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Photochemical carbon dioxide reduction with metal complexes

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Contents

Abstract

Transition-metal complexes, $CoHMD^{2+}$ (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and $Ru(bpy)_2(CO)X^{n+}$ (bpy = 2,2′-bipyridine, X = CO, Cl, H, etc.), mediate electron transfer in the photochemical reduction of CO_2. The thermodynamics and kinetics of CO_2 binding to $CoHMD^+$, and spectroscopic characterization of the CO_2 adducts of $CoHMD^+$ and $[Ru^I(bpy)(bpy^{\bullet -})(CO)]$ are described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbon dioxide reduction; Small molecule activation; Photocatalysis; Carboxylates; Macrocycles; Diimine

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1. Introduction

The reduction of carbon dioxide to produce carbon monoxide, formic acid or methanol is an important area relevant to the solution of problems related to global warming and the depletion of fossil fuels [1]. Photochemical carbon dioxide reduction poses a number of difficult scientific challenges. Because of the stability of carbon dioxide, energy is needed to drive the desired transformations; moreover, its inertness necessitates the use of catalysts. Transition-metal complexes are used as catalysts since they can absorb a significant part of the solar spectrum, have long-lived excited states, and can promote the activation of small molecules. Here we summarize earlier studies on photochemical CO_2 reduction and present our recent results on the characterization of intermediates such as the CO_2 adduct, and the kinetics and mechanisms of photochemical and electrochemical CO_2 reduction with cobalt macrocycles and $Ru(bpy)_2(CO)X^{n+}$ complexes (bpy = 2,2′-bipyridine, X = CO, Cl, H, etc.). The results are obtained using a variety of techniques including UV–vis, NMR, FT-IR spectroscopy, flash photolysis, pulse radiolysis, X-ray structure determinations, electrochemistry, XANES and EXAFS.

2. Photocatalytic CO_2 reduction

The potential for the reduction of CO_2 to $CO_2^{\bullet -}$ is -1.9 V versus NHE, making the one-electron reduction highly unfavorable. In addition, there is a large kinetic 'overvoltage' for the one-electron reduction because of structural differences between linear CO_2 and bent $CO_2^{\bullet -}$. In contrast, proton-assisted multielectron steps are much more favorable as shown below (at pH 7 in aqueous solution versus NHE) [2,3]:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \quad E^\circ = -0.61\ V \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad E^\circ = -0.53\ V \tag{2}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O \quad E^\circ = -0.20\ V \tag{3}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad E^\circ = -0.48\ V \tag{4}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^\circ = -0.38\ V \tag{5}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad E^\circ = -0.24\ V \tag{6}$$

Since the two-electron reduction to formic acid or CO requires a considerably lower potential than the one-electron reduction, electrolysis in the presence of catalysts can be carried out at considerably lower voltages. In the photochemical reduction of CO_2, the same considerations apply: the one-electron reduction to $CO_2^{\bullet -}$ requires extremely strong reducing agents that are generally difficult to produce by photochemical methods.

Table 1 summerizes the results from a large number of photoreduction studies of CO_2 by homogeneous and microheterogeneous photocatalysts. Although many

Table 1
Photocatalytic Reduction of CO_2[a]

