Comparative Study on Crystal Structures of $[Ru(bpy)_2(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4{\cdot}CH_3CN$, and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]{\cdot}3H_2O$ (bpy = 2,2′-Bipyridyl)

Hiroaki Tanaka, Biing-Chiau Tzeng,[†] Hirotaka Nagao, Shie-Ming Peng,[†] and Koji Tanaka[*]

Institute for Molecular Science, Department of Structural Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444, Japan

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The molecular structures of $[Ru(bpy)_2(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4{\cdot}CH_3CN$ as a model complex of $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]{\cdot}3H_2O$ have been determined by X-ray analysis. The observation that the Ru–C(O)OCH$_3$ bond distance of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ is shorter than the Ru–CO$_2$ one of $[Ru(bpy)_2(CO)(CO_2)]$ suggests that the multibond character of the Ru–CO$_2$ bond is not larger than that for Ru–C(O)OCH$_3$. One extra electron pair involved in $[Ru(bpy)_2(CO)(CO_2)]$ resulting from dissociation of a terminal proton of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ may be mainly localized in the CO$_2$ ligand rather than delocalized over the RuCO$_2$ moiety, and the extended three-dimensional network of hydrogen bonding between the CO$_2$ ligand and three hydrated water molecules compensates the increase in the electron density of the CO$_2$ moiety of $[Ru(bpy)_2(CO)(CO_2)]{\cdot}3H_2O$.

Introduction

Much attention has been paid to the activation of carbon dioxide on transition metal complexes.[1] Since the first characterization of $Ni(PCy_3)_2(\eta^2\text{-}CO_2)$,[3c] a variety of CO$_2$-metal complexes with η^1-,[2] η^2-,[3] μ^2-,[4] and μ^3-[5] CO$_2$ modes have been prepared. The η^1-CO$_2$ mode may be more suitable than other modes as active species in the reduction of CO$_2$ to CO and/or HCOOH, since $[M(\eta^1\text{-}CO_2)]^{n+}$ would be smoothly converted to $[M(C(O)OH)]^{(n+1)+}$ and $[M(CO)]^{(n+2)+}$. In high oxidation metal complexes, the η^1-CO$_2$ mode may be thermodynamically unstable due to an electronic repulsion between positively charged CO$_2$ carbon and metal atoms. The η^1-CO$_2$ mode, on the other hand, is favored by the charge-transfer interaction from the d_{z^2} orbital of the low oxidation metals such as Rh(I) and Co(I) to the π^* orbital of CO$_2$.[6] Despite intensive studies on catalytic CO$_2$ reduction by using homogeneous catalysts in recent years, there are only two reports[2] that determine the molecular structure of η^1-CO$_2$ complexes. It is, therefore, highly desired to elucidate the molecular structures of a series of η^1-CO$_2$, hydroxycarbonyl, and carbonyl metal complexes as possible active species in photo- and electrochemical CO$_2$ reductions.

We have reported that $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridyl) exists as equilibrium mixtures with $[Ru(bpy)_2(CO)(C(O)OH)]^+$ and its deprotonated species $[Ru(bpy)_2(CO)(CO_2)]$ (eqs 1 and 2) with the equilibrium constants, K_1

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \overset{K_1}{\rightleftharpoons} [Ru(bpy)_2(CO)(C(O)OH)]^+ \quad (1)$$

$$[Ru(bpy)_2(CO)(C(O)OH)]^+ + OH^- \overset{K_2}{\rightleftharpoons} [Ru(bpy)_2(CO)(CO_2)] + H_2O \quad (2)$$

and K_2, of 1.32×10^5 and 2.27×10^4 mol^{-1} dm^3, respectively, in H$_2$O, and the interconversion between $[Ru(bpy)_2(CO)(CO_2)]$ and $[Ru(bpy)_2(CO)(C(O)OH)]^+$ takes place in a diffusion-controlled reaction.[7] Those complexes function as active species in not only a water gas shift reaction[8] but also electro-[9] and photochemical[10] CO$_2$ reductions. Furthermore, two-electron reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ in dry CH$_3$CN under CO$_2$

[†] Department of Chemistry, National Taiwan University, Roosevelt Road Section 4, Taipei, Taiwan, Republic of China.

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(11) A prolonged electrolysis of $[Ru(bpy)_2(CO)(CO_2)]$ at −1.10 V in dry CH$_3$CN results in a slow decomposition of the η^1-CO$_2$ complex even under a CO$_2$ atmosphere.[9] Therefore, reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ under anhydrous conditions with CO$_2$ is not suitable for the synthesis of pure $[Ru(bpy)_2(CO)(CO_2)]$.

