Transition-Metal-Mediated Photochemical Disproportionation of Carbon Dioxide

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Efforts to activate carbon dioxide by transition-metal complexes[1] have centered primarily on its organometallic chemistry[2] and transition-metal-mediated electrochemistry[3] and, to a limited extent, on metal-mediated photochemical reduction.[4] A common feature of coordinated CO_2 reactivity emerging from studies of its interaction with electron-rich metal complexes is O-atom transfer, most commonly manifested as reductive disproportionation (eq 1, Sub = CO_2).[5] In a few instances O-transfer to a

Scheme I

$$L_nM + CO_2 \rightarrow L_nM(CO_2) \qquad (a)$$

$$L_nM(CO_2) \rightarrow L_nM{=}O \text{ or } L_nM(CO_3) + CO \qquad (b)$$

$$L_nM{=}O \text{ or } L_nM(CO_3) + Sub \rightarrow L_nM \text{ or } L_nM(CO_2) + SubO \qquad (c)$$

$$CO_2 + Sub\ (+2e^-) \rightarrow CO + SubO^{2-} \qquad (1)$$

substrate other than CO_2 has been observed such as to oxophilic metals,[6] isocyanides,[7] or phosphines,[8] the latter catalytically.[9] In an effort to expand the scope of these reactions and to overcome their thermodynamic limitations, we are seeking complexes which could mediate CO_2 splitting photochemically, as in Scheme I. It appeared that the molybdenocene system ($L_nM = Cp_2Mo$) might be a suitable one for this purpose since not only are several anticipated intermediates in the putative Scheme I known, i.e., Cp_2Mo,[10] Cp_2MoO,[11] Cp_2MoCO,[12] and $CpMo(CO_2)$,[13] but $CpMoL_{1,2}$ complexes in general appear to be photochemically active toward M–L scission.[14] Resulting from our initial investigations of the molybdenocene–CO_2 system, we provide here the first example of *photoinduced* disproportionation of coordinated carbon dioxide.

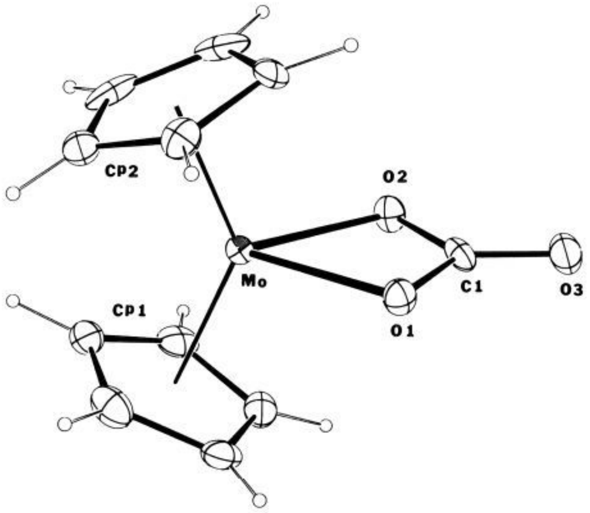

Figure 1. Perspective view of **2**. Thermal ellipsoids are shown at the 50% level, and hydrogen atoms are plotted as spheres of 0.05 Å radius: Mo–O(1), 2.098 (3); Mo–O(2), 2.095 (3); Mo–Cp_1, 1.977 (5); Mo–Cp_2, 1.986 (5); C(1)–O(1), 1.337 (6); C(1)–O(2), 1.322 (6); C(1)–O(3), 1.216(6); O(1)–Mo–O(2), 62.6 (1); Mo–O(1)–C(1), 93.4 (3); Mo–O(2)–C(1), 93.9 (3); O(1)–C(1)–O(2), 110.1 (4); O(1)–C(1)–O(3), 124.6 (5); O(2)–C(1)–O(3), 125.4 (4); Cp_1–Mo–Cp_2, 133.9 (2).

