

# Photoinduced Catalytic Organic-Hydride Transfer to CO<sub>2</sub> Mediated with Ruthenium Complexes as NAD<sup>+</sup>/NADH Redox Couple Models\*\*

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The catalytic organic-hydride transfer to CO<sub>2</sub> was first achieved through the photoinduced two-electron reduction of the [Ru(bpy)<sub>2</sub>(pbn)]<sup>2+</sup>/[Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> (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-1H-benzo[d]imidazole (BIH). The active species for the catalytic hydride transfer to carbon dioxide giving formate is [Ru(bpy)(bpy<sup>•-</sup>)(pbnHH)]<sup>+</sup> formed by one-electron reduction of [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> with BI<sup>•</sup>.

## Introduction

The increase in the atmospheric concentration of carbon dioxide (CO<sub>2</sub>) 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<sub>2</sub> into value-added chemical compounds,<sup>[1,2]</sup> such as methanol (CH<sub>3</sub>OH)<sup>[3,4]</sup> and formic acid (HCOOH)<sup>[5,6]</sup> under mild conditions. Direct one-electron reduction of CO<sub>2</sub> is a highly energy consuming process (−1.90 V vs. standard hydrogen electrode (SHE) in water at pH = 7),<sup>[7]</sup> and the resultant CO<sub>2</sub><sup>•-</sup> is hard to regulate its reactivity as a C<sub>1</sub> resource. In 1983, Lehn and his colleagues reported the first photochemical CO<sub>2</sub> reduction mediated with Re(bpy)(CO)<sub>3</sub>X (bpy = 2,2'-bipyridine, X = Cl, Br) having dual functions of a photosensitizer and a catalyst.<sup>[8]</sup> Since then, a large number of metal complexes including Mn,<sup>[9]</sup> Fe,<sup>[10–12]</sup> Co,<sup>[13–16]</sup> Ni,<sup>[17,18]</sup> Cu,<sup>[19,20]</sup> Mo,<sup>[21]</sup> Ru,<sup>[22–24]</sup> and Re<sup>[8,25,26]</sup> have

been shown to be active in the photochemical CO<sub>2</sub> reduction by the combination with a photosensitizer.<sup>[27,28]</sup> 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<sub>2</sub>. In addition to the reductive activation of CO<sub>2</sub> on metal ions, hydride transfer to CO<sub>2</sub> mediated with renewable organic hydride donors also may provide a new methodology to develop C<sub>1</sub> resources. Indeed, Musgrave and his colleagues found that 1,2,3-trimethylbenzimidazole as an organic hydride donor reacted with CO<sub>2</sub> to afford formate without the assistance of transition metals, though the reaction proceeded in a stoichiometric fashion but not catalytically.<sup>[29]</sup>

In biological systems, the NAD<sup>+</sup>/NADH (NAD = nicotinamide adenine dinucleotide) redox couple plays a pivotal role as a generator and/or a reservoir of hydride (H<sup>-</sup>), which is equivalent to one proton and two electrons.<sup>[30]</sup> Much information about organic NAD<sup>+</sup>/NADH model compounds has so far been accumulated to understand their unique redox and photo-physical properties as well as their photochemical and thermal reactivities.<sup>[31]</sup> 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<sup>+</sup> 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)<sub>2</sub> species via C–C bond formation.<sup>[32]</sup> In addition to the various organic NAD<sup>+</sup> and NADH model compounds, the reactivities of transition-metal hydrides are also examined to elucidate the hydricity of the bonds.<sup>[33]</sup> Recently, a ruthenium complex with an NAD<sup>+</sup> model ligand, [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> (pbn = 2-(pyridin-2-yl)benzo[b]-1,5-naphthyridine),<sup>[34,35]</sup> was shown to undergo photochemical two-electron reduction to afford the corresponding NADH-type complex [Ru(bpy)<sub>2</sub>(pbnHH)](PF<sub>6</sub>)<sub>2</sub> (pbnHH = 2-(pyridin-2-yl)-5,10-dihydrobenzo[b]-1,5-naphthyridine) under visible light irradiation in the presence of triethanolamine (TEOA) in CH<sub>3</sub>CN (see Scheme 1).<sup>[36]</sup>

