^{1}H NMR (90 MHz, CD_2Cl_2, −50 °C): 6.87–7.96 (m, 40 H, Ph), 4.64 and 2.85 (m, 2 × 2 H, PCH_2P), 0.63 (d, J_{HP} = 13 Hz, 18 H, PMe_3). ^{31}P NMR (36 MHz, CD_2Cl_2, −50 °C): 11.4–14.2 (m, 4 P, dppm), −22.9 to −28.7 (m, 2 P, PMe_3). IR (solid): $\nu(SO_2)$, 1153 (s) and 1042 cm^{-1}.

Preparation of RhCl(PMe_3)(dppm) (3). A solution of dppm (162 mg, 0.419 mmol) in toluene (2 mL) was added to a stirred solution of $[RhCl(COD)]_2$ (104 mg, 0.211 mmol) in 2 mL of toluene. PMe_3 (4.2 μL, 0.44 mmol) was injected into the rapidly stirred orange solution. A yellow precipitate formed which, after 0.5 h, was removed by filtration, washed with Et_2O, and dried in vacuo. Yield: 190 mg (75%). The product is slightly soluble in toluene, X-ray-quality crystals were grown from toluene/Et_2O.

^{1}H NMR (90 MHz, CD_2Cl_2): 7.36–8.51 (m, 20 H, Ph), 3.98 (t, J_{HP} = 13 Hz, 2 H, PCH_2P), 1.10 (d, J_{HP} = 7.6 Hz, 18 H, PMe_3). ^{31}P NMR (36 MHz, CD_2Cl_2, −50 °C): −4.1 to −19.7 (m, 2 P, dppm), −32.9 to −49.6 (m, 1 P, PMe_3). See the supplementary material for the structure determination.

Preparation of $[Rh_2(NO)_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2](BF_4)_2$ (4). Solid $NOBF_4$ (24 mg, 0.20 mmol) was added to a stirred brown solution of $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ (102 mg, 0.092 mmol) in 3 mL of CH_2Cl_2. A brown precipitate formed. After ca. 4 h the reaction volume was reduced in vacuo to ca. 1 mL, and the brown product was isolated by filtration and drying in vacuo. Yield: 114 mg (97%).

Alternatively, the reaction may be done as above in ethyl acetate. However, the resulting pale brown product (IR (mineral oil): ν(NO), 1635 (s sh), 1624 (s), 1592 (s) cm^{-1}), isolated as described above, is not **4** and has not been identified. When this solid is dissolved in CH_2Cl_2, crystals of a CH_2Cl_2 solvate of **4** precipitate within a few minutes. Yield: 76%.

IR (mineral oil mull): ν(NO), 1828 (s) cm^{-1}. Complex **4** is insoluble in noncoordinating or weakly coordinating solvents (THF). It dissolves in MeCN to give a green product with the following spectroscopic properties. IR (mineral oil mull): ν(NO), 1653 (m br) cm^{-1} (no MeCN peak was detected). ^{1}H NMR (90 MHz, CD_3CN): 7.24 (br, 40 H, Ph), 4.39 (quintet, J_{HP} = 5 Hz, 4 H, PCH_2P). ^{31}P NMR (36 MHz, CD_3CN): 7.1 (d, J_{PRh} = 103.5 Hz).

Structure Analyses. An abbreviated summary of crystallographic and data collection parameters for **4** is given in Table I. A full table, including the structure of **3**, and details of the structure determinations may be found in the supplementary material.

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Supplementary Material Available: Figures showing ORTEP diagrams of **3** and **4**, tables listing crystallographic and data collection parameters, positional parameters, anisotropic thermal parameters, and bond distances and angles for **3** and **4** and least-squares planes for **4**, and a summary describing structure determinations for **3** and **4** (11 pages); listings of structure factors for **3** and **4** (33 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry
and Biochemistry, University of California,
Los Angeles, California 90024, and
Department of Chemistry, University of California,
Santa Barbara, California 93106

Metallo–Oxo Complex Formation from Photochemical Cleavage of Bis(cyclopentadienyl)molybdenum Carbonate

Maher Henary,[†] William C. Kaska,[*,‡] and Jeffrey I. Zink[*,†]