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Table I. Data for Crystal Structure Analysis of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$, $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$, and $[Ru(bpy)_2(CO)_2](PF_6)_2$

formula	$C_{22}H_{22}N_4$-O_6Ru	$C_{49}H_{42}O_3N_5$-BRu	$C_{22}H_{16}F_{12}N_4$-O_2P_2Ru
fw	539.51	860.77	759.39
a, Å	8.672(2)	9.548(3)	12.034(2)
b, Å	12.279(1)	13.004(5)	16.434(3)
c, Å	20.820(4)	17.743(4)	13.925(3)
a, deg.	90.00	77.26(3)	90.00
b, deg.	97.48(6)	74.89(2)	94.88(1)
c, deg.	90.00	83.64(3)	90.00
Z; *V*, $Å^3$	4; 2190.1(7)	2; 2071.1(12)	4; 2743.9(9)
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
D_{calcd}, g/cm^3	1.64	1.38	1.84
θ range, deg.	<27.5	<25	<27.5
no. of data used ($F_o > 4\sigma(F_o)$)[a]	2370	7219	3770
no. of variables	299	532	389
final $R(F)$/ $R_w(F)$,[b] %	7.1/7.9	4.5/4.5	6.9/8.1

[a] $F_o > 2\sigma(F_o)$ for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$.
[b] $R(F) = (\sum\|F_o\| - |F_c\|)/\sum|F_o|$. $R_w(F) = [\sum W(|F_o| - |F_c|)^2]/\sum w|F_o|^2$.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$

Ru–C1	2.064(13)	Ru–N4	2.105(10)
Ru–C2	1.815(14)	C1–O1	1.245(16)
Ru–N1	2.073(10)	C1–O2	1.283(15)
Ru–N2	2.133(10)	C2–O3	1.145(17)
Ru–N3	2.204(10)		
C1–Ru–C2	88.5(6)	N1–Ru–N2	77.6(4)
C1–Ru–N1	88.7(5)	N2–Ru–N3	88.5(4)
C1–Ru–N2	86.6(4)	N3–Ru–N4	76.9(4)
C1–Ru–N3	172.6(5)	N4–Ru–N1	167.0(4)
C1–Ru–N4	97.7(5)	Ru–C1–O1	118.5(9)
C2–Ru–N1	96.7(5)	Ru–C1–O2	120.6(10)
C2–Ru–N2	172.7(5)	O1–C1–O2	120.9(12)
C2–Ru–N3	96.9(5)	Ru–C2–O3	178.8(11)
C2–Ru–N4	94.7(5)		

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$

Ru–C1	2.042(6)	Ru–N4	2.093(5)
Ru–C2	1.800(7)	C1–O1	1.191(8)
Ru–N1	2.070(5)	C1–O2	1.344(8)
Ru–N2	2.105(5)	O2–C3	1.463(9)
Ru–N3	2.151(5)	C2–O3	1.154(8)
C1–Ru–C2	88.5(3)	C2–Ru–N1	95.6(2)
C1–Ru–N1	89.8(2)	C2–Ru–N2	172.9(2)
C1–Ru–N2	89.1(2)	C2–Ru–N3	98.8(2)
C1–Ru–N3	169.9(2)	C2–Ru–N4	91.4(2)
C1–Ru–N4	95.9(2)	Ru–C1–O1	125.4(5)
N1–Ru–N2	77.7(2)	Ru–C1–O2	115.4(4)
N2–Ru–N3	84.5(2)	O1–C1–O2	119.2(6)
N3–Ru–N4	77.0(2)	C1–O2–C3	116.4(6)
N4–Ru–N1	171.1(2)	Ru–C2–C3	176.5(6)

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru(bpy)_2(CO)_2](PF_6)_2$

Ru–C1	1.865(10)	Ru–N3	2.073(7)
Ru–C2	1.906(9)	Ru–N4	2.083(6)
Ru–N1	2.095(6)	C1–O1	1.144(12)
Ru–N2	2.102(6)	C2–O2	1.125(11)
C1–Ru–C2	88.8(4)	N4–Ru–N1	169.5(3)
C1–Ru–N1	97.9(3)	C2–Ru–N1	89.5(3)
C1–Ru–N2	93.9(3)	C2–Ru–N2	175.9(3)
C1–Ru–N3	175.7(3)	C2–Ru–N3	93.1(3)
C1–Ru–N4	88.7(3)	C2–Ru–N4	98.9(3)
N1–Ru–N2	78.2(3)	Ru–C1–O1	176.4(8)
N2–Ru–N3	84.5(2)	Ru–C2–O2	177.2(7)
N3–Ru–N4	78.0(2)		

atmosphere produces $[Ru(bpy)_2(CO)(CO_2)]$[11] with evolving CO (eq 3).[10] We, therefore, proposed that $[Ru(bpy)_2(CO)(CO_2)]$

$$[Ru(bpy)_2(CO)_2]^{2+} + CO_2 + 2e^- \rightarrow [Ru(bpy)_2(CO)(CO_2)] + CO \quad (3)$$

formed in eq 2 is a kind of an η^1-CO_2 complex. The comparison of the molecular structures of $[Ru(bpy)_2(CO)(CO_2)]$, $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)_2]^{2+}$ may give fundamental information with respect to the smooth conversion among CO, C(O)OH, and CO_2 on the Ru atom. This paper describes the molecular structures of $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ as a model compound of $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(CO_2)]$. A part of this study has been reported elsewhere.[12]

Experimental Section

Materials. $[Ru(bpy)_2(CO)_2](PF_6)_2$ and $[Ru(bpy)_2(CO)(C(O)OH)]PF_6$ were prepared according to the literatures.[8,13] $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$ for X-ray structure analysis was similarly prepared as $[Ru(bpy)_2(CO)(C(O)OCH_3)]PF_6$.[8] A methanolic $(C_4H_9)_4NOH$ (Bu_4NOH) solution (0.347 M) was used without further purification. CH_3OH was dried over 4-Å molecular sieves. CH_3CN was distilled over calcium hydride.