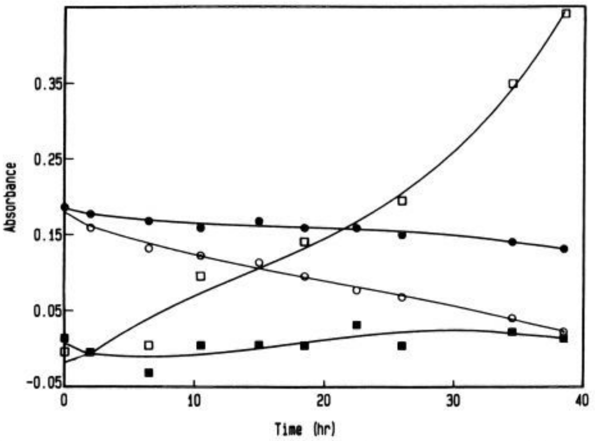

Figure 2. Infrared absorbance changes during the reaction of $Cp_2Mo(CO_2)$ (**1**) with CO_2 (THF, −10 °C) showing the disappearance of **1** (at 1740 cm^{-1})—(○) photolyzed, (●) dark—and the appearance of $Cp_2Mo(CO_3)$ (at 1630 cm^{-1})—(□) photolyzed, (■) dark.

Irradiation (>330 nm)[15] of a 0.05 M THF solution of Cp_2MoH_2 at −10 °C under 1 atm of CO_2 with continuous GC, IR, and ^1H NMR monitoring initially revealed the disappearance of the starting complex (1–3 h) and the formation of $[(C_5H_5)(C_5H_4)Mo]_2$,[16] $Cp_2Mo(\eta^2\text{-}CO_2)$[13] (**1**: IR 1740 cm^{-1}; ^1H NMR δ 5.07), and H_2.[17] Continued irradiation (3–30 h) resulted in the disappearance of **1** and the appearance of $Cp_2Mo(CO)$[12] (IR 1910

[†] Direct inquiries regarding X-ray diffraction results to this author.

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cm^{-1}, 4.48 ppm), free CO,[18] and a new complex **2** as a dark red precipitate with IR bands at 1670 and 1635 cm^{-1} (1620, 1590 cm^{-1} $^{13}CO_2$) and a single Cp resonance at 5.46 ppm.

$$\begin{array}{c} Cp_2MoH_2 + CO_2 \xrightarrow[THF]{h\nu} Cp_2Mo(\eta^2\text{-}CO_2) + [(C_5H_5)(C_5H_4)Mo]_2 + H_2 \\ \mathbf{1} \\ {\scriptstyle h\nu,\ CO_2}\Big\downarrow{\scriptstyle THF} \\ \mathbf{2} + Cp_2Mo(CO) + CO \end{array} \qquad (2)$$

The fact that isolated complex **2** released CO_2 when treated with aqueous HCl and that **2** was also produced from the reactions of $NaHCO_3$ or Na_2CO_3 with Cp_2MoCl_2 ($EtOH/H_2O$/20 °C) led us to suspect **2** to be a carbonate complex. Ultimately, single crystals of **2** were obtained from THF/ethanol, and its structure was established by X-ray diffraction.[19] Figure 1 shows **2** to be $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_3)$. The structure of **2** features a planar molybdenum–carbonate fragment which approximately bisects the angle defined by the two Cp–Mo vectors (133.9 (2)°). Symmetrical bidentate coordination of the carbonate ligand is reflected in the equal Mo–O lengths. Within the carbonate unit essentially localized bonding is indicated by the long C(1)–O(1) and C(1)–O(2) bonds (1.337 (6), 1.322 (6) Å) and short C(1)–O(3) (1.216 (6) Å).[20-22]

The formation of carbonate complex **2** during photolysis naturally raises the question of whether the **1** → **2** transformation is itself photoinduced. Indeed, the following results clearly provide an affirmative response on this point: (1) the rate of carbonate (**2**) formation from Cp_2MoH_2 during irradiation is roughly the same at both −10 and +40 °C (determined by isolation), and (2) at −10 °C *transformation of CO_2 complex **1** to **2** occurs appreciably only during irradiation.* Figure 2 shows the dramatically accelerated disappearance of CO_2 complex **1**[23] (and appearance of carbonate **2**[18]) when irradiated compared to a dark control, monitored by IR. The quantum yield for the **1** → **2** conversion at 366 nm was found to be 0.04 (±0.02),[24] almost as efficient as the photoexpulsion of H_2 from Cp_2MoH_2 (ca. 0.1).[14a]

Although elucidation of the **1** → **2** mechanism must await the results of experiments in progress, free Cp_2MoO (Scheme I) apparently *is not* an intermediate since its reaction with CO_2 (Δ or *hν*) to give **2** was found to be much slower ($t_{1/2} > 100$ h) than the **1** → **2** photoconversion.[25]

These results provide the first solution phase example of photochemical activation of a metal–carbon dioxide complex.[26] Studies to further characterize the photoreactivity of **1** and to expand the scope of transition-metal-medated photochemical oxidations with carbon dioxide are underway.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles and a structure of **2** showing numbering of Cp ring carbon atoms (5 pages). Ordering information is given on any current masthead page.