Sensitizer	Catalyst or relay	Donor	Product(s)	Φ^b mol einstein^{-1}	Ref.
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.049^c	[11]
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.096^d	[11]
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	$HCOO^-$	0.01	[12]
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	CO, H_2		[3]
$Ru(bpy)_3^{2+}$	Co^{2+}/Me_2phen	TEA	CO, H_2	0.012 (CO) 0.065 (H_2)	[13]
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	$HCOO^-$	0.14	[14–16]
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	$HCOO^-$, CO	0.03 ($HCOO^-$) 0.15 (CO)	[14–16]
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(H)^+$	TEOA	$HCOO^-$	0.15	[11]
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(X)^{n+}$, X = Cl and CO	TEOA	$HCOO^-$		[11]
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	CO, H_2		[17]
$Ru(bpy)_3^{2+}$	$Nicyclam^{2+}$	H_2A	CO, H_2	0.001 (CO)	[18,19]
$Ru(bpy)_3^{2+}$	$NiPr\text{-}cyclam^{2+}$	H_2A	CO, H_2	ca. 0.005 (CO)	[20]
$Ru(bpz)_3^{2+}$	Ru colloid	TEOA	CH_4	10^{-4} $(CH_4)^e$	[21,22]
$Ru(bpy)_3^{2+}$	bipyridinium$^+$, Ru or Os colloid	TEOA	CH_4 H_2	10^{-4} $(CH_4)^e$ 10^{-3} $(H_2)^e$	[22]
$ReCl(bpy)(CO)_3$		TEOA	CO	0.14	[23,24]
$ReBr(bpy)(CO)_3$		TEOA	CO	0.15	[25,26]
$[ReP(OEt)_3(bpy)(CO)_3]^+$		TEOA	CO	0.38	[27]
p-Terphenyl	$Cocyclam^{3+}$	TEOA	CO, $HCOO^-$, H_2	0.25^e (CO + HCOO −)	[28,29]
p-Terphenyl	$CoHMD^{2+}$	TEOA	CO, $HCOO^-$, H_2		[29,30]
Phenazine	$Cocyclam^{3+}$	TEOA	$HCOO^-$	0.07^e	[31]
FeTPP		TEA	CO		[32]
CoTPP		TEA	$HCOO^-$, CO		[33]

[a] Abbreviations used: TEOA = triethanolamine, MV^{2+} = methylviologen, TEA = triethylamine, bpy = 2,2′-bipyridine, Me_2phen = 2,9-Dimethyl-1,10-phenanthroline, BNAH = 1-benzyl-1,4-dihydronicotinamide, H_2A = ascorbic acid, cyclam = 1,4,8,11-tetraazacyclotetradecane and Pr-cyclam = 6-((N-R)pyridin-4-yl)methyl-1,4,8,11-tetraazacyclotetradecane where R = *p*-methoxybenzyl and benzyl, TPP = 5,10,15,20-tetraphenyl-21H,23H-porphine.

[b] Unless otherwise noted, the quantum yield of product formation is defined as the formation rate divided by the light intensity.

[c] With 15% water in DMF.

[d] With 15% water and excess bpy in DMF.

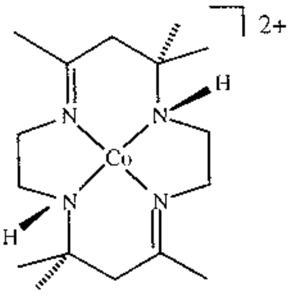
[e] Assuming two (or eight) photons produce one molecule of the product.

photoinduced stoichiometric reactions such as an insertion or addition of CO_2, reductive disproportionation to CO, metathesis of CN by CO_2, the formation of M–CO and M–OCHO complexes and, in rare cases, the formation of M=O together with CO are known [1,4–8], we limit our discussion to photocatalytic reactions using metal complexes as catalysts. Photoinduced CO_2 fixation systems containing enzymes are omitted [9,10].