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Introduction

Photochemical carbon–oxygen bond cleavage of carbon dioxide or the carbonate ion requires high-energy vacuum UV irradiation.[1] However, complexation of these molecules to a transition-metal ion lowers the energy required for this cleavage to occur.[2-4] In the case of the coordinated carbonate ion, two simple cleavage reactions are possible: breaking one carbon–oxygen bond gives carbon dioxide and the oxide ion, while breaking two carbon–oxygen bonds gives carbon monoxide and the elements of the peroxide ion. Both the oxide and the peroxide ions can act as ligands for early transition metals in high oxidation states.[5] Thus, photolysis of transition-metal carbonato complexes offers the possibility of synthesizing metal–oxo or metal–peroxo complexes from stable precursors.[6] This is especially appealing because carbon dioxide and carbonate ion are in thermodynamic equilibrium with water:

$$CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2-}$$

Photochemical synthesis of metal–oxo compounds is not well-known. Two recent examples from our laboratories include the photolysis of a dinuclear copper carbonato complex to produce a μ-oxo complex[7] and photolysis of a rhodium carbonato complex to produce a reactive oxo complex that further interacts with starting material to produce dimers.[6] An important goal is to produce a metal–oxo complex, which can be isolated, by photolysis of a carbonato complex. Ideally, the oxo complex should be stable enough to characterize and reactive enough to transfer oxygen to various substrates. We report here the synthesis and photochemical cleavage of bis(cyclopentadienyl)molybdenum carbonate to produce bis(cyclopentadienyl)molybdenum oxide and some further reactions to give oxygen gas.

Experimental Section

Materials. All of the reactions and photolyses were performed under purified argon. The photolyses were all performed in quartz cells, and the solutions or suspensions were stirred. The photolysis of the molybdenum carbonate also occurs in Pyrex vessels although the process takes longer. Tetrahydrofuran (THF) was distilled from benzophenone ketyl under argon[8] (THF must be used immediately after distillation or the photolysis will often not occur). An authentic sample of $(C_5H_5)_2Mo{=}O$ was prepared according to the literature.[9] Photolyses were performed only on samples of Cp_2MoCO_3 that were freshly prepared and stored below −10 °C in the refrigerator.

Preparation of $(C_5H_5)_2MoCO_3$. A degassed water solution of Na_2CO_3 (0.14 g, 1.32 mmol) was added to a degassed water solution of Cp_2MoBr_2 (Cp_2MoCl_2 can be used as well) (0.255 g, 0.66 mmol) (obtained by heating green Cp_2MoBr_2 in water until it dissolved), and the resulting mixture was stirred at room temperature until the green solution of molybdenum complex became burgundy colored. The resultant solution was filtered and concentrated by using a nitrogen stream or rotary evaporator. The product was purified by using EtOH/H_2O.[10] Anal. Calcd for $(C_5H_5)_2MoCO_3$: C, 46.16; H, 3.53. Found: C, 45.88; H, 3.33.

Physical Measurements. Electronic absorption spectra were obtained with a HP 8451 diode array spectrophotometer. The UV absorption spectrum of the molybdenum carbonate was obtained as a Nujol mull, whereas the UV spectrum of the reaction mixture, which included $Cp_2Mo{=}O$, was obtained in anhydrous THF in matched quartz cells at room temperature.

The photochemistry of the carbonate complex was studied by using a 200-W mercury lamp at 366 nm or an argon ion laser at 351.1 and 363.8 nm.

Infrared spectra were taken with the sample dispersed between AgCl plates, as Nujol mulls between CsI plates or in THF solution under argon

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[†] University of California, Los Angeles.

[‡] University of California, Santa Barbara.

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with a Bio-Rad Digilab FTS-60 FTIR spectrometer. Mass spectra were obtained with a BG 70-250HF double-focusing conventional geometry mass spectrometer.

Analyses were obtained by Desert Analytics, Box 41838, Tuscon, AZ 85717.

