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Photoinduced Catalytic Organic-Hydride Transfer to CO_2 Mediated with Ruthenium Complexes as NAD^+/NADH Redox Couple Models**

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The catalytic organic-hydride transfer to CO_2 was first achieved through the photoinduced two-electron reduction of the $[Ru(bpy)_2(pbn)]^{2+}$/$[Ru(bpy)_2(pbnHH)]^{2+}$ (bpy = 2,2′-bipyridine, pbn = 2-(pyridin-2-yl)benzo[*b*]-1,5-naphthyridine, and pbnHH = 2-(pyridin-2-yl)-5,10-dihydrobenzo[*b*]-1,5-naphthyridine) redox couple in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH). The active species for the catalytic hydride transfer to carbon dioxide giving formate is $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^+$ formed by one-electron reduction of $[Ru(bpy)_2(pbnHH)]^{2+}$ with $BI^{\bullet}$.

Introduction

The increase in the atmospheric concentration of carbon dioxide (CO_2) caused in part by the excessive use of fossil fuels has resulted in global warming. A feasible pathway to cope with such a global crisis is the chemical conversion of CO_2 into value-added chemical compounds,[1,2] such as methanol (CH_3OH)[3,4] and formic acid (HCOOH)[5,6] under mild conditions. Direct one-electron reduction of CO_2 is a highly energy consuming process (−1.90 V vs. standard hydrogen electrode (SHE) in water at pH = 7),[7] and the resultant $CO_2^{\bullet-}$ is hard to regulate its reactivity as a C_1 resource. In 1983, Lehn and his colleagues reported the first photochemical CO_2 reduction mediated with $Re(bpy)(CO)_3X$ (bpy = 2,2′-bipyridine, X = Cl, Br) having dual functions of a photosensitizer and a catalyst.[8] Since then, a large number of metal complexes including Mn,[9] Fe,[10–12] Co,[13–16] Ni,[17,18] Cu,[19,20] Mo,[21] Ru,[22–24] and Re[8,25,26] have been shown to be active in the photochemical CO_2 reduction by the combination with a photosensitizer.[27,28] Most of the reduction products are CO and/or HCOOH, in which coordinatively unsaturated low-valent metal complexes bearing a labile ligand work as the active sites for the reductive activation of CO_2. In addition to the reductive activation of CO_2 on metal ions, hydride transfer to CO_2 mediated with renewable organic hydride donors also may provide a new methodology to develop C_1 resources. Indeed, Musgrave and his colleagues found that 1,2,3-trimethylbenzimidazoline as an organic hydride donor reacted with CO_2 to afford formate without the assistance of transition metals, though the reaction proceeded in a stoichiometric fashion but not catalytically.[29]

In biological systems, the NAD^+/NADH (NAD = nicotinamide adenine dinucleotide) redox couple plays a pivotal role as a generator and/or a reservoir of hydride (H^-), which is equivalent to one proton and two electrons.[30] Much information about organic NAD^+/NADH model compounds has so far been accumulated to understand their unique redox and photophysical properties as well as their photochemical and thermal reactivities.[31] The first step in the photo- and electrochemical reactions is an intermolecular one-electron transfer, which inevitably generates reactive radical species. As a result, the reduction of NAD^+ analogs or the oxidation of NADH ones followed by a deprotonation usually generates their radical intermediates, which often cause intermolecular radical coupling to afford the corresponding dimeric $(NAD)_2$ species via C–C bond formation.[32] In addition to the various organic NAD^+ and NADH model compounds, the reactivities of transition-metal hydrides are also examined to elucidate the hydricity of the bonds.[33] Recently, a ruthenium complex with an NAD^+ model ligand, $[Ru(bpy)_2(pbn)](PF_6)_2$ (pbn = 2-(pyridin-2-yl)benzo[*b*]-1,5-naphthyridine),[34,35] was shown to undergo photochemical two-electron reduction to afford the corresponding NADH-type complex $[Ru(bpy)_2(pbnHH)](PF_6)_2$ (pbnHH = 2-(pyridin-2-yl)-5,10-dihydrobenzo[*b*]-1,5-naphthyridine) under visible light irradiation in the presence of triethanolamine (TEOA) in CH_3CN (see Scheme 1).[36]

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[**] *NAD = Nicotinamide adenine dinucleotide*

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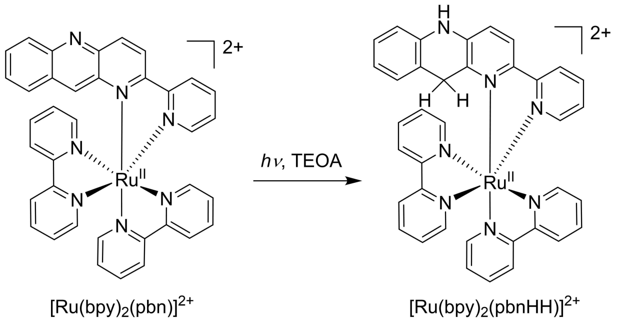
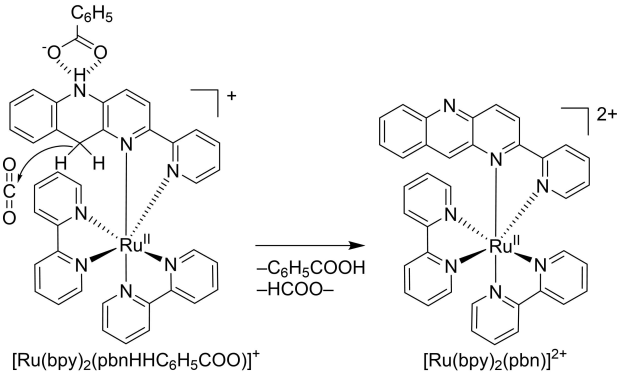


Scheme 1. Photoreduction of $[Ru(bpy)_2(pbn)]^{2+}$ affording $[Ru(bpy)_2(pbnHH)]^{2+}$ in the presence of TEOA as an electron and a proton source under visible light irradiation.