Preparation of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$. To a stirred H_2O/C_2H_5OH solution (100 cm^3, 1:1 v/v) of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (602 mg) was added a methanolic solution (5 cm^3) of Bu_4NOH (0.347 M). Slow evaporation of the resulting reddish yellow solution gave red crystals, which were washed with CH_3CN and dried under reduced pressure. Anal. Calcd for $C_{22}H_{22}N_4O_6Ru$: C, 48.98; H, 4.11; N, 10.38. Found: C, 48.86; H, 3.99; N, 10.37. Yield: 340 mg (80%). Infrared spectrum (KBr): $\nu(C{\equiv}O)$, 1911 cm^{-1}; $\nu(CO_2)$, 1428, 1242 cm^{-1}. ^{13}C NMR (67.8 MHz): δ 203.9 and 210.2 (CO_2 and CO), 158.2, 157.7, 157.1, 156.6, 155.9, 155.8, 150.0, 149.1, 140.0, 139.9, 139.8, 137.8, 127.9, 127.7, 127.5, 127.4, 124.7, 124.6, 124.2, 123.6 (bpy).

Reaction of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ with Iodomethane To Afford $[Ru(bpy)_2(CO)(C(O)OCH_3)]I$. A CD_3CN/CD_3OD solution (0.6 cm^3, 1:1 v/v) containing $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ (22.2 mg) and iodomethane (5.9 mg) was allowed to stand for 3 h under N_2 atmosphere. ^1H and ^{13}C NMR spectra of the resulting solution were consistent with those of $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4$ in the same solvent. ^1H NMR (270 MHz): δ 3.36 (s) (the methyl proton). ^{13}C NMR (67.8 MHz): δ 202.2 and 206.8 (CO and methoxycarbonyl); δ 158.0, 156.9, 156.5, 156.2, 155.7, 150.6, 149.0, 140.7, 140.6, 140.5, 139.3, 128.5, 128.5, 128.2, 128.0, 125.4, 125.1, 124.6, 124.2 (bpy); δ 49.9 (the methyl group).

^{13}C NMR Data for $[Ru(bpy)_2(CO)(C(O)OH)]PF_6$: δ 201.5 and 205.1 (CO and hydroxycarbonyl); δ 158.3, 157.2, 156.7, 156.4, 156.1, 150.5, 148.6, 141.0, 140.8, 140.8, 139.6, 128.7, 128.6, 128.4, 128.2, 125.6, 125.3, 124.9, 124.4 (bpy).

Physical Measurements and Product Analysis. Infrared spectra were obtained on a Shimadzu DR8000 spectrophotometer. ^1H and ^{13}C NMR data were obtained on a JEOL EX270 spectrometer. Elemental analyses were carried out at the Chemical Materials Center of Institute for Molecular Science. Electrochemical measurements were performed in a Pyrex cell equipped with a glassy-carbon working electrode, a Pt auxiliary electrode, an Ag/AgCl reference electrode, and a nozzle for bubbling of N_2 or CO_2. Cyclic voltammograms were obtained by use of a Hokuto Denko HR-101B potentiostat, a Hokuto Denko HB-107A function generator, and a Yokokawa Electric Inc. 3077 X-Y recorder.

X-ray Crystallographic Studies. The reflections of X-ray analysis were collected by θ–2θ technique ($0 < 2\theta < 55°$ for $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ and $[Ru(bpy)_2(CO)_2](PF_6)_2$, and $0 < 2\theta < 50°$ for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$ on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with Mo Kα radiation (0.7107 Å). The 2370 and 3770 independent reflections, for $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ and $[Ru(bpy)_2(CO)_2](PF_6)_2$, respectively, with $F_o > 4\sigma(F_o)$, and 7219 independent reflections for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$ with $F_o > 2\sigma(F_o)$ were used for the structure refinement. All of the calculations were carried out on a HITAC-M680H