Results

Photolysis of Cp_2MoCO_3. Irradiation of Cp_2MoCO_3 in anhydrous THF with an argon ion laser at 363.8 or 351.1 nm in a quartz cell causes disappearance of the starting material and formation of a green solution. The starting material is insoluble in all hydrocarbon solvents, chloroform, and dichloromethane. It is moderately soluble in methanol or ethanol and slightly soluble in THF. THF was chosen as the reaction medium because the photoproducts are soluble in THF and can be readily characterized. The initial conditions consist of a suspension of 0.001 g of Cp_2MoCO_3 in 10 mL of THF, which is sonicated for 0.5 h in an ice bath before photolysis is started. The absorption spectrum of the starting material in the solid state (Nujol mull) has an intense band at 270 nm, a shoulder at 325 nm, and a long tail to the red extending past 500 nm.

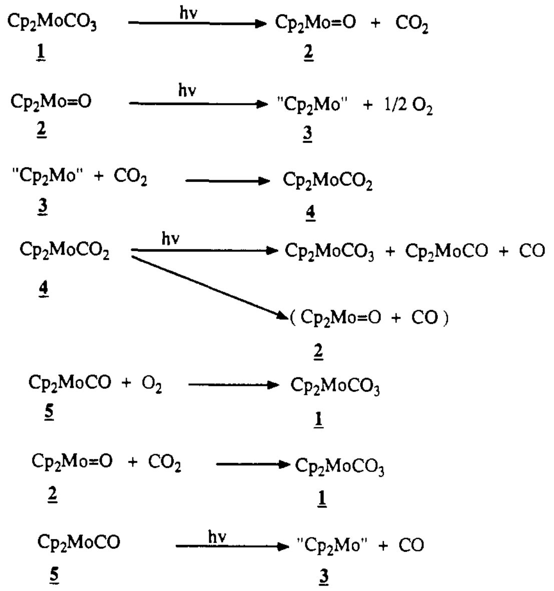
During the course of the photolysis (dilute suspension; 2 h), the burgundy-colored suspension becomes a clear green solution. The IR spectrum of the mixture that was monitored during photolysis shows a sharp new band at 2340 cm^{-1}, which was not present in the spectrum of the starting material. The IR spectrum of the starting material (Nujol mull) has bands at 1633 and 1320 cm^{-1}, which are characteristic of bidentate carbonato ligands.[11,12] The new band is identical with that observed in CO_2-saturated THF and is thus identified as the asymmetric stretch of free CO_2.[13] The CO_2 liberated during the course of the photolysis was also monitored by mass spectroscopy and gas chromatography. No oxygen or carbon monoxide was detected under the photolysis conditions described above.

The green solution produced by the photolysis has an electronic absorption spectrum that consists of a strong band at a wavelength less than 250 nm, shoulders at wavelengths between 300 and 400 nm, and a long tail extending to the red of the shoulders. These features are similar to those reported for $Cp_2Mo{=}O$.[14] Removal of the THF solvent under nitrogen gives a green solid. The infrared spectrum of the solid shows a strong band at 803 cm^{-1}, which is characteristic of the Mo=O stretch. In addition, a mass spectrum of the product gives a parent ion mass at $m/e = 245$, which is characteristic of $[Cp_2Mo{=}O]^+$. A ^1H NMR spectrum of the photolysis product in THF-d_8 showed that all of the Cp_2MoCO_3 had disappeared. The only product in THF under these dilute conditions was $Cp_2Mo{=}O$. By starting with dilute suspensions of Cp_2MoCO_3 (3–4 mg/10 mL of THF), photolysis is a very convenient way of making pure $Cp_2Mo{=}O$. The reaction can be monitored easily by following the disappearance of Cp_2MoCO_3 by ^1H NMR spectroscopy. The overall photochemical reaction under the low concentration conditions above is

$$Cp_2MoCO_3 \xrightarrow{h\nu} Cp_2Mo{=}O + CO_2$$

The quantum yield for the reaction cannot be accurately measured because the initial suspension scatters much of the incident light and the number of photons absorbed cannot be determined. Qualitatively, the reaction appears to be rather slow; irradiation of the suspension for more than 1 h with the filtered output of the 200-W mercury lamp is required to drive the reaction to near completion.

