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Photocatalytic CO$_2$ reduction under visible-light irradiation by ruthenium CNC pincer complexes

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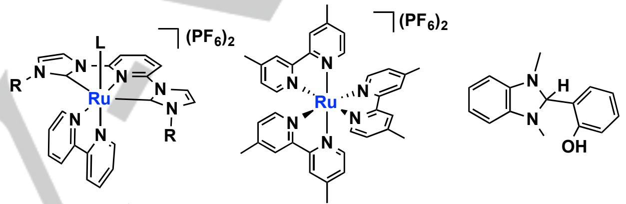
Abstract: Photocatalytic CO$_2$ reduction using a ruthenium photosensitizer, a sacrificial reagent (BI(OH)H) (1,3-dimethyl-2-(*o*-hydroxyphenyl)-2,3-dihydro-1*H*-benzo[d]imidazole), and a ruthenium catalyst were carried out. The catalysts contain a pincer ligand, 2,6-bis(alkylimidazol-2-ylidene)pyridine (CNC) and a bipyridine (bpy). Our photocatalytic reaction system resulted in HCOOH as a main product (selectivity 70 ~ 80%), a small amount of CO, and H$_2$. Comparative experiments (a coordinated ligand (NCMe vs. CO) and substituents (^{t}Bu vs. Me) of the CNC ligand in the catalyst) were performed. The TON$_{HCOOH}$ of carbonyl-ligated catalysts are higher than those of acetonitrile-ligated catalysts, and the carbonyl catalyst with the smaller substituents (Me) reached TON$_{HCOOH}$ = 5634 (24h), which is the best performance among the experiments.



L = NCMe, R = ^{t}Bu (**2a**)
L = NCMe, R = Me (**2b**)
L = CO, R = ^{t}Bu (**3a**)
L = CO, R = Me (**3b**)

[Ru(dmbpy)$_3$](PF$_6$)$_2$

BI(OH)H

Figure 1. Structures of catalysts, photosensitizer, and sacrificial reagent in this study.

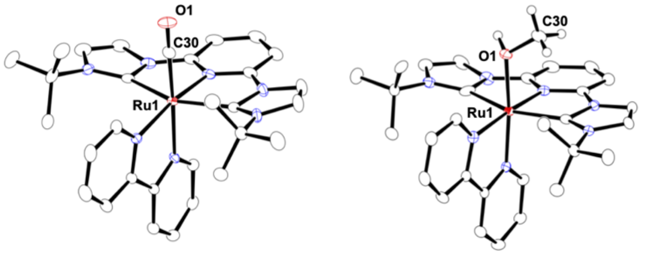


Figure 2. X-ray crystal structures of the cation part of [(^{tBu}CNC)Ru(bpy)(CO)](PF$_6$)$_2$ (**3a**) (left) and [(^{tBu}CNC)Ru(bpy)(HOMe)](PF$_6$)$_2$, (right). One of the two independent molecules of **3a** in the unit cell is shown. Thermal ellipsoids are set at 50% probability level. The counter PF$_6$ ions, crystallization solvents, and hydrogen atoms except for methanol protons in the methanol complex are omitted for clarity.

To realize a sustainable society, we must address the problem of energy/resource depletion. One possible solution is the use of carbon dioxide (CO$_2$), which is abundant and ubiquitous in the atmosphere. However, to do so CO$_2$ has to be reduced to useful substances, because it is the final carbon oxidation product. Ideally, sunlight (especially visible light) could be used as the energy for the reduction. Against this background, CO$_2$ reduction by visible light has been actively studied in recent years.[1]

Both homogeneous and heterogeneous[2] systems for CO$_2$ reduction have been explored. Although the latter is more practical, at present the former system appears to be more effective. The homogeneous system generally consists of a photosensitizer, a sacrificial reagent, and a catalyst which can be easily adjusted. Recently, the non-noble metal based molecular catalyst have been extensively investigated[1c, 3]. It has been proposed that the photosensitizer excited by visible light is reductively quenched by the sacrificial reagent to be a powerful reductant, and one electron is transferred from the reductant to the catalyst at a time.[1] Finally, CO$_2$ is reduced on the catalyst. In this study, we investigated the CO$_2$ reducing ability of ruthenium complexes having a 2,6-bis(alkylimidazol-2-ylidene)pyridine (CNC) ligand as the catalyst under visible light ($\lambda \geq 500$ nm) using a photosensitizer [Ru(dmbpy)$_3$](PF$_6$)$_2$ (dmbpy = 4,4'-dimethylbipyridine) and a sacrificial reagent BI(OH)H (1,3-dimethyl-2-(*o*-hydroxyphenyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole) which is very effective against this photosensitizer.[4] The performance of the catalyst was evaluated by the differences of substituents on the CNC ligand and ligands on the ruthenium atom. In 2015, we have reported that the CNC ruthenium complexes can readily incorporate CO$_2$ from air.[5a] This is the reason why we choose the CNC complexes as the catalyst. More recently, E. T. Papish et al. have reported several CO$_2$ reduction reactions using similar CNC complexes.[6] In this report, their comparisons are included.

