reported to be decamercurated upon treatment with mercuric trifluoroacetate.[16b] It should be anticipated that pentamercuration of cyclopentadienyl complexes will be frequently observed, provided that the complexes bear groups that impart sufficient solubility to the partially mercurated intermediates.

Complex 1 serves as a versatile synthon for pentahalocyclopentadienyl ligands and affords the pentaiodo and pentabromo derivatives upon treatment with aqueous KX_3. Moreover, the structure of 3 provides the first structural data for the pentaiodocyclopentadienyl ligand. We are continuing to work on the synthesis of mercurated metallocenes, their halogenated derivatives, and mechanistic studies aimed at probing the electronic character of mercury substituents in cyclopentadienyl complexes. These studies will be published in due course.

Supplementary Material Available: Tables listing positional parameters, thermal parameters, complete bond lengths and angles, and full experimental details for data collection and refinement for $3\cdot0.25CCl_4$, text giving experimental details for the preparation of 1-3 and their spectroscopic and analytical data, and a chart illustrating all of the possible isomers for 1 (11 pages). Ordering information is given on any current masthead page.

OM920417G

(16) For leading references, see: (a) Deacon, G. B.; Farquharson, G. J. *J. Organomet. Chem.* **1974**, *67*, C1; *Aust. J. Chem.* **1976**, *29*, 627. (b) Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1977**, *47*, 727; *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1977**, *20*, 1789.

Structure and Bonding of *cis*-$[Ru(bpy)_2(CO)(C(O)OCH_3)](B(C_6H_5)_4)\cdot CH_3CN$ (bpy = 2,2′-Bipyridine)

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Summary: The molecular structure of the title compound as a model for $[Ru(bpy)_2(CO)(C(O)OH)]^+$ was determined in order to elucidate the structural difference between $[Ru(bpy)_2(CO)(C(O)OH)]^+$ and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$, both of which are possible reaction intermediates in electrochemical and photochemical CO_2 reduction.

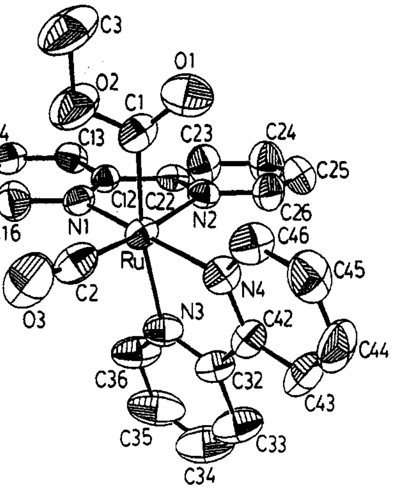

Figure 1. Molecular structure of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$. Selected bond distances (Å) and angles (deg): Ru–C1, 2.042 (6); Ru–C2, 1.800 (7); Ru–N1, 2.070 (5); Ru–N2, 2.105 (5); Ru–N3, 2.151 (5); Ru–N4, 2.093 (5); C1–O1, 1.191 (8); C1–O2, 1.344 (8); O2–C3, 1.463 (9); C2–O3, 1.154 (8); Ru–C1–O1, 125.4 (5); Ru–C1–O2, 115.4 (4); O1–C1–O2, 119.2 (6); C1–O2–C3, 116.4 (6); Ru–C2–O3, 176.5 (6).

Electrochemical[2] and photochemical[3] CO_2 reductions catalyzed by transition-metal complexes are of much interest in connection with the utilization of carbon resources. Elucidation of the bonding modes of CO_2 to those metal centers may afford fundamental information on the activation of CO_2 on the metal atoms. Among the η^1-,[4] η^2-,[5] μ_2-,[6] and μ_3-CO_2[7] metal complexes reported so far, η^1-CO_2

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(1) (a) The Graduate University for Advanced Studies. (b) National Taiwan University.

