4870 J. Am. Chem. Soc. 1988, 110, 4870-4871

# Carbon Dioxide Activation: Thermodynamics of $CO_2$ Binding and the Involvement of Two Cobalt Centers in the Reduction of $CO_2$ by a Cobalt(I) Macrocycle

Etsuko Fujita,* David J. Szalda,[1] Carol Creutz,* and
Norman Sutin*

*Chemistry Department, Brookhaven National
Laboratory, Upton, New York 11973*

*Received November 2, 1987*

Intense interest[2-7] in the transition-metal-promoted fixation of carbon dioxide has led us to explore the interaction of $CO_2$ with the cobalt(I) macrocycle, $CoL^+$ (L = [14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). Fisher and Eisenberg[6] reported the electrocatalytic activity of $CoL^{2+}$ in $CO_2$ reduction in $CH_3CN/H_2O$, and Gangi and Durand[7] established the reversible binding of $CO_2$ to $CoL^+$ in dry $Me_2SO$ by means of cyclic voltammetry. In earlier work $CoL^{2+}$ was found to mediate the photoreduction of water to $H_2$.[8] Here we describe the reversible binding of $CO_2$ to $CoL^+$ in $CH_3CN$ as characterized by UV–vis spectroscopy, a $CO_2$ reduction pathway involving two cobalt centers, and the formation, in the solid state, of a binuclear species containing the Co–C(OH)–O–Co moiety.

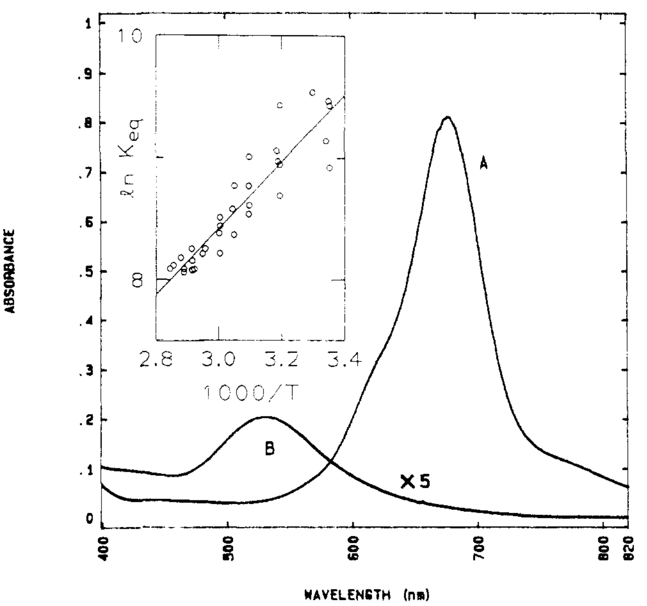

**Figure 1.** Absorption spectra of (A) $CoL^+$ $\lambda_{max}$ 678 nm ($\epsilon = 1.80 \times 10^4$ $M^{-1}$ $cm^{-1}$) and (B) $CoL(CO_2)^+$ $\lambda_{max}$ 530 nm ($\epsilon$ = 900 $M^{-1}$ $cm^{-1}$) in $CH_3CN$ at 25 °C. Insert: $\ln(K_1)$ versus $1000/T$. The $K_1$ values (eq 1) at 25–77 °C were calculated from the 530- and 680-nm absorbances of 0.1–1 mM $CoL(CO_2)^+$ solutions containing 0.01–0.1 M $CO_2$.[17]

---

[1] Permanent address: Department of Natural Sciences, Baruch College, Manhattan, NY 10010.

[2] For reviews of transition-metal–$CO_2$ chemistry, see: (a) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (b) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press; Oxford, 1982; Vol. 8, Chapter 50.4. (c) Ito, T.; Yamamoto, A. In *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (d) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (e) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (f) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *6*, 291.