We prepared four types of the CNC complexes; tert-butyl and methyl substituents on the CNC ligand and CH$_3$CN and CO ligands on ruthenium (Figure 1). Although

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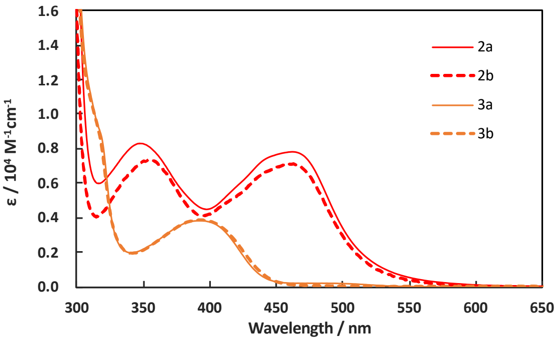

Figure 3. UV-vis absorption spectra of **2a**, **2b**, **3a**, and **3b**.

Table 1. The first reduction potentials of catalysts[a]

Complex	$E_{1/2}^{red}$ (V)[b]	E_{pc} (V)	E_{pa} (V)
2a	-1.39	-1.42	-1.35
2b	-1.47	-1.51	-1.43
3a	-1.21	-1.24	-1.17
3b	-1.24	-1.28	-1.19

[a] Measured in MeCN (1.0 mM). All values of the first reduction peaks are reported versus Ag/AgCl. Values are measured by CV in 0.1 M $^{n}Bu_4NPF_6$ using Pt counter and glassy carbon working electrode. [b] Quasi-reversible.

$[(^{R}CNC)Ru(bpy)Cl]PF_6$ (**1**) and $[(^{R}CNC)Ru(bpy)(NCMe)](PF_6)_2$ (**2**; [**Ru**-NCMe]) were prepared referring to literature methods,[5] $[(^{R}CNC)Ru(bpy)(CO)](PF_6)_2$ (**3**; [**Ru**-CO]) were synthesized by the substitution reactions of **1** in the presence of $AgPF_6$ through MeOH-ligated intermediates, which are confirmed as $[(^{tBu}CNC)Ru(bpy)(HOMe)](PF_6)_2$ by X-ray crystallographic analysis (Figure 2).

The UV-visible (UV-vis) absorption spectra of **2** and **3** are shown in Figure 3. According to a literature,[7] the lowest-energy transitions would contain $d_{\pi}(Ru) \rightarrow \pi*(bpy)$ MLCT without $d_{\pi}(Ru) \rightarrow \pi*(^{R}CNC)$ MLCT character. Compared to **2**, **3** display a significant blue shift in the lowest-energy absorption bands, because complexes **3** have a carbonyl ligand which lower the $d_{\pi}(Ru)$ energy level due to π-back donation. It is clear that the [**Ru**-NCMe] (**2a** and **2b**) absorb the irradiated light (≥ 500 nm), but not the [**Ru**-CO] (**3a** and **3b**). Cyclic voltammetry (CV) was used to evaluate the efficacy of complexes **2** and **3** to reduce CO_2 (Table 1 and Figure S1). Their first reduction waves, which are quasi-reversible, would be attributed to the bpy-based redox $(bpy^{\bullet-}/bpy)$. Although the effect of substituent groups (^{t}Bu vs. Me) of the CNC ligand on the redox potentials was small, the axial ligands (NCMe vs. CO) affected largely to their redox potentials. The reduction potentials of [**Ru**-CO] (**3a** and **3b**) are more positive than those of [**Ru**-NCMe] (**2a** and **2b**), which is reasonable because of the strong electron-withdrawing character of CO ligand. In any case, the electron transfer from the photosensitizer $[Ru(dmbpy)_3]^{2+}$ ($E_{1/2}(PS^{-}/PS)$ = –1.74 V vs. $Ag/AgNO_3$)[8] to their catalysts would be exergonic processes.

