was supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 02740254) from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Detailed information on the X-ray crystal analysis of **1b** and a mass spectral data table (observed and calculated abundances of isotopomers of M$^+$) for **1b** (18 pages); a table of observed and calculated structure factors for **1b** (7 pages). Ordering information is given on any current masthead page.

Reduction of Coordinated Carbon Dioxide by Transition-Metal Hydrides

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Received October 3, 1990

Summary: The reactions of $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (**1**) with the transition-metal hydrides $HCo(CO)_4$ and $H_2Fe(CO)_4$ have been examined. **1** reacts with excess $HCo(CO)_4$ rapidly at -78 °C to produce $[(\eta^5\text{-}C_5H_5)_2MoH(CO)]Co(CO)_4$ (**2**), $HCo_3(CO)_9$, and H_2O. $^{13}CO_2$-labeling experiments indicate that the original CO_2 in **1** is converted to coordinated CO in **2**. Complex **2** slowly converts to a novel unsymmetrically bridged hydrido complex $(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ (**3**) whose structure has been established by X-ray diffraction. Complex **1** also reacts with excess $H_2Fe(CO)_4$ to produce $[(\eta^5\text{-}C_5H_5)_2MoH(CO)][HFe_3(CO)_{11}]$ (**4**).

The attractiveness of carbon dioxide as a potential feedstock for organic chemicals has stimulated increasing interest in the organometallic chemistry of this abundant, yet typically unreactive molecule.[1] Nonetheless, proven examples of reactions of *coordinated* CO_2 are surprisingly few. In this regard, we have shown recently that $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (1) undergoes novel photoinduced disproportionation[2] and reacts readily with a variety of polar reagents E–Nu, giving complexes of the type $[(\eta^5\text{-}C_5H_5)_2Mo(CO)Nu]Nu$ and E–O–E, the result of O-transfer from coordinated CO_2.[3] In an effort to assess the potential benefits of cooperative bimetallic activation[4,5] for facilitating *catalytic* carbon dioxide reduction, we have begun to examine the interaction of 1 with representative transition-metal hydride complexes producible from dihydrogen. We report herein our initial observations, which include (1) the discovery of facile reduction of coordinated CO_2 in 1 by $HCo(CO)_4$ and $H_2Fe(CO)_4$, resulting in the formation of heterobimetallic carbonyl complex salts, and (2) the production of a novel unsymmetrically bridged hydridocarbonyl dinuclear complex.

We first examined the reaction of 1[2,6] with strongly acidic $HCo(CO)_4$ (pK_a = <0 in H_2O, 8.4 in CH_3CN[7]). Treatment of a CD_2Cl_2 solution of 1 with an excess (ca. 5 equiv) of $HCo(CO)_4$ at -90 °C resulted in an immediate darkening of the solution; ^1H NMR monitoring indicated complete consumption of 1 and the appearance of new absorptions at δ 5.60 (Cp), -8.30 (MH), and 1.62 (H_2O, confirmed by spiking). A preparative-scale reaction in toluene followed by addition of pentane afforded greenish yellow crystals of 2 (82% yield) whose NMR spectrum,[8] prominent M–CO IR absorptions at 1880 and 2030 cm^{-1}, and mass spectral data[8] suggested the presence of $[Co(CO)_4^-]$[9] and $[Cp_2Mo(CO)X^+]$[3,10] units. On the basis of these spectroscopic data and comparison with literature values,[11] 2 is identified as $[Cp_2Mo(CO)H][Co(CO)_4]$. Evaporation of the above solution afforded $HCo_3(CO)_9$[12] as the other