[3] Structures of $CO_2$-containing species: (a) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615–6. (b) Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 2391–1. (c) Bristow, G. R.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145–6. (d) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914–5. (e) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985–6. (f) Aresta, M.; Ballivet-Tkatchenko, D.; Bonnet, M. C.; Faure, R.; Loiseleur, H. *J. Am. Chem. Soc.* **1985**, *107*, 2994–5. (g) Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. For recent studies of reactions of $CO_2$ with transition-metal species, see: (h) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797–9. (i) Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698–9. (j) Keene, F. R.; Creutz, C.; Sutin, N. Coord. *Chem. Rev.* **1985**, *64*, 247. (k) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1986**, 56. (l) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L.; Guttierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 6424–5. (m) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956–62. (n) Alt, H. G.; Schwind, K. H.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *321*, C9–C12. (o) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223–31. (p) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181–6. (q) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826–8. (r) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1987**, *6*, 1805–7. (s) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970–973, and references cited therein.

[4] Only a few systems exhibit reversible binding: (a) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1974**, 615–6. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082–92.

[5] Recent studies of $CO_2$ electroreduction promoted by transition-metal complexes: (a) Bradley, M. G.; Tysak, T.; Graves, D. J.; Vlachopoulos, N. A. *J. Chem. Soc., Chem. Commun.* **1983**, 349. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328. (c) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315. (d) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. H. M. W.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 288. (e) Kapusta, S.; Hackerman, N. *J. Electrochem. Soc.* **1984**, *131*, 1511. (f) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033. (g) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (h) O'Toole, T. R.; Margerum, L. D.; Westmoreland, T. D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1416. (i) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461. (j) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (k) Behr, A.; Kanne, U. *J. Organomet. Chem.* **1986**, *317*, C41. (l) Daniele, S.; Ugo, P.; Bontempelli, G.; Fiorani, M. *J. Electroanal. Chem.* **1987**, *219*, 259. (m) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 597. (n) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 131. (o) DuBois, D. L.; Miedaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113. (p) Ishida, H.; Tanaka, K.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 1035. (q) Hoberg, H.; Gross, S.; Milchereit, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 571. (r) Ogura, K.; Uchida, H. *J. Chem. Soc., Dalton Trans.* **1987**, 1377 and references cited therein. For recent reports of homogeneous photoreduction, see: (s) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56. (t) Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553. (u) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105 and references cited therein.

[6] Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.

[7] Gangi, D. A.; Durand, R. R. *J. Chem. Soc., Chem. Commun.* **1986**, 697.

[8] Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.

[9] Goedken, V. L.; Kildahl, N. K.; Busch, D. H. *J. Coord. Chem.* **1977**, *7*, 89.

[10] Vasilevskis, J.; Olson, D. C. *Inorg. Chem.* **1971**, *10*, 1228.

[11] (a) Most of the solutions were prepared on a vacuum line with ultrapure $CH_3CN$ as solvent[11b] and Na(Hg) as reductant. Thus $[Na^+] \geq [CoL^+]$ in the reduced solution. For DMF, the $CoL^+$ was produced by electrolysis of $CoL^{2+}$ (b) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley, New York, 1986.

[12] $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) of $CoL(CO_2)^+$, DMF (containing 0.1 M TPAP) 523 (800), 316 (4800); $CH_3CN$ 530 (900), 310 (6040). Molar absorptivities assume 100% conversion from $CoL^{2+}$. Unlike $Co^{(II)}L$ complexes[9] $CoL(CO_2)^+$ exhibits no absorption in the near-IR.

[13] (a) Except for a slight decrease in the Ni(I) absorption, the UV–vis spectrum of $NiL^+$ in $CH_3CN$ did not change upon addition of $CO_2$; addition of CO generated a bright green solution of $NiL(CO)^+$[13b] ($\lambda_{max}$ 620 nm ($\epsilon$ 31), 410 sh (1500), 345 (3600), 301 (3300), 238 (8100)). (b) Gagnē, R. R.; Ingle, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 1444.

[14] As judged from $^1H$ NMR spectra of freshly prepared solutions in $CD_3CN$.