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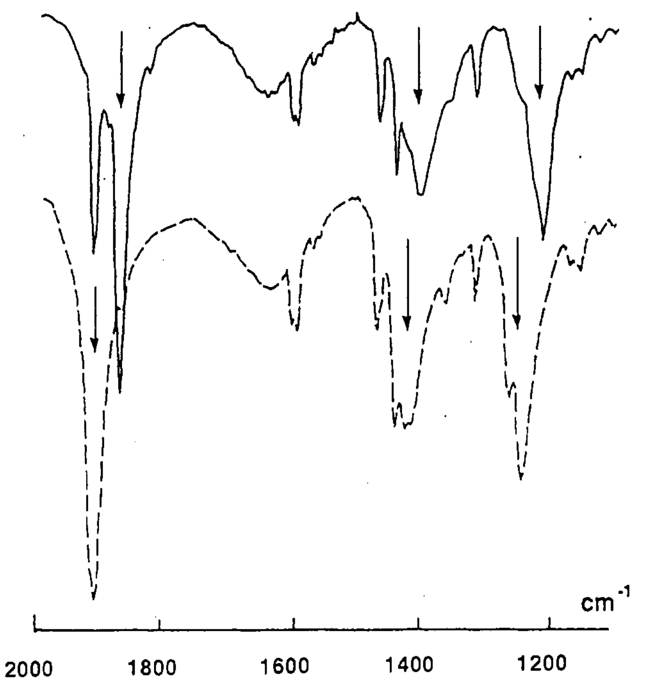

Figure 1. Infrared spectra (KBr) of $[Ru(bpy)_2(CO)(CO_2)]$ (dotted line) and of $[Ru(bpy)_2(CO)(CO_2)]$ after being dissolved in $CH_3OH/H_2{}^{18}O$ (99% enriched) (5:1, v/v) (solid line).

computer, using the UNICS III program. The structures were solved by the heavy-atom method. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in the structure factor calculations. The data for crystal structures analysis are shown in Table I. Selected bond distances and angles for $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$, $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$, and $[Ru(bpy)_2(CO)_2](PF_6)_2$ are shown in Tables II–IV.

Results and Discussion

Isolation of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$. A colorless H_2O/C_2H_5OH (1:1 v/v) solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ rapidly changed to yellow by an addition of an equimolar amount of a methanolic Bu_4NOH. Concentration of the solution afforded $[Ru(bpy)_2(CO)(C(O)OH)]PF_6$ as a yellow solid, which shows strong $\nu(C{\equiv}O)$ and $\nu(C{=}O)$ bands at 1946 and 1619 cm^{-1}.[8] These bands were shifted to 1904 and 1586 cm^{-1} after the hydroxycarbonyl complex was dissolved in $CH_3OH/CH_3CN/H_2{}^{18}O$ (5:2:1 v/v) for 30 min. On the other hand, the H_2O/C_2H_5OH (1:1 v/v) solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ turned to reddish yellow by an addition of 2 equiv of Bu_4NOH. Slow evaporation of the reddish yellow solution gave red single crystals of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$. The infrared spectrum of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ shows the $\nu(C{\equiv}O)$ band at 1911 cm^{-1} and the $\nu(CO_2)$ bands at 1428 and 1242 cm^{-1} (Figure 1). Those bands were shifted to 1869, 1407 and 1213 cm^{-1} after the complex was dissolved in $CH_3OH/H_2{}^{18}O$ (99% enriched) (5:1 v/v) for 3 h. Thus, the oxygen atoms of both CO_2 and CO of $[Ru(bpy)_2(CO)(CO_2)]$ are replaced by that of $H_2{}^{18}O$ (Figure 1, eq 4).

$$[Ru(bpy)_2(CO)(CO_2)] + 3H_2{}^*O \rightleftharpoons [Ru(bpy)_2(C^*O)(C^*O_2)] + 3H_2O \quad (4)$$

The ^{13}C NMR spectrum of $[Ru(bpy)_2(CO)_2](PF_6)_2$ showed the CO carbon at 190.3 ppm in CD_3CN, and the CO and CO_2 signals of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ were observed at 203.9 and 210.2 ppm in CD_3OD. An addition of an equimolar amount of a methanolic solution of Bu_4NOH to the $[Ru(bpy)_2(CO)_2](PF_6)_2$ solution resulted in a complete disappearance of the 190.3 ppm signal, and the CO and COOH carbons of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ appeared at 201.5 and 205.1 ppm with 19 signals of two nonequivalent 2,2′-bipyridyl ligands. Such selective formation of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ in the reaction of an equimolar amount of OH^- with $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN is quite contrast to that in H_2O, where $[Ru(bpy)_2(CO)(C(O)OH)]^+$ always exists as an equilibrium mixture with either $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)(CO_2)]$, or both of them. In fact, a further addition of a methanolic solution of Bu_4NOH (about 1.2 molar excess) to the CH_3CN solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ caused an appearance of two signals of 203.9 and 210.2 ppm of $[Ru(bpy)_2(CO)(CO_2)]$ in addition to the 201.5 and 205.1 ppm signals of $[Ru(bpy)_2(CO)(C(O)OH)]^+$.[14] This result indicates that the interconversion between $[Ru(bpy)_2(CO)(C(O)OH)]^+$ and $[Ru(bpy)_2(CO)(CO_2)]$ in CD_3CN/CD_3OD is very slow compared with that in H_2O.