(2) (a) Dubois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8753. (b) Atoguchi, T.; Aramata, A.; Kazusaka, A.; Enyo, M. *J. Chem. Soc., Chem. Commun.* **1991**, 156. (c) Tsai, J. C.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 29. (d) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343. (e) Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1990**, 2155. (f) Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 86. (g) Tamaura, Y.; Tabata, M. *Nature (London)* **1990**, *346*, 255. (h) Ruiz, J.; Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 812. (i) Tomohiro, T.; Uoto, K.; Okuno, H. *J. Chem. Soc., Chem. Commun.* **1990**, 194. (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) (a) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1988**, 339. (b) Mandler, D.; Willner, I. *J. Am. Chem. Soc.* **1987**, *109*, 7884. (c) Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553. (d) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105. (e) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 1035. (f) Hawecher, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (g) Ziessel, R.; Hawecher, J.; Lehn, J.-M. *Helv. Chim. Acta* **1986**, *69*, 1065. (h) Hawecher, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56. (i) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161. (j) Kitamura, N.; Tazuke, S. *Chem. Lett.* **1983**, 1109. (k) Hawecher, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536.

(4) (a) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914. (b) Harlow, R. L.; Kinney, J. B.; Herskovitz, T. *J. Chem. Soc., Chem. Commun.* **1980**, 813. (c) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(5) (a) Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. (b) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145. (c) Aresta, M.; Nobile, F. *J. Chem. Soc., Chem. Commun.* **1975**, 636.

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complexes have been proposed as active species in electrochemical and photochemical CO_2 reductions.[2a] We have reported the molecular structure of an η^1-CO_2 complex of ruthenium, $[Ru(bpy)_2(CO)(CO_2)]\cdot 3H_2O$[8] (bpy = 2,2′-bipyridine) (1), which exists as equilibrium mixtures with $[Ru(bpy)_2(CO)(C(O)OH)]^+$ (2) and $[Ru(bpy)_2(CO)_2]^{2+}$ (3) in H_2O[9] (eqs 1 and 2). 2 and 3 are possible precursors for

$$\underset{1}{[Ru(bpy)_2(CO)(CO_2)]} + H^+ \rightleftarrows \underset{2}{[Ru(bpy)_2(CO)(C(O)OH)]^+} \quad (1)$$

$$\underset{2}{[Ru(bpy)_2(CO)(C(O)OH)]^+} + H^+ \rightleftarrows \underset{3}{[Ru(bpy)_2(CO)_2]^{2+}} + H_2O \quad (2)$$

the formation of CO and $HCOO^-$, respectively, in electrochemical[10] and photochemical[11] CO_2 reduction. Disproportionation of 2 to 1 and 3 in an aqueous and an organic solution caused serious difficulties in growing single crystals of 2. The molecular structure of $[Ru(bpy)_2(CO)(C(O)OCH_3)]^+$ as a model compound for 2, therefore, is of great interest from the viewpoint of elucidation of the interconversion between 1 and 2 by a diffusion-controlled reaction. This communication reports the crystal structure of $[Ru(bpy)_2(CO)(C(O)OCH_3)](B(C_6H_5)_4)\cdot CH_3CN$ (4) and comparison of the bond characters between Ru–$C(O)OCH_3$ in 4 and Ru–CO_2 in 1.

The reaction of 1 with CH_3I in CH_3OH affords $[Ru(bpy)_2(CO)(C(O)OCH_3)]I$ in almost quantitative yield, and the PF_6 salt of 4 is also synthesized by the reaction of the PF_6 salt of 3 with CH_3ONa.[9] Single crystals of 4 were obtained by slow evaporation of an acetonitrile solution containing the $(B(C_6H_5)_4)_2$ salt of 3 and 1 equiv of CH_3ONa. The Ru atom is octahedrally coordinated, and the methoxycarbonyl moiety is in a cis position with the carbonyl ligand (Figure 1).[12] The bond distances and angles for the 2,2′-bipyridine ligands of 4 are similar to those for 1 and also close to those of the other 2,2′-bipyridine complexes of ruthenium.[13] The C1–O1 and C1–O2 bond distances for 4 are 1.191 (8) and 1.344 (8) Å, respectively. It is worthy of note that the average of the C1–O1 and C1–O2 bonds (1.268 Å) for 4 is essentially same as that of the two C–O bonds in the CO_2 moiety of 1 (1.264 Å). The Ru–C1 distance (2.042 (6) Å) for 4 is close to the metal–carbon bond distance for the previously reported (methoxycarbonyl)rhodium complex (2.041 (5) Å).[14] The fact, however, that the Ru–C1 distance for 4 is shorter than the Ru–CO_2 bond distance for 1 (2.064 (13) Å) indicates that the multibond character of the Ru–$C(O)OCH_3$ bond in 4 is not smaller than that of the Ru–CO_2 bond of 1, although a metal–CO_2 bond in $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$ is proposed to have a carbene character ($W{=}CO_2^{2-}$) of the Fisher type.[15] On the basis of the similarity of the ^{13}C NMR chemical shifts of the carbonyl and methoxycarbonyl carbons (δ 202.2 and 206.8) of 4[16] with those of the carbonyl and hydroxycarbonyl carbons of 2 (δ 201.5 and 205.1) in CD_3OD, the electronic structure of the methoxycarbonyl carbon of 4 may be close to that of the hydroxycarbonyl carbon of 2. This assumption implies that a negative charge resulting from dissociation of the proton from the hydroxycarbonyl moiety of 2 (eq 1) is mainly localized on the CO_2 group of 1 rather than delocalized on the $RuCO_2$ moiety. The localization may enable a smooth reversible conversion to 2 in H_2O (eq 1), similar to the case for organic carboxylic acids.

