

($\nu_{\text{asym}}(\text{CO}_2)$). Raman (solid, 6328-Å excitation; cm^{-1}): 287 ($\nu_{\text{sym}}(\text{W}-\text{W})$).

[$\text{W}_2(\text{O}_2\text{C}-t\text{-Bu})_4$]. $\text{W}_2(\text{O}_2\text{C}-t\text{-Bu})_4$ (1.0 g, 1.3 mmol) was dissolved in 40 mL of benzene. With constant stirring, 0.16 g (0.65 mmol) of I_2 dissolved in 5 mL of benzene was added dropwise to the tungsten solution. After 3 h, a light gray solid was isolated by filtration, washed several times with fresh benzene and then hexane, and dried in vacuo; yield 1.1 g, 95%.

Anal. Calcd for $\text{W}_2\text{O}_8\text{C}_{20}\text{H}_{36}\text{I}$: C, 26.72; H, 4.37; I, 14.11. Found: C, 26.92; H, 4.20; I, 14.85. IR (Fluorolube mull; cm^{-1}): 1491 ($\nu_{\text{asym}}(\text{CO}_2)$). ESR (solid, 25 °C, 9.64 GHz): $g_{\text{iso}} = 1.794$.

$\text{W}_2(\text{O}_2\text{CMe})_4$. (N.B. This procedure must be followed as closely as possible to obtain a pure product in the quoted yield.) Freshly sublimed $\text{W}_2(\text{O}_2\text{CCF}_3)_4$ (1.0 g, 1.22 mmol) was dissolved in 5 mL of 60 °C toluene with stirring. A suspension of 1.5 g (5 mmol) of powdered tetrabutylammonium acetate in 10 mL of toluene was added, in one portion, to the tungsten solution. Precipitation of a bright yellow solid occurred within a few seconds after the addition. The mixture was stirred vigorously for a total of 30 s and then filtered rapidly through a 30-mL medium-porosity sintered-glass frit. The yellow solid was washed successively with 3×10 mL of methylene chloride and 2×10 mL of hexane and then dried in vacuo; yield 0.65–0.70 g, 80–90%.

Anal. Calcd for $\text{W}_2\text{O}_8\text{C}_8\text{H}_{12}$: C, 15.91; H, 2.00. Found: C, 16.41; H, 2.11. ^1H NMR (THF- d_6 , 360.1 MHz; ppm): 2.91 (s). IR (Fluorolube mull; cm^{-1}): 1485 ($\nu_{\text{asym}}(\text{CO}_2)$). Raman (solid, 6328-Å excitation; cm^{-1}): 304 ($\nu_{\text{sym}}(\text{W}-\text{W})$). UV-vis (THF, λ_{max} , nm): 375 ($\epsilon 1.50 \times 10^4$). MS (70 eV): m/e 604 (P^+) (see text).

X-ray Structure Determination of $\text{W}_2(\text{O}_2\text{C}-t\text{-Bu})_4\cdot 2\text{PPh}_3$.⁴⁷ Large, well-formed yellow-orange blocks were obtained by slow cooling of a saturated toluene solution. Inside a nitrogen-filled glovebag, a small fragment of 0.1-mm maximum dimension was cleaved, mounted on a

glass fiber with silicon grease, and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer. A systematic search of a limited hemisphere of reciprocal space revealed diffraction maxima that could be indexed as monoclinic, with systematic absences suggesting space group $\text{C}2/c$ or $\text{C}c$. Successful solution and refinement of the structure indicated the centrosymmetric choice was correct.

Diffraction data were collected at -163 ± 4 °C, and the structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. Several of the hydrogen atoms were located in a difference Fourier map phased on the refined non-hydrogen parameters, but attempts to refine them were unsuccessful. For this reason, all hydrogens were included as fixed atom contributors, by using idealized positions.

A final difference Fourier map contained several peaks of magnitude $1.8\text{--}2.4 \text{ e } \text{Å}^{-3}$ in the vicinity of the tungsten and numerous peaks of magnitude $0.6\text{--}1.2 \text{ e } \text{Å}^{-3}$ elsewhere.

Acknowledgment. The authors are grateful to the National Science Foundation for financial support and the Wrubel Computing Center, Indiana University, for a generous gift of computing time. We thank Dr. Melvin Luetkens, Jr., for his assistance in obtaining the tungsten-183 NMR and ESR spectra. A.P.S. thanks Professors M. H. Chisholm (Indiana), F. A. Cotton (Texas A & M), and R. A. Andersen (Berkeley) for preprints of their work on tungsten dimer chemistry and Professor B. E. Bursten (Ohio State) for helpful discussions on the SCF- $\text{X}\alpha$ -SW method.

Registry No. 1, 86728-84-9; 2, 88921-50-0; 3, 94110-43-7; 4, 94070-84-5; $\text{W}_2(\text{O}_2\text{CCF}_3)_4$, 77479-85-7; $\text{Mo}_2(\text{O}_2\text{C}-t\text{-Bu})_4$, 55946-68-4; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 36608-07-8; $\text{MoW}(\text{O}_2\text{C}-t\text{-Bu})_4$, 60511-37-7; W, 7440-33-7; Mo, 7439-98-7.

