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Carbon–Carbon Bond Formation in the Electrochemical Reduction of Carbon Dioxide Catalyzed by a Ruthenium Complex

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A carbonyl ligand of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (**1**) (bpy = 2,2′-bipyridine) or $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (**2**) (trpy = 2,2′:6′,2″-terpyridine) is reversibly converted to hydroxycarbonyl and η^1-CO_2 moieties by treatment with OH^-. **1** and **2** also react with $NaBH_4$ to afford CH_3OH *via* formyl and hydroxymethyl complexes, and the molecular structures of **2** and $[Ru(bpy)_2(CO)(CH_2OH)]PF_6$ (**3**) were determined by X-ray structure analysis. Crystal data: **2**, $C_{26}H_{19}N_5OP_2F_{12}Ru$, monoclinic, space group $C2/c$, $a = 34.683(3)$ Å, $b = 10.168(2)$ Å, $c = 24.640(3)$ Å, $\beta = 133.35(1)°$, $V = 6318(1)$ Å^3, $Z = 8$, and $R = 0.046$ ($R_w = 0.060$) for 5844 data with $F_o > 3\sigma(F_o)$; **3**, $C_{22}H_{19}N_4O_2PF_6Ru$, monoclinic, space group $C2/c$, $a = 30.931(4)$ Å, $b = 7.487(1)$ Å, $c = 24.873(3)$ Å, $\beta = 124.68(1)°$, $V = 4736(1)$ Å^3, $Z = 8$, and $R = 0.059$ ($R_w = 0.070$) for 2880 data with $F_o > 3\sigma(F_o)$. The controlled-potential electrolysis of **2** at −1.75 V *vs* $Ag|Ag^+$ in CO_2-saturated C_2H_5OH/H_2O (8:2 v/v) at −20 °C produced HC(O)H, CH_3OH, H(O)CCOOH, and $HOCH_2COOH$ together with CO and HCOOH, while the electrochemical CO_2 reduction in the presence of **1** gave only CO and HCOOH under similar electrolysis conditions. The achievement of the multi-electron reduction of CO_2 by **2** as the first example in homogeneous reactions is ascribed to $[Ru(bpy)(trpy)(CHO)]^+$ formed by two-electron reduction of **2** in protic media.

Introduction

Much attention has been paid to electrochemical reduction of CO_2 as a potential C1 source for chemicals and fuels.[1,2] A variety of transition metal complexes have been shown to be active as catalyst precursors. The reduction products in those homogeneous reactions, however, have been limited to CO and HCOOH.[1] On the other hand, direct electrochemical reduction of CO_2 on a Cu electrode in H_2O affords highly reduced products such as CH_4, CH_2CH_2, C_2H_5OH, and C_3H_7OH in addition to CO and HCOOH.[2f] It is, therefore, highly desired to construct a homogeneous reaction system capable of multi-electron reduction of CO_2 accompanied by carbon–carbon bond formation to utilize CO_2 as a source for other organic products. Both metal–formato and metallocarboxylato complexes have been proposed as reaction intermediates in homogeneous electrochemical CO_2 reduction; the former is formed by CO_2 insertion into metal–hydride bonds, and the latter is generated by an electrophilic attack of CO_2 at low-valent metal centers.[1e,3] We have reported that $[Ru(bpy)_2(CO)_2]^{2+}$ exists as an equilibrium mixture with $[Ru(bpy)_2(CO)(C(O)OH)]^+$ and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (eqs 1 and 2) in

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \rightleftharpoons [Ru(bpy)_2(CO)(C(O)OH)]^+ \quad (1)$$

$$[Ru(bpy)_2(CO)(C(O)OH)]^+ + OH^- \rightleftharpoons [Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)] + H_2O \quad (2)$$

aqueous solutions,[4] and those three complexes are involved in the production of CO and HCOOH and in the CO_2 carrier in its electro- and photochemical reduction in protic media.[5] The reversible conversion between CO and CO_2 on Ru is also evidenced by the molecular structures of those complexes.[6] The smooth conversion from CO_2 to CO *via* C(O)OH on a Ru complex (eqs 1 and 2) implies that reduction and carboxylation of the carbonyl ligated on a Ru has fundamental significance not only for the multi-electron reduction of CO_2 but also for carbon–carbon bond formation. This paper describes chemical reactivities of the carbonyl ligands of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (**1**) and of $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (**2**) and the capability for the multi-electron reduction of CO_2 by those two complexes. A part of this study has been reported elsewhere.[7]

Experimental Section

Materials. *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$, [RuCl(bpy)(trpy)]Cl, $[Ru(dppe)_2(CO)_2](PF_6)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane), and $[Ru(dmpe)_2(CO)_2](PF_6)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane)

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were prepared according to the literature methods.[8-10] Sodium acenaphthylenide was prepared in a THF solution. CH_3CN was distilled over calcium hydride. Gaseous $^{13}CO_2$ was generated by addition of H_2SO_4 to $Ba^{13}CO_3$ (98 atom %), trapped at 77 K, and then allowed to evaporate slowly by warming to room temperature. Other chemicals were obtained as reagent grade.

Physical Measurements. Infrared spectra were obtained on a Shimadzu FTIR-8100 spectrophotometer. ^1H and ^{13}C NMR were measured on a JEOL EX270 spectrometer. Electronic absorption spectra were measured on a Hewlett Packard 8452A diode array spectrophotometer. FAB-mass and GC-mass spectra were obtained on a Shimadzu/Kratos Concept 1S and a Shimadzu GC-mass QP-1000EX, respectively. Elemental analyses were carried out at the Chemical Materials Center of the Institute for Molecular Science. Electrochemical measurements were performed with a Hokuto Denko HAB-151 potentiostat and a Riken Denshi Co. F-72F X-Y recorder using a glassy-carbon disk working electrode (ϕ = 3 mm), a Pt auxiliary electrode, and an $Ag|Ag^+$ reference electrode purchased from BAS Co.[11]

Preparations. *cis*-$[Ru(bpy)_2(CO)_2](PF_6)_2$ (1). An aqueous solution (50 mL) of *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ (500 mg) was heated at 140 °C under 20 atm of CO for 24 h. The solution was cooled to room temperature and filtered to remove insoluble materials. An aqueous solution of NH_4PF_6 (350 mg/5 mL) was added to the filtrate, and then the mixture was kept in a refrigerator for 2 h. Pale yellow *cis*-$[Ru(bpy)_2(CO)_2](PF_6)_2$ was collected by filtration, washed with H_2O, and dried *in vacuo*. Yield: 80%. IR spectrum (KBr): $\nu(C\equiv O)$ 2091, 2039 cm^{-1}.

