voked to explain exchange in a sterically hindered alcohol. The dihydrogen ligand in $IrH(H_2)(bq)(PR_3)_2^+$ is more acidic than in the tungsten complex and more easily deprotonated.

It has been suggested[3c] that adventitious water mediates the enigmatic H/D scrambling observed on our dihydrogen complexes, possibly by a deprotonation mechanism similar to the above. However, the relatively slow rate (days) of $D_2/H_2O$ exchange determined in solutions containing $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ would argue against this. Even though the $M-\eta^2\text{-}D_2 + H_2 \rightarrow M-\eta^2\text{-}HD + HD$ statistical scrambling occurs over a similar time frame (ca. 1–2 days for bulk reaction, solution or solid state), a very fast rate of $D_2/H_2O$ reaction would be required for a trace amount of water to actively exchange with a much larger amount (up to 10 mmol) of hydrogen. Furthermore, we have found that $H_2/D_2$ scrambling occurs over *catalytic* amounts of *solid* $W(CO)_3(PCy_3)_2$ *thoroughly dried in vacuo*, which surely would preclude deprotonation by $H_2O$.[41] Additional studies of these isotopic exchange processes are planned to obtain mechanistic information.

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**Supplementary Material Available:** Tables of general displacement parameter expressions (*U*'s) (2 pages). Ordering information is given on any current masthead page.

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# Organometallic Oxides: Oxidation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ with $O_2$ To Form *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$, *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$, and $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$

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Oxidation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ by air in $CHCl_3$ gave $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$, in an unprecedented reaction in which an oxygen atom was inserted into a $C_5$ ring. The previously reported complexes $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ and $(\eta\text{-}C_5Me_5)MoCl(O)_2$ were also obtained from the oxidation. The structure of $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ has been determined by X-ray diffraction (orthorhombic, $a$ = 15.971 (1) Å, $b$ = 16.825 (1) Å, $c$ = 23.597 (1) Å, space group *Pcab*, $Z$ = 8, $R'$ = 0.051). The anion is a derivative of the classic $\{[Mo(O)(\mu\text{-}O)_2]_6(\mu_6\text{-}O)\}^{2-}$, in which a terminal oxygen has been replaced by $\eta\text{-}C_5Me_5$. The strong trans effect of Mo=O manifests itself across the $Mo_6(\mu_6\text{-}O)$ octahedron to the $Mo-(\eta\text{-}C_5Me_5)$ unit. Irradiation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ in the presence of $O_2$ gave *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ and *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$, whose structures have been determined by X-ray diffraction. *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ is orthorhombic, with $a$ = 8.581 (7) Å, $b$ = 39.610 (6) Å, $c$ = 56.650 (8) Å, space group *F2dd*, $Z$ = 32, and $R$ = 0.195. $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ is monoclinic, with $a$ = 8.451 (8) Å, $b$ = 28.771 (16) Å, $c$ = 10.925 (14) Å, $\beta$ = 107.2 (10)°, space group $P2_1/c$, Z = 4, and $R$ = 0.073. These diamagnetic dinuclear compounds have long Mo—Mo distances (2.72 and 2.80 Å, respectively). Extended Hückel calculations show that there is very little Mo—Mo bonding, and the formal Mo—Mo description required by the 18-electron rule is incorrect.

## Introduction

Cubanes of general formula $[(\eta\text{-}C_5R_5)M(\mu_3\text{-}A)]_4$ (M = d-block element; A = p-block element, usually from group 16) have interesting electronic and magnetic properties. In the cases where M = Mo, Fe and A = S, they may also be models for the active sites of ferridoxins and nitrogenase.[1] As part of our research into cyclopentadienylmetal oxides, we have discussed the molecular and electronic structures of $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$ (R = H,[2] Me;[3] $R_5$ = $H_4Me$[4]). An extremely desirable cubane for comparison purposes would be $[(\eta\text{-}C_5R_5)Mo(\mu_3\text{-}O)]_4$. However, this molecule presents a considerable synthetic challenge. The route used to prepare $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$, namely oxidation of $(\eta\text{-}C_5R_5)_2Cr$ with $N_2O$,[5] cannot be used for molybdenum since $(\eta\text{-}C_5R_5)_2Mo$ compounds are unknown. The routes used to prepare $[(\eta\text{-}C_5R_5)Mo(\mu_3\text{-}S)]_4$ (the reaction between $[(\eta\text{-}C_5R_5)Mo(CO)_2]_2$ and $[(\eta\text{-}C_5R_5)Mo(\mu\text{-}\eta^2\text{-}SC_3H_6S)]_2$[6] or between $[(\eta\text{-}C_5R_5)Mo(\mu\text{-}Cl)_2]_2$ and LiSH[7]) are also not available because the starting materials do not exist or because they do not react in an analogous manner when oxygen replaces sulfur.