Scheme I



When more concentrated suspensions (0.06 g/10 mL of THF or greater) are photolyzed, the solution becomes green from the presence of $Cp_2Mo{=}O$. Carbon dioxide, oxygen, and carbon monoxide can be detected by mass spectroscopy. The relative amounts of these gases are 27.7%, 5.8%, and 8.0%, respectively, on the basis of mass spectroscopy. The amount of $Cp_2Mo{=}O$ and the ratio of the gases formed varied with the photolysis times. Short photolysis times (2 h or less) invariably show no extra gases except carbon dioxide. Long photolysis times (in excess of 2 h) give variable amounts of gases. Infrared spectra of the crude photolysis mixture show the presence of $Cp_2Mo{=}O$, which has a $\nu(Mo{=}O)$ stretching band at 803 cm^{-1}; a band at 1910 cm^{-1}, characteristic of Cp_2MoCO; and a band at 1633 cm^{-1}, for excess Cp_2MoCO_3. A ^1H NMR spectrum in THF-d_8 shows the presence of $Cp_2Mo{=}O$ at 5.43 ppm, Cp_2MoCO at 4.48 ppm, and Cp_2MoCO_3 at 5.54 ppm.[21] In a typical experiment, photolysis for 3 h gave a 75% yield of pure $Cp_2Mo{=}O$. Since Cp_2MoCO_3 is convenient to make and store in the cold, photolysis represents another way to make small amounts of $Cp_2Mo{=}O$, which is not storable even under vacuum for any length of time. The very limited solubility of Cp_2MoCO_3 in THF makes it easy to separate from the very soluble $Cp_2Mo{=}O$.

After the photolysis, there is a very small amount of yellow-brown material left that is soluble in DMSO. A multiplet at 5.66 ppm is observed in the ^1H NMR spectrum. This has not been identified.

Discussion

The primary photochemical process is cleavage of the carbonate ligand of Cp_2MoCO_3 in both dilute and concentrated suspensions to release CO_2 and generate $Cp_2Mo{=}O$. This result is the same as that of our previous report on late-transition-metal carbonates like Cp^*RhCO_3 that photochemically cleave to give $Cp^*Rh{=}O$ and CO_2.[6] Metallo–oxo complexes thus generated are important because there is a potential for oxygen transfer to organic substrates or inorganic substrates, and metallo–oxo cycles can be formed.[14–18] We were surprised to observe that concentrated suspensions of Cp_2MoCO_3 photochemically release oxygen gas, in addition to carbon monoxide and carbon dioxide. We are not certain whether the oxygen is directly released from Cp_2MoCO_3 or from the $Cp_2Mo{=}O$ photoproduct. Tyler[19] has reported that the quantum yield for the formation of oxygen from $Cp_2Mo{=}O$ is not high. He also reports that $Cp_2Mo{=}O$ does not transfer

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oxygen to substrates, yet it can release oxygen in a probable photochemical bimolecular reaction. Scheme I is a summary of our photochemical results with dilute and concentrated suspensions of Cp_2MoCO_3 and of other known reactions in the literature.[19-21] The photolysis of dilute suspensions of Cp_2MoCO_3 involves several pathways. One pathway gives only $Cp_2Mo{=}O$ (there is some unreacted Cp_2MoCO_3 when the photolysis time is very short). No oxygen or carbon monoxide is detected in the gas phase. The second pathway we propose is that if any oxygen is produced either from cleavage of Cp_2MoCO_3 or more likely from $Cp_2Mo{=}O$, it interacts with **5** to re-form **1**. We propose that **5** is produced from the reaction of "Cp_2Mo" with CO_2 that is generated from the initial decomposition of Cp_2MoCO_3. Thus no CO- or MoCO-containing products will be observed when dilute suspensions of Cp_2MoCO_3 are photolyzed less than 2 h. A combination of different kinetics and different amounts of material produced preclude the formation of oxygen and carbon monoxide at short photolysis times, cf. Scheme I. After photolysis of dilute suspensions for 1 h, the UV spectrum of the green solution showed that some Cp_2MoCO_3 remains along with the $Cp_2Mo{=}O$ that is formed. After 2 h of photolysis and Cp_2MoCO_3 concentrations of up to 4 mg/10 mL of THF, no Cp_2MoCO_3 is left, and the solutions are clear green.