$[Ru(bpy)(trpy)(CO)](PF_6)_2$ (2). This complex was prepared by a procedure similar to that for *cis*-$[Ru(bpy)_2(CO)_2](PF_6)_2$ by using *cis*-[RuCl(bpy)(trpy)]Cl (500 mg) in place of $[RuCl_2(bpy)_2]\cdot 2H_2O$. Yield: *ca* 80%. Anal. Calcd for $C_{26}H_{19}N_5OP_2F_{12}Ru$: C, 38.63; H, 2.37; N, 8.66. Found: C, 38.67; H, 2.43; N, 8.63. IR spectrum (KBr): $\nu(C\equiv O)$ 2004 cm^{-1}. Electronic absorption spectrum: λ_{max}/nm ($\epsilon/mol^{-1}\cdot cm^{-1}$) 264 ($4.01 \times 10^4$), 284 ($4.01 \times 10^4$), and 316 ($3.20 \times 10^4$) in CH_3CN.

***cis*-$[Ru(bpy)_2(CO)(CH_2OH)]PF_6$ (3).** To a CH_3CN solution (10 mL) of *cis*-$[Ru(bpy)_2(CO)_2](PF_6)_2$ (200 mg) at −20 °C, an aqueous solution of $NaBH_4$ (20 mg/2 mL) was added under N_2 atmosphere. The mixture was allowed to stand for 2 h at −10 °C. Concentration of the resulting red solution by one-fourth gave an orange powder, which was collected by filtration and dried *in vacuo*. Yield: 80%. Anal. Calcd for $C_{22}H_{19}N_4O_2PF_6Ru$: C, 42.80; H, 3.10; N, 9.07. Found: C, 42.67; H, 3.38; N, 9.14. IR spectrum (KBr): $\nu(C\equiv O)$ 1925 cm^{-1}. ^1H NMR (270 MHz, CD_3CN): δ 4.34, 4.37, 4.45, and 4.47 (AB pattern of C^*H_2OH, J_{AB} = 7.24 Hz). FAB-mass spectrum: (M + Na) and (M − PF_6). Electronic absorption spectrum: 248 (5.80×10^4), 282 (6.43×10^4), 346 (1.40×10^4), and 460 (7.01×10^3) in CH_3CN.

$[Ru(bpy)(trpy)(C(O)OH)]PF_6\cdot 1.5H_2O$. A CH_2ClCH_2Cl solution (50 mL) of $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (50 mg) was stirred in the presence of the solid $(CH_3)_4NOH\cdot 5H_2O$ (30 mg) for 15 h under N_2, resulting in a deep violet solution. This mixture was filtered to remove unreacted $(CH_3)_4NOH\cdot 5H_2O$. After the solution was concentrated to one-fifth volume under reduced pressure, diethyl ether (10 mL) was added resulting in a deep violet precipitate. This was collected by filtration and dried *in vacuo*. Yield: 50%. Anal. Calcd for $C_{26}H_{23}N_5O_{3.5}PF_6Ru$: C, 44.14; H, 3.28; N, 9.90. Found: C, 44.40; H, 3.75; N, 9.98. IR spectrum (KBr): $\nu(C{=}O)$ 1653 cm^{-1}. FAB-mass spectrum: ((M − PF_6) + H). Electronic absorption spectrum: 240 (3.73×10^4), 282 (3.25×10^4), 294 (3.61×10^4), 318 (3.25×10^4), and 502 (1.22×10^4) in CH_3CN.

X-ray Structure Analysis. The single crystals of **2** and **3** were obtained by diffusing diethyl ether over a CH_3CN solution of **2** and **3**. A yellow cubic crystal of **2** and a red prismatic crystal of **3** having approximate dimensions of 0.25 × 0.25 × 0.27 mm and 0.35 × 0.33 × 0.21 mm, respectively, were mounted on glass fiber with epoxy resin. Crystal data are summarized in Table 1. The reflections were collected by the θ-2θ scan technique ($2\theta < 55°$ for **2** and $2\theta < 50°$ for **3**) on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The 5844 and 2880 independent reflections for **2** and **3** with $|F_o| > 3\sigma(|F_o|)$ were used for the structure refinements. All the calculation were carried out on a Silicon Graphics IRIS indigo computer system using TEXSAN.[12] The structures were solved by direct methods and expanded using Fourier techniques. Empirical absorption corrections were made using the program DIFABS,[13] resulting in transmission factors ranging from 0.90 to 1.15 for **2** and from 0.92 to 1.20 for **3**. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in idealized positions. Refinements were carried out using full-matrix least-squares procedures. The final atomic coordinates and temperature factors are available as supplementary material.

Table 1. Crystal Data for $[Ru(bpy)(trpy)(CO)](PF_6)_2$ and $[Ru(bpy)_2(CO)(CH_2OH)]PF_6$

	$[Ru(bpy)(trpy)(CO)](PF_6)_2$	$[Ru(bpy)_2(CO)(CH_2OH)]PF_6$
formula	$C_{26}H_{19}N_5OP_2F_{12}Ru$	$C_{22}H_{19}N_4O_2PF_6Ru$
fw	808.47	617.45
a, Å	34.683(3)	30.931(4)
b, Å	10.168(2)	7.487(1)
c, Å	24.640(3)	24.873(3)
β, deg	133.35(1)	124.68(1)
V, Å3	6318(1)	4736(1)
Z	8	8
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)
T, °C	23	23
λ, Å	0.710 69	0.710 69
D_{calcd}, g cm^{-3}	1.70	1.73
μ, cm^{-1}	6.99	8.05
tot. no. of data collcd	7558	4514
no. of idp data	5844	2880
no. of variables	424	325
final R/R_w[a]	0.046/0.060	0.059/0.070

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.