Scheme 2. Stoichiometric hydride transfer to CO_2 from the 1:1 adduct of $[Ru(bpy)_2(pbnHH)](PF_6)_2$ and $C_6H_5COO^-$ under dry conditions.

The reduced complex $[Ru(bpy)_2(pbnHH)]^{2+}$ formed the 1:1 adduct with benzoate ($C_6H_5COO^-$) via $C_6H_5COO^-\cdots HN$ hydrogen bond, in which the hydricity of pbnHH was effectively enhanced, and reacted with CO_2 with generating $HCOO^-$ in a stoichiometric reaction in CH_3CN (Scheme 2).[37] The expanded capability of the hydricity of $[Ru(bpy)_2(pbnHH)]^{2+}$ would lead to construct a new reaction system that is able to reduce CO_2 catalytically using a renewable organic hydride donor. This paper reports the first catalytic hydride transfer to CO_2 driven by the two-electron $[Ru(bpy)_2(pbn)]^{2+}/[Ru(bpy)_2(pbnHH)]^{2+}$ redox couple and the subsequent one-electron reduction of $[Ru(bpy)_2(pbnHH)]^{2+}$ in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as an electron source with a proton source in CH_3CN.

Results and Discussion

A Ru-NAD model complex, $[Ru(bpy)_2(pbn)](PF_6)_2$ was smoothly reduced to $[Ru(bpy)_2(pbnHH)](PF_6)_2$ as a Ru-NADH one under visible light irradiation in CH_3CN/TEOA (4:1, *v*/*v*).[35] A similar photo-illumination of $[Ru(bpy)_2(pbn)](PF_6)_2$ in CH_3CN/Et_3N (9:1, *v*/*v*) containing Et_3NHPF_6 also produced $[Ru(bpy)_2(pbnHH)](PF_6)_2$. The selective formation of $[Ru(bpy)_2(pbnHH)]^{2+}$ in the photochemical reduction was confirmed by the ^1H NMR spectra of the final CD_3CN/Et_3N solution containing Et_3NHPF_6 (Figure S1 in the Supporting Information), indicating that Et_3N and Et_3NHPF_6 worked as an electron and a proton source, respectively, in the reaction.

Furthermore, the CO_2 bubbling into the yellow CH_3CN/Et_3N (9:1, *v*/*v*) solution of $[Ru(bpy)_2(pbnHH)](PF_6)_2$ resulted in a quick color change to a reddish color probably due to the formation of $[Ru(bpy)_2(pbn)](PF_6)_2$. The observations of not only the reduction of $[Ru(bpy)_2(pbn)]^{2+}$ to $[Ru(bpy)_2(pbnHH)]^{2+}$ under visible light irradiation in CH_3CN/Et_3N in the presence of Et_3NH^+ but also the regeneration of $[Ru(bpy)_2(pbn)]^{2+}$ by the bubbling of CO_2 into the $[Ru(bpy)_2(pbnHH)]^{2+}$ solution drove us to construct a catalytic system aimed at the hydride transfer to CO_2 by the photoinduced two-electron of the $[Ru(bpy)_2(pbn)]^{2+}/[Ru(bpy)_2(pbnHH)]^{2+}$ redox couple.

However, the reaction of $[Ru(bpy)_2(pbn)](PF_6)_2$ (1 mM) in a CO_2-saturated CH_3CN/Et_3N (9:1, *v*/*v*) solution containing Et_3NHPF_6 (10 mM) under visible light irradiation generated only a very small amount of $HCOO^-$ (turnover number (TON) = 0.091, entry 1 in Table 1). Although the yield of $HCOO^-$ was very low, this result implied the occurrence of the photoinduced reduction of $[Ru(bpy)_2(pbn)]^{2+}$ followed by the hydride transfer from the resultant $[Ru(bpy)_2(pbnHH)]^{2+}$ to CO_2 in the one-pot reaction. A similar CO_2 reduction using $[Ru(bpy)_2(pbnHH)](PF_6)_2$ also produced a very small amount of $HCOO^-$ (entry 2 in Table 1).

To evaluate the effect of different proton sources on the CO_2 reduction, the redox behavior of $[Ru(bpy)_2(pbn)](PF_6)_2$ was examined in CH_3CN/Et_3N containing CH_3COOH in place of Et_3NHPF_6 (entry 3 in Table 1). Irradiation of the reddish solution containing $[Ru(bpy)_2(pbn)](PF_6)_2$ with visible light caused gradual color change to yellow one (from black to red curve in Figure S2). The bubbling of CO_2 into the yellow solution (from red to blue curve in Figure S2) regenerated the reddish solution. The photochemical CO_2 reduction using 0.5 mM of $[Ru(bpy)_2(pbn)](PF_6)_2$ under the same reaction conditions also produced $HCOO^-$ (entry 4 in Table 1). The yields of $HCOO^-$ produced in the presence of CH_3COOH were still very low

Table 1. Amounts of $HCOO^-$ produced in the CO_2 reduction by $[Ru(bpy)_2(pbn)](PF_6)_2$ in the presence of Et_3NHPF_6 or CH_3COOH in CH_3CN/Et_3N (9:1, *v*/*v*, 2 mL) under visible light irradiation.

