

and axial ligation, must be able to modulate reactivity toward halide ions of the (P⁺)(Fe^{IV}O)X/P(Fe^{IV}O) couple in proteins. It is interesting to note, however, that the remarkable reactivity of (TMP⁺)(Fe^{IV}O)X toward hydrocarbons⁸ is not reflected in an especially high one-electron redox potential.

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Registry No. TMP(Fe^{IV}O), 93085-16-6; (TMP⁺)Fe^{III}(ClO₄)₂, 93842-71-8; (TMP⁺)(Fe^{IV}O)Cl, 95724-71-3; (TMP⁺)(Fe^{IV}O)Br, 95724-72-4; (TMP⁺)(Fe^{IV}O)ClO₄, 95724-73-5; TMPFeCl, 77439-21-5; TMPFeOH, 77439-20-4; TMPFeClO₄, 93862-22-7; Cl₂, 7782-50-5; Br₂, 7726-95-6; *m*-chloroperoxybenzoic acid, 937-14-4.

Carbon Dioxide and Formaldehyde Coordination on Molybdenocene to Metal and Hydrogen Bonds of the C₁ Molecule in the Solid State

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Fixation of carbon dioxide and formaldehyde in their intact form on a metal center is a primary goal in metal-promoted transformations of a C₁ molecule, provided it forms metal-carbon bonds. Formation of formaldehyde^{1,2} and carbon dioxide complexes³ is, however, a quite rare reaction, in spite of the various strategies applied so far. Some to be mentioned utilized metal-carbenes, metal-nucleophiles, and bifunctional complexes.¹⁻³ All these compounds must possess a special ensemble of properties which seems very difficult to match and which are different for carbon dioxide and formaldehyde.

Coordination of formaldehyde has been achieved by a few complexes only,^{1,2} all having a carbene-type reactivity by which they add to a >C=O double bond. Dicyclopentadienylmolybdenum(II)⁴ [cp₂Mo] (cp = η⁵-C₅H₅) was shown to be, along with vanadocene,⁵ one of the most versatile metallic carbenes. Its generation may be, however, a crucial point. Displacement of a relatively weakly bonded ligand to the [cp₂Mo] moiety may overcome this difficulty and provide a slow reaction producing crystalline materials. Complex [cp₂Mo(PhC≡CPh)] (I)⁶ has been used as starting material, where the Ph₂C₂ ligand can be replaced

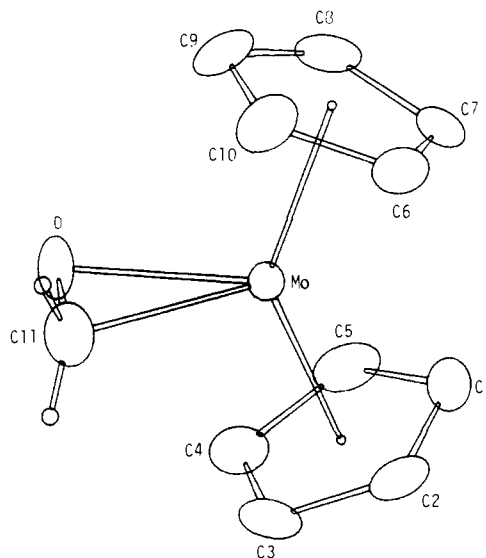


Figure 1. An ORTEP diagram of complex II. Bond lengths (Å) and angles (deg) are the following: C11-O1 = 1.360 (9), Mo-C11 = 2.152 (8), Mo-O = 2.056 (4), cp1-Mo-cp2 = 139.0 (3).

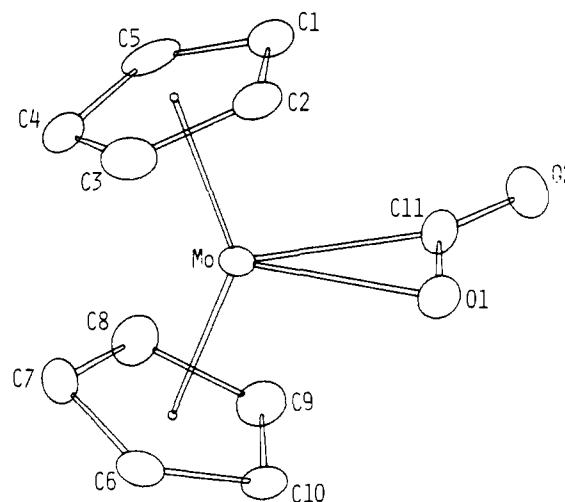
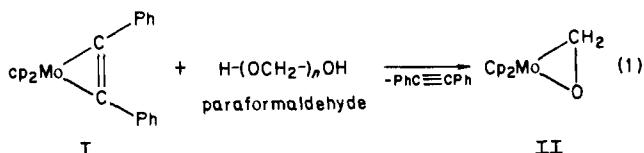


Figure 2. A view of complex III, molecule A. Bond distances (Å) and angles (deg) are the following: Mo-O1, 2.160 (7); Mo-C11, 2.112 (11); C11-O1, 1.288 (14); C11-O2, 1.201 (14); cp1-Mo-cp2, 141.3 (3).

by either formaldehyde or carbon dioxide.