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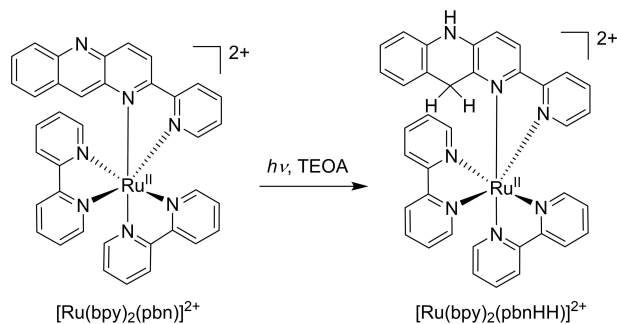
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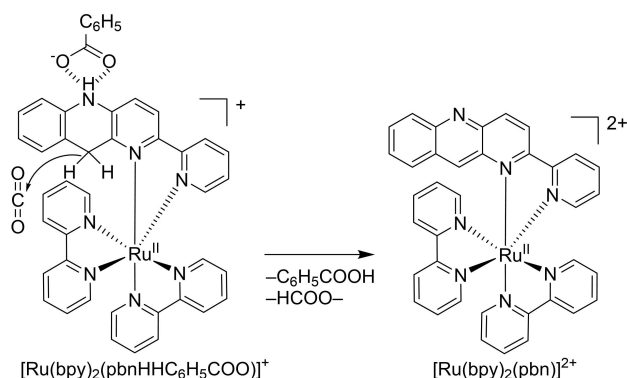
[\*\*] NAD = Nicotinamide adenine dinucleotide

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



**Scheme 2.** Stoichiometric hydride transfer to  $\text{CO}_2$  from the 1:1 adduct of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  and  $\text{C}_6\text{H}_5\text{COO}^-$  under dry conditions.

The reduced complex  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  formed the 1:1 adduct with benzoate ( $\text{C}_6\text{H}_5\text{COO}^-$ ) via  $\text{C}_6\text{H}_5\text{COO}^- \cdots \text{HN}$  hydrogen bond, in which the hydricity of pbnHH was effectively enhanced, and reacted with  $\text{CO}_2$  with generating  $\text{HCOO}^-$  in a stoichiometric reaction in  $\text{CH}_3\text{CN}$  (Scheme 2).<sup>[37]</sup> The expanded capability of the hydricity of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  would lead to construct a new reaction system that is able to reduce  $\text{CO}_2$  catalytically using a renewable organic hydride donor. This paper reports the first catalytic hydride transfer to  $\text{CO}_2$  driven by the two-electron  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}/[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  redox couple and the subsequent one-electron reduction of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  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  $\text{CH}_3\text{CN}$ .

## Results and Discussion

A Ru-NAD model complex,  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  was smoothly reduced to  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  as a Ru-NADH one under visible light irradiation in  $\text{CH}_3\text{CN}/\text{TEOA}$  (4:1, v/v).<sup>[35]</sup> A similar photo-illumination of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}/\text{Et}_3\text{N}$  (9:1, v/v) containing  $\text{Et}_3\text{NHPF}_6$  also produced  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$ . The selective formation of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  in the photochemical reduction was confirmed by the  $^1\text{H}$  NMR spectra of the final  $\text{CD}_3\text{CN}/\text{Et}_3\text{N}$  solution containing  $\text{Et}_3\text{NHPF}_6$  (Figure S1 in the Supporting Information), indicating that  $\text{Et}_3\text{N}$  and  $\text{Et}_3\text{NHPF}_6$  worked as an electron and a proton source, respectively, in the reaction.