Stoichiometry of the Reaction of 2 with OH^-. The stoichiometry of the reaction between **2** and OH^- was determined by the change in the absorbance at 502 nm of the electronic absorption spectra of CH_3CN solutions containing various concentrations of **2** and a methanolic solution of Bu_4NOH (3.64×10^{-1} mol L^{-1}) under the total concentration of 2.48×10^{-4} mol L^{-1}.

Reaction of 1 and 2 with $NaBH_4$. A given amount (25–200 μL) of an aqueous $NaBH_4$ solution (0.50 mmol L^{-1}) was added to CH_3CN solutions (1.0 mL) of **1** or **2** (25 μmol) at −20 °C, and the solution was stirred for 30 min at that temperature. After the mixture was warmed to room temperature, it was stirred for 4 h. The amount of CH_3OH formed was then determined by GC. The measurement of ^1H NMR spectra of the reaction of **1** or **2** with BH_4^- was conducted after mixing a CD_3CN solution of **1** and **2** (0.6 mL) with a given amount of an aqueous solution of $NaBH_4$ (40 μL) at −30 °C.

Reduction of Carbon Dioxide. The reduction of carbon dioxide was carried out under controlled-potential electrolysis in a CO_2-saturated C_2H_5OH/H_2O (8/2 v/v) solution containing **1** or **2** and LiCl as supporting electrolyte. This was performed in an electrolysis cell with two compartments: one for an Hg pool working electrode and an $Ag|Ag^+$ reference electrode and the other for a Pt auxiliary electrode, which is separated from the working electrode by a cation-exchange membrane (Nafion film). Both compartments were connected to a volumetric flask filled with Nujol through a stainless steel tube. Test solutions were saturated with CO_2 by bubbling for 30 min and stirred magnetically to attain the thermal equilibrium of CO_2 between liquid and gaseous phases. The controlled-potential electrolysis was performed with a Hokuto Denko HA-501 potentiostat, and the electricity consumed in the electrolysis was measured with a Hokuto Denko HF-201 coulometer.

Products Analysis. Gaseous products, CO and H_2, were sampled from the gaseous phase with a pressure-locked syringe at regular intervals in the electrolysis and analyzed on a Shimadzu GC-8A gas chromatograph equipped with a 2-m column filled with Molecular Sieve 13X at 40 °C using He as a carrier gas. The amounts of HC(O)H and CH_3OH in the solution were determined by a Hitachi 262-50 gas chromatograph equipped with a 2-m column filled with Gaskuropack 54 at 150 °C using He as a carrier gas. The amounts of HCOOH in the solutions were measured by a Shimadzu IP-3A isotachophoretic analyzer. Carboxylic acids, H(O)CCOOH and $HOCH_2COOH$, were first converted to H(O)-

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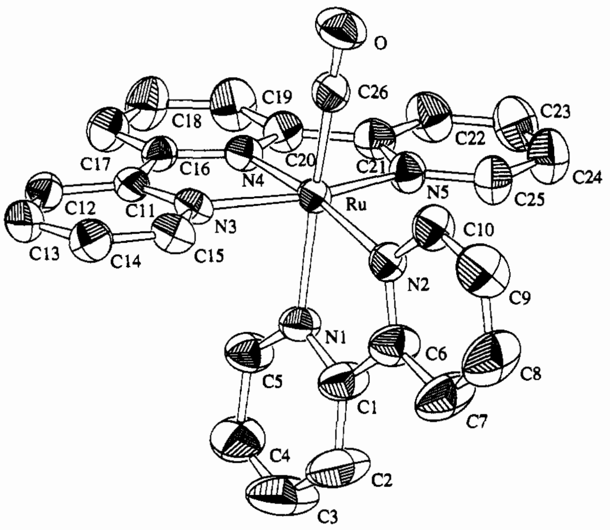

Figure 1. Molecular structure of $[Ru(bpy)(trpy)(CO)]^{2+}$ with atom labeling. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of $[Ru(bpy)(trpy)(CO)](PF_6)_2$

Ru–N1	2.114(3)	Ru–N5	2.086(3)
Ru–N2	2.093(3)	Ru–C26	1.844(4)
Ru–N3	2.086(3)	C26–O	1.160(4)
Ru–N4	1.988(3)		
N1–Ru–N2	77.9(1)	N4–Ru–N5	79.6(1)
N3–Ru–N4	78.7(1)	Ru–C26–O	175.2(3)

$CCOOCH_3$ and $HOCH_2COOCH_3$ by treatment of the crude products with CH_2N_2 in diethyl ether and then analyzed on a Shimadzu GCMS-QP1000EX.

Results and Discussion

Structure of $[Ru(bpy)(trpy)(CO)](PF_6)_2$. The molecular structure of $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (**2**) as an analog of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (**1**) was determined by X-ray structure analysis from the viewpoint of the reversible conversion among $[\mathbf{1}]^{2+}$, $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(CO_2)]$ in H_2O, which play key roles in the two-electron reduction of CO_2. **2** was prepared by the reaction of $[RuCl(bpy)(trpy)]^+$ with CO (20 atm) at 140 °C. The crystal structure of $[\mathbf{2}]^{2+}$ is depicted in Figure 1. The selected bond distances and angles in the molecules are listed in Table 2. The Ru–C26 (1.844(4) Å) and C26–O (1.160(4) Å) bond distances of **2** are shorter and longer than the Ru–C (1.865 and 1.906 Å) and C–O (1.144 and 1.125 Å) bond distances, respectively, of **1**. The short Ru–C26 and long C26–O bond distances of **2** compared with the corresponding bond distances of **1** may reflect the $\nu(C{\equiv}O)$ band at 2004 cm^{-1} for the former and those at 2093 and 2039 cm^{-1} for the latter.[6]