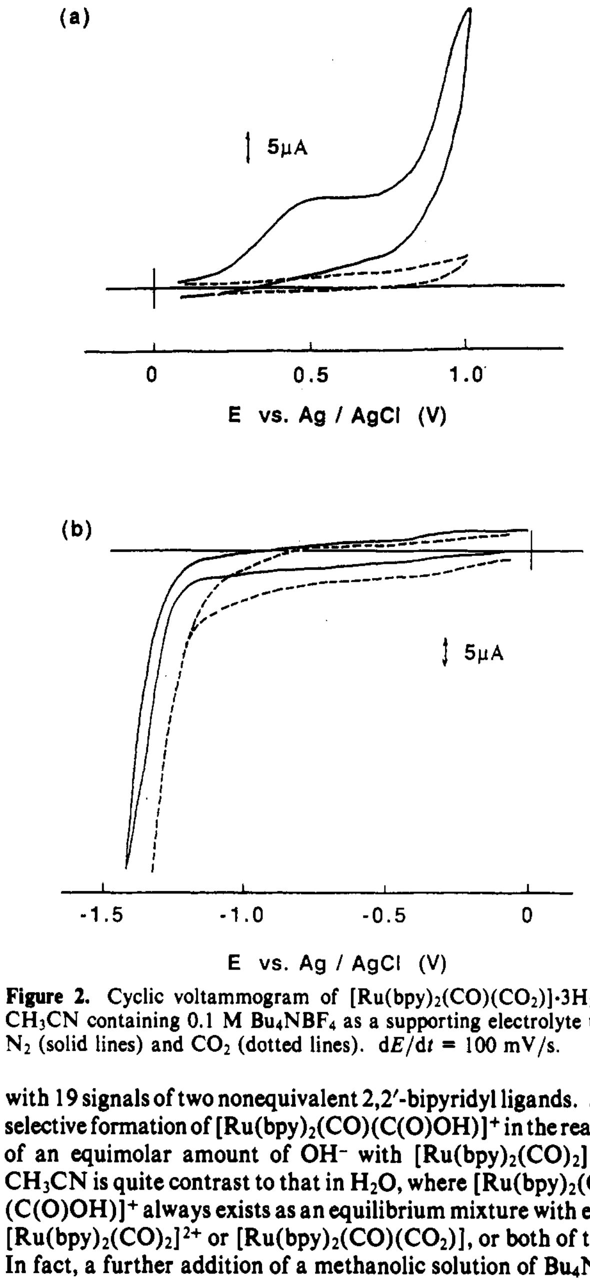

Figure 2. Cyclic voltammogram of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ in CH_3CN containing 0.1 M Bu_4NBF_4 as a supporting electrolyte under N_2 (solid lines) and CO_2 (dotted lines). dE/dt = 100 mV/s.

Cooper et al. have demonstrated that $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$ produced in the reaction of $W(CO)_6$ with Li under CO_2 at −78 °C in THF undergoes an oxide-abstraction reaction by CO_2 to regenerate $W(CO)_6$ at room temperature (eq 5).[15] Such an

$$[W(CO)_5(\eta^1\text{-}CO_2)]^{2-} + CO_2 \rightarrow W(CO)_6 + CO_3{}^{2-} \quad (5)$$

unusual oxide-abstraction reaction by CO_2 may be rationalized by a strong nucleophilicity of the oxygen atom of the CO_2 ligand. In contrast to eq 5, $[Ru(bpy)_2(CO)(CO_2)]$ is quite stable in

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[14] The concentration of the ruthenium complexes became too low to detect the ^{13}C NMR signals when the CH_3CN solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ was mixed with a 2 mol excess of methanolic solution of Bu_4NOH.

[15] Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797.

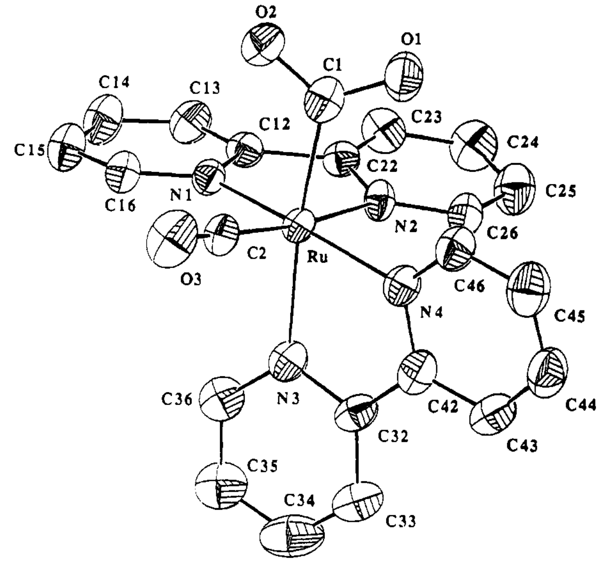

Figure 3. Molecular structure of $[Ru(bpy)_2(CO)(CO_2)]$.