Photocatalytic CO_2 reduction was performed in a glass tube containing DMA/TEOA (dimethylacetamide/triethanolamine) (5.0 mL, 4:1 v/v), catalyst **2** or **3** (10 μM), $[Ru(dmbpy)_3](PF_6)_2$ (50 μM), and BI(OH)H (0.10 M). The CO_2-saturated solution was irradiated at λ ≥ 500 nm using a 450 W high-pressure Hg lamp combined with a K_2CrO_4 solution filter. Formate was analyzed by capillary electrophoresis, while the gaseous products (CO and H_2) were analyzed by gas chromatography (GC-TCD). Table 2 summarizes the results of the photocatalytic reactions and total turnover numbers of the reduced products are shown in Figure 4. The time courses of obserbed products (TON) using **3b** are shown in Figure 5. Use of complexes **2** and **3** led to formation of formic acid as a main product with H_2 and a small amount of CO (entry 1-4). Best performance is TON_{HCOOH} = 5634 (24h) for **3b** (entry 4). Even in the absence of the catalyst, a small amount of HCOOH and CO were detected because decomposition of the photosensitizer $[Ru(dmbpy)_3]^{2+}$ would generate other active catalysts (entry 5).[1e] However, presence of the catalyst (**2** or **3**) increased the total amount of the reduced products (HCOOH and CO) more than about 10 folds. Control experiments in the absence of the photosensitizer (entry 6), the

Table 2. The results of photocatalytic CO_2 reduction for 24 h[a], [b]

				Product (μmol)			TON (selectivity %)		
Entry	Catalyst	Sensitizer	Sacrificial reagent	HCOOH	CO	H_2	HCOOH	CO	H_2
1	**2a**	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	165	6.5	28	3296 (83)	129 (3)	556 (14)
2	**2b**	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	230	11	72	4593 (73)	224 (4)	1438 (23)
3	**3a**	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	190	6.5	25	3792 (86)	129 (3)	505 (11)
4	**3b**	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	282	15	95	5634 (72)	300 (4)	1897 (24)
5	–	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	21	3	8.9	-	-	-
6	**3b**	–	BI(OH)H	0	0.43	4.4	0	8.6 (9)	87 (91)
7	**3b**	$[Ru(dmbpy)_3]^{2+}$	–	0	~ 0	1	0	~ 0	20 (100)
8[c]	**3b**	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	0	0	15	0	0	307 (100)
9[d]	**3b**	$[Ru(dmbpy)_3]^{2+}$	BI(OH)H	0	0	0	0	0	0

[a] In a typical run, a CO_2-saturated DMA/TEOA (4/1) solution containing the catalyst (10 μM), sensitizer (50 μM), and sacrificial reagent (0.1 M) was irradiated for 24h using a 450 W high-pressure Hg lamp combined with a K_2CrO_4 solution filter under CO_2 atmosphere. [b] Products (μmol) values were averaged over three reactions. [c] Under Ar atmosphere. [d] Under dark. TON = mol number of the product/mol number of the catalyst.

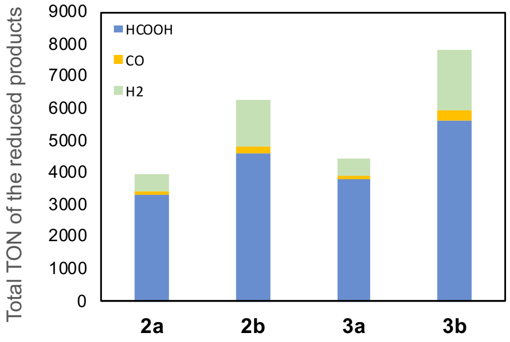

Figure 4. Total turnover number (TON) graphs of the reduced products (HCOOH, CO, and H_2) after 24 h.

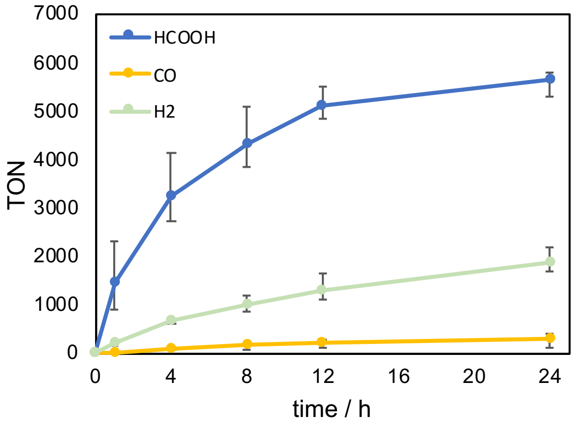

Figure 5. Turnover numbers (TON) for formation of HCOOH, CO, and H_2 as a function of irradiation time during photocatalytic reaction of **3b**. Each data point is the average of three runs.

sacrificial reagent (entry 7), or CO_2 (entry 8) led to no formation of HCOOH. Catalyst **3b** can function both as a photosensitizer and a catalyst, but the performance was very low (TON_{CO} = 8.6) (entry 6). Even under Ar, H_2 was detected (TON_{H2} = 307) in our photocatalytic reaction conditions (entry 8).