Entry	Ruthenium complex [mM]	Et_3NHPF_6 [mM]	CH_3COOH [mM]	$HCOO^-$ [mM] (TON)
1	$[Ru(bpy)_2(pbn)](PF_6)_2$ (1)	10	–	0.091 (0.091)
2	$[Ru(bpy)_2(pbnHH)](PF_6)_2$ (1)	10	–	0.083 (0.083)
3	$[Ru(bpy)_2(pbn)](PF_6)_2$ (1)	–	280	0.15 (0.15)
4	$[Ru(bpy)_2(pbn)](PF_6)_2$ (0.5)	–	590	0.13 (0.26)

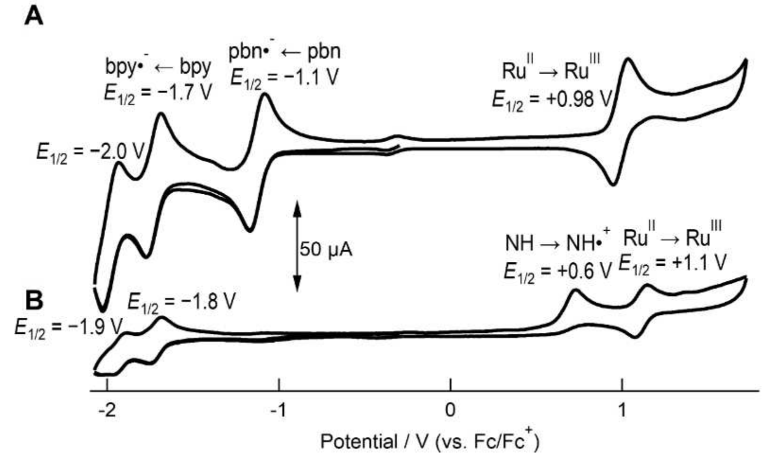


Figure 1. CVs of (A) $[Ru(bpy)_2(pbn)]^{2+}$ and (B) $[Ru(bpy)_2(pbnHH)]^{2+}$ in a CH_3CN solution containing 0.1 м Bu_4NClO_4 with a scan rate of 0.1 V s^{-1}.

(TON = 0.15, 0.26: entries 3, 4 in Table 1), but larger than the values obtained in the presence of Et_3NHPF_6.

The pbnHH group of $[Ru(bpy)_2(pbnHH)]^{2+}$ forms an adduct with a base, such as CH_3COO^- or $C_6H_5COO^-$, through a hydrogen bond at the NH position, which effectively enhances the hydricity of the pbnHH ligand (Scheme 2). The deprotonation of the NH group of $[Ru(bpy)_2(pbnHH)]^{2+}$ assisted by bases triggers a hydride transfer to CO_2 with the generation of $HCOO^-$ and $[Ru(bpy)_2(pbn)]^{2+}$. In other words, an excess amount of proton sources would crucially depress the release of hydride from pbnHH, indicating that $[Ru(bpy)_2(pbnHH)]^{2+}$ essentially has a very weak hydride donor ability in the absence of a base. Further one- or two-electron reduction of the complex, therefore, may create the function of providing a hydride to CO_2 even in the presence of excess protons.

Both $[Ru(bpy)_2(pbn)](PF_6)_2$ and $[Ru(bpy)_2(pbnHH)](PF_6)_2$ showed the metal centered reversible Ru^{II}/Ru^{III} redox couples at $E_{1/2} = +0.98$ and $+1.1$ V, respectively, in CH_3CN as shown in their cyclic voltammograms (CVs) in Figure 1. The pbn-localized $[Ru(bpy)_2(pbn)]^{2+}/[Ru(bpy)_2(pbn^{\bullet-})]^{+}$ redox couple at $E_{1/2} = -1.1$ V, and the subsequent bpy-centered $[Ru(bpy)_2(pbn^{\bullet-})]^{+}/[Ru(bpy)(bpy^{\bullet-})(pbn^{\bullet-})]^{0}$ and $[Ru(bpy)(bpy^{\bullet-})(pbn^{\bullet-})]^{0}/[Ru(bpy^{\bullet-})_2(pbn^{\bullet-})]^{-}$ ones were observed at $E_{1/2} = -1.7$ and -2.0 V, respectively (Figure 1A). The pbn-localized redox wave disappeared in the CV of $[Ru(bpy)_2(pbnHH)](PF_6)_2$ (Figure 1B). A newly appeared irreversible oxidation wave at $E_{1/2} = +0.6$ V is assigned to the $[Ru(bpy)_2(pbnHH)]^{2+}/[Ru(bpy)_2(pbnHH^{\bullet+})]^{3+}$ couple. The two bpy-centered $[Ru(bpy)_2(pbnHH)]^{2+}/[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ and $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}/[Ru(bpy^{\bullet-})_2(pbnHH)]^{0}$ redox couples emerged at $E_{1/2} = -1.8$ and -1.9 V, respectively (Figure 1B). Introduction of CO_2 into the solution caused an increase of the cathodic currents at more negative potential than the $[Ru(bpy)_2(pbnHH)]^{2+}/[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ redox couple, indicating the occurrence of hydride transfer from $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ to CO_2 (Figure S3).

The electronic absorption spectra of $[Ru(bpy)_2(pbn)](PF_6)_2$ and $[Ru(bpy)_2(pbnHH)](PF_6)_2$ in CH_3CN showed their metal-to-ligand charge transfer (MLCT) bands at 530 and 418 nm, respectively (Figure 2). The emission bands from the exited states, $[Ru^{III}(bpy)_2(pbn^{\bullet-})]^{2+*}$ and $[Ru^{III}(bpy)(bpy^{\bullet-})(pbnHH)]^{2+*}$, appeared at 550 and 650 nm, respectively (Figure S4A). The intensity of the 550 nm emission band of $[Ru(bpy)_2(pbn)]^{2+*}$ decreased with the addition of Et_3N to the solution (Figure S4A). The reductive quenching of $[Ru^{III}(bpy)_2(pbn^{\bullet-})]^{2+*}$ by Et_3N was followed by the protonation of the resultant $[Ru^{II}(bpy)_2(pbn^{\bullet-})]^{+}$ and the subsequent disproportionation of $[Ru^{II}(bpy)_2(pbnH^{\bullet})]^{2+}$ generates the two electron-reduced $[Ru^{II}(bpy)_2(pbnHH)]^{2+}$ and the original $[Ru^{II}(bpy)_2(pbn)]^{2+}$.

