Crystal structure of cis-(carbonyl)(.eta.1-carbon dioxide)bis(2,2'-bipyridyl)ruthenium, an active species in catalytic carbon dioxide reduction affording carbon monoxide and HCOO-

Hiroaki Tanaka, Hirotaka Nagao, Shie Ming Peng, and Koji Tanaka

Organometallics, **1992**, 11 (4), 1450-1451• DOI: 10.1021/om00040a010 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

1450 *Organometallics* **1992**, *11*, 1450–1451

Crystal Structure of *cis*-(Carbon monoxide)(η^1-carbon dioxide)bis(2,2′-bipyridyl)ruthenium, an Active Species in Catalytic CO_2 Reduction Affording CO and $HCOO^-$

Hiroaki Tanaka, Hirotaka Nagao, Shie-Ming Peng,[1] and Koji Tanaka*

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

Received December 19, 1991

Summary: A reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with 2 equiv of Bu_4NOH in H_2O/EtOH (1:1 v/v) affords an η^1-CO_2 complex, $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$. An addition of an aqueous HCl solution to a MeOH solution of $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ quantitatively regenerates $[Ru(bpy)_2(CO)_2]^{2+}$.

Much attention has been paid to electro- and photochemical CO_2 reduction using homogeneous catalysts, and a variety of transition-metal complexes have been shown to be active as catalyst precursors in those homogeneous reactions.[2] Among these metal complexes, $[Ru(bpy)_2(CO)_2]^{2+}$ is of interest in the ability to catalyze not only electro-[3] and photochemical CO_2 reduction[2i] but also the water-gas shift reaction (WGSR)[4] as a reverse reaction of CO_2 reduction. A carbonyl carbon of $[Ru(bpy)_2(CO)_2]^{2+}$ undergoes a reversible nucleophilic attack of OH^- to form $[Ru(bpy)_2(CO)C(O)OH]^+$ in a neutral aqueous solution (eq 1), and $[Ru(bpy)_2(CO)(COO)]$ has been proposed to be

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

$$[Ru(bpy)_2(CO)C(O)OH]^+ + OH^- \rightleftharpoons [Ru(bpy)_2(CO)(COO)] + H_2O \tag{2}$$

formed by dissociation of the hydroxycarbonyl proton of $[Ru(bpy)_2(CO)C(O)OH]^+$ in alkaline solutions (eq 2).[4] $[Ru(bpy)_2(CO)(COO)]$ is inactive in the WGSR but is considered to be the key intermediate in the CO_2 reduction. This communication reports the crystal structure of the key intermediate, $[Ru(bpy)_2(CO)(COO)]$, in a catalytic cycle of the CO_2 reduction.

A colorless H_2O/EtOH (1:1 v/v) solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ rapidly changed to yellow by addition of an equimolar amount of Bu_4NOH in MeOH, and the crude product showed strong $\nu(C{\equiv}O)$ and $\nu(C{=}O)$ bands at 1946 and 1619 cm^{-1} for $[Ru(bpy)_2(CO)(C(O)OH)](PF_6)$ (eq 1), as described elsewhere.[4] On the other hand, an H_2O/EtOH (1:1 v/v) solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ turned to red by addition of 2 equiv of Bu_4NOH. Slow evaporation of the red solution gave single crystals of a neutral complex, $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$,[5] which displayed two strong IR bands at 1911 and 1242 cm^{-1} assignable to $\nu(C{\equiv}O)$ and $\nu(CO_2)$, since those bands were shifted to 1869 to 1213 cm^{-1}, respectively, after treatment of $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ with $H_2{}^{18}O$ (97%). Also, addition of an aqueous HCl solution to a methanolic solution of $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ quantiatively regenerated the colorless $[Ru(bpy)_2(CO)_2]^{2+}$. These observations suggest that the CO_2 adduct of eq 2 proposed so far[4] exists as a neutral CO_2 adduct in the solid state.