In the absence of $(\eta\text{-}C_5R_5)_2Mo$, the carbonyl dimers $[(\eta\text{-}C_5R_5)Mo(CO)_n]_2$ ($n$ = 2, 3) are attractive candidates for oxidation to $[(\eta\text{-}C_5R_5)Mo(\mu_3\text{-}O)]_4$. The oxidation of $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ by $O_2$ was first investigated by Green

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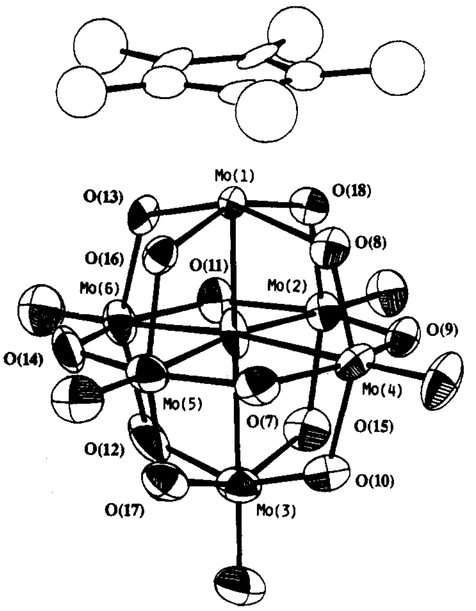

**Figure 1.** Structure of the [(η-C$_5$Me$_5$)Mo$_6$O$_{18}$]$^-$ anion as determined by X-ray diffraction.

and co-workers.[8,9] The products were *syn*-[(η-C$_5$H$_5$)Mo(O)(μ-O)]$_2$, [(η-C$_5$H$_5$)Mo(O)$_2$]$_2$(μ-O), and (η-C$_5$H$_5$)MoCl(O)$_2$. More recently, oxidation of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ to [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) and (η-C$_5$Me$_5$)MoCl(O)$_2$ has been reported.[10] These oxidations were all exhaustive; that is, they were conducted under conditions of an unlimited supply of O$_2$. No attempts to characterize intermediates were recorded. We therefore decided to investigate the oxidation of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ further, with a view to isolating intermediates and possibly clusters such as [(η-C$_5$Me$_5$)Mo(μ$_3$-O)]$_4$. These investigations have resulted in the new compounds *syn*-[(η-C$_5$Me$_5$)MoCl]$_2$(μ-Cl)$_2$(μ-O), *syn*-[(η-C$_5$Me$_5$)MoCl]$_2$(μ-Cl)(μ-CO$_3$H)(μ-O), and [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$], which are reported here. The insertion of an oxygen atom into a C$_5$ ring, as in the formation of [C$_5$Me$_5$O]$^+$, is an unprecedented reaction.

## Results and Discussion

**Formation of [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$].** Oxidation of a chloroform solution of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ by air gave a mixture of [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) and (η-C$_5$Me$_5$)MoCl(O)$_2$, as was previously reported by Faller and Ma.[10] However, we noticed that a third product was formed. The amount of this product increased with time and also increased as the initial concentration of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ was increased. There was no reaction between [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ and N$_2$O. The new product was considerably less soluble in CHCl$_3$ than [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) or (η-C$_5$Me$_5$)MoCl(O)$_2$. It was purified by recrystallization from acetone/chloroform and shown by spectroscopy, elemental analysis, and X-ray crystallography to be the salt [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$] (Figures 1 and 2). The structure of this salt is discussed below.