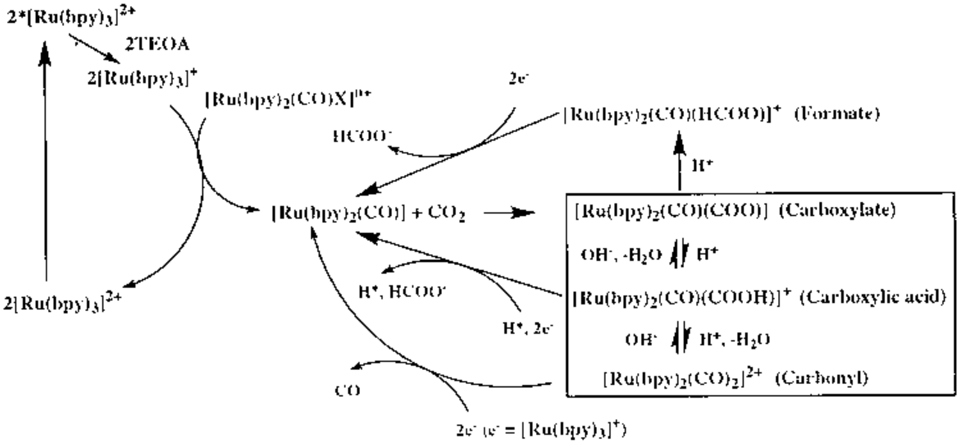
The systems used for photochemical CO_2 reduction studies can be divided into several groups: (1) $Ru(bpy)_3{}^{2+}$ both as a photosensitizer and a catalyst; (2) $Ru(bpy)_3{}^{2+}$ as a photosensitizer and another metal complex as a catalyst; (3) $Ru(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{2+}$-type complexes as photosensitizers in microheterogeneous systems; (4) $ReX(CO)_3(bpy)$ or a similar complex both as a photosensitizer and a catalyst; (5) porphyrins both as photosensitizer and catalyst; and (6) organic photosensitizers and a metal complex as catalysts. We are particularly interested in photochemical CO_2 reduction with cobalt macrocycles and $Ru(bpy)_2(CO)X^{n+}$ (bpy = 2,2′-bipyridine, X = CO, Cl, H, etc.) as catalysts in categories (2) and (6).

Photochemical CO_2 reduction to CO (and formate in some cases) has been reported in a catalytic system using $Ru(bpy)_3{}^{2+}$ as the sensitizer, $CoHMD^{2+}$ (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, see Scheme 1) as the electron relay catalyst, and ascorbate as a sacrificial reductive quencher [17]. These systems also produce H_2 via reduction of water. When $CoHMD^{2+}$ is used as a catalyst at pH 4, the system produces a mixture of CO and H_2 with low selectivity ($CO/H_2 = 0.06–0.3$, depending on the conditions). $[Co^{III}HMD(H^-)]^{2+}$, which forms by protonation of $Co^{I}HMD^+$, has been suggested to be a common intermediate [17,34] for CO and H_2 production in the photocatalytic system, however, new studies [30] indicate that this may be incorrect (see Section 3).

DMF solutions containing $Ru(bpy)_3{}^{2+}$, $Ru(bpy)_2(CO)X^{n+}$ (X = CO, Cl, H, etc.), and TEOA as an electron donor have been used for photochemical CO_2 reduction [11,14–16]. These systems produce formate as the major product and CO as a minor product. The total quantum yield reaches 15%. It is reported that water is needed for formation of formate, however the addition of a large amount of water decreases the efficiency of formate production. The addition of bpy increased the efficiency, probably to avoid the photolabilization of bpy from the $Ru(bpy)_3{}^{2+}$



Scheme 1. *N*-*rac*-$CoHMD^{2+}$.



Scheme 2. Proposed mechanism for the CO_2 reduction by $Ru(bpy)_2(CO)X^{n+}$.

species. Tanaka et al. and Ziessel et al. reject $[Ru(bpy)_2(CO)(H)]$ as an intermediate. This is contrary to what was found in electrochemical CO_2 reduction by T.J. Meyer et al. [35]. The evidence Tanaka and Ziessel found indicates that $[Ru(bpy)_2(CO)(Cl)]^+$ and the hydride have almost the same activity. The proposed mechanism (Scheme 2) involves the reduction of $[Ru(bpy)_2(CO)Cl]^+$ by two electrons to produce $[Ru(bpy)_2(CO)]$, which reacts with CO_2 to form $[Ru(bpy)_2(CO)(COO)]$. $[Ru(bpy)_2(CO)(COO)]$ and $[Ru(bpy)_2(CO)(COOH)]^+$ are prepared by the addition of two and one OH^-, respectively to $[Ru(bpy)_2(CO)_2]^+$ [36–41]. These are air stable species, and have been characterized by X-ray diffraction and various types of spectroscopy. In the photochemical system, it is proposed that the reverse reactions are taking place to form CO [11,14–16]. The production of formate is assumed to be involved in the isomerization of the carboxylate complex associated with protonation, or reduction of the carboxylic acid adduct associated with protonation. Unfortunately, Meyer et al. could not isolate the singly- or doubly-reduced hydride and its CO_2 insertion product [35].