[15] Upon cooling to ~ −40 °C, however, the solution becomes brownish yellow, but the purple hue (530-nm band) returns when the solution is warmed to room temperature. A small sample of the tan solid was obtained at −70 °C from THF–$CH_3CN$: IR (Nujol) 1653 $cm^{-1}$, 1559 $cm^{-1}$. The thermochromism, which may be due to addition of a solvent molecule to $CoL(CO_2)^+$, is being further investigated.

[16] Anal. Calcd for $CoL(CO_2)(ClO_4)\cdot0.5NaClO_4\cdot0.5CH_3CN$: Co, 10.44; $ClO_4$, 26.41; Na, 2.03; C, 38.27; H, 5.98; N, 11.21. Found: Co, 10.0; $ClO_4$, 25.8; Na, 2.46; C, 38.94; H, 6.19; N, 10.71. When $CoL^+$ was first crystallized from $CH_3CN$[10] to separate it from $Na^+$, a sample of lower $Na^+$ content was obtained: Anal. Calcd for $CoL(CO_2)(ClO_4)\cdot0.25NaClO_4$: Co, 11.48; Na, 1.12; $ClO_4$, 24.21. Found: Co, 11.5; Na, 1.38; $ClO_4$, 23.3. IR (Nujol) 1700, 1663, 1643, and 1607 $cm^{-1}$.

0002-7863/88/1510-4870$01.50/0

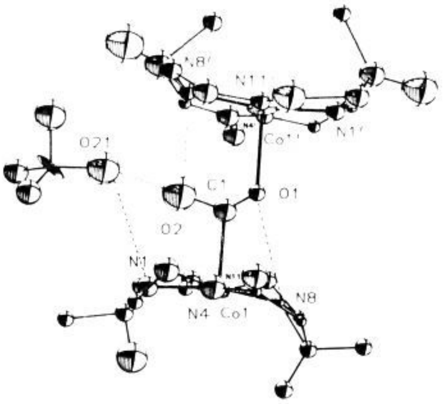

**Figure 2.** An ORTEP view of the $(CoL)_2(CO_2H)^{3+}$ unit **1** and one perchlorate anion (thermal ellipsoids at 50% probability level) with hydrogen atoms omitted. (Note that the presence of the proton in the $CO_2H$ group is inferred from the short O2-to-O21 distance (see below). In view of the structural disorder (see Supplementary Material), the alternative formulation $(CoL)_2(CO_2)^{3+}$ cannot be entirely ruled out.[21]) The labeling scheme is as indicated with N4 out of the plane and N11 behind the plane. The primed atoms are related to the unprimed atoms by a pseudoinversion center located between C1 and O1 of the carbon dioxide. Both Co centers are five coordinate, with four coordination sites being filled by the macrocycle and the fifth by the carbon (C1) or oxygen (O1) of the bridging $CO_2H$. A hydrogen bond between O2 (of $CO_2H$) and O21 (of $ClO_4^-$) (distance 2.38 (8) Å) is proposed. There are intradimer hydrogen bonds between N8′ and O2 and N8 and O1 as well as a weak hydrogen bond between N1 and O21 of the perchlorate anion. Selected bond distances (Å), unprimed (primed): Co(1)–N(1), 1.95 (4), (1.96 (4)); Co(1)–N(4), 2.06 (5), (1.84 (4)); Co(1)–N(8), 1.68 (3), (2.04 (4)); Co(1)–N(11), 1.98 (3), (1.85 (4)); Co(1)–C(1), 2.06 (6); Co(1′)–O(1), 2.28 (3).