Supplementary Material Available: Tables of calculated hydrogen atom positions, anisotropic thermal parameters, and observed and calculated structure factors for $\text{W}_2(\text{O}_2\text{C}-t\text{-Bu})_4\cdot 2\text{PPh}_3$ (14 pages). Ordering information is given on any current masthead page.

(47) General procedures have been described in a previous publication. See: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* 1980, 19, 2755.

Contribution from the Department of Chemistry,
The University of Michigan, Ann Arbor, Michigan 48109

Air Oxidation of the $\text{CpMo}(\text{CO})_3^-$ Anion. Molecular Structure of the $(\eta^2\text{-Carbonato})\text{dicarbonylcyclopentadienylmolybdenum(II)}$ Anion, $\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})^-$

M. DAVID CURTIS* and KYOUNG R. HAN

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Air (or dioxygen) reacts with the $\text{CpMo}(\text{CO})_3^-$ anion in acetone solution to give initially the deep red carbonato anion $\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})^-$. This anion may be isolated as the tetraethylammonium salt. Upon continued reaction with O_2 , the carbonato anion is further oxidized to $\text{Mo}_2\text{O}_7^{2-}$, which precipitates with the counterion in essentially quantitative yield. No other metal-containing species are detected in solution. The crystal structure of $[\text{Et}_4\text{N}][\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})]$ has been determined: triclinic, space group $\text{P}\bar{1}$ (No. 2); a, b, c (Å) = 8.103 (3), 11.824 (3), 9.572 (4); α, β, γ (deg) = 90.12 (3), 93.18 (3), 90.52 (3); $V = 915.6$ (6) Å³; $Z = 2$. The structure was solved by a Patterson and successive difference maps to $R = 0.042$, $R_w = 0.051$ based on 3091 data with $I > 3\sigma(I)$. The anion has the typical four-legged piano stool structure. Some average bond distances (Å): $\text{M}-\text{CO}$, 1.94; $\text{Mo}-\text{O}$, 2.13; $\text{O}-\text{C}$, 1.31; $\text{O}=\text{C}$, 1.229 (5).

Introduction

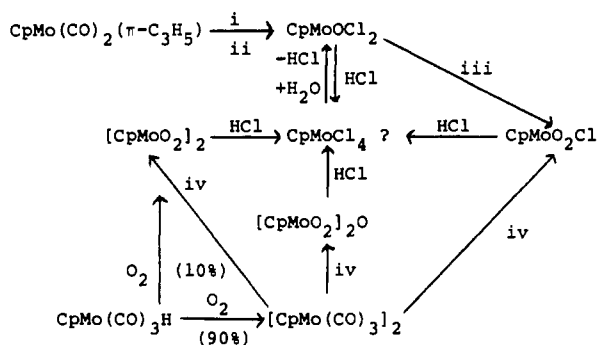
Oxidation reactions, especially those involving metal-catalyzed reactions of dioxygen, are receiving renewed interest.^{1,2} In order to understand the interaction of dioxygen with coordinated ligands in a catalytic cycle, some knowledge of such interactions in stoichiometric reactions is necessary. Molybdenum is widely associated with catalysis of redox reactions in both biological and industrial processes and displays a wide range of stable oxidation states.³ It is therefore important to determine the ways in which

dioxygen interacts with ligands coordinated to molybdenum.

Cousins and Green⁴ have investigated the reactions of dioxygen with a variety of cyclopentadienyl (Cp) compounds of molybdenum. Their results are summarized in Scheme I. It is interesting to note that $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ reacts to give $(\text{CpMoO}_2)_2$ and CpMoO_2Cl in the presence of chloroform. Cousins and Green also report that the hydride $\text{CpMo}(\text{CO})_3\text{H}$ reacts to give the dioxide dimer $(\text{CpMoO}_2)_2$, albeit in low yield. The major product

(1) (a) Voge, H. H.; Adama, C. R. *Adv. Catal.* 1967, 17, 151. (b) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* 1981, 30, 133.
(2) Sheldon, R. A.; Kochi, J. "Metal Catalyzed Oxidation of Organic Compounds"; Academic Press: New York, 1981.

(3) (a) Dolphin, D., Ed. "Biometric Chemistry"; American Chemical Society: Washington, DC, 1980; Adv. Chem. Ser. No. 191. (b) Massoth, F. E. *Adv. Catal.* 1978, 27, 266. (c) Barry, H. F., Mitchell, P. C. H., Eds. *Chem. Uses Molybdenum, Proc. Int. Conf.*, 4th 1982.
(4) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* 1964, 1567; *J. Chem. Soc. A* 1969, 16.

Scheme 1^a

^a i = HCl/Et₂O; ii = CHCl₃/O₂; iii = O₂/Et₂O; iv = O₂/hν in CHCl₃.

of the oxidation of the hydride in absence of coordinating ligands, e.g., chloride, is the dimer Cp₂Mo₂(CO)₆.⁵ Here, we report yet another mode of oxidation of a simple Cp-molybdenum complex, viz., the anion CpMo(CO)₃⁻. This anion reacts with dioxygen to give the η²-carbonato complex CpMo(CO)₂(η²-O₂CO), according to eq 1. The molecular structure of the anion is also reported.