In the photochemical reduction of CO_2, reduced metal catalysts, metal hydride complexes, metal formate complexes, and metallocarboxylates are postulated as intermediates. However, the kinetics and mechanisms of CO_2 reduction still remain unclear in many cases. In order to design more efficient systems for the photochemical reduction of CO_2 we need to understand factors controlling both the photochemical and the catalytic processes including photoexcitation and deactivation of the photosensitizer, precursor complex formation, charge transfer, energy transfer, back electron transfer, successor complex dissociation, interaction with CO_2, bond formation and cleavage, and regeneration of the catalyst. Our research at BNL focuses on kinetic and mechanistic studies of photochemical CO_2 reduction mediated by transition-metal complexes as catalysts as shown below.

3. CO_2 reduction by cobalt macrocycles

Previously we [30,42–48] and others [49] characterized the interaction of low-spin d^8 *N-rac*-Co^IHMD^+ with CO_2 in CH_3CN and in H_2O. The CO_2 binding constants in CH_3CN [43] and in H_2O [46] are 1.2×10^4 and 4.5×10^8 M^{-1}, respectively. The complex is thermochromic, being purple at room temperature and yellow at low temperature (-100°C) with $\Delta H° = -7.0$ kcal mol^{-1} and $\Delta S° = -27$ cal K^{-1} mol^{-1} for Eq. (8) in CH_3CN [44]. The spectra of Co^IHMD^+, $[CoHMD(CO_2)]^+$, and $[CoHMD(CO_2)(CH_3CN)]^+$ are shown in Fig. 1. The pressure dependence of the equilibrium constant shows that increasing pressure shifts the equilibrium toward the six-coordinate species with an overall reaction volume $\Delta V° = -17.7 \pm 1.0$ ml mol^{-1} at 15°C [48].

$$CoHMD^+ + CO_2 \rightleftharpoons [CoHMD(CO_2)]^+ \tag{7}$$

$$[CoHMD(CO_2)]^+ + CH_3CN \rightleftharpoons [CoHMD(CO_2)(CH_3CN)]^+ \tag{8}$$

The coordination number, geometry, and electronic properties have been studied using XANES [47]. The edge positions (E_0) of the CoHMD complexes studied here are extremely sensitive to the oxidation state of the metal (Fig. 2). The edge energy, relative to $Co^{II}HMD^{2+}$, decreases (1 eV) upon reduction and increases (2 eV) upon oxidation. The $1s-4p_z$ pre-edge peak, located ca. 6 eV below the main edge in the XANES spectrum for $Co^{II}HMD^{2+}$, is characteristic of a four-coordinate square-planar geometry. The E_0 for $[CoHMD(CO_2)]^+$ at room temperature is similar to that of $Co^{II}HMD^{2+}$ ($\Delta E_0 = +0.2$ eV, which is within the reproducibility of the measurements), and is consistent with theoretical estimates that the bound CO_2 receives 0.71 electrons mainly from the Co d_z^2 orbital [50,51]. The six-coordinate $[CoHMD(CO_2)(CH_3CN)]^+$ species shows a 1.2 eV shift towards Co(III) from

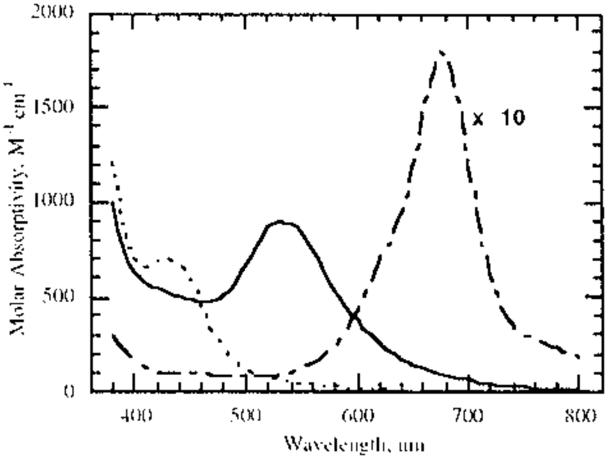


Fig. 1. UV–vis spectra of Co^IHMD^+ (— - —), 5-coordinate $CoHMD(CO_2)^+$ (—), and 6-coordinate $[Co^{III}HMD(CO_2{}^{2-})(CH_3CN)]^+$ (- - - -) in CH_3CN.