Reaction of 2 with Nucleophiles. A variety of hydroxycarbonyl complexes have been prepared by reactions of cationic carbonyl complexes with water and hydroxyl ion.[14] Although the equilibria among $[\mathbf{1}]^{2+}$, $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ in H_2O (eqs 1 and 2) are easily monitored by the characteristic electronic absorption spectra, the aqueous solution of **2** did not show any spectral changes in H_2O up to pH 13. By contrast, addition of a methanolic solution of Bu_4NOH (5.98×10^{-5}–2.39×10^{-4} mol L^{-1}) to a CH_3CN solution of **2** (2.39×10^{-4} mol L^{-1}) results in an appearance of an absorption band at 502 nm in the electronic absorption spectrum, and the absorbance of the band increased with increasing amounts of OH^- (Figure 2). The 502-nm band completely disappeared by addition of CF_3COOH to the solution. The change in the absorbance at the 502-nm band of the CH_3CN solutions containing various concentrations of **2** and a methanolic solution of Bu_4NOH with a total concentration of 2.48×10^{-4} mol L^{-1} (continuous variation method) demonstrated the 1:1 adduct formation (eq 3) but did

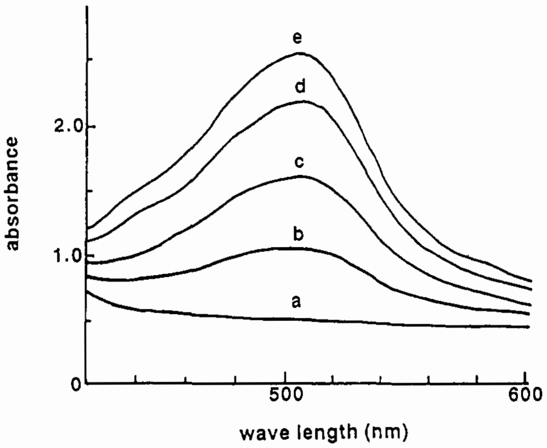

Figure 2. Electronic absorption spectra of $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (2.39×10^{-4} mol L^{-1}) in CH_3CN in the presence of various concentration of Bu_4NOH: 0 (a); 5.98×10^{-5} mol L^{-1} (b); 1.20×10^{-4} mol L^{-1} (c); 1.79×10^{-4} mol L^{-1} (d); 2.39×10^{-4} mol L^{-1} (e).

$$[Ru(bpy)(trpy)(CO)]^{2+} + OH^- \rightleftharpoons [Ru(bpy)(trpy)(C(O)OH)]^+ \quad (3)$$

$$[Ru(bpy)(trpy)(C(O)OH)]^+ + OH^- \rightleftharpoons [Ru(bpy)(trpy)(CO_2)] + H_2O \quad (4)$$

not give an evidence for a 1:2 stoichiometry (eq 4) in CH_3CN/CH_3OH. In accordance with this, the ^{13}C NMR spectrum for the 1:1 mixture of **2** in CD_3CN and a methanolic solution of Bu_4NOH showed a new signal at δ 208 assigned to the hydroxycarbonyl carbon of $[Ru(bpy)(trpy)(C(O)OH)]^+$ (eq 3) (δ 205 for $[Ru(bpy)_2(CO)(C(O)OH)]^+$).[6] The lack of a signal assigned to the CO_2 carbon of $[Ru(bpy)(trpy)(CO_2)]$ (eq 4) in the presence of excess of Bu_4NOH indicates that dissociation of the hydroxycarbonyl proton of $[Ru(bpy)(trpy)(C(O)OH)]^+$ (eq 4) is negligible in CH_3CN/CH_3OH. Concentration of the CH_3CN/CH_3OH solution of the 1:1 mixture of **2** and Bu_4NOH resulted in precipitation of deep violet $[Ru(bpy)(trpy)(C(O)OH)]PF_6$ ($\nu(C{=}O)$ 1634 cm^{-1}) together with a small amount of **2** ($\nu(C{\equiv}O)$ 2004 cm^{-1}). On the other hand, the IR spectrum of the products obtained by the reaction of **2** with a solid of $(CH_3)_4NOH$ (2.6 molar excess) in CH_3CN showed two new strong bands at 1464 and 1281 cm^{-1} in addition to the $\nu(C{=}O)$ band of $[Ru(bpy)(trpy)(C(O)OH)]PF_6$ at 1634 cm^{-1}.[15] From the comparison of the IR spectrum of $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ ($\nu(CO_2)$ 1428, 1213 cm^{-1}),[6] the 1464- and 1281-cm^{-1} bands are reasonably assigned to $\nu(CO_2)$ bands of $[Ru(bpy)(trpy)(\eta^1\text{-}CO_2)]$. Attempts to separate $[Ru(bpy)(trpy)(C(O)OH)]^+$ and $[Ru(bpy)(trpy)(CO_2)]$ from the crude products were unsuccessful. Quantitative regeneration of **2** by dissolution of the reaction products into H_2O also suggested the formation of both complexes in the reaction of **2** with $(CH_3)_4NOH$ in CH_3CN (eqs 3 and 4). The extent of the dissociation of the hydroxycarbonyl proton of $[Ru(bpy)(trpy)(C(O)OH)]^+$ (eq 4) appears to depend on the solvents, since the reaction of **2** with solid $(CH_3)_4NOH$ in CH_2ClCH_2Cl afforded a pure PF_6 salt of $[Ru(bpy)(trpy)(C(O)OH)]^+$.

Similar to **1**, the catalytic ability of **2** in electrochemical CO_2 reduction is inferred by analogy with the reversible conversion among CO_2, COOH, and CO on the Ru atom (eqs 3 and 4).

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[14] *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*; Sullivan, B. P., Krist, K., Guard, H. E., Eds.; Elsevier Science Publishers BV: Amsterdam, 1993; p 19–67.

[15] The $\nu(C{=}O)$ band of **2** completely disappeared in the IR spectrum of the crude product.

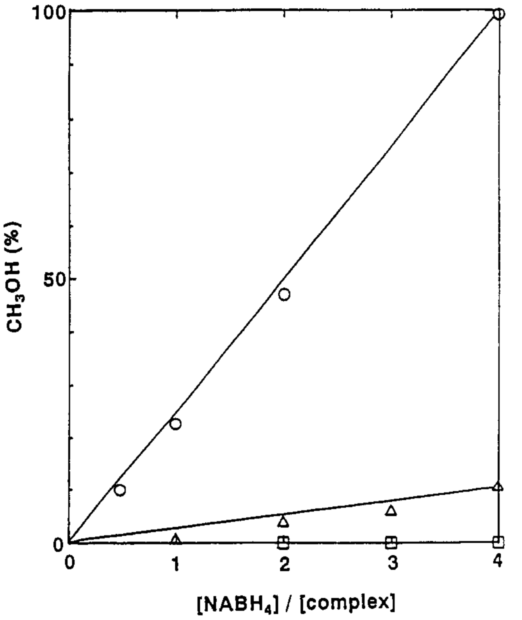

Figure 3. Yields of CH_3OH in the reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (△), $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (○), and $[RuL_2(CO)_2](PF_6)_2$ (L = dppe and dmpe) (□) with various amounts of $NaBH_4$ in CH_3CN/H_2O.