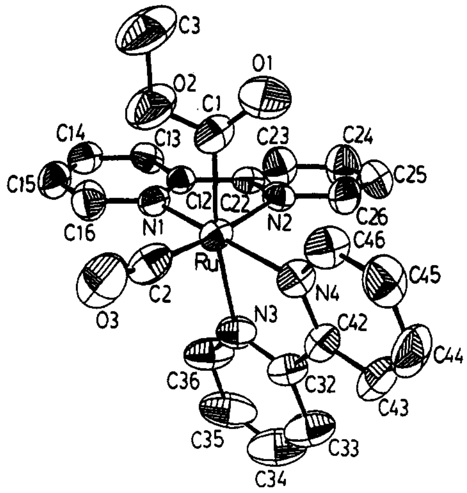

Figure 4. Molecular structure of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$.

CH_3OH at room temperature, as described above. The ^{13}C NMR of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ in CO_2-saturated CD_3OH, however, revealed the formation of both $[Ru(bpy)_2(CO)(C(O)OH)]^+$ (201.5 and 205.1 ppm) and $CD_3OC(O)O^-$ (161.4 ppm), and neither $[Ru(bpy)_2(CO)(CO_2)]$ nor $[Ru(bpy)_2(CO)_2]^{2+}$ was detected in the solution. The absence of $[Ru(bpy)_2(CO)_2]^{2+}$ in the CO_2-saturated CD_3OH indicates that $[Ru(bpy)_2(CO)(CO_2)]$ does not undergo an oxide-abstraction reaction by CO_2. On the basis of the $pK_a = 9.5$ of $[Ru(bpy)_2(CO)(C(O)OH)]^+$, protonation of $[Ru(bpy)_2(CO)(CO_2)]$ affording $[Ru(bpy)_2(CO)(C(O)OH)]^+$ in CO_2-saturated CD_3OH is explained by enhancement of the acidity of CD_3OH due to concomitant formation of $CD_3OCO_2^-$ (eq 6). The conversion of $[Ru(bpy)_2(CO)(CO_2)]$ to $[Ru(bpy)_2(CO)(C(O)OH)]^+$ in CO_2-saturated CH_3OH was also observed in a cyclic voltammogram (CV); the CV of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ shows an irreversible anodic wave at +0.53 V vs Ag/AgCl (a solid line in Figure 2a) and a strong cathodic current at potential more negative than −1.25 V in CH_3OH under an N_2 atmosphere (a solid line in Figure 2b). The anodic +0.53-V wave completely disappears in CO_2-saturated CH_3OH (a dotted line in Figure 2a), and the reduction of CO_2 takes place at potentials more negative than −1.18 V (a dotted line in Figure 2b). Those results may make clear the roles of $[Ru(bpy)_2(CO)(CO_2)]$ and $[Ru(bpy)_2(CO)(C(O)OH)]^+$ in a previous electrochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$, where $[Ru(bpy)_2(CO)(C(O)OH)]^+$ resulting from $[Ru(bpy)_2(CO)(CO_2)]$ functions as the active species for the formation of $HCOO^-$ in CO_2-saturated CH_3OH.[16]

$$[Ru(bpy)_2(CO)(CO_2)] + CH_3OH + CO_2 \rightarrow [Ru(bpy)_2(CO)(C(O)OH)]^+ + CH_3OCO_2^- \quad (6)$$

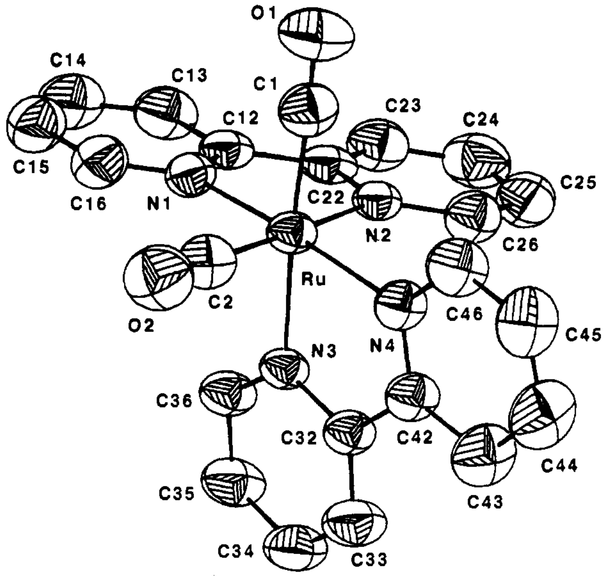

Figure 5. Molecular structure of $[Ru(bpy)_2(CO)_2]^{2+}$.

