</sup> (L = HMD, OMD, and DMD) is confirmed by transient spectra in the actual photocatalytic CO<sub>2</sub> reduction system. The kinetics of the formation and disappearance of the intermediates have been measured and are consistent with the mechanism shown below.



The rate constant for electron transfer from the *p*-terphenyl radical anion to Co<sup>II</sup>L<sup>2+</sup> is probably diffusion controlled due to



the large driving force. This rapid reaction prevents competitive degradation of TP to dihydroterphenyl derivatives. The  $\text{Co}^{\text{I}}\text{L}^+$  produced reacts efficiently to form the  $\text{CO}_2$  adduct while the hydride formation is suppressed by limiting the amount of a proton source. The  $\text{CO}_2$  binding rate constants and the equilibrium constants obtained by flash photolysis measurements on the catalytic system are consistent with those previously obtained by conventional methods in acetonitrile. The present flash photolysis study clearly shows evidence that these reactions proceed rapidly and the cobalt macrocycle provides two electrons to the  $\text{CO}_2$  moiety to produce a stable  $\text{SCo}^{\text{III}}\text{L}(\text{CO}_2^{2-})^+$  species. The rate determining step in the photocatalytic system seems to be the second electron transfer to  $\text{SCo}^{\text{III}}\text{L}(\text{CO}_2^{2-})^+$ , followed by a bond-breaking step as shown in eq 13. The previous continuous photolysis experiments indicated that the continuously formed  $\text{TP}^{\bullet-}$  may be a source of the second electron.

In order to improve the quantum yield of CO production in the photocatalytic system, several factors should be considered: (1) relatively large amounts of cobalt complexes are needed because of the slow chemical  $\text{CO}_2$  reduction reaction; (2) steric hindrance and reduction potentials are important factors not only for the  $\text{CO}_2$  binding to reduced mediators but also for

CO production in the photochemical  $\text{CO}_2$  system; and (3) the proton source should be carefully chosen to avoid the formation of a  $\text{Co}^{\text{III}}\text{LH}^{2+}$  species.

**Acknowledgment.** We thank Drs. Norman Sutin and Carol Creutz for their helpful comments. T.O. thanks the Japan Society for the Promotion of Science for a Research Fellowship for Young Scientists. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

**Supplementary Material Available:** Figures plotting pseudo-first-order rate constants vs concentration for  $\text{Co}^{\text{II}}\text{HMD}^{2+}$ ,  $\text{Co}^{\text{II}}\text{-DMD}^{2+}$ , and  $\text{Co}^{\text{II}}\text{OMD}^{2+}$  (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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