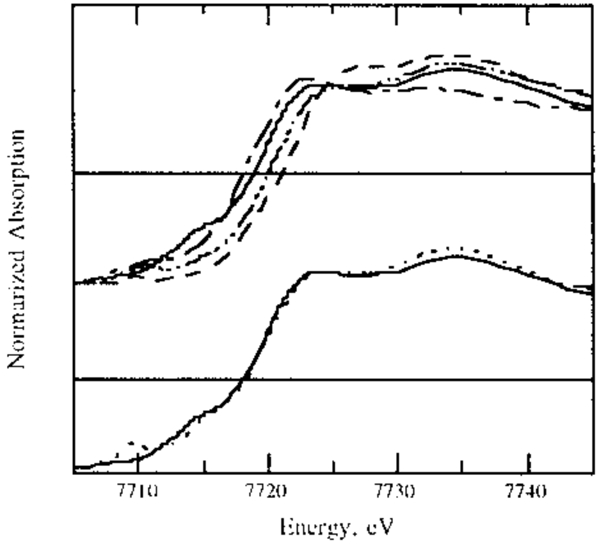


Fig. 2. XANES spectra for a series of CoHMD complexes. Top: $[CoHMD(CO)](ClO_4)$ in CH_3CN at room temperature (— - —) $[CoHMD](ClO_4)_2$ in CH_3CN at 150 K (—), $[Co^{III}HMD(CO_2^{2-})(CH_3CN)](ClO_4)$ in CH_3CN at 150 K (— - - - —), and $[Co^{III}HMD(CO_3)](ClO_4)$ in H_2O at room temperature (- - -). Bottom: $[CoHMD(CO_2)](ClO_4)$ in CH_3CN at room temperature (- - -) and $[CoHMD](ClO_4)_2$ in CH_3CN at 150 K (—).

$Co^{II}HMD^{2+}$ and is interpreted as a Co(III)–CO_2^{2-} carboxylate complex. This assignment is consistent with the change of the asymmetric ν_{CO_2} from 1706 cm^{-1} for $[CoHMD(CO_2)]^+$ to 1544 cm^{-1} for $[CoHMD(CO_2)(CH_3CN)]^+$ [45]. Although the Co(III) carboxylates have been postulated as intermediates in CO_2 reduction and water–gas shift reactions, the XANES results provide the first unambiguous evidence that active metal catalysts, such as $Co^{I}HMD^+$, can promote two-electron transfer to the bound CO_2. This reversible intramolecular two-electron-transfer process, responsive to temperature and pressure changes, could be of fundamental importance to processes dealing with the reduction of CO_2.

Cobalt macrocycles mediate electron transfer in the photoreduction of CO_2 with *p*-terphenyl as a photosensitizer and a tertiary amine as a sacrificial electron donor in a 5:1 acetonitrile/methanol mixture, leading to efficient and selective formation of both CO and HCO_2^- without producing much H_2 [29]. The total quantum yield of CO and HCO_2^- is 0.25 at 313 nm in the presence of TEOA and cocyclam^{3+} (see Table 1). The kinetics and mechanism of this system have been studied by continuous and flash photolysis techniques in the presence of TEA and $CoHMD^{2+}$ [30]. Transient spectra provide evidence for the sequential formation of the *p*-terphenyl radical anion, the $Co^{I}HMD^+$ complex, the $[CoHMD(CO_2)]^+$ complex and the $[S–Co^{III}HMD-(CO_2^{2-})]^+$ complex (S = solvent) in the catalytic system.