Although multi-electron reduction of CO_2 by homogeneous catalysts has not been reported so far, it may become feasible if the carbonyl ligands of **1** and **2** are reduced without fission of the Ru–CO bond. It is well-known that a cationic Re–carbonyl complex[16] is stepwise reduced to formyl, hydroxymethyl, and methyl complexes by BH_4^-. In addition, Os,[17] Fe,[18] Ir,[19] Mo, and W[20] formyl complexes are also reduced to methyl derivatives by treatments with various hydride donors. So, the reduction of the carbonyl ligands of **1** and **2** by BH_4^- was conducted. An aqueous solution of $NaBH_4$ was allowed to react with **1** and **2** at −20 °C for 30 min, and then the mixture was further stirred at room temperature for 4 h. GC analysis of the resulting solution revealed the formation of CH_3OH. The yield of CH_3OH increased with increasing the amount of BH_4^- used. Especially, the carbonyl ligand of **2** is quantitatively reduced to CH_3OH by treatment with 4 equiv of BH_4^- generating $[Ru(bpy)(trpy)(CH_3CN)]^{2+}$, while the carbonyl ligand of **1** is reduced to CH_3OH in a 10% yield under the same reaction conditions (Figure 3). Thus, the carbonyl ligand of **2** is much more subject to reduction than that of **1**. The ^1H NMR spectrum of the 1:1 mixture of **1** and $NaBH_4$ in CD_3CN/H_2O (15:1 v/v) at −20 °C showed a new signal at 13.9 ppm, which disappeared at 5 °C. After the reaction mixture was warmed to room temperature, an AB pattern (J_{AB} = 7.24 Hz) of methylene protons of $[Ru(bpy)_2(CO)(CH_2OH)]PF_6$ (**3**) (see below) emerged. These results indicate that **1** undergoes successive reduction by BH_4^- to afford $[Ru(bpy)_2(CO)(CHO)]^+$ and $[Ru(bpy)_2(CO)(CH_2OH)]^+$. The signal at 13.9 ppm observed at low temperature, therefore, is reasonably assigned to the formyl proton of $[Ru(bpy)_2(CO)(CHO)]^+$.[21] In addition, the reaction of **3** with 2 equiv of $NaBH_4$ in CH_3CN/H_2O for 4 h produced CH_3OH in a 9% yield. It is, therefore, concluded that **3** is the precursor to CH_3OH. Similarly, the ^1H NMR spectrum of the 1:1 mixture of **2** and $NaBH_4$ in CD_3CN/H_2O at −30 °C also showed a new signal at 14.0 ppm assignable to the formyl proton of $[Ru(bpy)(trpy)(CHO)]^+$ by analogy with the reaction of **1** with BH_4^-. The formyl proton signal slowly weakened in intensity at −20 °C and almost disappeared at −10 °C, suggesting that $[Ru(bpy)(trpy)(CHO)]^+$ is much more labile than $[Ru(bpy)_2(CO)(CHO)]^+$ in CH_3CN/H_2O. Although **3** was isolated in the reaction of **1** with BH_4^-, $[Ru(bpy)(trpy)(CH_2OH)]^+$ was not confirmed in careful measurement of temperature- and time-dependent ^1H NMR spectra of the mixture of **2** with BH_4^- in CD_3CN/H_2O. The quantitative generation of CH_3OH and $[Ru(bpy)(trpy)(CH_3CN)]^{2+}$ in the reaction of **2** with 4 equiv of BH_4^- (Figure 3) may, therefore, be explained by a rapid reaction of $[Ru(bpy)(trpy)(CH_2OH)]^+$ with proton (eq 5). It is worthy

$$[Ru(bpy)(trpy)(CH_2OH)]^+ + H^+ \rightarrow [Ru(bpy)(trpy)(CH_3CN)]^{2+} + CH_3OH \quad (5)$$

to note that the reaction of $[Ru(dppe)_2(CO)_2](PF_6)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) and $[Ru(dmpe)_2(CO)_2](PF_6)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with BH_4^- produce $[Ru(dppe)_2(CO)(CHO)]^+$ and $[Ru(dmpe)_2(CO)(CHO)]^+$,[22] but no CH_3OH was formed in those reactions even in the presence of large excess of BH_4^- (Figure 3).

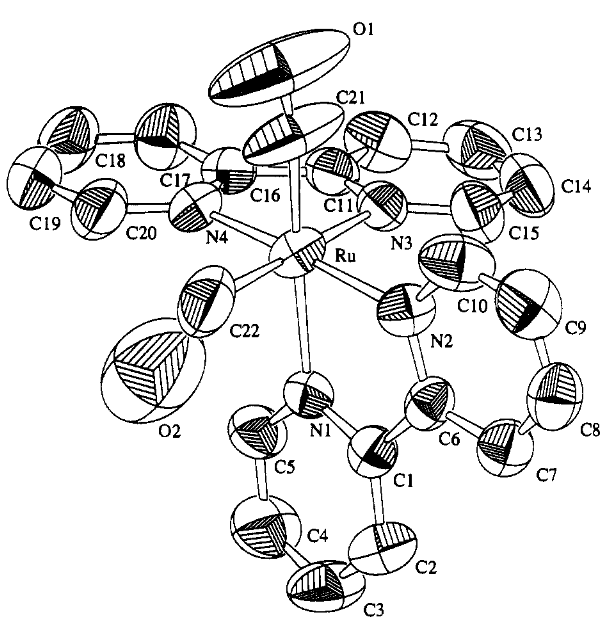

Figure 4. Molecular structure of $[Ru(bpy)_2(CO)(CH_2OH)]^+$ with atom labeling. Hydrogen atoms are omitted for clarity.