The photolysis of more concentrated suspensions of Cp_2MoCO_3 in THF shows the presence of small ratios of oxygen and carbon monoxide. These gases are formed because more starting material is present than can be photolyzed and secondly because "Cp_2Mo" can form a complex with CO_2 to form Cp_2MoCO_2,[20] which in turn can form Cp_2MoCO,[21] just as it does with dilute suspensions. The ratio of oxygen is low because most of it is being consumed in the side reaction of Cp_2MoCO_3 regeneration or interaction with $Cp_2Mo{=}O$.[19] If there were no CO_2 present, then the amount of oxygen would be substantial as Tyler[19] reports with just photolysis of $Cp_2Mo{=}O$ alone.

Conclusion

Photochemical fragmentation of an early-transition-metal carbonate generates carbon dioxide and the metallo-oxo complex $Cp_2Mo{=}O$. More concentrated suspensions generate oxygen gas.

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Contribution from the Loker Hydrocarbon Research Institute,
Department of Chemistry, University of Southern California,
Los Angeles, California 90089-1661,
and Department of Chemistry,
Dalhousie University,
Halifax, Nova Scotia, Canada, B3H 4J3

A New Electronegativity Scale. 12. Intrinsic Lewis Acid Strength for Main-Group Elements

Yu-Ran Luo[†] and Sidney W. Benson*[‡]

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We have recently discovered a good linear relation, (Figure 1) between the new electronegativity scale, V_X, and Brown's scale of Lewis acid strength, S_a, for 28 main-group elements in their highest oxidation state. This new V_X scale was found to give the best correlation for S_a in a comparison with other available electronegativity scales.

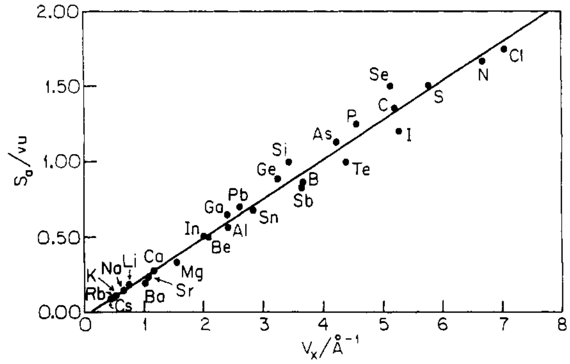

Figure 1. Relation between the new scale of electronegativity[5] and Lewis acid strengths[1] of main-group elements.

Table I. Correlation Coefficients of Lewis Acid Strengths with Various Electronegativities

rank order	scales	correln coeff
1	Luo-Benson[5]	0.9906
2	Zhang[16]	0.9839
3	Allred-Rochow[17]	0.9803
4	Boyd-Markus[18]	0.9778
5	Allen[19]	0.9764
6	Pauling[20]	0.9755
7	revised Mulliken[21]	0.9355

Very recently, inorganic crystal structures for over 14 000 coordination environments involving nearly 100 different cations were analyzed by Brown.[1] The average coordination number to oxygen observed in a large sample of compounds, N_t, was used to calculate a scale of cation Lewis acid strengths, S_a, i.e.

$$S_a = V/N_t \qquad (1)$$

where S_a is in valence units (vu), which represents the electron pairs per bond, and V is the oxidation state of the cation. There are linear relations[1,2] between Brown's scale of Lewis acid strength and some scales of electronegativity, such as Zhang's X_Z, Allred-Rochow's, X_{AR},[1] and Allen's, X_A, scales:

$$X_Z = 1.18S_a + 0.771 \qquad (2)$$

$$X_{AR} = 4.90S_a \qquad (3)$$

$$X_A = (S_a/1.18)^{0.5} \qquad (4)$$

The values of S_a allow one to predict which Lewis acids will bond to which Lewis bases using the observation that both numerical strengths must be equal for maximum bonding.

We have reported a new scale of electronegativity.[3,4] This scale gave the least scatter and the highest correlation coefficient with heats of formation of alkyl derivatives of main-group elements.[5] It has been used very satisfactorily for estimating heats of formation of different alkyl derivatives,[3,4] group parameters for additivity schemes, ionization potentials of main-group atoms,[7] thermochemistry of silicon-containing compounds,[8] homopolar

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[†] Dalhousie University.

[‡] University of Southern California.

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