Experimental Section

Oxidation of [Et₄N][CpMo(CO)₃]. This yellow salt is sparingly soluble in THF and EtOH but is quite soluble in acetone. Passing air or dry oxygen through a yellow solution in acetone gave rise to an immediate red coloration. The ν_{CO} bands due to the CpMo(CO)₃⁻ anion (1885 (vs), 1775 (vs), 1740 (vs) cm⁻¹) diminished in new bands at 1940 (vs), 1815 (vs), 1670 (w, sh), 1640 (sh), and 1620 (s) cm⁻¹ appeared. The oxidation was halted when the new bands reached their maximum intensity (continued oxidation caused a diminution of the intensities of all ν_{CO} bands concomitant with the formation of an off-white precipitate—see below). The red solution was then concentrated under N₂. The concentrated solution was cooled to 0 °C to give well-formed, red crystals (ca. 15% isolated yield). ¹H NMR (acetone-d₆): δ 5.6 (5 H, Cp), 3.5 (q, 8 H, N-CH₂), 1.4 (tt, 12 H, N-CH₂CH₃). IR (KBr): 3000 (w), 1940 (s), 1815 (s), 1670 (w), 1630 (sh), 1615 (s), 1450 (m), 1400 (w), 1246 (m), 1180 (mw), 1018–1005–995 (w, unresolved), 890 (vw), 825 (w), 785 (m), 738 (w), 504 (2), 432 (2), 388 (w), 320 (w) cm⁻¹.

If the flow of O₂ or air was not interrupted when the intensity of the ν_{CO} bands started to diminish, then an off-white solid started to precipitate and, eventually, all the ν_{CO} bands disappeared. The solid was collected by filtration and washed with acetone. It was then dissolved in MeOH and reprecipitated by addition of acetone to give a white solid, shown to be [Et₄N]₂[Mo₂O₇]. ¹H NMR (CD₃OD): δ 2.65 (q, 2 H), 1.65 (tt, 3 H). IR: ν_{Mo-O} 871, 775 cm⁻¹. Anal. Calcd for C₈H₂₀Mo₂NO₇: C, 22.14; H, 4.61; N, 3.23; Found: C, 22.88; H, 4.74; N, 3.27.

The supernatant solution above [Et₄N]₂[Mo₂O₇] remained dark red or orange but contained no Mo. The color apparently arose from oxidation of the Cp groups.

Oxidation of [PPN][CpMo(CO)₃] and [Bu₄N][CpMo(CO)₃]. The salt [PPN][CpMo(CO)₃] (PPN⁺ = Ph₃P=N=PPh₃⁺), 1.0 g (1.3 mmol), was dissolved in 40 mL of acetone, and dry O₂ was passed through the solution. After 0.5 h, a white solid (0.6 g) had formed and the solution was deep red. The white solid was shown to be (PPN)₂Mo₂O₇: Anal. Calcd for C₇₂H₆₀Mo₂N₂O₇P₄: C, 62.64; H, 4.35; Mo, 13.89; P, 8.98; O, 10.13; Found: C, 62.88; H, 4.26; Mo, 13.68; P, 8.90; O (by difference), 10.28.

The filtrate from the white solid was concentrated to a volume of ca. 5 mL and, upon standing, yielded 0.35 g of unreacted [PPN][CpMo(CO)₃]. Therefore, the yield of (PPN)₂Mo₂O₇, based on unrecovered CpMo(CO)₃⁻, is quantitative. The IR spectrum of the solution showed only trace amounts of the carbonato complex.

A similar oxidation by dry air of [n-Bu₄N][CpMo(CO)₃] (0.9 g, 1.8 mmol) in 5 mL of Me₂CO gave, after 0.5 h, 0.4 g of white solid, which gave an IR spectrum indicative of (n-Bu₄N)₂Mo₂O₇ (ν_{Mo-O} = 870, 775 cm⁻¹), and a red oil, which was shown by IR and NMR analyses to be an approximately equimolar mixture of CpMo(CO)₃⁻ and CpMo(CO)₂(η²-O₂CO)⁻ ions as their tetrabutylammonium salts. The carbo-

Table I. Summary of Crystallographic Statistics

formula	[(C ₂ H ₅) ₄ N][[(C ₅ H ₅)Mo(CO) ₂ (η ² -CO ₃)] (C ₁₆ H ₂₅ MoNO ₅)
mol wt	407.1
color, form	dark red, rhomboids
cryst size/mm	0.33 × 0.12 × 0.16
a, b, c/Å	8.103 (3), 11.824 (3), 9.572 (4)
α, β, γ/deg	90.12 (3), 93.18 (3), 90.52 (3)
space group; Z; V/Å ³	P1; 2; 915.6 (6)
ρ(obsd)/g cm ⁻³	1.44
(flotation in CCl ₄ /hexane)	
ρ(calcd)/g cm ⁻³	1.48
radiation	Mo Kα (graphite monochromator)
takeoff angle/deg	4°
scan mode	θ/2θ
2θ(max)/deg	60°
scan speed/deg s ⁻¹	2–15
scan width	Mo Kα ₁ – 0.8° to Mo Kα ₂ + 0.8°
bkgd:scan time ratio	0.8
μ/cm ⁻¹	7.20
I/I ₀ (max, min)	0.92, 0.89
temp	ambient (ca. 21 °C)
no. of unique data collected	4244
no. of data with I > 3σ(I)	3091
check reflns (hkl)	401, 234, 060
R(F), R _w (F)	0.042, 0.051
goodness of fit	1.63
largest Δ/σ	0.03
no. of variables	208