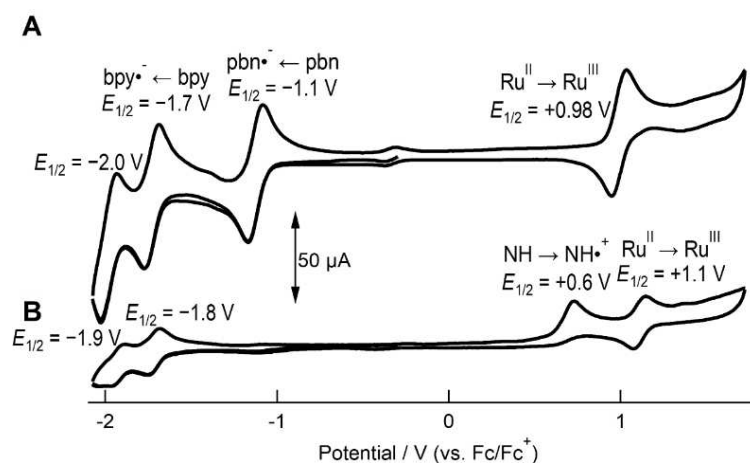
Furthermore, the  $\text{CO}_2$  bubbling into the yellow  $\text{CH}_3\text{CN}/\text{Et}_3\text{N}$  (9:1, v/v) solution of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  resulted in a quick color change to a reddish color probably due to the formation of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$ . The observations of not only the reduction of  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  to  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  under visible light irradiation in  $\text{CH}_3\text{CN}/\text{Et}_3\text{N}$  in the presence of  $\text{Et}_3\text{NH}^+$  but also the regeneration of  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  by the bubbling of  $\text{CO}_2$  into the  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  solution drove us to construct a catalytic system aimed at the hydride transfer to  $\text{CO}_2$  by the photoinduced two-electron of the  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}/[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  redox couple.

However, the reaction of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  (1 mM) in a  $\text{CO}_2$ -saturated  $\text{CH}_3\text{CN}/\text{Et}_3\text{N}$  (9:1, v/v) solution containing  $\text{Et}_3\text{NHPF}_6$  (10 mM) under visible light irradiation generated only a very small amount of  $\text{HCOO}^-$  (turnover number (TON) = 0.091, entry 1 in Table 1). Although the yield of  $\text{HCOO}^-$  was very low, this result implied the occurrence of the photoinduced reduction of  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  followed by the hydride transfer from the resultant  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  to  $\text{CO}_2$  in the one-pot reaction. A similar  $\text{CO}_2$  reduction using  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  also produced a very small amount of  $\text{HCOO}^-$  (entry 2 in Table 1).

To evaluate the effect of different proton sources on the  $\text{CO}_2$  reduction, the redox behavior of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  was examined in  $\text{CH}_3\text{CN}/\text{Et}_3\text{N}$  containing  $\text{CH}_3\text{COOH}$  in place of  $\text{Et}_3\text{NHPF}_6$  (entry 3 in Table 1). Irradiation of the reddish solution containing  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  with visible light caused gradual color change to yellow one (from black to red curve in Figure S2). The bubbling of  $\text{CO}_2$  into the yellow solution (from red to blue curve in Figure S2) regenerated the reddish solution. The photochemical  $\text{CO}_2$  reduction using 0.5 mM of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  under the same reaction conditions also produced  $\text{HCOO}^-$  (entry 4 in Table 1). The yields of  $\text{HCOO}^-$  produced in the presence of  $\text{CH}_3\text{COOH}$  were still very low

**Table 1.** Amounts of  $\text{HCOO}^-$  produced in the  $\text{CO}_2$  reduction by  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  in the presence of  $\text{Et}_3\text{NHPF}_6$  or  $\text{CH}_3\text{COOH}$  in  $\text{CH}_3\text{CN}/\text{Et}_3\text{N}$  (9:1, v/v, 2 mL) under visible light irradiation.

Entry	Ruthenium complex [mM]	$\text{Et}_3\text{NHPF}_6$ [mM]	$\text{CH}_3\text{COOH}$ [mM]	$\text{HCOO}^-$ [mM] (TON)
1	$[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$ (1)	10	–	0.091 (0.091)
2	$[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$ (1)	10	–	0.083 (0.083)
3	$[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$ (1)	–	280	0.15 (0.15)
4	$[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$ (0.5)	–	590	0.13 (0.26)



**Figure 1.** CVs of (A)  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  and (B)  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  in a  $\text{CH}_3\text{CN}$  solution containing 0.1 M  $\text{Bu}_4\text{NClO}_4$  with a scan rate of  $0.1 \text{ V s}^{-1}$ .

(TON=0.15, 0.26: entries 3, 4 in Table 1), but larger than the values obtained in the presence of  $\text{Et}_3\text{NHPF}_6$ .