Upon introduction of $CO_2$ into intensely blue $CoL^+$ solutions in $CH_3CN$ or DMF[9-11] at room temperature, a pale purple $CO_2$ adduct formed immediately.[12] No such reaction was found for $NiL^+$.[13] Solutions of the $CO_2$ adduct are diamagnetic,[14] and a 1:1 adduct (eq 1) is the dominant cobalt species over the concentration range 0.1–6 mM Co(I), 0.1–1 atm $CO_2$, at 25 °C.[15]

$$\mathrm{Co([14]diene)^+ + CO_2 = Co([14]diene)(CO_2)^+} \qquad (1)$$

The solid perchlorate salt,[16] isolated from $CH_3CN$ following rapid addition of THF, has C–O stretching frequencies (IR (Nujol): $\nu$(C=N) 1657 $cm^{-1}$; $\nu$(C–O) 1653, 1304, 1222 $cm^{-1}$, confirmed by $^{13}CO_2$ labeling) that are quite similar to those reported for a $Co(salen)CO_2$ derivative (1650, 1280, 1215 $cm^{-1}$)[4b] and are consistent with substantial transfer of charge to $CO_2$.

When solutions of the adduct were heated at reduced $CO_2$ pressure, partial dissociation to the parent complex was observed. Thus eq 1 could be characterized by UV–vis spectroscopy (Figure 1):[17] $\Delta G_1°(298) = (-5.5 \pm 1.0)$ kcal mol$^{-1}$, $\Delta H_1° = (-5.4 \pm 1.0)$ kcal mol$^{-1}$, $\Delta S_1° = (+0.4 \pm 3)$ cal K$^{-1}$ mol$^{-1}$. The binding constant $K_1 = (1.2 \pm 0.5) \times 10^4$ M$^{-1}$ at 298 K in $CH_3CN$ is slightly smaller than that ($7 \times 10^4$ M$^{-1}$) reported for DMSO,[7] possibly reflecting the greater "solvation" of $CO_2$ in $CH_3CN$ (solubility $S = 0.28$ M atm$^{-1}$ at 298 K[17]) than in DMSO ($S = 0.082$ M atm$^{-1}$);[7] when referred to gaseous $CO_2$ as standard state, the equilibrium constants are within experimental error of one another. The values of $\Delta H_1°$ and $\Delta S_1°$ reflect a complicated set of factors including the binding and immobilization of a linear, $CH_3CN$-solvated $CO_2$ and the transfer of substantial charge from the metal to $CO_2$.

Dilute solutions of $CoL(CO_2)^+$ are extremely stable in $CH_3CN$: a 0.3 mM solution decayed only ~15% in 10 days at 23 °C. In fact, the disappearance of $CoL(CO_2)^+$ is second order, $-d[CoL(CO_2)^+]/dt = k_{app}[CoL(CO_2)^+]^2$ ($k_{app} = (1.0 \pm 0.1) \times 10^{-3}$ M$^{-1}$ s$^{-1}$ at 23 °C, 0.1–1 atm $CO_2$, 0.1–6 mM $CoL(CO_2)^+$). The reaction products[18] are (yields based on initial Co(II)) $CoL^{2+}$ (1.0), CO (0.3), $H_2$ (0.08), and $NaHCO_3$ (0.8). The $H_2$ and $NaHCO_3$ likely arise from trace water (ca 30 ppm), and precipitation of $NaHCO_3$ is driven by its extreme insolubility in $CH_3CN$.[11] The second-order rate law suggests either direct reaction of two $CoL(CO_2)^+$ species resulting in electron and "oxide" transfer (yielding CO and $CO_3^{2-}/HCO_3^-$) or an "inner-sphere" mechanism involving a binuclear intermediate. Although the UV–vis spectral studies provide no evidence for binuclear species under the conditions of the solution equilibrium studies,[19] evidence for such a species **1**, shown in Figure 2, is found in the solid state.[20] The involvement of a binuclear species such as **1**, which contains the LCo–C(OH)O–CoL moiety,[21] in the formation of CO would be consistent with the observed rate law in $CH_3CN$ provided that there is an additional $CO_2$ (acting as $O^{2-}$ or $OH^-$ acceptor) in the activated complex.