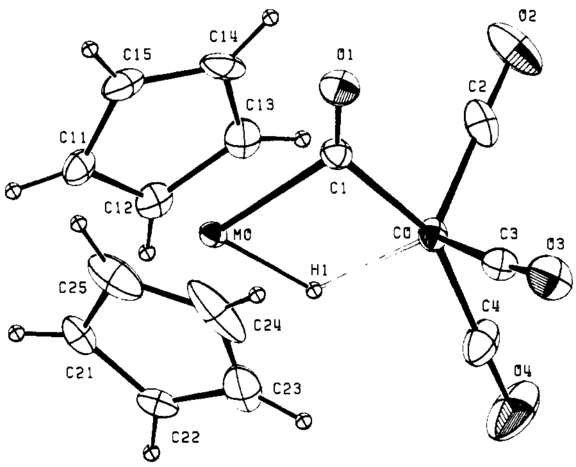

Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ (**3**). Selected bond distances (Å): Mo–Co 2.8449 (4); Mo–C(1) 2.190 (2); Co–C(1) 1.905 (2); C(1)–O(1) 1.181 (3); Mo–H(1) 1.64 (3); Co–H(1) 1.88 (3); Mo–Cp(1) 1.969 (1); Mo–Cp(2) 1.965 (2); Co–C(2) 1.768 (3); Co–C(3) 1.772 (3); Co–C(4) 1.818 (3). Selected bond angles (deg): Cp(1)–Mo–Cp(2) 141.5 (1); C(1)–Mo–H(1) 81 (1); C(1)–Co–H(1) 83 (1); C(1)–Co–C(2) 92.0 (1); C(1)–Co–C(3) 89.7 (1); C(1)–Co–C(4) 158.0 (1); C(2)–Co–C(3) 113.0 (1); C(2)–Co–C(4) 103.7 (1); C(3)–Co–C(4) 97.9 (1).

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(1) Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: W. Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

(2) Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

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(4) The reduction of a bimetallic μ-carboxylate complex by Cp_2ZrHCl has been reported: Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

(5) Several examples of bimetallic and trimetallic complexes of CO_2 exist, but little is known of their reactivity; see: Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Chem. Soc.* **1982**, *104*, 5082. Also see other examples cited in ref 4.

(6) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

(7) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, CA, 1987; p 91.

(8) ^1H NMR (acetone-d_6) 5.85 (s, 10 H), -8.2 (s, 1 H); MS for 2 (12 eV DIP) *m/e* 256 ($Cp_2{}^{98}MoCO$), 228 ($Cp_2{}^{98}Mo$), 172 ($HCo(CO)_4$), 144 ($HCo(CO)_3$), 116 ($HCo(CO)_2$), 88 ($HCo(CO)$).

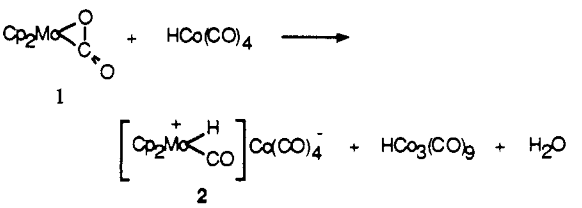
(9) Edgell, W. F.; Hedge, S.; Barbetta, A. *J. Am. Chem. Soc.* **1987**, *100*, 1406.

(10) Bell, L. G.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *135*, 173.

(11) Mugnier, Y.; Moise, C. *J. Organomet. Chem.* **1963**, *248*, C33.

(12) Green-black solid: IR (KBr) 2060, 2030, 1850, 1830 cm^{-1}; MS (70 eV, DIP) *m/e* 430 (M$^+$), 429 ($Co_3(CO)_9$), 401 ($Co_3(CO)_8$). Literature data for $HCo_3(CO)_9$: Fachinetti, G.; Balocchi, L.; Secco, F.; Venturini, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 204. Fachinetti, G.; Pucci, S.; Zanuzzi, P.; Methong, U. *Ibid.* **1979**, *18*, 619.