nato complex could not be separated from the unreacted CpMo(CO)₃⁻ due to the nearly identical solubilities of the two salts in all solvents tested.

Crystal Structure Determination of [Et₄N][CpMo(CO)₂(η²-O₂CO)]. A crystal suitable for X-ray diffraction was selected from the crop of crystals obtained from acetone as described above. The crystalline material appeared homogeneous under the microscope. The crystal was sealed in a thin-walled capillary and mounted on a Syntex P2₁ diffractometer. Relevant crystal and data collection statistics are collected in Table I. The unit cell was obtained from 15 accurately centered reflections randomly distributed in reciprocal space (20° ≤ 2θ ≤ 45°). Intensities of three check reflections were measured after every 50 data points. The average intensity of these check reflections decayed 8% during the data collection, but this small decrease was not corrected for. The octants scanned were h, ±k, ±l.

The Mo atom was located in a Patterson map. Following one cycle of refinement on x, y, z and the scale factor (R = 33%), a difference map showed the positions of 10 more atoms. Following one cycle of refinement on these 11 atoms (R = 26%), all the remaining non-hydrogen atoms were located. Following isotropic convergence (two cycles), all atoms were refined anisotropically and a subsequent difference map revealed the locations of all hydrogens save one. These were entered into the atom list but not refined. The final agreement indices are given in Table I; Table II gives the atomic coordinates, and Table III shows the temperature factors. Bond distances and angles are collected in Tables IV and V, respectively. Programs used in the structure determination are given in ref. 6. Table VI (supplementary material) lists the positions of the hydrogen atoms, and Table VII (supplementary material) lists the F_o vs. F_c values.

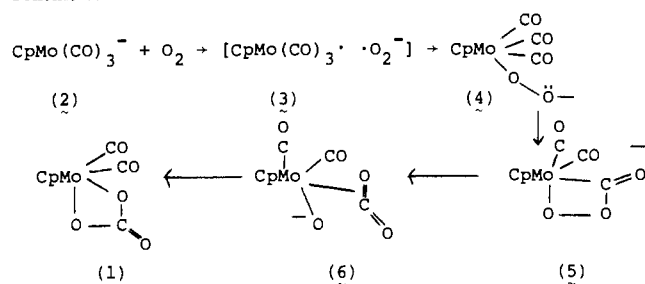
Results and Discussion

Acetone solutions of CpMo(CO)₃⁻ react with O₂ or dry air to give the η²-carbonato anion CpMo(CO)₂(η²-O₂CO)⁻ (1) (eq 1). Prolonged oxidation converts the carbonato complex to the hep-

- (6) Computations were carried out on an Amdahl 470/V6 computer. Computer programs used during the structural analysis were SYNCOR (data reduction by W. Schmonsees), FORDAP (Fourier refinement by Z. Zalkin), ORFLS (full-matrix, least-squares refinement by Busing, Martin, and Levy), ORFFE (distances, angles, and their esd's by Busing, Martin, and Levy), ORTEP (thermal ellipsoid drawings by C. K. Johnson), HATOMS (hydrogen atom positions by A. Zalkin), PLANES (least-squares planes by D. M. Blow), and ABSORB (absorption correction program by D. Templeton and L. Templeton). Scattering factors were obtained from: Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2 and 2.3.1.

Table II. Fractional Atomic Coordinates for $[\text{Et}_4\text{N}][\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})]$