On the other hand, the emission spectrum of $[Ru^{III}(bpy)(bpy^{\bullet-})(pbnHH)]^{2+*}$ was not affected by the addition of an

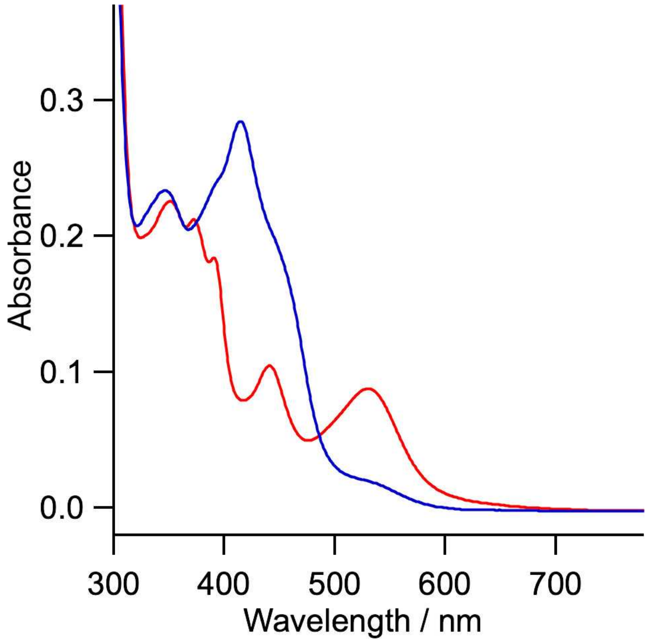


Figure 2. Electronic absorption spectra of $[Ru(bpy)_2(pbn)](PF_6)_2$ (red line) and $[Ru(bpy)_2(pbnHH)](PF_6)_2$ (blue line) in CH_3CN.

excess amount of Et_3N because of the extremely short lifetime of its excited state (Figure S4B). Thus, $[Ru(bpy)_2(pbn)]^{2+}$ was smoothly reduced to $[Ru(bpy)_2(pbnHH)]^{2+}$ in the presence of Et_3N under photoillumination, while $[Ru^{II}(bpy)_2(pbnHH)]^{2+}$ was inert under the similar conditions.

Therefore we examined the reactivity of $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ against CO_2. The UV/Vis absorption spectrum of $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ generated by means of the electrolysis of $[Ru(bpy)_2(pbnHH)]^{2+}$ (0.2 mM) at −1.7 V in CH_3CN containing 0.1 M Bu_4NClO_4 (Figure S5 dashed black line) showed a band at 420 nm but no absorption band above 500 nm. An addition of CO_2-saturated CH_3CN to the solution resulted in significant decrease of the 420 nm band and increase of the absorbance at 500–600 nm (Figure S5 red line). The pattern of the final spectrum is close to a mixture of $[Ru(bpy)_2(pbn)]^{2+}$ and $[Ru(bpy)_2(pbnHH)]^{2+}$ (Figure S2), which also indicated the occurrence of hydride transfer from $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ to CO_2.

BIH acts as a good sacrificial electron donor in photochemical reactions.[38] The one-electron oxidation of BIH ($E_{1/2} = -0.07$ V vs. Fc/Fc$^+$) in the presence of a base is followed by the proton releases, in which the rate of the deprotonation of $BIH^{\bullet}$ was $k_{dp} = 1.1 \times 10^5$ $M^{-1}s^{-1}$.[38] The oxidation potential of the resultant $BI^{\bullet}$ is −2.06 V (vs. Fc/Fc$^+$),[39] and negative enough to reduce $[Ru(bpy)_2(pbnHH)]^{2+}$ ($E_{1/2} = -1.8$ V, Figure 1B) to produce $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$. The TON of $HCOO^-$ increased from 8.8 to 41 (entries 1 and 2 in Table 2) when the concentration of $[Ru(bpy)_2(pbn)](PF_6)_2$ decreased from 1.0 to 0.2 mM. In addition, CO (0.66 μmol) was produced together with $HCOO^-$. The stability of $[Ru(bpy)_2(pbn)]^{2+}$ and $[Ru(bpy)_2(pbnHH)]^{2+}$ in CH_3CN under visible light irradiation was investigated by analyzing the reaction mixture using high-performance liquid chromatography. A trace amount of a free bpy liberated from the complexes was detected from the reaction mixture. Irradiation with visible light to $[Ru(bpy)_3]^{2+}$ in CH_3CN is known to cause a partial release of a bpy ligand from the complex, and the resultant $[Ru(bpy)_2]$ species has an ability to reduce CO_2 to CO.[8] The coordinatively saturated Ru atoms in $[Ru(bpy)_2(pbn)]^{2+}$ and $[Ru(bpy)_2(pbnHH)]^{2+}$ apparently have no ability to activate CO_2 at the Ru centers. the high selectivity of HCOOH formation in the present photochemical CO_2 reduction is ascribed to the hydride transfer from the renewable organic hydride of $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ to CO_2. When the concentration of $[Ru(bpy)_2(pbn)](PF_6)_2$ decreased to 0.1 and 0.05 mM, $HCOO^-$ were produced with TON = 63 and 56, respectively (entries 3 and 4 in Table 2). The ^{13}C NMR spectra of a CD_3CN/TEOA (9:1, *v/v*, 1 mL) solution containing $[Ru(bpy)_2(pbn)](PF_6)_2$ (0.2 mM) and BIH (22 mM) under $^{13}CO_2$ atmosphere did not exhibit any signal around 168 ppm before light irradiation (Figure S6). After irradiation of visible light for 48 h, the solution displayed the appearance of the singlet signal at 168.7 ppm attributable to $H^{13}COOH$.[40] Furthermore, the similar photochemical CO_2 reduction using ^{12}CO did not display a signal assignable HCOOH in the ^{13}C NMR spectra under normal resolution conditions. Thus, all the HCOOH molecules produced in the present study resulted from CO_2, and were safely ruled out the possibility of decomposition products of organic molecules.