Supplementary Material Available: For this structure study, tables of atomic parameters and *U* values (4 pages). Ordering information is given on any current masthead page.

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(6) John, G. R.; Johnson, B. F. G.; Lewis, J.; Wong, K. C. *J. Organomet. Chem.* 1979, *169*, C23.

(7) (a) Eady, C. R.; Guy, J. J.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* 1976, 602. (b) Beck, W.; Raab, K.; Nagel, U.; Steimann, M. *Angew. Chem., Int. Ed. Engl.* 1982, *115*, 2271. (c) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Mann, B. E.; Caulton, K. G. *Inorg. Chem.* 1990, *29*, 128.

(8) Tanaka, H.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Organometallics* 1992, *11*, 1450.

(9) Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* 1986, *5*, 724.

(10) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* 1987, *6*, 181.

(11) Ishida, H.; Terada, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* 1990, *29*, 905.

(12) Crystal data for 4: $C_{49}H_{42}O_3N_5BRu$, $M_r = 860.77$, triclinic space group $P1$, $a = 9.548$ (3) Å, $b = 13.004$ (5) Å, $c = 17.743$ (4) Å, $\alpha = 77.26$ (3)°, $\beta = 74.89$ (2)°, $\gamma = 83.64$ (3)°, $V = 2071.1$ (12) Å^3, $Z = 2$, $D_c = 1.380$ g cm^{-3}, $F(000) = 844$, $\lambda = 0.70930$ Å, $\mu(\text{Mo K}\alpha) = 4.25$ cm^{-1}, crystal dimensions 0.03 × 0.25 × 0.30 mm. $R_F = 0.045$ for 7219 unique reflections with $F > 2\sigma(F)$ and 532 variables. Data were collected by θ–2θ techniques ($0 < 2\theta < 50°$) 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.

(13) Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczek, F. R.; Selbin, J. *Inorg. Chem.* 1985, *24*, 4078.

(14) Burk, P. L.; Engen, D. V.; Campo, K. S. *Organometallics* 1984, *3*, 493.

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

(16) Other observed signals on a ^{13}C NMR spectrum are as follows (67.8 MHz, CD_3OD): 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 (the 2,2′-bipyridine ligands); δ 49.9 (the methyl group).

Phase-Transfer Photolysis of Metal Hexacarbonyls

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Summary: The photochemical conversion of $M(CO)_6$ (M = Cr, Mo, W) to $M(CO)_5X^-$ (X = halogen) across a hexane/water interface leads to a separation of the reactant and product. This process may be of general importance for synthetic applications. Under suitable conditions inner-filter effects and secondary photolysis can be avoided.

Photochemical reactions in microheterogeneous media have been investigated extensively.[1,2] In particular excited-state electron transfer of metal complexes has been

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(1) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.

(2) Thomas, J. K. *The Chemistry of Excitation at Interfaces*; ACS Monograph 181; American Chemical Society: Washington, DC, 1984.

0276-7333/92/2311-3172$03.00/0