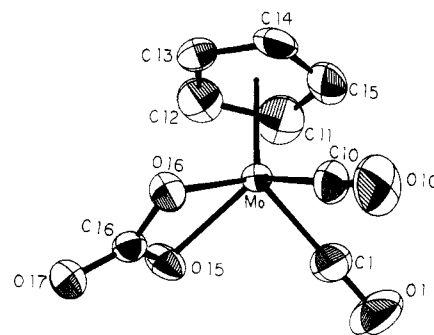
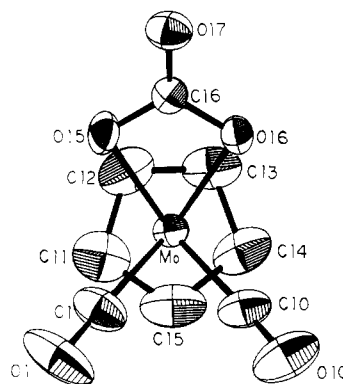
atom	x	y	z
Mo	0.30676 (4)	0.17409 (3)	0.25702 (4)
C1	0.4737 (7)	0.1507 (4)	0.4074 (6)
O1	0.5759 (6)	0.1360 (4)	0.4953 (5)
N1	0.2516 (3)	0.4345 (3)	0.7501 (3)
C2	0.4068 (5)	0.3710 (4)	0.7126 (4)
C4	0.2966 (5)	0.5131 (4)	0.8745 (4)
C3	0.4705 (7)	0.2894 (5)	0.8236 (6)
C5	0.1643 (6)	0.5971 (4)	0.9056 (5)
C6	0.1897 (5)	0.5020 (4)	0.6221 (4)
C7	0.3013 (7)	0.5950 (4)	0.5811 (5)
C8	0.1177 (5)	0.3543 (4)	0.7925 (5)
C9	0.0744 (7)	0.2600 (5)	0.6836 (6)
C10	0.5140 (6)	0.1499 (4)	0.1687 (6)
O10	0.6382 (5)	0.1331 (4)	0.1198 (5)
C15	0.2319 (6)	-0.0107 (4)	0.2400 (7)
C11	0.1413 (7)	0.0346 (5)	0.3463 (7)
C12	0.0251 (6)	0.1118 (5)	0.2836 (6)
C13	0.0482 (6)	0.1164 (4)	0.1423 (6)
C14	0.1770 (6)	0.0409 (5)	0.1127 (6)
O17	0.2284 (4)	0.4903 (3)	0.2467 (3)
C16	0.2540 (4)	0.3880 (4)	0.2505 (4)
O15	0.2454 (4)	0.3257 (2)	0.3615 (3)
O16	0.2942 (4)	0.3282 (2)	0.1427 (3)

Scheme II

taoxodimolybdenum(VI) anion, $\text{Mo}_2\text{O}_7^{2-}$. No compounds other than the starting anion, the carbonato complex, and the $\text{Mo}_2\text{O}_7^{2-}$ ion are observed in the IR spectra of the reaction mixtures. It appears as though $\text{CpMo}(\text{CO})_3^-$ is first converted to 1. As the concentration of 1 increases, its rate of oxidation to $\text{Mo}_2\text{O}_7^{2-}$ becomes comparable to the rate of oxidation of $\text{CpMo}(\text{CO})_3^-$. Consequently, the reaction must be monitored by IR or other means and stopped when the concentration of carbonato species is a maximum. This seems to occur at about 50% conversion of the $\text{CpMo}(\text{CO})_3^-$ anion when air is used as the oxidizing medium. When pure dioxygen is used, it is more difficult to stop the oxidation at the carbonato stage, and $\text{Mo}_2\text{O}_7^{2-}$ is rapidly produced.

When Et_4N^+ is the counterion, the salt $[\text{Et}_4\text{N}][\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})]$ preferentially crystallizes. However, the solubilities of this salt and $[\text{Et}_4\text{N}][\text{CpMo}(\text{CO})_3]$ are so similar that only a small fraction (ca. 30%) of the carbonato species in solution may be crystallized before $[\text{Et}_4\text{N}][\text{CpMo}(\text{CO})_3]$ coprecipitates. When $n\text{-Bu}_4\text{N}^+$ is used as the counterion, a mixture of $[\text{Bu}_4\text{N}][\text{CpMo}(\text{CO})_3]$ and $[\text{Bu}_4\text{N}][\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})]$ is obtained as a red oil. With PPN^+ as the counterion and pure O_2 as the oxidant, only a trace of the carbonato species is produced. The major product in this case is the PPN^+ salt of $\text{Mo}_2\text{O}_7^{2-}$, obtained in quantitative yield based on unrecovered $\text{CpMo}(\text{CO})_3^-$.

In the infrared spectrum, the C—O stretches of the coordinated carbonato group give rise to two prominent bands at 1615 (ν_1) and 1246 (ν_3) cm^{-1} . These two bands correlate with the doubly degenerate ν_3 mode of the free carbonate ion.⁷ It has been proposed that the degree of splitting of the carbonate ν_3 mode is related to the covalency of the M—O bonds.⁸ The splitting ob-

**Figure 1.** ORTEP plot of the $\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})^-$ anion (1) with numbering scheme.**Figure 2.** ORTEP plot of 1 viewed along the Mo—Cp (centroid) axis.

served here is comparable to those observed in several η^2 -carbonato complexes of Co,⁷ Ru,⁹ and Ir,^{10,11} suggesting a similar degree of covalency in all these complexes. Additional carbonyl vibrational modes are at 1018 (ν_2) (partially obscured by a mode due to the Et_4N^+ cation), 890 (ν_8), 825 (ν_3), and 738 (ν_6) cm^{-1} .