Table 2. Amounts of $HCOO^-$, H_2, and CO produced in the reduction of CO_2 by $[Ru(bpy)_2(pbn)](PF_6)_2$ in CH_3CN/TEOA (9:1, *v/v*, 1 mL) with BIH (22 mM) under visible-light irradiation (48 h).

Entry	$[Ru(bpy)_2(pbn)](PF_6)_2$ [mM]	Amount formed (TON) $HCOO^-$ [mM]	H_2 [μmol]	CO [μmol]
1[a]	1.0	8.8 (8.8)	0.33 (0.33)	2.6 (2.6)
2	0.2	8.2 (41)	0.10 (0.5)	0.66 (3.3)
3	0.1	6.3 (63)	0.28 (2.8)	1.1 (11)
4	0.05	2.8 (56)	0.21 (4.2)	0.35 (7.0)

[a] Visible light irradiation for 30 h.

The present photochemical CO_2 reduction produced formic acid accompanied by CO and H_2 evolution in the initial 4 h (Figure S7 and Table S1). After 4 h, the rate of formic acid formation gradually decreased, and CO evolution completely stopped. The high catalytic activity toward the photochemical CO_2 reduction in the initial 4 h clearly indicates that $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ works as the active catalyst toward the organic hydride transfer to CO_2 generating formic acid.

Photochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(pbn)](PF_6)_2$ in the presence of BIH and various proton sources was also conducted (see Table 3). When CH_3COOH was used, $HCOO^-$ was formed with TON of 0.85 (entry 1 in Table 3). However, when EtOH was used instead, $HCOO^-$ was detected with a larger TON of 5 (entry 2 in Table 3). Similar photochemical CO_2 reduction in the presence of H_2O as a proton source generated $HCOO^-$ with a TON of 41 (entry 3 in Table 3). Thus, $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$ works as the active catalyst in the hydride transfer to CO_2 in the presence of EtOH or H_2O as a proton source.

The proposed reaction mechanism of the developed catalytic organic hydride transfer to CO_2 is illustrated in Scheme 3. The photoexcited $[Ru^{III}(bpy)_2(pbn^{\bullet-})]^{2+*}$ generated through the illumination at the MLCT band of $[Ru(bpy)_2(pbn)]^{2+}$ undergoes reductive quenching by BIH to give $[Ru^{II}(bpy)_2(pbn^{\bullet-})]^{2+}$ and $BIH^{\bullet+}$. The protonation of the $pbn^{\bullet-}$ framework of the $[Ru^{II}(bpy)_2(pbn^{\bullet-})]^{2+}$ in the presence of an ROH (i.e., TEOA, EtOH, or H_2O) produces $[Ru(bpy)_2(pbnH^{\bullet})]^{2+}$ and $BI^{\bullet}$ (the left path in Scheme 3).[35] Disproportionation of $[Ru(bpy)_2(pbnH^{\bullet})]^{2+}$ generates $[Ru(bpy)_2(pbnHH)]^{2+}$ and $[Ru(bpy)_2(pbn)]^{2+}$ (the central path) and the subsequent reduction of $[Ru(bpy)_2(pbnHH)]^{2+}$ by $BI^{\bullet}$ affords $[Ru(bpy)(bpy^{\bullet-})(pbnHH)]^{+}$, which works as the active catalyst, transferring hydride to CO_2 to produce $HCOO^-$ with regenerating $[Ru(bpy)_2(pbnH^{\bullet})]^{2+}$ (the right path).

Table 3. Amounts of $HCOO^-$ and TON in the catalytic reduction of CO_2 by $[Ru(bpy)_2(pbn)](PF_6)_2$ in CH_3CN in the presence of BIH (22 mM) and a proton source under visible light irradiation (48 h).

Entry	$[Ru(bpy)_2(pbn)](PF_6)_2$ [mM]	Proton source [mL]	CH_3CN [mL]	$HCOO^-$ [mM] (TON)
1	0.2	CH_3COOH (0.05)	0.95	0.17 (0.85)
2	0.2	EtOH (0.1)	0.9	1.0 (5)
3	0.2	H_2O (0.1)	0.9	8.1 (41)