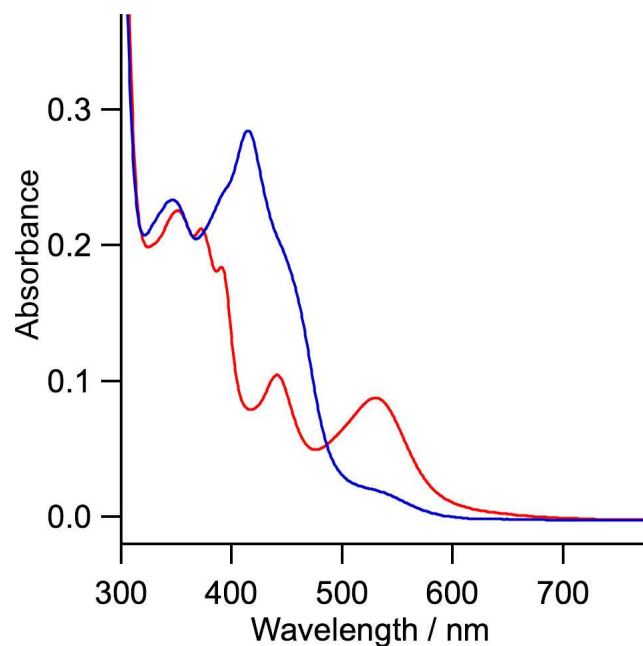
The pbnHH group of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  forms an adduct with a base, such as  $\text{CH}_3\text{COO}^-$  or  $\text{C}_6\text{H}_5\text{COO}^-$ , through a hydrogen bond at the NH position, which effectively enhances the hydricity of the pbnHH ligand (Scheme 2). The deprotonation of the NH group of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  assisted by bases triggers a hydride transfer to  $\text{CO}_2$  with the generation of  $\text{HCOO}^-$  and  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ . In other words, an excess amount of proton sources would crucially depress the release of hydride from pbnHH, indicating that  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$  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  $\text{CO}_2$  even in the presence of excess protons.

Both  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  and  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  showed the metal centered reversible  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  redox couples at  $E_{1/2} = +0.98$  and  $+1.1 \text{ V}$ , respectively, in  $\text{CH}_3\text{CN}$  as shown in their cyclic voltammograms (CVs) in Figure 1. The pbn-localized  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}/[\text{Ru}(\text{bpy})_2(\text{pbn}^{\bullet-})]^+$  redox couple at  $E_{1/2} = -1.1 \text{ V}$ , and the subsequent bpy-centered  $[\text{Ru}(\text{bpy})_2(\text{pbn}^{\bullet-})]^+ / [\text{Ru}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbn}^{\bullet-})]^0$  and  $[\text{Ru}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbn}^{\bullet-})]^0 / [\text{Ru}(\text{bpy}^{\bullet-})_2(\text{pbn}^{\bullet-})]^-$  ones were observed at  $E_{1/2} = -1.7$  and  $-2.0 \text{ V}$ , respectively (Figure 1A). The pbn-localized redox wave disappeared in the CV of  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  (Figure 1B). A newly appeared irreversible oxidation wave at  $E_{1/2} = +0.6 \text{ V}$  is assigned to the  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}/[\text{Ru}(\text{bpy})_2(\text{pbnHH}^{\bullet+})]^{3+}$  couple. The two bpy-centered  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}/[\text{Ru}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbnHH})]^+$  and  $[\text{Ru}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbnHH})]^+ / [\text{Ru}(\text{bpy}^{\bullet-})_2(\text{pbnHH})]^0$  redox couples emerged at  $E_{1/2} = -1.8$  and  $-1.9 \text{ V}$ , respectively (Figure 1B). Introduction of  $\text{CO}_2$  into the solution caused an increase of the cathodic currents at more negative potential than the  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}/[\text{Ru}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbnHH})]^+$  redox couple, indicating the occurrence of hydride transfer from  $[\text{Ru}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbnHH})]^+$  to  $\text{CO}_2$  (Figure S3).

The electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  and  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}$  showed their metal-to-

ligand charge transfer (MLCT) bands at 530 and 418 nm, respectively (Figure 2). The emission bands from the excited states,  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{pbn}^{\bullet-})]^{2+*}$  and  $[\text{Ru}^{\text{III}}(\text{bpy})(\text{bpy}^{\bullet-})(\text{pbnHH})]^{2+*}$ , appeared at 550 and 650 nm, respectively (Figure S4A). The intensity of the 550 nm emission band of  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+*}$  decreased with the addition of  $\text{Et}_3\text{N}$  to the solution (Figure S4A). The reductive quenching of  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{pbn}^{\bullet-})]^{2+*}$  by  $\text{Et}_3\text{N}$  was followed by the protonation of the resultant  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{pbn}^{\bullet-})]^+$  and the subsequent disproportionation of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{pbnH}^{\bullet})]^{2+}$  generates the two electron-reduced  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{pbnHH})]^{2+}$  and the original  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{pbn})]^{2+}$ .

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



**Figure 2.** Electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  (red line) and  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$  (blue line) in  $\text{CH}_3\text{CN}$ .

excess amount of Et<sub>3</sub>N because of the extremely short lifetime of its excited state (Figure S4B). Thus, [Ru(bpy)<sub>2</sub>(pbn)]<sup>2+</sup> was smoothly reduced to [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> in the presence of Et<sub>3</sub>N under photoillumination, while [Ru<sup>II</sup>(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> was inert under the similar conditions.

Therefore we examined the reactivity of [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup> against CO<sub>2</sub>. The UV/Vis absorption spectrum of [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup> generated by means of the electrolysis of [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> (0.2 mM) at -1.7 V in CH<sub>3</sub>CN containing 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> (Figure S5 dashed black line) showed a band at 420 nm but no absorption band above 500 nm. An addition of CO<sub>2</sub>-saturated CH<sub>3</sub>CN 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)<sub>2</sub>(pbn)]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> (Figure S2), which also indicated the occurrence of hydride transfer from [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup> to CO<sub>2</sub>.

BIH acts as a good sacrificial electron donor in photochemical reactions.<sup>[38]</sup> The one-electron oxidation of BIH ( $E_{1/2} = -0.07$  V vs. Fc/Fc<sup>+</sup>) in the presence of a base is followed by the proton releases, in which the rate of the deprotonation of BIH<sup>\*</sup> was  $k_{dp} = 1.1 \times 10^5$  M<sup>-1</sup>s<sup>-1</sup>.<sup>[38]</sup> The oxidation potential of the resultant BI<sup>\*</sup> is -2.06 V (vs. Fc/Fc<sup>+</sup>),<sup>[39]</sup> and negative enough to reduce [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> ( $E_{1/2} = -1.8$  V, Figure 1B) to produce [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup>. The TON of HCOO<sup>-</sup> increased from 8.8 to 41 (entries 1 and 2 in Table 2) when the concentration of [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> decreased from 1.0 to 0.2 mM. In addition, CO (0.66 μmol) was produced together with HCOO<sup>-</sup>. The stability of [Ru(bpy)<sub>2</sub>(pbn)]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> in CH<sub>3</sub>CN 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)<sub>3</sub>]<sup>2+</sup> in CH<sub>3</sub>CN is known to cause a partial release of a bpy ligand from the complex, and the resultant [Ru(bpy)<sub>2</sub>] species has an ability to reduce CO<sub>2</sub> to CO.<sup>[8]</sup> The coordinatively saturated Ru atoms in [Ru(bpy)<sub>2</sub>(pbn)]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> apparently have no ability to activate CO<sub>2</sub> at the Ru centers. The high selectivity of HCOOH formation in the present photochemical CO<sub>2</sub> reduction is ascribed to the hydride transfer from the renewable organic hydride of [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup> to CO<sub>2</sub>. When the concentration of [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> decreased to 0.1 and 0.05 mM, HCOO<sup>-</sup> were produced with TON=63 and 56, respectively

**Table 2.** Amounts of HCOO<sup>-</sup>, H<sub>2</sub>, and CO produced in the reduction of CO<sub>2</sub> by [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN/TEOA (9:1, v/v, 1 mL) with BIH (22 mM) under visible-light irradiation (48 h).