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[18] $Cp_2Mo(CO)$ photodissociates CO under these conditions[14] so that ^1H NMR monitoring initially shows parallel growth of **2** and $Cp_2Mo(CO)$ followed by gradual decline of the latter.

[19] Crystal data: Crystals of **2** were unstable at room temperature but stable at low temperature. Anal. Calcd for $C_{11}H_{10}MoO_3$: C, 46.2; H, 3.4; Mo, 33.5. Found: C, 45.5; H, 3.8; Mo, 32.7. $M_r = 286.14$, monoclinic space group $P2_1/n$ (nonstandard setting of $P2_1/c$), $a = 6.019$ (1) Å, $b = 12.752$ (2) Å, $c = 12.129$ (2) Å, $\beta = 94.60$ (3)°; $V = 927.9$ Å^3, $Z = 4$, $D_c = 2.048$ g cm^{-3}, $F(000) = 568$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 12.5$ cm^{-1}. Cell dimensions and intensities of 1627 reflections were measured at −135 (2) °C ($2\theta_{max} = 50°$, $\pm h,k,l$) on an Enraf-Nonius CAD-4 diffractometer fitted with a low-temperature device. The structure was solved by the heavy-atom method and refined anisotropically by full-matrix least-squares (hydrogen atoms were refined isotropically). All calculations were carried out by using the SHELX-76 program. For 1529 unique observed reflections [$I > 2\sigma(I)$] the final $R = 0.029$, $R_w = 0.034$, GOF = 1.6. $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

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[23] The $Cp_2Mo(CO_2)$ employed in these experiments was isolated in ca. 33% yield by irradiation of Cp_2MoH_2 for 4 h followed by THF removal in vacuo and trituration with CO_2-saturated toluene (to remove unreacted Cp_2MoH_2 and $Cp_2Mo(CO)$).

[24] Lamp intensity was determined by using ferrioxalate actinometry at the 366-nm Hg line (band pass filter). Disappearance of **1** was monitored in the IR at 1745 cm^{-1}. The modest quantum yield may reflect the incursion of competing nonproductive processes, e.g., photoexpulsion/recombination of CO_2 and/or radiative decay to ground state.

[25] Furthermore, no Cp_2MoO was detected by IR or ^1H NMR during the photolysis of **1**.

[26] The studies listed in ref 4 involve photochemical production of a reduced metal complex which reacts thermally with CO_2 to give CO. Photooxidation of $M(CO)_6$ (M = Cr, W) by CO_2 in an argon matrix (20 K) has been observed, apparently via photoactivation of a transient CO_2 complex (ref 27).

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The Gas-Phase Chemistry of the Silaacetylide Anion, $HCSi^-$

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The tandem flowing afterglow selected ion flow tube (FA-SIFT) is a versatile instrument which is especially suited to the investigation of the gas-phase chemistry of unusual ions.[1] We have used this instrument to generate the silaacetylide anion, $HC{\equiv}Si^-$,[11] and wish to report some chemistry of this interesting ion, particularly reactions which support the structure given over that of its tautomer. Ions of this type are of interest because of recent studies on the preparation of the neutral silicon–nitrogen triple bond[2] and the silicon–silicon triple bond synthon.[3] Our work represents the first report on the parent compound, $H_2C{=}Si{:}$.[4,11] A host of other unsaturated silicon anions can also be studied by this technique, and we report preliminary results on the chemistry of an ion of mass 43 to which we tentatively assign the structure $H_2Si{=}CH^-$.

In the FA-SIFT a mixture of anions of different masses can be produced by direct electron impact at 1 Torr helium pressure on silicon-containing neutrals in the first flow tube. Under these conditions, secondary reactions of ions with neutral precursors give rise to a rich array of ionic products. For example, electron impact on methylsilane produces over 20 anions corresponding in mass to Si^-, SiC^-, Si_2^-, and Si_2C^-, together with many of their hydrogenated analogues. At the end of this flow tube the ions

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[†] Denver.

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