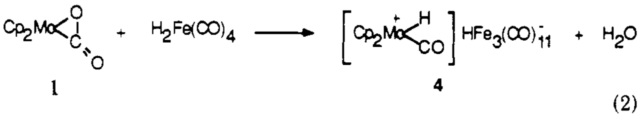
major Co-containing product (eq 1). That **2** is derived from a reaction of coordinated CO_2 was demonstrated by the formation of $[Cp_2Mo(^{13}CO)H][Co(^{13}CO)_4]$ in the reaction of $HCo(CO)_4$ with $Cp_2Mo(\eta^2\text{-}^{13}CO_2)$.[13]


(1)

Interestingly, when CH_2Cl_2/pentane solutions of **2** were allowed to stand for 2–3 days at −20 °C, red crystals of a new complex **3** deposited. IR, ^1H NMR, and MS analyses of **3**[14] indicated the presence of both Cp_2Mo, $Co(CO)_{3,4}$, bridging carbonyl, and metal hydride units. X-ray diffraction analysis of **3**[15] revealed the novel structure $Cp_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ shown in Figure 1.

We presume that **3** arises via loss of CO from **2**. Although the structure and bonding of **3** will be discussed fully in a later account, the following features are especially significant: (1) *the bridging hydride atom*, which was located unambiguously and with high precision, *resides markedly closer to the larger Mo atom*,[16] suggesting a stronger interaction with this metal; and (2) **3** is 2 electrons short of the closed-shell electron count of 36, raising interesting questions about metal–metal and metal–hydride bonding.

Complex **1** also was found to react, albeit more slowly (ca. 10 h at −20 °C in toluene), with an excess of the less acidic $H_2Fe(CO)_4$ (pK_a = 4.0 in H_2O, 11.4 in CH_3CN[7]), resulting in the formation of a deep-red solution. Addition of pentane caused precipitation of burgundy red crystals of **4** (ca. 100%). IR, ^1H NMR, MS, and X-ray diffraction analyses[18] have been employed to establish the identity of **4** as $[(\eta^5\text{-}C_5H_5)_2Mo(CO)H][HFe_3(CO)_{11}]$[19] (eq 2). ^1H NMR monitoring of this reaction in CD_2Cl_2 revealed the initial formation of an unidentified intermediate that decays as **4**, and H_2O is generated.


(2)

Reactions of the CO_2 complex **1** with both $HCo(CO)_4$ and $H_2Fe(CO)_4$ have thus been found to produce salts of the type $[Cp_2MoH(CO)][M_x(CO)_y]$, which fix the original coordinated CO_2 as CO and produce H_2O as the oxygen sink, a formal stoichiometric water gas shift reaction (eq 3). Since control experiments have demonstrated the lack

$$CO_2 + H_2 \dashrightarrow CO + H_2O \qquad (3)$$

of reactivity between CO_2 itself and $HCo(CO)_4$ and $H_2Fe(CO)_4$, the reactions indicated by eqs 1 and 2 illustrate a rare example of cooperative bimetallic activation of CO_2. The contrast between the earlier reported cleavage of coordinated CO_2 in **1** by HX and R_3SiX[3] (giving $Cp_2Mo(CO)X^+$) (eq 4) and by $H_xM'(CO)_y$ (forming Cp_2Mo-

$$Cp_2Mo(CO_2) + 2\ E\text{-}X \dashrightarrow Cp_2Mo(CO)X^+X^- + E\text{-}O\text{-}E \qquad (4)$$

$(CO)H^+$, eqs 1 and 2) should also be noted. Whether the formation of the carbonyl hydride cationic complexes in eqs 1 and 2 reflects an instability of the Mo–Co and Mo–Fe σ-bonded alternatives (thermodynamic) or rather a fundamentally different mechanism of H-transfer steps remains to be seen. Nonetheless, the ability of these and other transition-metal complexes to activate and transfer dihydrogen[20] raises the attractive possibility that bimetallic *catalytic* systems can be devised for CO_2 reduction.

Acknowledgment. We are grateful for support provided by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (89ER 13997) and to Pressure Chemical Co. for a gift of cobalt carbonyl.