It is interesting to speculate on the mechanism of formation of the carbonato group. A possible mechanism is shown in Scheme II. The anion transfers an electron to dioxygen such that the total spin ($S = 1$) is conserved. The spin in the radical pair 3 can then relax and subsequently form the peroxy anion 4. The peroxy group can then add to a carbonyl group to form the cyclic peroxo acyl 5. This four-membered ring can undergo a scission analogous to that observed for metallacyclobutanes in the olefin metathesis reaction¹² forming the carbon dioxide complex 6. Ring closure by attack of the oxo ligand on the carbon of the coordinated carbon monoxide leads to the final carbonato complex 1. Peroxo-acyl intermediates, e.g. 5, have been proposed previously,^{10,11,13} and a similar type of intermediate has been invoked in the oxygen atom transfer from a complexed nitro group to an adjacent carbonyl group.¹⁴

As mentioned above, exhaustive oxidation of the mixture gives essentially quantitative conversion of anion 2 to the corresponding tetraalkylammonium salt of the $\text{Mo}_2\text{O}_7^{2-}$ anion. The salts prepared by this method show $\nu_{\text{Mo-O}}$ stretching modes at 870 and 775 cm^{-1} . Day et al. have noted that bulky cations stabilize the $\text{Mo}_2\text{O}_7^{2-}$ ion relative to other molybdenum oxoanions.¹⁵ The Mo—O stretching frequencies observed here are in agreement with those previously reported.¹⁵

X-ray Structure of $[\text{Et}_4\text{N}][\text{CpMo}(\text{CO})_2(\eta^2\text{-O}_2\text{CO})]$. Figures 1 and 2 show two views of the anion. The coordination about the

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Table III. Temperature Factors for [Et₄N][CpMo(CO)₂(η²-O₂CO)]

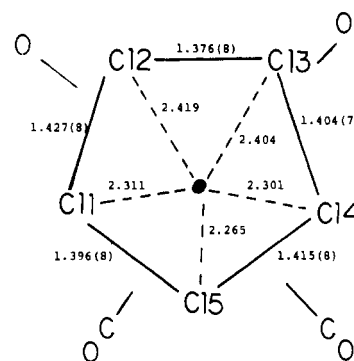
atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃	B ^a Å ²
Mo	2.19 (1)	2.30 (2)	2.65 (2)	0.02 (1)	-0.29 (1)	-0.42 (1)	2.34 (1)
C1	5.35 (25)	3.04 (25)	5.43 (26)	-0.41 (18)	-1.74 (20)	0.48 (18)	4.27 (14)
O1	8.89 (28)	5.62 (24)	8.21 (26)	-0.74 (19)	-5.34 (23)	2.02 (19)	6.09 (13)
N1	2.20 (11)	3.07 (16)	1.96 (12)	-0.25 (10)	0.23 (9)	-0.24 (10)	2.35 (7)
C2	3.11 (17)	4.03 (24)	3.21 (18)	0.66 (14)	0.51 (13)	-0.79 (15)	3.28 (11)
C4	3.36 (17)	3.81 (22)	2.04 (15)	-0.04 (14)	-0.16 (12)	-0.60 (13)	2.92 (10)
C3	5.25 (27)	5.77 (33)	5.31 (27)	2.37 (23)	-0.23 (21)	-0.16 (22)	5.08 (15)
C5	4.62 (21)	3.96 (25)	2.97 (18)	0.15 (17)	0.75 (15)	-0.83 (15)	3.66 (12)
C6	3.73 (18)	3.82 (22)	1.82 (15)	-0.40 (15)	-0.12 (12)	0.24 (13)	2.94 (10)
C7	6.17 (28)	4.25 (27)	3.25 (20)	-0.78 (20)	0.92 (18)	0.71 (17)	4.24 (14)
C8	3.29 (17)	3.11 (22)	3.72 (19)	-0.66 (14)	0.84 (14)	0.24 (15)	3.24 (11)
C9	6.18 (29)	4.69 (30)	5.44 (28)	-2.34 (23)	0.71 (22)	-1.02 (21)	4.97 (15)
C10	2.92 (18)	4.07 (26)	6.21 (27)	0.58 (16)	-0.02 (17)	-0.60 (19)	4.14 (13)
O10	3.90 (18)	8.05 (29)	10.50 (32)	1.17 (17)	2.11 (19)	-1.43 (23)	6.43 (13)
C15	4.08 (22)	2.32 (25)	9.23 (39)	-0.69 (17)	-0.78 (24)	-0.60 (23)	4.31 (15)
C11	4.37 (23)	4.08 (28)	7.40 (33)	-1.33 (20)	0.29 (22)	1.06 (23)	4.83 (14)
C12	2.96 (18)	4.38 (28)	7.19 (32)	-1.00 (17)	1.06 (19)	-0.72 (22)	4.33 (14)
C13	2.81 (18)	3.99 (27)	7.15 (32)	-0.32 (16)	-1.65 (18)	-1.48 (21)	3.94 (13)
C14	4.01 (21)	4.27 (28)	6.93 (31)	-0.28 (18)	-0.84 (20)	-3.14 (23)	4.21 (14)
O17	4.20 (14)	2.62 (18)	4.65 (16)	0.14 (11)	-0.24 (11)	-0.15 (11)	3.71 (9)
C16	2.31 (14)	2.88 (25)	2.77 (17)	-0.24 (12)	-0.08 (11)	-0.28 (13)	2.62 (11)
O15	5.46 (16)	2.78 (15)	2.24 (12)	0.14 (11)	0.67 (10)	-0.47 (9)	3.16 (8)
O16	4.45 (14)	3.04 (14)	2.28 (11)	0.51 (10)	0.50 (9)	0.25 (9)	3.09 (7)