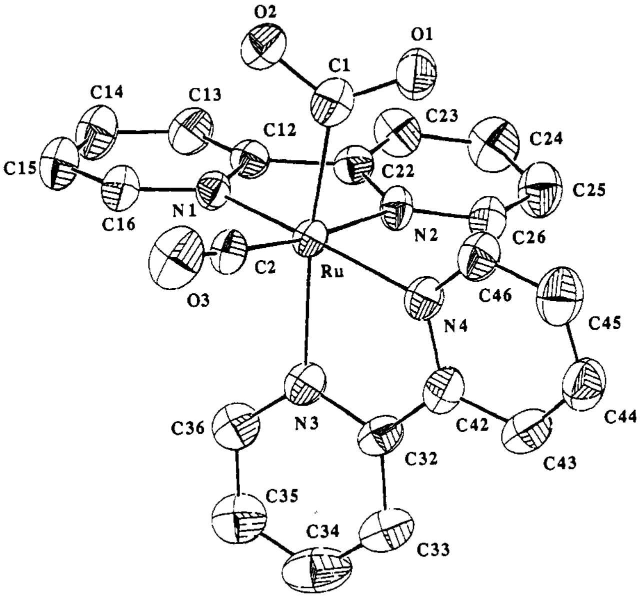

Figure 1. Molecular structure of $[Ru(bpy)_2(CO)(COO)]$. Selected bond distances (Å) and angles (deg): Ru–C1, 2.064 (13); Ru–C2, 1.814 (14); Ru–N1, 2.073 (10); Ru–N2, 2.133 (10); Ru–N3, 2.204 (10); Ru–N4, 2.105 (10); C1–O1, 1.245 (16); C1–O2, 1.283 (15); C2–O3, 1.150 (17); Ru–C1–O1, 118 (1); Ru–C1–O2, 121 (1); O1–C1–O2, 121 (1); Ru–C2–O3, 179 (1).

The structure of $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ is shown in Figure 1.[6] The ruthenium is octahedrally coordinated by a CO, an η^1-CO_2 in a cis position, and four nitrogen atoms of 2,2′-bipyridine ligands. Both CO and CO_2 exhibit a strong trans influence; the Ru–N3 (trans to CO_2) distance

---

[1] Visiting professor at the Institute for Molecular Science. Permanent address: Department of Chemistry, National Taiwan University, Roosevelt Road Section 4, Taipei, Taiwan, Republic of China.

[2] (a) Atoguchi, T.; Aramata, A.; Kazusaka, A.; Enyo, M. *J. Chem. Soc., Chem. Commun.* **1991**, 156. (b) Tsai, J. C.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 29. (c) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343. (d) Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. *J. Chem. Soc.*, Dalton *Trans.* **1990**, 2155. (e) Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 86. (f) Tamaura, Y.; Tabata, M. *Nature* (*London*) **1990**, *346*, 255. (g) Ruiz, J.; Guerchais, V.; Astruc, D. *J. Chem. Soc.*, Chem. *Commun.* **1989**, 812. (h) Tomohiro, T.; Uoto, K.; Okuno, H. *J. Chem. Soc., Chem. Commun.* **1990**, 194. (i) Ishida, H.; Terada, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1990**, *29*, 905. (j) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8*, 1822. (k) Tukahara, K.; Wilkins, R. G. *Inorg. Chem.* **1989**, *28*, 1605. (l) Silavwe, N. D.; Goldman, A. S.; Ritter, R.; Tyler, D. R. *Inorg. Chem.* **1989**, *28*, 1231. (m) Sugimura, K.; Kuwabata, S.; Yoneyama, H. *J. Am. Chem. Soc.* **1989**, *111*, 2361. (n) Hurrell, H. C.; Mogstad, A. L.; Usifer, D. A.; Potts, K. T.; Abruna, H. D. *Inorg. Chem.* **1989**, *28*, 1080. (o) Tanaka, K.; Wakita, R.; Tanaka, T. *J. Am. Chem. Soc.* **1989**, *111*, 2428 and references therein.

[3] Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181.

[4] Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* **1986**, *5*, 724.

[5] Anal. Calcd for $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$, $C_{22}H_{22}N_4O_6Ru$: C, 48.98; H, 4.11; N, 10.38. Found: C, 48.86; H, 3.99; N, 10.37.

[6] Crystal data for $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$: $C_{22}H_{22}N_4O_6Ru$, monoclinic space group $P2_1/n$, a = 8.672 (2) Å, b = 12.279 (1) Å, c = 20.820 (4) Å, β = 97.32 (2)°, V = 2190.1 (7) Å^3, Z = 4, D_c = 1.64 g cm^{-3}, $R_F = 0.071$ for 2370 unique reflections ($\theta < 27.5°$) with $F > 4\sigma(F)$ and 299 variables. Data were collected on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with Mo Kα radiation. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed contributions.