Note Added in Proof. The structure of **2** has been confirmed by X-ray diffraction.[21]

Supplementary Material Available: Tables of atomic coordinates, positional and thermal parameters, and interatomic distances and angles (5 pages). Ordering information is given on any current masthead page.

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(13) A 50% enriched sample of $Cp_2Mo(\eta^2\text{-}^{13}CO_2)$ was treated with excess $HCo(^{12}CO)_4$ in CH_2Cl_2 at −78 °C. The resulting $[Cp_2Mo(CO)H]$-$Co(CO)_4$ when analyzed by IR and MS (12 eV, DIP) was found to have 4 atom % ^{13}CO in the $Cp_2Mo(CO)H^+$ unit and 20 atom % in the $Co(CO)_4$ fragment, an approximately statistical distribution expected from rapid scrambling between the cationic and anionic fragments.

(14) **3**: IR (KBr) 2040, 1965, 1915, 1740 cm^{-1}; ^1H NMR (C_6D_6) 4.02 (s, 10 H), −5.2 (br s, 1 H); MS (12 eV, DIP) *m/e* 256 ($Cp_2{}^{98}MoCO$), 228 ($Cp_2{}^{98}Mo$), 180 ($CpCo(CO)_2$), 152 (CpCoCO), 124 (CpCo).

(15) X-ray crystal data for **3** (data collected at −110 °C) $[C_{14}H_{11}O_4CoMo]$: M_r = 398.11, monoclinic space group $P2_{1/n}$, a = 21.958 (5) Å, b = 7.625 (2) Å, c = 8.204 (2) Å, β = 98.16 (3) Å, V = 1359.7 $Å^3$, Z = 4, D_c = 1.945 g cm^{-3}, $F(000)$ = 784, $\lambda(Mo\ K\alpha)$ = 0.71069 Å, $\mu(Mo\ K\alpha)$ = 20.3 cm^{-1}. Cell dimensions and intensities of 3040 reflections ($2\Theta_{max}$ = 55°) were measured. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically, and the least-squares refinement coverged at the final R = 0.029. A difference Fourier map showed all H atoms with peak heights between 0.56 and 0.93 e $Å^3$; the hydride atom had a peak height of 0.67 e $Å^3$ but was not included in the refinement. A subsequent difference Fourier map showed one peak at 0.68 e $Å^3$ at the location of the hydride, while the next highest peak was at 0.34 e $Å^3$. All the hydrogen atoms were refined with an isotropic temperature factor; the temperature factor of the hydride was third highest among the H atoms but not unusual in value and refined properly to its final value. All calculations were carried out by using the SHELX-76 program. For 2399 unique observed reflections [$I > 2\sigma(I)$], the final R = 0.020, R_w = 0.025, and GOF = 0.98.

(16) Out of hundreds of metal–hydride X-ray structure determinations, relatively few high precision structures exhibit significantly unsymmetrical H bridging. Among the heterobimetallic structures, with very few exceptions (ref 17), the H is located closer to the smaller metal.

(17) Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1314.

(18) **4**: IR (KBr) 2070, 2030, 1990, 1950, 1930, 1720 cm^{-1}; ^1H NMR (acetone-d_6) 5.85 (s, 10 H), −8.2 (s, 1 H), −14.85 (s, 1 H); MS (12 eV, DIP) *m/e* 256 ($Cp_2{}^{98}MoCO$), 228 ($Cp_2{}^{98}Mo$); MS (neg. CI, NH_3) 448 ($Fe_3(CO)_{10}^-$), 420 ($Fe_3(CO)_9^-$), 392 ($Fe_3(CO)_8^-$), 168 ($Fe(CO)_4^-$). X-ray crystal data: monoclinic, space group $P2_1/c$, a = 12.183 (4) Å, b = 12.004 (4) Å, c = 17.355 (6) Å, β = 94.13 (3)°. Spectroscopic and unit cell parameters are in agreement with those reported for **4** in ref 19.

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(21) Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. Unpublished results, 1990.