We have isolated hydroxymethyl complex **3** as the precursor to CH_3OH in the reaction of **1** with 1.5 equiv of BH_4^-. Although Re,[16] Os,[17] Fe,[18] and Ir[19] hydroxymethyl complexes have been characterized so far, the molecular structure by X-ray analysis has been determined only for $[Ir(H)(PMe_3)_4(CH_2OH)]PF_6$.[19a] The X-ray structure analysis of **3** reveals the octahedral coordination geometry with four nitrogen atoms of two bpy ligands and two carbon atoms of carbonyl and hydroxymethyl ligands as shown in Figure 4. The selected bond distances and angles in the molecules are listed in Table 3. The large thermal ellipsoids of carbon and oxygen atoms (C21, C22, O1, O2) of carbonyl and

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(16) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811–2815; *J. Organomet. Chem.* **1973**, *173*, C9–C12. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsey, S. G. *J. Mol. Catal.* **1981**, *13*, 43–59. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927–1933. (d) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371–3373. (e) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741–743.

(17) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49–C51.

(18) Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430–431.

(19) (a) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580–1586. (b) Thorn, D. L. *Organometallics* **1982**, *1*, 197–204; *J. Am. Chem. Soc.* **1980**, *102*, 7109–7110.

(20) Treichel, O. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328–1334.

(21) The ^{13}C NMR spectrum of mixture of **1** and 1 equiv of $NaBH_4$ in CD_3CN/H_2O at −20 °C showed carbonyl carbon at δ 205 and formyl carbon at δ 269.

(22) (a) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M. Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2501–2507. (b) Barratt, D. S.; Glidewell, C.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1079–1081.

Table 3. Selected Bond Distances (Å) and Angles (deg) of $[Ru(bpy)_2(CO)(CH_2OH)]PF_6$

Ru-N1	2.125(6)	Ru-C21	1.85(1)
Ru-N2	2.058(6)	Ru-C22	2.09(1)
Ru-N3	2.151(6)	C21-O1	1.11(1)
Ru-N4	2.073(6)	C22-O2	1.30(1)
N1-Ru-N2	78.2(2)	Ru-C21-O1	170(1)
N3-Ru-N4	77.4(2)	Ru-C22-O2	108.4(8)

hydroxymethyl ligands may be due to the disorder between these two sites or around the Ru-C21 and Ru-C22 bonds. The Ru-C-O angle (Ru-C22-O2 108.4(8)°) is an indication of the coordination to Ru with the sp^3 hybrid carbon of the hydroxymethyl group. The $Ru-CH_2OH$ bond distance (Ru-C22 = 2.09(1) Å) is longer than the Ru-CO bond distance (Ru-C21 = 1.85(1) Å). Furthermore, the long Ru-C22 bond distance of the $Ru-CH_2OH$ moiety of **3** compared with those of the $Ru-CO_2$ (2.06(1) Å) and $Ru-C(O)OCH_3$ (2.042(6) Å) ones for $[Ru(bpy)_2(CO)(\eta^1-CO_2)]$ and $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$, respectively,[6] may also reflect the bond characters of those Ru-C bonds. Other bond distances and angles of the bpy ligands are similar to those in other ruthenium complexes containing those ligands.[6,23]

Reduction of Carbon Dioxide. The cyclic voltammogram (CV) of **1** shows an irreversible two-electron reduction wave at -1.35 and -1.40 V *vs* Ag|Ag$^+$ at 20 °C and -20 °C, respectively, in CH_3CN under N_2 (solid lines in Figure 5a,b). On the basis of the fact that the irreversible two-electron reduction of **1** at room temperature results from the spontaneous Ru-CO bond cleavage,[5] **1** still readily loses CO upon two-electron reduction even at -20 °C. The CV of **2** at 20 °C displays an almost reversible $[Ru(bpy)(trpy)(CO)]^{2+/+}$ redox couple (E_{pc} = -1.39 and E_{pa} = -1.31 V) in the potential range of -1.0 to -1.6 V (Figure 5c). When the potential range is expanded to -1.9 V, one cathodic (-1.69 V) and two anodic waves (-1.46 and -1.20 V) newly appear in addition to the $[Ru(bpy)(trpy)(CO)]^{2+/+}$ couple (a solid line in Figure 5c). The weak anodic waves at -1.46 and -1.20 V presumably arise from an ECE process, since both the $[Ru(bpy)(trpy)(CO)]^{2+/+}$ (E_{pc} = -1.41 and E_{pa} = -1.33 V) and the $[Ru(bpy)(trpy)(CO)]^{+/0}$ (E_{pc} = -1.76 and E_{pa} = -1.62 V) redox couples clearly emerge at -20 °C, and the -1.46 and -1.20 V anodic waves completely disappear in the CV of **2** at that temperature (Figure 5d). The appearance of the $[Ru(bpy)(trpy)(CO)]^{+/0}$ couple at -20 °C indicates that the Ru-CO bond of $[Ru(bpy)(trpy)(CO)]^0$ is maintained at least in the CV time scale. The CVs of **1** and **2** in CO_2-saturated CH_3CN exhibit catalytic currents due to the reduction of CO_2 at potentials more negative than -1.6 V at 20 °C (dotted lines in Figure 5a,c). Thus, both complexes have the ability to catalyze electrochemical CO_2 reduction.

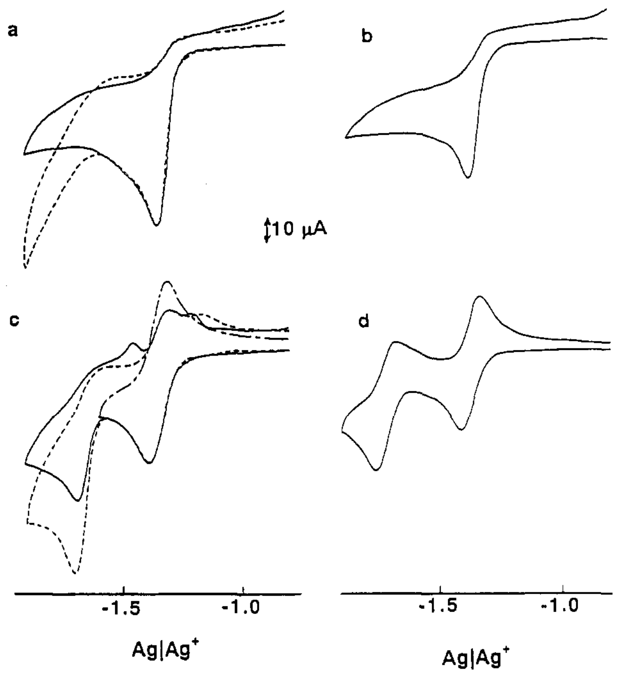

Figure 5. Cyclic voltammograms of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (2.05×10^{-3} mol L^{-1}) (a and b) and $[Ru(bpy)(trpy)(CO)](PF_6)_2$ (2.01×10^{-3} mol L^{-1}) (c and d) in CH_3CN under N_2 (solid lines) and CO_2 atmosphere (dotted lines).