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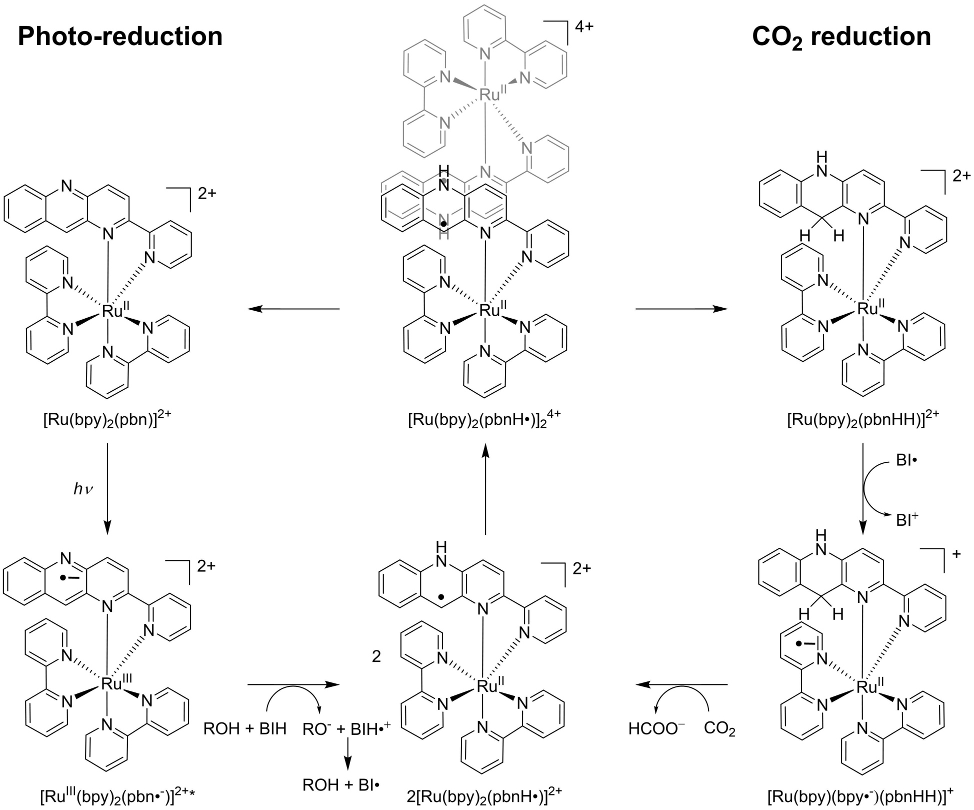
Photo-reduction
CO$_2$ reduction
4+
2+
$[Ru(bpy)_2(pbn)]^{2+}$
$[Ru(bpy)_2(pbnH•)]_2^{4+}$
$[Ru(bpy)_2(pbnHH)]^{2+}$
hν
BI•
BI$^+$
$[Ru^{III}(bpy)_2(pbn•^-)]^{2+*}$
2
ROH + BIH
RO$^-$ + BIH•$^+$
ROH + BI•
$2[Ru(bpy)_2(pbnH•)]^{2+}$
HCOO$^-$
CO$_2$
+
$[Ru(bpy)(bpy•^-)(pbnHH)]^+$

Scheme 3. Proposed mechanism of the photoassisted catalytic hydride transfer to CO_2 catalyzed by $[Ru(bpy)_2(pbn)](PF_6)_2$ in the presence of BIH and an ROH (i.e., TEOA, EtOH, or H_2O) in CH_3CN.

Thus, the first catalytic organic hydride transfer to CO_2 is achieved through the photoinduced two-electron reduction of the $[Ru(bpy)_2(pbn)]^{2+}$/$[Ru(bpy)_2(pbnHH)]^{2+}$ redox couple followed by a further one-electron reduction of $[Ru(bpy)_2(pbnHH)]^{2+}$ with BI$^•$ formed during the reductive quenching of the excited state of $[Ru^{III}(bpy)_2(pbn^{•-})]^{2+}*$ in the presence of BIH and ROH.

Conclusions

Here, the photoinduced reduction of $[Ru(bpy)_2(pbn)]^{2+}$ in the presence of BIH as an electron donor and ROH (i.e., TEOA, EtOH, or H_2O) as a proton donor produced $[Ru(bpy)_2(pbnH^•)]^{2+}$ together with BI$^•$. The subsequent disproportionation of $[Ru(bpy)_2(pbnH^•)]^{2+}$ gives $[Ru(bpy)_2(pbnHH)]^{2+}$, which was further reduced by BI$^•$ to generate a highly reactive species, $[Ru(bpy)(bpy^{•-})(pbnHH)]^+$. It is worthy of noting that the hydride transfer from $[Ru(bpy)(bpy^{•-})(pbnHH)]^+$ to CO_2 was not disturbed by the presence of an excess amount of a proton source. The regeneration of $[Ru(bpy)_2(pbnH^•)]^{2+}$ accompanied by $HCOO^-$ production constructs the catalytic cycle of the CO_2 reduction. The present study is the first catalytic organic hydride transfer to CO_2 using the photoinduced two-electron reduction of $[Ru(bpy)_2(pbn)]^{2+}$ in the presence of BIH and ROH with maximal TON of 63.

Experimental Section

General

The ^1H and ^{13}C NMR spectra in CD_3CN were recorded using a JEOL AL-400 and ECA-600 spectrometers (400 and 151 MHz), respectively; residual CD_2HCN ($\delta = 1.94$ ppm) and $^{13}CD_3CN$ ($\delta = 118.3$ ppm) were used as an internal reference. The electronic absorption spectra were measured using a Hitachi U-3500 spectrophotometer. A light source was Asahi Spectra MAX-303 with a 300 W xenon lamp using a UV/Vis type mirror module. The amount of HCOOH in a liquid phase was determined by a liquid chromatograph equipped with a conductivity detector (Prominence Organic Acid Analysis System, SHIMADZU). Electrochemical measurements were carried out with a BAS CV-50 W voltametric analyzer with a conventional three-electrode system: cyclic voltammetry using an Ag/Ag$^+$ electrode as a reference electrode, a glassy carbon electrode as a working electrode, and a platinum needle as an auxiliary electrode. The redox potentials were determined versus ferrocene/ferrocenium (Fc/Fc$^+$). Cyclic voltammograms were recorded in CH_3CN/0.1 м Bu_4NClO_4 with a scan rate of 0.1 $V s^{-1}$ at ca. 1 mм sample solutions. The fluorescence emission spectra were obtained using a Hamamatsu Photonics C9920-03G spectrometer.