^a Equivalent isotropic B value.Table IV. Bond Distances (Å) in [Et₄N][CpMo(CO)₂(η²-O₂CO)]

(a) Anion			
Mo-C1	1.941 (5)	C1-O1	1.162 (6)
-C10	1.945 (5)	C10-O10	1.152 (6)
-O16	2.127 (3)	C16-O15	1.300 (5)
-O16	2.128 (3)	-O16	1.307 (5)
-C15	2.265 (5)	-O17	1.229 (5)
-C14	2.301 (4)	C11-C12	1.427 (8)
-C11	2.311 (5)	-C15	1.396 (8)
-C13	2.404 (4)	C12-C13	1.376 (8)
-C12	2.419 (5)	C13-C14	1.420 (7)
-C16	2.570 (5)	C14-C15	1.415 (8)
(b) Cation			
N-C2	1.530 (5)	C2-C3	1.509 (7)
-C4	1.535 (5)	C4-C5	1.509 (6)
-C6	1.528 (5)	C6-C7	1.485 (7)
-C8	1.508 (5)	C8-C9	1.550 (7)

Table V. Selected Bond Angles (deg) in [Et₄N][CpMo(CO)₂(η²-O₂CO)]

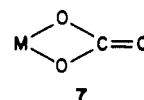
(a) Anion			
C1-Mo-C10	73.5 (2)	O15-Mo-C11	105.6 (2)
-O15	87.1 (2)	-C12	87.4 (2)
-O16	121.4 (2)	-C13	103.1 (2)
O15-Mo-O16	60.8 (1)	-C14	138.1 (2)
C10-Mo-O15	124.4 (2)	-C15	141.0 (2)
-O16	85.8 (2)	O16-Mo-C11	141.8 (2)
Mo-C1-O1	178.5 (6)	-C12	106.8 (2)
-C10-O10	177.8 (5)	-C13	89.2 (2)
-O16-C16	94.0 (2)	-C14	105.5 (2)
-O16-C16	93.8 (2)	-C15	141.6 (2)
O15-C16-O16	111.4 (4)	C1-Mo-C11	90.8 (2)
-O17	124.6 (4)	-C12	120.0 (2)
O16-C16-O17	124.0 (4)	-C13	148.3 (2)
C12-C11-C16	107.7 (5)	-C14	128.3 (2)
C13-C12-C11	108.5 (5)	-C15	94.7 (2)
C14-C13-C12	108.2 (5)	C10-Mo-C11	125.7 (2)
C15-C14-C13	107.7 (5)	-C12	147.4 (2)
C11-C15-C14	107.8 (5)	-C13	120.7 (2)
		-C14	90.6 (2)
		-C15	93.1 (2)
(b) Cation			
C2-N-C4	108.6 (3)	C6-N-C8	109.6 (3)
-C6	108.2 (3)	N-C2-C3	114.1 (4)
-C8	111.5 (3)	-C4-C5	114.3 (3)
C4-N-C6	111.0 (3)	-C6-C7	115.0 (3)
-C8	108.0 (3)	-C8-C9	113.8 (3)

Figure 3. Diagram of the Mo-C and C-C distances in **1**.

Mo atom is the usual four-legged piano stool. As seen in Figure 2, the carbonyl groups eclipse the C-C bonds of the Cp group while the oxygen atoms of the carbonato group eclipse the carbon atoms. This arrangement is in keeping with the general observation that the best π -accepting ligands eclipse the C-C bonds in CpML₂L'₂ complexes.¹⁶

The carbonato group might be expected to behave as a strong π -donor ligand. Such π -donation should then be manifested in a shorter bond to the π -accepting carbonyls. In fact, the Mo-CO distances (1.94 Å) in **1** are shorter than the usual Mo-CO distances (1.98–2.00 Å) usually found in CpMo(CO)_nL_{4-n} complexes. In the salt [Cp₃Mo₃(CO)₆S⁺][CpMo(CO)₃]⁻, the average Mo-CO distances in the cation and anion are 1.98 and 1.92 Å, respectively.¹⁷ Thus, the Mo-CO π -bond order in **1** seems to be approaching that found in anion **2**. The relatively low C-O stretching frequencies (1920, 1810 cm⁻¹) found for **1** support the argument for extensive back-donation to the carbonyls in **1**.