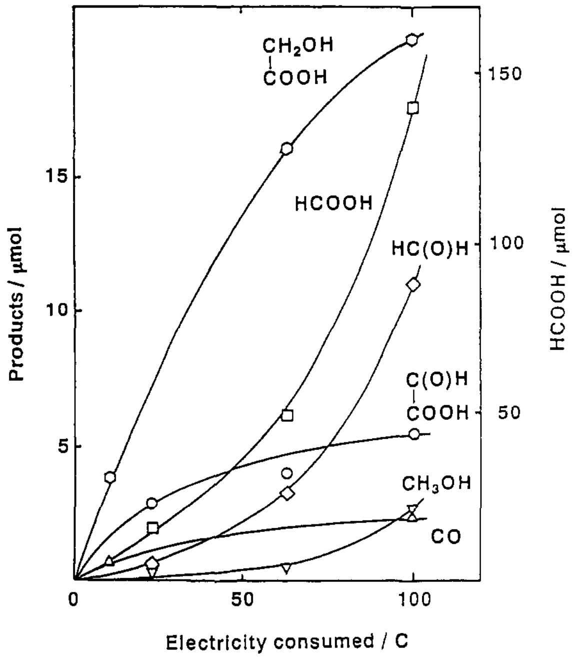

Figure 6. Plots of the amounts of CO (△), HCOOH (□), HC(O)H (◇), CH_3OH (▽), CH(O)COOH (○), and $CH_2(OH)COOH$ (○) *vs* the electricity consumed in the reduction of CO_2 by $[Ru(bpy)(trpy)(CO)](PF_6)_2$ under the controlled-potential electrolysis.

The controlled-potential electrolysis of **2** at -1.60 V in CO_2-saturated DMF/H_2O (2:8 v/v, pH 9) at room temperature produced CO, HCOOH, and H_2 with current efficiencies (η) of 35, 30, and 20%, respectively, and a trace amount of CH_3OH (η = 0.4%) was formed in the electrolysis. A green solid, however, gradually precipitated after about 80 C passed in the electrolysis. The stability of the catalyst in the electrochemical CO_2 reduction was improved in less protic solvents; the electrochemical CO_2 reduction by **2** in CO_2-saturated $EtOH/H_2O$ (8:2 v/v) at -1.70 V at room temperature also gave CO, HCOOH, and H_2 with a small amount of CH_3OH (η = 0.3%), but no precipitate was observed during the electrolysis. Although electrochemical reduction of CO_2 in the presence of **2** at room temperature afforded only a trace amount of CH_3OH as the six-electron reduction product, the same reduction conducted at -20 °C produced a variety of reduction products such as HC(O)H, H(O)CCOOH, $HOCH_2COOH$, and CH_3OH in addition to CO and HCOOH (Figure 6). Furthermore, the electrochemical $^{13}CO_2$ reduction by **2** under similar conditions gave $H(O)^{13}C^{13}COOH$ and $HO^{13}CH_2{}^{13}COOH$ (determined as $H(O)^{13}C^{13}COO^{12}CH_3$ and $HO^{13}CH_2{}^{13}COO^{12}CH_3$, respectively, by GC-mass). Thus, **2** has the ability to catalyze four- and six-electron reduction of CO_2 accompanied by carbon-carbon bond formation as the first example in homogeneous electrochemical reduction of CO_2. The electronic absorption spectrum of the electrolyte after reoxidation of the final solution at -0.5 V was almost consistent with that of the initial solution, and the IR absorption spectrum of the reaction

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(23) (a) Tanaka, H.; Tzeng, B.-C.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Organometallics* **1992**, *11*, 3171-3172. (b) Tanaka, H.; Nagao, H.; Tanaka, K. *Inorg. Chem.* **1992**, *31*, 1971-1973.

residue also showed the strong $\nu(C{\equiv}O)$ band of **2**. Thus, **2** is regenerated in the catalytic cycle of the present CO_2 reduction. On the other hand, neither CH_3OH, HC(O)H, H(O)CCOOH, nor $HOCH_2COOH$ was produced at all under the similar electrochemical reduction of CO_2 by **1** at −20 °C, and only CO and HCOOH were formed similar to the catalyzed reduction at 20 °C.