0276-7333/92/2311-1450$03.00/0

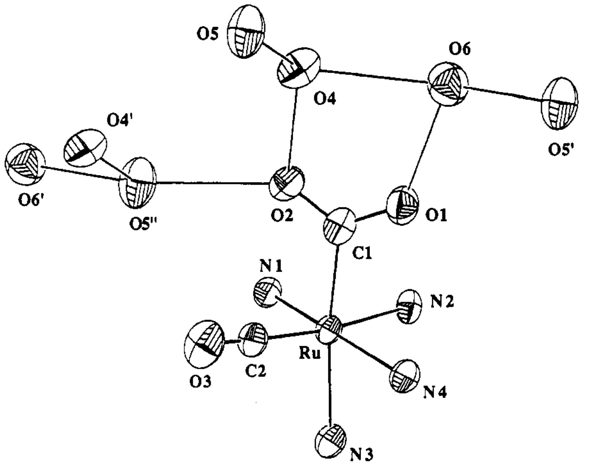

Figure 2. Three-dimensional network of hydrogen bonding in $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$. Distances (Å): O1–O6, 2.653 (15); O2–O4, 2.711 (14); O4–O6, 2.751 (15); O4–O5, 2.800 (14); O6–O5′, 2.870 (14); O2–O5″, 2.764 (14); O5″–O4′, 2.800 (14); O5″–O6′, 2.870 (14).

(2.204 (10) Å) is longer than the Ru–N4 (trans to bpy) distance (2.105 (10) Å). Similarly, the Ru–N2 (trans to CO) distance (2.133 (10) Å) is longer than the Ru–N1 (trans to bpy) distance (2.073 (10) Å). The CO is linearly coordinated to Ru with an Ru–C2–O3 angle of 179 (1)°. The most interesting feature in the complex is the Ru–CO_2 fragment; the Ru–C distance is 2.064 (13) Å, the Ru–C–O angles are 121 (1) and 118 (1)°, respectively, and the C–O distances are 1.245 (16) and 1.283 (15) Å, respectively, with an O–C–O angle of 121 (1)°. These values are like those observed in the other η^1-CO_2 compelxes reported so far, $[Rh(\eta^1\text{-}CO_2)Cl(diars)_2]$[7] and $[Co(pr\text{-}salen)KCO_2\cdot THF]_n$.[8] The other interesting feature is the extended three-dimensional network of hydrogen bondings observed between the complex and three hydrated water molecules (Figure 2). Each water molecule is connected by three hydrogen bondings; 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 distances of 2.653 (15), 2.751 (15), and 2.870 (14) Å, respectively. The hydrogen-bonding network of $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ results in a distinct difference in solubility of hydrated and anhydrous $[Ru(bpy)_2(CO)(COO)]$; $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ is only soluble in MeOH and EtOH and almost insoluble in CH_3CN, DMSO, and DMF, while anhydrous $[Ru(bpy)_2(CO)(COO)]$ prepared similarly in dry CH_3CN in place of H_2O/EtOH is quite soluble in most organic solvents.

Recently, Meyer et al. have reported that the one-electron-reduction product of $[Ru(bpy)_2(CO)H]^+$ reacts with CO_2 to form a formato complex, $[Ru(bpy)_2(CO)O(O)CH]$, which produces $HCOO^-$ upon another one-electron reduction.[9] The fact, however, that electrochemical reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ at −1.10 V (vs SCE) in dry CH_3CN under a CO_2 atmosphere gives $[Ru(bpy)_2(CO)(COO)]$[10] and CO (eq 3)[3] supports the notion that a selective electrochemical CO_2 reduction to not only CO[3] but also $HCOO^-$[11] by $[Ru(bpy)_2(CO)_2]^{2+}$ proceeds through rapid interconversions among $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)C(O)OH]^+$, and $[Ru(bpy)_2(CO)(COO)]$, depending on the acidity of the proton source in the reaction media.

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

Registry No. $[Ru(bpy)_2(CO)_2](PF_6)_2$, 75550-97-9; $[Ru(bpy)_2(CO)_2(C(O)OH)](PF_6)$, 86536-99-4; $[Ru(bpy)_2(CO)_2(COO)]\cdot 3H_2O$, 139495-15-1; $[Ru(bpy)_2(CO)_2(COO)]$, 86536-98-3.

Supplementary Material Available: For this structure study, tables of atomic parameters with averaged thermal parameters and anisotropic thermal parameters (3 pages); a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

---

[7] Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* 1983, *105*, 5914.

[8] Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* 1982, *104*, 5082.

[9] Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* 1991, *30*, 86.

[10] A prolonged electrolysis of $[Ru(bpy)_2(CO)(COO)]$ at −1.10 V in dry CH_3CN results in a slow decomposition of the η^1-CO_2 complex even under a CO_2 atmosphere.[3] Therefore, reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ under anhydrous conditions with CO_2 is not suitable for the synthesis of pure $[Ru(bpy)_2(CO)(COO)]$.

[11] Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* 1987, 131.