The reversible 1:1 binding of $CoL^+$ to $CO_2$ in $CH_3CN$ and $Me_2SO$[7] reflects the strongly nucleophilic character of this low-spin $d^8$ metal center. However, $CO_2$ binding alone does not yield sufficient activation to lead to $CO_2$ reduction in these media. Instead the involvement of two $CoL^+$ centers is implicated. Although single-centered, two-electron reduction is conceivable for the cobalt systems, it is not a significant pathway in $CH_3CN$. A third pathway involving reaction of $CO_2$ with the hydride $CoL(H)^{2+}$ (the conjugate acid of $CoL^+$)[22] could be significant under electrocatalytic conditions.[6] The rich diversity of $CO_2$ binding and reduction modes in the Co[14]diene system is the focus of continuing studies.

**Acknowledgment.** We thank E. Norton for performing analyses for Co, Na, $ClO_4^-$, $HCO_2^-$, and $C_2O_4^{2-}$. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

**Supplementary Material Available:** Description of collection and reduction of X-ray data, structure refinement, description of structure, tables of atomic coordinates, thermal parameters, and bond distances and bond angles, and drawing of packing interactions (26 pages); table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

---

(17) The solubility of $CO_2$ in $CH_3CN$ as a function of temperature was determined by adding to a $CO_2$-saturated sample a known excess of aqueous $Ba(OH)_2$ which was back-titrated with standard HCl. Our solubility value, 0.28 M atm$^{-1}$ at 298 K, is an order of magnitude larger than that[5l] reported for $CH_3CN$ with 0.1 M TBAP.

(18) (a) Carbon monoxide and $H_2$ were determined by GC (molecular sieve 5A; He or Ar carrier); $NaHCO_3$, by IR and microanalysis. (b) The dependence of $k_{app}$ on [$H_2O$] is presently under study: Fujita, E., work in progress.

(19) From the spectrophotometric studies of eq 1, $K_2 \leq 1$ is obtained.

$$\mathrm{2CoL(CO_2)^+ \rightleftharpoons [CoL]_2CO_2^{2+} + CO_2} \qquad (2)$$

(20) (a) Diamond-shaped crystals of the perchlorate salt of **1** (IR (Nujol) 1661, 1643, 1610 $cm^{-1}$) were grown from THF/$CH_3CN$ over 5 days at −5 °C. Crystal data are as follows: $[Co(N_4C_{16}H_{32})]_2(CO_2H)(ClO_4)_3 \cdot 2CH_3CN$; 0.20 × 0.23 × 0.47 mm crystal, $Pca2_1$ (no. 29), $a = 23.263$ (13) Å, $b = 10.378$ (4) Å, $c = 21.551$ (4) Å, $V = 5203$ (6) Å$^3$, $Z = 4$, $\rho$(calcd) = 1.410 g/cm$^3$, $\rho$(obsd) = 1.43 g/cm$^3$ ($CCl_4$ and hexane). Enraf-Nonius Cad-4 diffractometer, $\mu = 8.66$ cm$^{-1}$ (Mo K$\alpha$) (no absorption correction applied), 23 °C, $2\theta_{max} = 40°$, $N_{refl} = 5550$, $(I > 0) = 3356$, $N_{av} = 2083$ ($R_{av} = 0.032$), ($F_o > 1.5\sigma(F_o)$) is 1449. $R = 14.0$, $R_w = 12.9$. Heavy atom solution, full-matrix least-squares refinement (SHELX-76) all non-hydrogen atoms isotropic except Co and Cl, all hydrogens were placed at calculated positions and refined with a common isotropic thermal parameter. (Data collection was attempted at 150 K, but after 3 days new peaks appeared, indicating an increase in the unit cell volume—possibly due to a phase change.) A full report of the structure will be published elsewhere. (b) The atom numbering scheme is given in the following: Goedken, V. L.; Merrell, P. H.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 3397–3405.

(21) An alternative interpretation (in which $CO_2$, not $CO_2H$, is bridging) is discussed in the Supplementary Material.

(22) (a) Tait, A. M.; Hoffman, M. Z.; Hayon, E. J. *J. Am. Chem. Soc.* **1976**, *98*, 86. (b) Creutz, C.; Fujita, E.; Schwarz, H. A.; Sutin, N.; Wishart, J. F., work in progress.