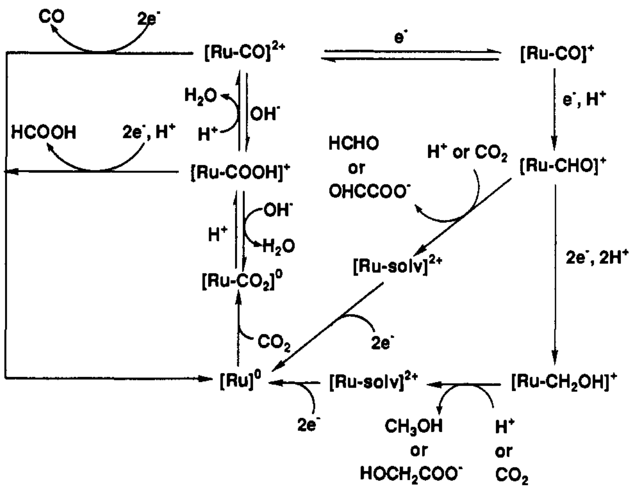
Possible Mechanism of CO_2 Reduction by 2. The reactions of **1** and **2** with BH_4^- in CH_3CN/H_2O produce CH_3OH, and both complexes catalyze electrochemical two-electron reduction of CO_2 affording CO and HCOOH at room temperature. By analogy to the reactivity of **1** and **2** toward OH^- (eqs 1–4), the two-electron reduction of CO_2 by **2** is inferred to proceed *via* $[Ru(bpy)(trpy)(CO_2)]$ and $[Ru(bpy)(trpy)(C(O)OH)]^+$ (eqs 6 and 7) similar to the reaction mechanism by **1**.[5] The remarkable difference between **1** and **2** in the multi-electron reduction of CO_2 at low temperature may be ascribed to the lability of $[Ru(bpy)_2(CO)_2]^0$ and the stability of $[Ru(bpy)(trpy)(CO)]^0$ at −20 °C. As expected from the reaction of **2** with BH_4^- at −20 °C, $[Ru(bpy)(trpy)(CHO)]^+$ is likely to be generated in the reaction of $[Ru(bpy)(trpy)(CO)]^0$ with proton. To confirm this, **2** was reduced by 1.9 equiv of a THF solution of sodium acenaphthylenide in CD_3CN at −20 °C, and then 1 equiv of H_2O was added to the solution at that temperature. The ^1H NMR spectrum of the solution at −20 °C showed a new broad peak centered at δ 13.7.[24] Although the chemical shift of the signal slightly differs from that of the formyl proton of $[Ru(bpy)(trpy)(CHO)]^+$ (δ 14.0, prepared by the reaction of **2** with BH_4^-), the δ 13.7 signal may be assigned to the formyl proton by attributing a paramagnetic shift to a contaminant such as $[Ru(bpy)(trpy)(CO)]^+$ in the solution. Furthermore, the δ 13.7 signal observed at −20 °C completely disappeared at −10 °C. Such thermal lability of the complex also supports the formation of $[Ru(bpy)(trpy)(CHO)]^+$ in the reaction of $[Ru(bpy)(trpy)(CO)]^0$ with a proton at −20 °C (eq 8). It has been suggested that alkali metal ions interact with carbonyl ligands in highly reduced organometallic complexes.[25] The reaction of eq 8 , therefore, may proceed *via* protonation of the electron-rich carbonyl oxygen of $[Ru(bpy)(trpy)(CO)]^0$, affording a kind of a hydroxyalkylidyne $[Ru(bpy)(trpy)(COH)]^+$, and a subsequent isomerization to the formyl complex $[Ru(bpy)(trpy)(CHO)]^+$.[3,26] We cannot, however, exclude another reaction path such as protonation of Ru(0) giving a seven-coordinated hydride Ru(II) complex, followed by a hydride migration to carbonyl carbon. The similar treatment of **1** with 2 equiv of sodium acenaphthylenide and then 1 equiv of H_2O at −20 °C did not show any signals assignable to the formyl proton around 14 ppm in the ^1H NMR spectrum. These results indicate that the reaction of the two-electron reduced form of **2** with proton is equivalent to that of **2** with hydride. On the other hand, the two-electron reduction of **1** readily causes the Ru–CO bond cleavage as expected from the irreversible cathodic wave in the CV of **1** at −20 °C. Thus, $[Ru(bpy)(trpy)(CHO)]^+$ is considered to be the key compound in the multi-electron reduction of CO_2 by **2**. The reduction of $[Ru(bpy)(trpy)(CHO)]^+$ in protic media will afford HC(O)H or $[Ru(bpy)(trpy)(CH_2OH)]^+$, the latter of which is the possible precursor to CH_3OH. Alternatively, carboxylation of $[Ru(bpy)(trpy)(CHO)]^+$ and $[Ru(bpy)(trpy)(CH_2OH)]^+$ possibly gives H(O)CCOOH and $HOCH_2COOH$,[27] respectively. The participation of $[Ru(bpy)(trpy)(CO)]^0$ and $[Ru(bpy)(trpy)(CHO)]^+$ in the catalytic cycle of the electrochemical reduction of CO_2 by **2** at −20 °C reasonably explains the formation of HC(O)H, CH_3OH, H(O)CCOOH, and $HOCH_2COOH$, as shown in Scheme 1. The lack of the capability of **2** in the multi-electron reduction of CO_2 at room temperature, therefore, is ascribed to the thermal lability of $[Ru(bpy)(trpy)(CO)]^0$. The view that protonation of the carbonyl ligand for the two-electron reduced form of **2** and the reduction of the carbonyl ligand of **2** by hydride gave the same product may provide a new catalytic system for the electrochemical reduction of both CO_2 and CO by homogeneous catalysts.

$$[Ru(bpy)(trpy)(CO)]^{2+} + 2e^- + CO_2 \rightarrow [Ru(bpy)(trpy)(CO_2)] + CO \quad (6)$$

$$[Ru(bpy)(trpy)(C(O)OH)]^+ + 2e^- + H^+ + CO_2 \rightarrow [Ru(bpy)(trpy)(CO_2)] + HCOOH \quad (7)$$

$$[Ru(bpy)(trpy)(CO)]^0 + H^+ \rightarrow [Ru(bpy)(trpy)(CHO)]^+ \quad (8)$$

Scheme 1



Acknowledgment. We thank Assistant Professor Hideki Masuda of Nagoya Institute of Technology for his advice on the X-ray structure analysis. This work was supported by a Grant-in Aid for Science Research No. 03453105 from the Ministry of Education.

Supplementary Material Available: For **1** and **3**, tables of atomic coordinates and thermal parameters and bond lengths and angles and ORTEP drawings with atomic labeling (22 pages). Ordering information is given on any current masthead page.

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(24) In the absence of H_2O, the formation of $[Ru(bpy)(trpy)(CHO)]^+$ was not confirmed in the ^1H NMR spectrum of CD_3CN/THF solution containing **2** and 1.8 equiv of sodium acenaphthylenide.

(25) Ellis, J. E.; Stein, B. K.; Frerichs, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 4066–4075.

(26) (a) Nicholas, K. M. *Organometallics* **1982**, *1*, 1713–1715. (b) Nevinger, L. R.; Keister, J. B.; Maher, J. *Organometallics* **1990**, *9*, 1900–1905.

(27) $HOCH_2COOH$ was also produced by direct reduction of H(O)CCOOH on a glassy-carbon electrode at −1.70 V in $EtOH/H_2O$ at −20 °C.