$$TP + TEA + h\nu \rightarrow TP^{\bullet -} + TEA^{\bullet +} \qquad (9)$$

$$\mathrm{TP}^{\bullet -} + \mathrm{Co^{II}HMD^{2+}} \rightarrow \mathrm{TP} + \mathrm{Co^{I}HMD^{+}} \tag{10}$$

$$\mathrm{Co^{I}HMD^{+}} + \mathrm{CO_2} \rightleftharpoons \mathrm{CoHMD(CO_2)^{+}} \tag{11}$$

$$\mathrm{CoHMD(CO_2)^{+}} + \mathrm{S} \rightleftharpoons [\mathrm{S\text{-}Co^{III}HMD\text{-}(CO_2{}^{2-})}]^{+} \tag{12}$$

$$[\mathrm{S\text{-}Co^{III}HMD\text{-}(CO_2{}^{2-})}]^{+} + \mathrm{HA} \rightleftharpoons [\mathrm{S\text{-}Co^{III}HMD\text{-}(COOH^{-})}]^{2+} + \mathrm{A}^{-}$$
$$\mathrm{HA} = \mathrm{HTEA^{+}},\ \mathrm{MeOH},\ \mathrm{H_2O} \tag{13}$$

$$[\mathrm{S\text{-}Co^{III}HMD\text{-}(COOH)^{-}}]^{2+} + \mathrm{e}^{-} \rightarrow \mathrm{Co^{II}HMD^{2+}} + \mathrm{CO} + \mathrm{OH}^{-}$$
$$\mathrm{e}^{-} = \mathrm{TP}^{\bullet -},\ \mathrm{Co^{I}HMD^{+}},\ \mathrm{Et_2NC^{\bullet}HCH_3} \tag{14}$$

The electron-transfer rate constant for the reaction of *p*-terphenyl radical anion with $\mathrm{Co^{II}HMD^{2+}}$ is 1.1×10^{10} $\mathrm{M^{-1}\ s^{-1}}$ and is probably diffusion controlled because of the large driving force (ca. 1.1 V). Flash photolysis studies yield a rate constant 1.7×10^{8} $\mathrm{M^{-1}\ s^{-1}}$ and an equilibrium constant 1.1×10^{4} $\mathrm{M^{-1}}$ for the binding of $\mathrm{CO_2}$ to $\mathrm{Co^{I}HMD^{+}}$ in the catalytic system. These are consistent with the values previously obtained by conventional methods in acetonitrile. The $\mathrm{Co^{I}HMD^{+}}$ produced reacts efficiently to form the $\mathrm{CO_2}$ adduct while the hydride formation is suppressed by limiting the amount of a proton source. Our study clearly shows evidence that the cobalt macrocycle provides two electrons to the $\mathrm{CO_2}$ moiety to produce a stable $\mathrm{SCo^{III}HMD(CO_2{}^{2-})^{+}}$ species. The rate-determining step in the photocatalytic system seems to be the second electron transfer to $\mathrm{SCo^{III}HMD(CO_2{}^{2-})^{+}}$, followed by a bond breaking step as shown in Eq. (14). The continuously formed $\mathrm{TP}^{\bullet -}$ may be a source of the second electron.

4. $\mathrm{CO_2}$ reduction by $[\mathrm{Ru(bpy)_2(CO)X}]^{n+}$ (X = CO, Cl, and H)

DMF solutions containing $\mathrm{Ru(bpy)_3{}^{2+}}$, $[\mathrm{Ru(bpy)_2(CO)X}]^{n+}$ (X = CO, Cl, H, etc.), and TEOA as an electron donor produce formate and CO from $\mathrm{CO_2}$ by photochemical processes [30]. We are characterizing the reaction of the reduced $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$, $[\mathrm{Ru(bpy)_2(CO)Cl}]^{+}$, or $[\mathrm{Ru(bpy)_2(CO)(H)}]^{+}$ with $\mathrm{CO_2}$ in $\mathrm{CH_3CN}$ to find out if $[\mathrm{Ru(bpy)_2(CO)(COO)}]$ is produced as proposed (see Scheme 2). It should be noted that $\mathrm{Ru(bpy)_3^{+}}$, produced by quenching the excited state of $\mathrm{Ru(bpy)_3{}^{2+}}$ by TEOA, cannot reduce $[\mathrm{Ru(bpy)_2(CO)(Cl)}]^{+}$ and $[\mathrm{Ru(bpy)_2(CO)(H)}]^{+}$ to form the doubly- and singly-reduced species, respectively, as shown in Table 2. Instead, a species like $[\mathrm{Ru(bpy)_2(CO)(S)}]^{2+}$ (S = solvent) may be involved in photocatalytic $\mathrm{CO_2}$ systems.