In comparison with eqs 5 and 6, the nucleophilicity of the CO_2 ligand of $[Ru(bpy)_2(CO)(CO_2)]$ may be much less than that of $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$. It has, however, been reported that a neutral η^1-CO_2 complex $[IrCl(dmpe)_2(\eta^1\text{-}CO_2)]$ can be converted to the corresponding methoxycarbonyl complex $[IrCl(dmpe)_2(C(O)OCH_3)]FSO_3$ by a treatment with a strong methylation agent such as CH_3FSO_3.[17] In the present study, $[Ru(bpy)_2(CO)(C(O)OCH_3)]I$ was quite smoothly obtained in the reaction of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ with CH_3I in CH_3OH (eq 7). It is worthy to note that $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ can be also synthesized by the reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with CH_3ONa in CH_3OH (eq 8).[8] Thus,

$$[Ru(bpy)_2(CO)(CO_2)] + CH_3I \rightarrow [Ru(bpy)_2(CO)(C(O)OCH_3)]I \quad (7)$$

$$[Ru(bpy)_2(CO)_2]^{2+} + CH_3O^- \rightarrow [Ru(bpy)_2(CO)(C(O)OCH_3)]^+ \quad (8)$$

$[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ can be prepared not only by an electrophilic attack of CH_3I to $[Ru(bpy)_2(CO)(CO_2)]$ but also by a nucleophilic attack of CH_3O^- to $[Ru(bpy)_2(CO)_2]^{2+}$.

X-ray Structure Analysis. A comparison of the molecular structures of $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(CO_2)]$ is particularly interested in the viewpoint of the smooth interconversion among those complexes in H_2O. Although colorless and red single crystals of $[Ru(bpy)_2(CO)_2](PF_6)_2$ and $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ suitable for X-ray crystal analysis were obtained successfully, attempts to grow single crystals of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ were unsuccessful. The crystal structure of $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$, therefore, was determined as a model compound of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ based on the view that the molecular structure of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ can be safely presumed by that of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$. The

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(16) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 131.

(17) Harlow, R. L.; Kinney, J. B.; Herskovitz, T. *J. Chem. Soc., Chem. Commun.* **1980**, 813.

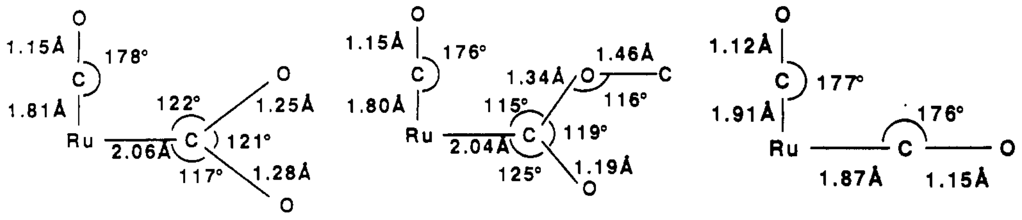

Figure 6. Bond distances and angles of $Ru(CO)(CO_2)$, $Ru(CO)(C(O)OCH_3)$, and $Ru(CO)_2$ moieties.

molecular structures of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$, $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$, and $[Ru(bpy)_2(CO)_2](PF_6)_2$ are shown in Figures 3–5. Two 2,2′-bipyridyl ligands of three complexes are in a cis position, and the bond distances and angles of the 2,2′-bipyridyl ligands are similar to those observed in the other 2,2′-bipyridyl–ruthenium complexes reported so far.[18] So, the structural difference in the present complexes is focused on the $Ru(CO)_2$, $Ru(CO)(C(O)OCH_3)$, and $Ru(CO)(CO_2)$ moieties (Figure 6). Although the lengths of the C1–O1 (1.144(12) Å) and C2–O2 bonds (1.125(11) Å) for $[Ru(bpy)_2(CO)_2]^{2+}$ are not so different from those of the C2–O3 bonds for $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ and $[Ru(bpy)_2(CO)(CO_2)]$ (1.154(8) and 1.145(17) Å, respectively), the wavenumber of $\nu(C{\equiv}O)$ bands decreases in the order $[Ru(bpy)_2(CO)_2]^{2+}$ (2093 and 2039 cm^{-1}), $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ (1960 cm^{-1}), and $[Ru(bpy)_2(CO)(CO_2)]$ (1911 cm^{-1}). This may be correlated with the difference in the electron donor ability of CO, CO_2CH_3, and CO_2 ligands. In accordance with this, both Ru–N2 (trans to CO) and Ru–N3 (trans to CO, CO_2CH_3, or CO_2) bond distances for the present complexes have a tendency to lengthen in the same order: $[Ru(bpy)_2(CO)_2]^{2+}$, 2.102(6) and 2.073(7) Å; $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$, 2.105(5) and 2.151(5) Å; and $[Ru(bpy)_2(CO)(CO_2)]$, 2.133(10) and 2.204(10) Å.