Materials

$[Ru(bpy)_2(pbn)](PF_6)_2$,[35] $[Ru(bpy)_2(pbnHH)](PF_6)_2$,[35] and BIH[38,39] were prepared according to previously reported procedures. Solvents and reagents for preparation of compounds were obtained from commercial suppliers and utilized as supplied. CO_2 for photoinduced reduction was purchased from Nippon Ekitan, Tokyo, Japan. $^{13}CO_2$ was prepared by the reaction of $Ba^{13}CO_3$ (Isotec, US) with aqueous 5% H_2SO_4. Et_3N and TEOA used as electron sources, CH_3COOH and EtOH used as proton sources, and CH_3CN for a reduction solvent were purchased from Nacalai Tesque, Kyoto, Japan and used without further purification. H_2O used as a proton source was prepared as a distilled water by a YAMATO AutoStill WG250 system.

Photoinduced catalytic CO_2 reduction

A typical procedure is as follows (entry 2 in Table 2). The mixture of $[Ru(bpy)_2(pbn)](PF_6)_2$ (196 μg, 0.2 μmol) and BIH (5.0 mg, 22 μmol) was dissolved in dry CH_3CN/TEOA (9:1, *v/v*, 1 mL). To the reaction mixture was bubbling CO_2 over 30 min. The reaction mixture was stirred under visible light irradiation for 48 h and analyzed by the aforementioned liquid chromatograph.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: carbon dioxide · hydride transfer · formate · organic hydride · photoreduction · ruthenium complex

[1] a) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163–170; b) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg. Chem.* **2005**, *44*, 6802–6827.

[2] a) T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387; b) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem. Soc. Rev.* **2009**, *38*, 89–99; c) M. D. Doherty, D. C. Grills, J. T. Muckerman, D. E. Polyansky, E. Fujita, *Coord. Chem. Rev.* **2010**, *254*, 2472–2482; d) C. Finn, S. Schnittger, L. J. Yellowlees, J. B. Love, *Chem. Commun.* **2012**, *48*, 1392–1399.

[3] a) S. N. Riduan, Y. G. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.* **2009**, *48*, 3322–3325; *Angew. Chem.* **2009**, *121*, 3372–3375; b) A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839–9843; *Angew. Chem.* **2009**, *121*, 10023–10027; c) E. B. Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev, A. B. Bocarsly, *J. Am. Chem. Soc.* **2010**, *132*, 11539–11551.

[4] C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125.

[5] R. D. Richardson, E. J. Holland, B. K. Carpenter, *Nat. Chem.* **2011**, *3*, 301–303.

[6] a) H. Hayashi, S. Ogo, T. Abura, S. Fukuzumi, *J. Am. Chem. Soc.* **2003**, *125*, 14266–14267; b) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168–14169; c) Y. Maenaka, T. Suenobu, S. Fukuzumi, *J. Am. Chem. Soc.* **2012**, *134*, 367–374; d) J. F. Hull, Y. Himeda, W. H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* **2012**, *4*, 383–388; e) Y. Maenaka, T. Suenobu, S. Fukuzumi, *Energy Environ. Sci.* **2012**, *5*, 7360–7367; f) P. Kang, C. Cheng, Z. F. Chen, C. K. Schauer, T. J. Meyer, M. Brookhart, *J. Am. Chem. Soc.* **2012**, *134*, 5500–5503.

[7] J. Bonin, M. Chaussemier, M. Robert, M. Routier, *ChemCatChem* **2014**, *6*, 3200–3207.

[8] J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* **1983**, 536–538.

[9] L. Rotundo, J. Filippi, R. Gobetto, H. A. Miller, R. Rocca, C. Nervi, F. Vizza, *Chem. Commun.* **2019**, *55*, 775–777.

[10] C. Cometto, L. Chen, P.-K. Lo, Z. Guo, K.-C. Lau, E. Anxolabéhère-Mallart, C. Fave, T.-C. Lau, M. Robert, *ACS Catal.* **2018**, *8*, 3411–3417.

[11] R. Bonetto, R. Altieri, M. Tagliapietra, A. Barbon, M. Bonchio, M. Robert, A. Sartorel, *ChemSusChem* **2020**, *13*, 4111–4120.

[12] C. Costentin, M. Robert, J.-M. Savéant, *Acc. Chem. Res.* **2015**, *48*, 2996–3006.

[13] J. Shen, R. Kortlever, R. Kas, Y. Y. Birdja, O. Diaz-Morales, Y. Kwon, I. Ledezma-Yanez, K. J. P. Schouten, G. Mul, M. T. M. Koper, *Nat. Commun.* **2015**, *6*, 8177–8185.

[14] Z. Guo, S. Cheng, C. Cometto, E. Anxolabéhère-Mallart, S.-M. Ng, C.-C. Ko, G. Liu, L. Chen, M. Robert, T.-C. Lau, *J. Am. Chem. Soc.* **2016**, *138*, 9413–9416.

[15] T. Ouyang, H.-J. Wang, H.-H. Huang, J.-W. Wang, S. Guo, W.-J. Liu, D.-C. Zhong, T.-B. Lu, *Angew. Chem. Int. Ed.* **2018**, *57*, 16480–16485; *Angew. Chem.* **2018**, *130*, 16718–16723.

[16] T. Akai, M. Kondo, S. K. Lee, H. Izu, T. Enomoto, M. Okamura, Y. Saga, S. Masaoka, *Dalton Trans.* **2020**, *49*, 1384–1387.

[17] J. Schneider, H. Jia, K. Kobiro, D. E. Cabelli, J. T. Muckerman, E. Fujita, *Energy Environ. Sci.* **2012**, *5*, 9502–9510.

[18] J. D. Froehlich, C. P. Kubiak, *J. Am. Chem. Soc.* **2015**, *137*, 3565–3573.