The reduction potentials of $\mathrm{Ru(bpy)_2(CO)X^{n+}}$ species are summarized in Table 2. While the two-electron reduction wave in the cyclic voltammogram of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ in $\mathrm{CH_3CN}$ at -1.0 V (vs SCE) is not affected by $\mathrm{CO_2}$, the second reduction wave of $[\mathrm{Ru(bpy)_2(CO)Cl}]^{+}$ at -1.55 V indicates an increase in current under $\mathrm{CO_2}$. The current depends on the electrolytes used. A very intense blue color develops with reduction of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ by Na–Hg, which is indicative of a metal center reduction. The resulting solution does not react with

Table 2
Reduction potentials (vs. SCE) of $Ru(bpy)_2(CO)X^{n+}$ species

Complex	Solvent	Reduction potentials (V)	Ref.
$[Ru(bpy)_3]^{2+}$	CH_3CN	−1.34	[52]
$[Ru(bpy)_2(CO)_2]^{2+}$	CH_3CN	−1.0 ($2e^-$)	This work
$[Ru(bpy)_2(CO)_2]^{2+}$	DMF	−0.95 ($2e^-$)	[16]
$[Ru(bpy)_2(CO)(H)]^{+}$	CH_3CN	−1.45, −1.65	This work, [35]
$[Ru(bpy)_2(CO)(Cl)]^{+}$	CH_3CN	−1.33, −1.55	This work
$[Ru(bpy)_2(CO)(Cl)]^{+}$	DMF	−1.24, −1.48	[16]
$[Ru(bpy)_2(CO)(CH_3CN)]^{2+}$	CH_3CN	−1.10, −1.35	[35]
$[Ru(bpy)_2(CO)(OCOH)]^{+}$	CH_3CN	−1.35, −1.52	[35]
$[Ru(bpy)_2(CO)(COO)]$	DMF	−1.30, −1.50	[15]

CO_2. With or without CO_2, a black species is precipitated and the solution becomes almost colorless. The species is $[Ru(bpy)(CO)_2]_n$, produced by loss of a bpy ligand, as investigated by Ziessel et al. in the electrochemical CO_2 reduction using the Ru mono- and bis-bpy carbonyl species on an electrode surface [53,54]. Interestingly, both Tanaka's and Ziessel's groups reported a decrease in catalytic activity with formation of a black precipitate during photoreduction of CO_2. Therefore the proposed mechanism of CO production from $[Ru(bpy)_2(CO)_2]^{2+}$ with two molecules of $Ru(bpy)_3^+$ serving as the electron source may not be involved in photochemical CO_2 reduction.

The first reduction of $[Ru(bpy)_2(CO)Cl]^+$ seems to be bpy-centered. However, within a few minutes, two visible absorption features due to the bpy radical anion disappear, indicating intramolecular electron transfer is taking place to form $[Ru^I(bpy)_2(CO)]$ with loss of a Cl^- ligand. The Ru(I) species does not react with CO_2. The second reduction is the formation of a Ru(I) bpy radical, $[Ru^I(bpy)(bpy^{\bullet -})(CO)]$. Upon addition of CO_2, the solution changes from reddish purple to brown and produces one or more species exhibiting IR stretching bands at 1966, 1935, 1252 cm^{-1}. These stretching frequencies do not agree with published