Entry	[Ru(bpy) <sub>2</sub> (pbn)](PF <sub>6</sub> ) <sub>2</sub> [mM]	Amount formed (TON)		
		HCOO <sup>-</sup> [mM]	H <sub>2</sub> [μmol]	CO [μmol]
1 <sup>[a]</sup>	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.

(entries 3 and 4 in Table 2). The <sup>13</sup>C NMR spectra of a CD<sub>3</sub>CN/TEOA (9:1, v/v, 1 mL) solution containing [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> (0.2 mM) and BIH (22 mM) under <sup>13</sup>CO<sub>2</sub> 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<sup>13</sup>COOH.<sup>[40]</sup> Furthermore, the similar photochemical CO<sub>2</sub> reduction using <sup>12</sup>CO did not display a signal assignable HCOOH in the <sup>13</sup>C NMR spectra under normal resolution conditions. Thus, all the HCOOH molecules produced in the present study resulted from CO<sub>2</sub>, and were safely ruled out the possibility of decomposition products of organic molecules.

The present photochemical CO<sub>2</sub> reduction produced formic acid accompanied by CO and H<sub>2</sub> 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<sub>2</sub> reduction in the initial 4 h clearly indicates that [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup> works as the active catalyst toward the organic hydride transfer to CO<sub>2</sub> generating formic acid.

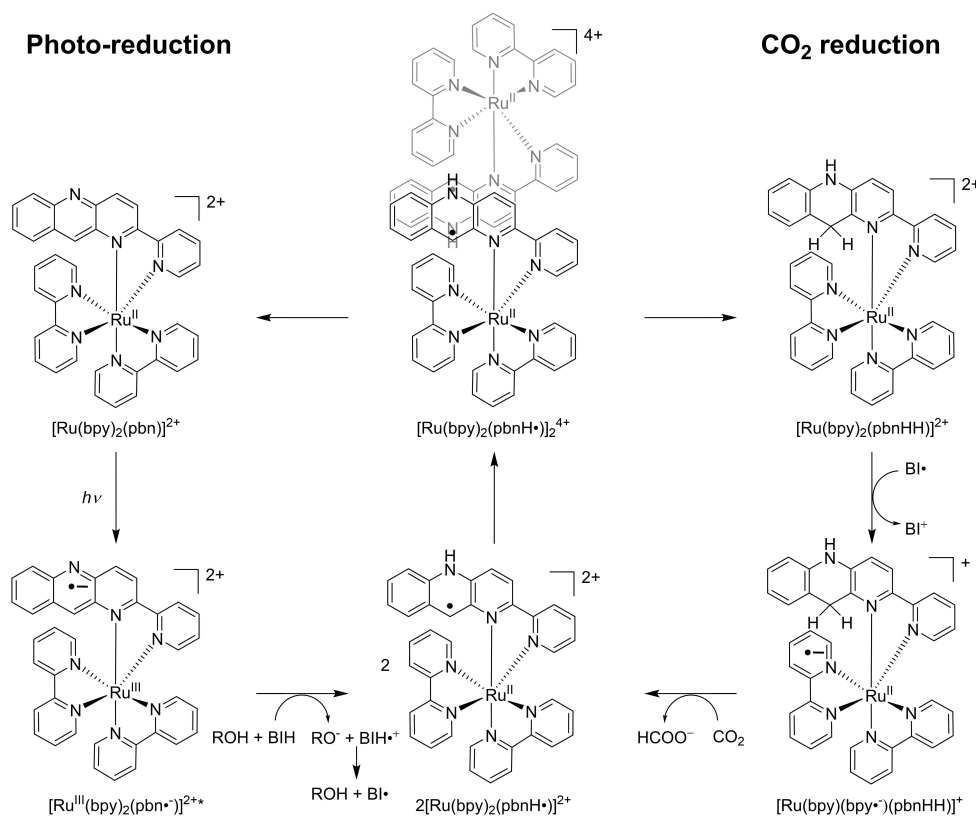
Photochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> in the presence of BIH and various proton sources was also conducted (see Table 3). When CH<sub>3</sub>COOH was used, HCOO<sup>-</sup> was formed with TON of 0.85 (entry 1 in Table 3). However, when EtOH was used instead, HCOO<sup>-</sup> was detected with a larger TON of 5 (entry 2 in Table 3). Similar photochemical CO<sub>2</sub> reduction in the presence of H<sub>2</sub>O as a proton source generated HCOO<sup>-</sup> with a TON of 41 (entry 3 in Table 3). Thus, [Ru(bpy)(bpy<sup>\*</sup>)(pbnHH)]<sup>+</sup> works as the active catalyst in the hydride transfer to CO<sub>2</sub> in the presence of EtOH or H<sub>2</sub>O as a proton source.