The most interesting features in $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ and $[Ru(bpy)_2(CO)(CO_2)]$ are the bond lengths and angles of the $Ru–CO_2$ fragments. The Ru–C1 bond distance of the former is 2.042(6) Å with Ru–C1–O1 (125.4(5)°), Ru–C1–O2 (115.4(4)°), and O1–C1–O2 (119.2(6)°), and that of the latter is 2.064(13) Å with Ru–C1–O1 (118.5(9)°), Ru–C1–O2 (120.6(10)°), and O1–C1–O2 (120.9(12)°). The $Ru–CO_2$ bond distance of $[Ru(bpy)_2(CO)(CO_2)]$ is close to the CO_2–metal distances in $[Rh(\eta^1\text{-}CO_2)Cl(diars)_2]$ and $[Co(pr\text{-}salen)\text{-}KCO_2\cdot THF]_n$,[3] and the $Ru–CO_2CH_3$ bond length of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ is also similar to metal–CO_2CH_3 ones of other methoxycarbonyl–metal complexes.[19] Although a double bond character has been suggested in the $W–CO_2$ bond of $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$, the fact that the Ru–C1 distance of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ is shorter than that of $[Ru(bpy)_2(CO)(CO_2)]$ suggests that the multibond character for the $Ru–CO_2$ bond is not always larger than that for the $Ru–C(O)OCH_3$ bond. A difference in the C1–O1 (1.245 (16) Å) and C1–O2 (1.283 (15) Å) bond distances of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ may be associated with a difference in the number of hydrogen bondings of O2 with two solvated water (O4 and O5″) and that of O1 with another solvated water (O6) (see below). It is, however, worthy to note that the C1–O1 (1.245(16) Å) and C1–O2 (1.283(15) Å) bond distances of $[Ru(bpy)_2(CO)(CO_2)]$ are intermediate between those of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ (1.191(8) and 1.344(8) Å), and the average of the C1–O1 and C1–O2 bond distances of the former (1.264 Å) is almost consistent with that of the latter (1.268 Å). The C1–O1 and C1–O2 bonds of $[Ru(bpy)_2(CO)(CO_2)]$, therefore, are approximated by a bond order of 1.5, and the one extra electron-pair involved in $[Ru(bpy)_2(CO)(CO_2)]$ resulting from dissociation of the terminal proton of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ may be mainly localized in the CO_2 ligand rather than delocalized over the $RuCO_2$ moiety.

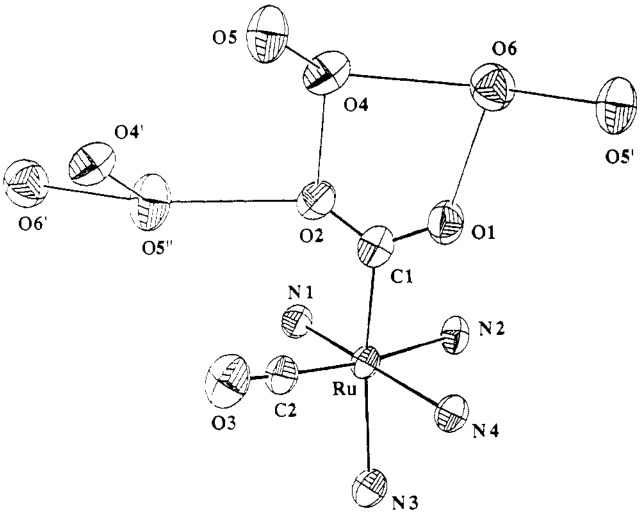

Figure 7. Three-dimensional network of hydrogen bonding of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$.

The increase in the electron density of the CO_2 moiety of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ compared with that of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ may be compensated for by the existence of the extended three-dimensional network of hydrogen bonding observed between the complex and three hydrated water molecules (Figure 7). Each water molecule is connected by three hydrogen bonds; e.g., O4 (water) is connected to O2 (CO_2), O5 (water), and O6 (water) with distances of 2.711(14), 2.800(14), and 2.751(14) Å, respectively. Similarly, O5 is connected to O2 (CO_2), O4 (water), and O6 (water) with distances of 2.764(14), 2.800(14), and 2.870(14) Å, respectively, and O6 is connected to O1 (CO_2), O4 (water) and O5 (water) with 2.653(15), 2.751(15), and 2.870(14) Å, respectively. The hydrogen-bonding network of $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ results in a distinct difference in the solubility of hydrated and anhydrous $[Ru(bpy)_2(CO)(CO_2)]$; $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ is only soluble in H_2O, CH_3OH, and C_2H_5OH and is almost insoluble in CH_3CN, DMSO, and DMF, while anhydrous $[Ru(bpy)_2(CO)(CO_2)]$ prepared similarly in dry CH_3CN is quite soluble in most organic solvents.

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Supplementary Material Available: For these structure studies, tables of atomic parameters with averaged thermal parameters and anisotropic thermal parameters for $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$ and $[Ru(bpy)_2(CO)_2](PF_6)_2$, atomic parameters with U values for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$, tables of bond distances and angles for all three compounds, and numbering diagrams for $[Ru(bpy)_2(CO)(C(O)OCH_3)]B(C_6H_5)_4\cdot CH_3CN$ and the PF_6^- anions in $[Ru(bpy)_2(CO)_2](PF_6)_2$ (21 pages). Ordering information is given on any current masthead page.

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