A toluene solution of I was reacted with paraformaldehyde at 80 °C. The suspension was filtered while warm and, on cooling, the resulting solution yielded crystals of II (Figure 1);^{7,8}



The structure of II was proven by an X-ray analysis.⁹ It is very

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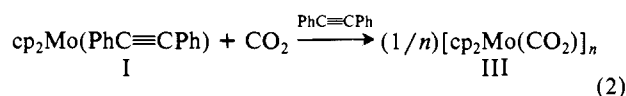
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(8) A toluene (50 mL) solution of I (2.09 g) was heated up to 80 °C for 20 min in the presence of an excess of paraformaldehyde. The suspension was filtered while warm, and the resulting solution was cooled to -15 °C. Crystals of II suitable for an X-ray analysis were collected (0.56 g). The unreacted starting material I was recovered from the mother solution by addition of *n*-hexane and cooling. Longer reaction time and higher temperature can increase the yield. Anal. Calcd for C₁₁H₁₂O₂Mo: C, 51.58; H, 4.72. Found: C, 51.60; H, 4.72. ν(CO) (Nujol) 1157 vs; ¹H NMR spectrum (CDCl₃, Me₄Si) δ 3.05 (2 H, s, CH₂), 4.75 (10 H, s, cp); the mass spectrum showed the parent peak at *m/e* 258 and other peaks whose position and intensity are in agreement with the natural isotopic mixture of molybdenum.

close to that reported for $\text{cp}_2\text{V}(\text{CH}_2\text{O})$,¹ with the two bent cp ligands making a cavity in the equatorial plane for the formaldehyde fragment. The C–O bond length [1.360 (9) Å] is very close to those of the other formaldehyde complexes,^{1,2} except for that in $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{O})]$ [1.59 (1) Å].^{2a} The Mo–O bond [2.056 (4) Å] is significantly shorter than the Mo–C bond distance [2.252 (8) Å], similar to the vanadocene derivative.¹ A significant structural feature is the hydrogen bonding formed from the oxygen atoms interacting with the hydrogens from C1 and C7 of an adjacent molecule [C1...O, 3.318 (8); H1...O, 2.330 (69) Å; C1–H1...O, 163 (4)°; C7...O, 3.439 (8); H7...O, 2.404 (64) Å; C7–H7...O, 158 (5)°].¹⁰

Diphenylacetylene was displaced in complex I by carbon dioxide carrying out the reaction in toluene¹¹ at room temperature. Complex III was isolated as crystalline solid,



having a C=O stretching band at 1745 cm^{-1} in solution (THF), which is shifted down to 1705 cm^{-1} in the solid state (Nujol).¹¹

A view of complex III is shown in Figure 2, with the most relevant bond distances and angles.¹² In the asymmetric unit there are two crystallographic independent molecules, $[\text{cp}_2\text{Mo}(\text{CO}_2)]$ denoted by A and B, whose geometries are not significantly different. The two cp ligands are bent to make a cavity in the equatorial plane for the CO_2 unit $\eta^2\text{-C,O}$ bonded to the metal. Structural parameters for the cp_2Mo unit are as reported for complex II. Mo–C and Mo–O bond distances in the $[\text{Mo}(\text{CO}_2)_2(\text{CN-}i\text{-Pr})(\text{PMe}_3)_3]$.¹³ The M–O bond distance in complex III is significantly longer than that found in II. Both C–O bond distances maintain a double-bond character with the longest one [C11A–O1A, 1.288 (14) Å] involved in the interaction with the metal, while the other one is C11A–O2A = 1.201 (14) Å. These distances compare very well with those reported for [Ni-

$(\text{PCy}_3)_2(\text{CO}_2)]$ [1.22 (2) and 1.17 (2) Å]¹⁴ and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Nb}(\text{CH}_2\text{SiMe}_3)(\text{CO}_2)]$ [1.283 (8) and 1.216 (8) Å].¹⁵ It is worthy to note that the molecules are held together by a network of $\text{CH}\cdots\text{O}$ contacts which can be considered as hydrogen bonds (Figure 3, supplementary material).^{10,16}

Carbon dioxide in complex III can be viewed as experiencing bifunctional activation: the electron-rich active site is the Mo atom and weakly acid hydrogen atoms interacting at the oxygens complete the activation.¹⁷ Such a bifunctional interaction would be responsible for the difference in the C–O stretching frequency going from solid state (1705 cm^{-1} , Nujol) to the solution (1745 cm^{-1} , THF).¹¹ This feature may have interesting suggestions on how fixation of CO_2 occurs in bifunctional systems containing protonic acids, including solvents, and how to devise strategies for the fixation of CO_2 . Complex III is a rather unique complex of CO_2 , since the metallic fragment to which CO_2 is bonded is rather robust and it is not a phosphine-type ligand, which can be involved in promoting transformations of CO_2 -like deoxygenation.