[19] A. Mouchfiq, T. K. Todorova, S. Dey, M. Fontecave, V. Mougel, *Chem. Sci.* **2020**, *11*, 5503–5510.

[20] U. R. Pokharel, F. R. Fronczek, A. W. Maverick, *Nat. Commun.* **2014**, *5*, 5883–5888.

[21] J. A. Buss, D. VanderVelde, G. T. Agapie, *J. Am. Chem. Soc.* **2018**, *140*, 10121–10125.

[22] Z. Chen, J. J. Concepcion, M. K. Brennaman, P. Kang, M. R. Norris, P. G. Hoertz, T. J. Meyer, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15606–15611.

[23] J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah, G. K. S. Prakash, *J. Am. Chem. Soc.* **2016**, *138*, 778–781.

[24] S. K. Lee, M. Kondo, G. Nakamura, M. Okamura, S. Masaoka, *Chem. Commun.* **2018**, *54*, 6915–6918.

[25] J. A. Keith, K. A. Grice, C. P. Kubiak, E. A. Carter, *J. Am. Chem. Soc.* **2013**, *135*, 15823–15829.

[26] B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining, T. J. Meyer, *J. Chem. Soc. Chem. Commun.* **1985**, 1414–1416.

[27] C. J. Gagliardi, B. C. Westlake, C. A. Kent, J. J. Paul, J. M. Papanikolas, T. J. Meyer, *Coord. Chem. Rev.* **2010**, *254*, 2459–2471.

[28] a) S. Fukuzumi, in *Physical Inorganic Chemistry: Reactions, Processes, and Applications* (Ed. A. Bakac), Wiley, Hoboken, Germany, **2010**, Ch. 2; b) K. Kamogawa, Y. Shimoda, K. Miyata, K. Onda, Y. Yamazaki, Y. Tamaki, O. Ishitani, *Chem. Sci.* **2021**, *12*, 9682–9693.

[29] C.-H. Lim, S. Ilic, A. Alherz, B. T. Worrell, S. S. Bacon, J. T. Hynes, K. D. Glusac, C. B. Musgrave, *J. Am. Chem. Soc.* **2019**, *141*, 272–280.

[30] a) U. Eisner, J. Kuthan, *Chem. Rev.* **1972**, *72*, 1–42; b) C. Walsh, *Acc. Chem. Res.* **1980**, *13*, 148–155; c) D. M. Stout, A. I. Meyers, *Chem. Rev.* **1982**, *82*, 223–243.

[31] S. Fukuzumi, in *Advances in Electron-Transfer Chemistry* Vol. 2 (Ed. P. S. Mariano), JAI, Greenwich, CT, **1992**, Ch. 2, and references therein.

[32] J. Gébicki, A. Marcinek, J. Zielonka, *Acc. Chem. Res.* **2004**, *37*, 379–386.

[33] K. M. Waldie, A. L. Osericher, M. H. Reineke, A. F. Sasayama, C. P. Kubiak, *ACS Catal.* **2018**, *8*, 1313–1324.

[34] a) S. Fukuzumi, J. Yuasa, N. Satoh, T. Suenobu, *J. Am. Chem. Soc.* **2004**, *126*, 7585–7594; b) A. Kobayashi, H. Konno, K. Sakamoto, A. Sekine, Y. Ohashi, M. Iida, O. Ishitani, *Chem. Eur. J.* **2005**, *11*, 4219–4226; c) B. W. Cohen, D. E. Polyansky, R. Zong, H. Zhou, T. Ouk, D. E. Cabelli, R. P. Thummel, E. Fujita, *Inorg. Chem.* **2010**, *49*, 8034–8044.

[35] T. Koizumi, K. Tanaka, *Angew. Chem. Int. Ed.* **2005**, *44*, 5891–5894; *Angew. Chem.* **2005**, *117*, 6041–6044.

[36] a) D. Polyansky, D. Cabelli, J. T. Muckerman, E. Fujita, T. Koizumi, T. Fukushima, T. Wada, K. Tanaka, D. Polyansky, *Angew. Chem. Int. Ed.* **2007**, *46*, 4169–4172; *Angew. Chem.* **2007**, *119*, 4247–4250; b) T. Fukushima, E. Fujita, J. T. Muckerman, D. E. Polyansky, T. Wada, K. Tanaka, *Inorg. Chem.* **2009**, *48*, 11510–11512; c) T. Fukushima, T. Wada,

H. Ohtsu, K. Tanaka, *Dalton Trans.* **2010**, *39*, 11526–11534; d) H. Ohtsu, K. Tanaka, *Chem. Commun.* **2012**, *48*, 1796–1798.

[37] H. Ohtsu, K. Tanaka, *Angew. Chem. Int. Ed.* **2012**, *51*, 9792–9795; *Angew. Chem.* **2012**, *124*, 9930–9933.

[38] a) Y. Tamaki, K. Koike, T. Morimoto, O. Ishitani, *J. Catal.* **2013**, *304*, 22–28; b) R. N. Sampaio, D. C. Grills, D. E. Polyansky, D. J. Szalda, E. Fujita, *J. Am. Chem. Soc.* **2020**, *142*, 2413–2428; c) Y. Hu, F. Zhan, Q. Wang, Y. Sun, C. Yu, X. Zhao, H. Wang, R. Long, G. Zhang, C. Gao, W. Zhang, J. Jiang, Y. Tao, Y. Xiong, *J. Am. Chem. Soc.* **2020**, *142*, 5618–5626; d) X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J.-P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501–2516.

[39] Y. Kuramochi, O. Ishitani, H. Ishida, *Coord. Chem. Rev.* **2018**, *373*, 333–356.

[40] M. Irikura, Y. Tamaki, O. Ishitani, *Chem. Sci.* **2021**, *12*, 13888–13896.

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