Table 3
IR stretching frequencies for Ru complexes

Complex	Medium	IR stretching frequencies, cm^{-1}		Ref.
		ν_{CO}	ν_{CO_2}	
$[Ru(bpy)_2(CO)]+CO_2$	CD_3CN with Na^+	1966, 1935	1252	This work
$[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$	KBr	1911	1428 (weak), 1242	[38]
$[Ru(bpy)_2(CO)(COO)]$	CD_3CN with Na^+	1936	1252	This work
$[Ru(bpy)_2(CO)(COO)]$	CD_3CN with Li^+	1950	1283	This work
$[Ru(bpy)_2(CO)(COOH)]^+$	CD_3CN	1968		This work
$[\{(bpy)_2(CO)Ru\}_2(COO)]^{2+}$	KCl	1954	1507, 1176	[58]

KBr data for $Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ [37] (see Table 3). Although the carboxylate, $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ [37], is not soluble in CH_3CN, the addition of salts causes its dissolution. In the presence of Li^+ or Na^+ the carboxylate is slowly converted to the carboxylic acid in CH_3CN with a trace amount of water. In the presence of Mg^{2+} the carboxylate is immediately converted to $[Ru(bpy)_2(CO)_2]^{2+}$. The interaction of the bound CO_2 of $Ru(bpy)_2(CO)(COO)$ with a cation or proton shifts the CO and CO_2 stretching frequencies dramatically as shown in Table 3. Such effects of alkali metal cation are not new. Cutler et al. recently found a similar trend on the IR shift of CO stretching using $FeCp^*(CO)(COO)^-$ ($Cp^* = 1,2,3,4,5$-pentamethylcyclopenta-dienyl) [55]. Floriani [56] and Savéant [57] reported a large effect of alkali metal cations on the stability and reactivity of metal CO_2 adducts such as Co(I)Salen–CO_2 and Fe(0)TPP–CO_2, respectively. The order of reactivity of these Lewis acid synergists is reported to be Mg^{2+} ca. $Ca^{2+} > Ba^{2+} > Li^+ > Na^+$ from cyclic voltammetry of FeTPPCl with CO_2. This result is consistent with our results for $Ru(bpy)_2(CO)(COO)$ with alkali metals.

Na–Hg was used as the reductant in our experiments of CO_2 addition to the doubly reduced species in CH_3CN. Therefore, the resulting solution contains Na^+, and the IR bands should correspond to those with Na^+. In fact, two absorption peaks at 1935 and 1252 cm^{-1} are due to the carboxylate and a peak at 1966 cm^{-1} is due to the carboxylic acid adduct. The small differences in the IR stretching frequencies between this product (the first entry in Table 3) and authentic samples (the third and fifth entries) might be due to the Na^+ concentration differences in the solutions.

5. Conclusion

This article has summarized recent studies in our laboratory. $CoHMD^{2+}$ has been used successfully as a catalyst for photochemical CO_2 reduction because of the small $Co^{II}HMD^{2+}/Co^{I}HMD^+$ reorganization energy, the fast CO_2 binding to $Co^{I}HMD^+$ (1.7×10^8 M^{-1} s^{-1}) and the large K_{CO_2}. Our XANES results clearly indicate that active metal catalysts, such as $Co^{I}HMD^+$, can promote two-electron transfer to the bound CO_2 (reduce CO_2 to ${CO_2}^{2-}$) and thereby facilitate reduction of CO_2. The slow step in the photoreduction of CO_2 is likely to be the C–O bond rupture of the bound carboxylic acid, produced by protonation of $[S-Co^{III}HMD({CO_2}^{2-})]^+$, upon reaction with the electron donor. Unfortunately, the UV–vis transient spectrum of $[S-Co^{III}HMD({CO_2}^{2-})]^+$ is too weak to permit the study of proton dependence, its disappearance and its further reactions.

The doubly reduced species $[Ru^{I}(bpy)(bpy^{\bullet -})(CO)]$ reacts with CO_2 in CH_3CN. The reaction seems to produce $[Ru(bpy)_2(CO)(COO)]$ together with $[Ru(bpy)_2(CO)(COOH)]^+$. IR of $[Ru(bpy)_2(CO)(COO)]$ shows a marked alkali metal cation dependence. Investigations of kinetics and mechanisms of photochemical reduction of CO_2 continue with $[Ru(bpy)_2(CO)(COO)]$ and $[Ru(bpy)_2(CO)H]^+$.

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