Isotopic labeling experiment under $^{13}CO_2$ atmosphere was performed to determine the source of the carbon atoms in the produced formic acid. Before irradiation, in the $^{13}C\{^1H\}$ NMR spectrum of a DMF-d_7/TEOA (4:1 v/v) solution consisting of catalyst **3b** (10 μM), $[Ru(dmbpy)_3](PF_6)_2$ (50 μM), and BI(OH)H (0.10 M), a signal assignable to $^{13}CO_2$ is observed at 125.2 ppm (Figure S3). Irradiation resulted in both decrease of the $^{13}CO_2$ signal and appearance of a signal at 167.2 ppm, which is assignable to an equilibrium mixture of $H^{13}COOH$ and $H^{13}COO^-$ [4]. The ^1H NMR spectra confirmed the formation of the labeled formic acid (8.56 ppm, a doublet signal, $^1J_{CH}$ = 185 Hz) along with trace amount of signal for the non-labeled formic acid (Figure S4). These results clearly show that the formic acid originated from the reduction of CO_2.

The similar CNC ruthenium complex, $[(CNC^{OMe})RuCl(NCMe)_2]OTf$, where a 4-methoxy group is introduced to the pyridyl moiety in CNC ligand, has been reported.[6a,b] The use of this complex for the photocatalytic CO_2 reduction in CH_3CN with photosensitizer $[Ir(ppy)_3]$ resulted in selective production of CO (TON_{CO} = 227 (selectivity 97%)), but in DMF with photosensitizer $[Ru(bpy)_3]^{2+}$ production of formate was dominant (TON_{HCOOH} = 143 (selectivity 90%)). More recently, alternation of imidazole to benzimidazole moiety and coordination of a bpy ligand led to formation of CO (TON_{CO} = 55) without photosensitizer.[6c] Interestingly, the low loading of the catalyst (1.0 nM) afforded TON_{CO} = 33,000. In contrast, our system shows high performance in the photocatalytic CO_2 reduction, leading to production of formate.

Comparison of TON (24 h) of HCOOH based on differences in the axial ligands ([**Ru**-NCMe] vs. [**Ru**-CO]) showed that TON_{HCOOH} (24 h) of [**Ru**-CO] (**3a** and **3b**) are higher than those of [**Ru**-NCMe] (**2a** and **2b**), respectively. This may be due to the presence of the absorption band ($\lambda \geq 500$ nm) in [**Ru**-NCMe], which reduce the performance of the catalyst. Alternatively, differences in the substituents (R = ^{t}Bu vs. Me) resulted in higher TON for the catalyst having Me substituents (**2b** and **3b**), but with lower selectivity of HCOOH because of increment of H_2 production. The steric hindrance of the ^{t}Bu substituents should account for the results.[9] The bulkier substituents (^{t}Bu) should prevent access of CO_2 to the metal center, whereas the smaller substituents (Me) should allow access of protons as well as CO_2 to the metal center, leading to lower selectivity of HCOOH.

In summary, we achieved TON_{HCOOH} = 5634 (selectivity 72%) (24h) by photocatalytic CO_2 reduction using visible light. Our ruthenium catalysts contain a CNC and a bpy ligands. The carbonyl complex with smaller substituents (Me groups) (**3b**) resulted in the best performance within the four complexes.

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Keywords: photocatalytic CO_2 reduction • pincer ligand • ligand effect • carbonyl complexes • ruthenium

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[9] see ref. 6c; Similar steric effect in the photocatalytic CO_2 reduction has been observed using the analogous CNC complex with Me or Ph substituents. The performance of the complex with smaller substituents (Me groups) is better than that of the other complex (Ph groups).

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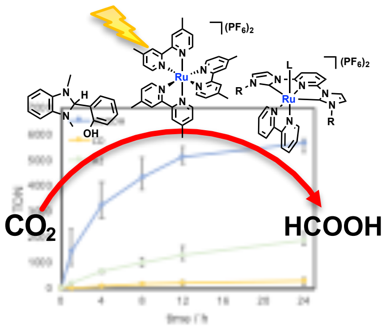

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