The C-O distances in the carbonato group indicate a considerable localization of the bonds as in **7**. The C16-O17 length



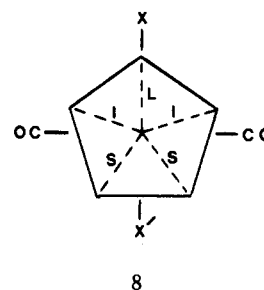
is 1.229 (5) Å, i.e. essentially the same as the C=O bond in aldehydes and ketones (1.22 Å), but is considerably longer than

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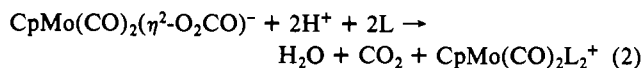
the C=O bond in organic carbonates (ca. 1.16 Å).¹⁸ The remaining two C—O bond lengths (average 1.30 Å) are slightly shorter than the C—O bonds in organic carbonates (1.28–1.37 Å, average 1.34 Å). The angles about the carbonate carbon (C16) are comparable to those in ethylene and vinylene carbonate.¹⁸

The distances from Mo to the Cp carbons and the C—C distances within the Cp ring show some interesting variations (Figure 3). Such alterations in bond lengths have been treated theoretically,^{16,19,20} but the simplest rationalization of the observed trends in the Mo—C distances is that the longer Mo—C distances "trans" (Figure 3) to the carbonyls are a manifestation of the trans influence commonly seen in square-planar complexes (see discussion in ref 21). In all the structures of the type *cis*-CpM(CO)₂L₂, the M—C(Cp) bond length pattern is as in Figure 3. In *trans*-CpM(CO)₂XX', the pattern appears to be that shown in 8, where X' is higher in the spectrochemical series than X (L = long, I = intermediate, S = short). The same pattern is seen in CpMo(CO)₃X complexes (let X' = CO in 8).^{22,23}

Reactivity. Only a few reactions of the carbonate anion, 1, have been investigated. Treatment of 1 with trifluoroacetic acid in the



presence of Ph₃P, Et₃P, or (MeO)₃P gave corresponding *cis*-CpMo(CO)₂L₂⁺ complexes, identified by IR spectra.²⁴ Presumably, the carbonate group is protonated and then lost as CO₂ and water:



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Supplementary Material Available: Tables VI and VII, giving H atom positions and *F*_o vs. *F*_c values (13 pages). Ordering information is given on any current masthead page.

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Contribution from the School of Science, Griffith University, Nathan, Queensland 4111, Australia, and Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia

Lewis Base Adducts of Group 11 Metal Compounds.[†] 10. The 1:1 Heterobimetallic Adduct of Tris(pyrrolidinecarbodithioato)cobalt(III) with Copper(I) Bromide

LUTZ M. ENGELHARDT,^{1a} PETER C. HEALY,^{1b} ROCCO I. PAPASERGIO,^{1a} and ALLAN H. WHITE*^{1a}

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Reaction of copper(I) bromide with tris(pyrrolidinecarbodithioato)cobalt(III) has yielded a 1:1 adduct that has been characterized by single-crystal X-ray structure determination. Crystals are triclinic, *P* $\bar{1}$, *a* = 15.385 (4) Å, *b* = 15.025 (4) Å, *c* = 11.088 (4) Å, α = 76.01 (2)°, β = 79.67 (2)°, and γ = 78.18 (2)°; the structure was refined by least-squares methods to a residual of 0.036 for 4369 independent observed reflections. The complex is dimeric, of the type (Co(dtc)₃)CuBr₂Cu(Co(dtc)₃), with two such units in the cell. The copper is four-coordinate by two bromine atoms and two sulfur atoms from independent carbodithioate ligands, the approach of the copper to the latter being along the pseudo-2-fold axis of the Co(dtc)₃ species. Cu...Cu is 2.697 (2) Å.

Introduction

In the more symmetrical pseudo-square-planar and pseudo-*D*₃ ("octahedral") bis- and tris(1,1-dithio chelate)metal complexes, each of the sulfur atoms is coordinated to only one metal atom; it is well-known that the bonding capacities of these sulfur atoms is not saturated since it is possible for them to be utilized for bridging purposes to yield oligonuclear species as in, e.g., [Ru₂(S₂CN-*i*-Pr₂)₃]⁺, [Ru₂(CO)₂(S₂CNEt₂)₄], and [Ru₃(CO)₃Cl₂(S₂CNEt₂)₄].² Apart from a number of well-studied examples of oligomer formation of this type in homonuclear systems, however, little advantage appears to have been taken of the apparent capacity of such species to enable the coordination complex itself to act as a chelating agent for the purpose of coordinating other metals to form heteronuclear species. Within the 1:1 dithio chelate field, the only example structurally characterized that

appears to exploit this possibility is that of [Fe{CN(*p*-ClC₆H₄)₂(S₂CNET₂)₂ZnI₂}]₃,³ wherein the zinc atom becomes four-coordinate by chelation by a pair of sulfur atoms from different carbodithioate ligands. More conventional bridging thiol groups are to be found in species such as [(piperidine *N*-oxide(1-))₂Mo(μ-S)₂Cu μ-Cl]₂.⁴ We find that the addition of tris-(*N,N*-disubstituted carbodithioato)cobalt(III) complexes dissolved in acetonitrile to solutions of copper(I) halide in the same solvent yield dark amorphous precipitates. Crystalline compounds may be obtained by taking the solvent in a flat dish and allowing the two species to slowly diffuse together from deposits of solid at the extremities of the dish, air being excluded. In this manner an adduct of tris(pyrrolidinecarbodithioato)cobalt(III)(Co(dtc)₃) with

[†]The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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