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Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles and a listing of structure factor amplitudes for complexes II and III and Figure 3 showing the hydrogen bonding framework in complex III involving molecules A and B (12 pages). Ordering information is given on any current masthead page.

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(16) The metal-bonded oxygen atoms are involved in the formation of one hydrogen bond; the uncoordinating ones form two hydrogen bonds. The environment of the two molecules is, however, different. Molecule A forms centrosymmetric dimers through the hydrogen bonds C9A–H9A...O2A and is linked to adjacent B molecules through four hydrogen bonds involving both cyclopentadienyl rings. Molecule B is linked through hydrogen bond only to molecules A and only one of the two cyclopentadienyl rings is engaged in the formation of hydrogen bonds.

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(9) Crystal data: $\text{C}_{11}\text{H}_{12}\text{MoO}$, $M_r = 256.2$, monoclinic, space group $C2/c$ (from systematic absences and structural analysis), $a = 13.576$ (2) Å, $b = 6.825$ (1) Å, $c = 20.751$ (3) Å, $\beta = 104.21$ (1)°; $V = 1863.9$ (5) Å³, $Z = 8$; $D_c = 1.826$ g cm^{-3} ; $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu(\text{Mo K}\alpha) = 13.3$ cm^{-1} ; crystal dimensions $0.10 \times 0.24 \times 0.50$ mm. Intensities of 3617 reflections were measured at room temperature ($2.5 < \theta < 26.0$) on a Philips 1100 diffractometer by using Mo $K\alpha$ radiation, 1947 independent reflections, agreement between equivalent reflections = 0.026. The structure was solved by the heavy-atom method and refined by full-matrix least squares. All calculations were carried out using the SHELX-76 program. For 1414 unique observed reflections [$I > 3\sigma(I)$] the final R value is 0.031.

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(11) A toluene (50 mL) or THF (50 mL) solution of I (2.0 g) was reacted at room temperature and atmospheric pressure with carbon dioxide. The reaction is very slow. After a week a weak band appeared at 1745 cm^{-1} , while some crystalline solid precipitated. The amount of crystalline solid increased by cooling the solution at -15 °C (0.41 g). The unreacted starting complex I can be recovered from the mother solution. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Mo}$: C, 48.89; H, 3.70. Found: C, 49.27; H, 3.73. By gentle heating and under 20 atm of CO_2 the reaction is significantly faster and the yield higher. The CO band falls at 1705 (Nujol) and 1745 cm^{-1} (THF solution). Its solubility in THF is rather poor. The reaction of I with CO_2 can be followed by IR and the appearance of the band at 1745 is very slow. When dissolved by gentle heating in THF, complex III shows a strong band at 1745 cm^{-1} . With continued heating in vacuo, a band at 1700 cm^{-1} appeared, which increased slowly with time. This change cannot be reversed by restoring the CO_2 atmosphere. We did not clearly identify the new species having the band at 1700 cm^{-1} in solution.

(12) Crystal data: $\text{C}_{11}\text{H}_{10}\text{MoO}_2$, $M_r = 270.2$, monoclinic, space group $P2_1/c$ (from systematic absences), $a = 7.754$ (3) Å, $b = 13.04$ (6) Å, $c = 19.045$ (7) Å, $\beta = 100.70$ (4)°; $V = 1892$ (1) Å³, $Z = 8$, $D_c = 1.896$ g cm^{-3} ; $F(000) = 1072$, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu(\text{Mo K}\alpha) = 13.2$ cm^{-1} ; crystal dimensions $0.32 \times 0.22 \times 0.35$ mm. Intensities of 4707 reflections were measured at room temperature ($3.0 < \theta < 25.0$) on a Philips PW 1100 diffractometer using Mo $K\alpha$ radiation resulting in 3440 independent reflections (agreement between equivalent reflections 0.070). The structure was solved by the heavy-atom method and refined anisotropically by full-matrix least squares. All calculations were carried out using the SHELX-76 program. For 2153 unique observed reflections [$I > 3\sigma(I)$] the final R value is 0.054.

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Dithioether-Containing Cyclic Peptides

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The design and synthesis of cyclic analogues of linear peptide hormones and neurotransmitters have attracted considerable interest in recent years. This interest often has been motivated by the desire to develop analogues with increased receptor selectivity, antagonist activity, or prolonged duration of action and is generally based upon evidence for or suspicion of a biologically active conformation of the native peptide that includes some specific folded structure. The rationale for the cyclic analogue then is to stabilize this proposed folded conformation. Among the many approaches utilized for preparing cyclic peptides,¹ several successful examples have employed pairs of cysteine and/or penicillamine (β,β -dimethylcysteine) residues with subsequent cyclization through the side chains to yield conformationally restricted disulfide-containing peptides.^{2–5} These successes notwithstanding, cyclization via disulfide bond formation suffers from one major drawback. Generally, for a given native peptide relatively few residues can be replaced without drastic activity losses. Thus,

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