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

**Table 3.** Amounts of HCOO<sup>-</sup> and TON in the catalytic reduction of CO<sub>2</sub> by [Ru(bpy)<sub>2</sub>(pbn)](PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN in the presence of BIH (22 mM) and a proton source under visible light irradiation (48 h).

Entry	[Ru(bpy) <sub>2</sub> (pbn)](PF <sub>6</sub> ) <sub>2</sub> [mM]	Proton source [mL]	CH <sub>3</sub> CN [mL]	HCOO <sup>-</sup> [mM] (TON)
1	0.2	CH <sub>3</sub> COOH (0.05)	0.95	0.17 (0.85)
2	0.2	EtOH (0.1)	0.9	1.0 (5)
3	0.2	H <sub>2</sub> O (0.1)	0.9	8.1 (41)





**Scheme 3.** Proposed mechanism of the photoassisted catalytic hydride transfer to  $\text{CO}_2$  catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  in the presence of BIH and an ROH (i.e., TEOA, EtOH, or  $\text{H}_2\text{O}$ ) in  $\text{CH}_3\text{CN}$ .

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

## Conclusions

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

## Experimental Section

### General

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in  $\text{CD}_3\text{CN}$  were recorded using a JEOL AL-400 and ECA-600 spectrometers (400 and 151 MHz), respectively; residual  $\text{CD}_2\text{HCN}$  ( $\delta = 1.94$  ppm) and  $^{13}\text{CD}_3\text{CN}$  ( $\delta = 118.3$  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  $\text{HCOOH}$  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-50W voltametric analyzer with a conventional three-electrode system: cyclic voltammetry using an  $\text{Ag}/\text{Ag}^+$  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 ( $\text{Fc}/\text{Fc}^+$ ). Cyclic voltammograms were recorded in  $\text{CH}_3\text{CN}/0.1$  M  $\text{Bu}_4\text{NClO}_4$  with a scan rate of  $0.1$   $\text{V s}^{-1}$  at ca. 1 mM sample solutions. The fluorescence emission spectra were obtained using a Hamamatsu Photonics C9920-03G spectrometer.

### Materials

$[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$ ,<sup>[35]</sup>  $[\text{Ru}(\text{bpy})_2(\text{pbnHH})](\text{PF}_6)_2$ ,<sup>[35]</sup> and BIH<sup>[38,39]</sup> were prepared according to previously reported procedures. Solvents and reagents for preparation of compounds were obtained from commercial suppliers and utilized as supplied.  $\text{CO}_2$  for

photoinduced reduction was purchased from Nippon Ekitan, Tokyo, Japan.  $^{13}\text{CO}_2$  was prepared by the reaction of  $\text{Ba}^{13}\text{CO}_3$  (Isotec, US) with aqueous 5%  $\text{H}_2\text{SO}_4$ .  $\text{Et}_3\text{N}$  and TEOA used as electron sources,  $\text{CH}_3\text{COOH}$  and  $\text{EtOH}$  used as proton sources, and  $\text{CH}_3\text{CN}$  for a reduction solvent were purchased from Nacalai Tesque, Kyoto, Japan and used without further purification.  $\text{H}_2\text{O}$  used as a proton source was prepared as a distilled water by a YAMATO AutoStill WG250 system.

### Photoinduced catalytic $\text{CO}_2$ reduction

A typical procedure is as follows (entry 2 in Table 2). The mixture of  $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$  (196  $\mu\text{g}$ , 0.2  $\mu\text{mol}$ ) and BIH (5.0 mg, 22  $\mu\text{mol}$ ) was dissolved in dry  $\text{CH}_3\text{CN}/\text{TEOA}$  (9:1, v/v, 1 mL). To the reaction mixture was bubbling  $\text{CO}_2$  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

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