Further investigation showed that a mixture of [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) and (η-C$_5$Me$_5$)MoCl(O)$_2$ (1:2 ratio), when dissolved in chloroform, acetone, or ether, gave [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$] on exposure to air over a 10-day period, in the complete absence of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$. Solutions of [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) in hexane or benzene did not give [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$] when exposed to air for any length of time. On the other hand, solutions of (η-C$_5$Me$_5$)MoCl(O)$_2$ did give the salt when exposed to air, but only very slowly and in low yield. Molybdenum blue[11] was also formed. In dry chloroform, (η-C$_5$Me$_5$)MoCl(O)$_2$ did not give the salt when exposed to dry O$_2$. It was found previously that (η-C$_5$Me$_5$)MoCl(O)$_2$ was converted into [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) by H$_2$O.[12] We conclude that [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$] was formed from a mixture of (η-C$_5$Me$_5$)MoCl(O)$_2$, [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O), and O$_2$ and/or H$_2$O. The salt was not formed directly from [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$.

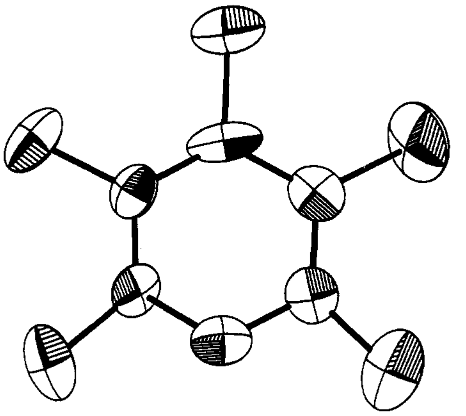

**Figure 2.** The [C$_5$Me$_5$O]$^+$ cation associated with [(η-C$_5$Me$_5$)Mo$_6$O$_{18}$]$^-$.

The mechanism of this remarkable reaction, in which an oxygen atom was inserted into the C$_5$ ring of C$_5$Me$_5$, remains obscure. However, some relevant observations are of interest. It was observed previously that (η-C$_5$Me$_5$)MoCl(O)$_2$ was a catalyst for the epoxidation of olefins by alkyl hydroperoxides.[13] No oxidation of the η-C$_5$Me$_5$ ligand of (η-C$_5$Me$_5$)MoCl(O)$_2$ was observed during the epoxidation. The known[12,14,15] peroxo complex (η-C$_5$Me$_5$)MoCl(η-O$_2$)(O) was inert toward olefins.[13] In agreement with this, we found that a mixture of (η-C$_5$Me$_5$)MoCl(η-O$_2$)(O) and [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O) did not give [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$]. Also, oxidation of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$ with H$_2$O$_2$ and HCl gave a mixture of (η-C$_5$Me$_5$)MoCl(O)$_2$, [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O), and (η-C$_5$Me$_5$)MoCl(O$_2$)(O), but no [C$_5$Me$_5$O][(η-C$_5$Me$_5$)Mo$_6$O$_{18}$]. We conclude that (η-C$_5$Me$_5$)MoCl(O)$_2$ catalyzed the slow insertion (via epoxidation) of an oxygen atom into the η-C$_5$Me$_5$ ligand of [(η-C$_5$Me$_5$)Mo(O)$_2$]$_2$(μ-O). The lack of any product containing chlorine, other than (η-C$_5$Me$_5$)MoCl(O)$_2$, is further evidence for the catalytic role of this complex. However, the remarkable insertion reaction appeared to require the concomitant formation of [(η-C$_5$Me$_5$)Mo$_6$O$_{18}$]$^-$ by an equation such as (1). The reason the formation of [(η-C$_5$Me$_5$)Mo$_6$O$_{18}$]$^-$ is so important to the insertion remains a mystery.

$$3[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O}) + 2\text{O}_2 \xrightarrow{(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2} [\text{C}_5\text{Me}_5\text{O}][(\eta\text{-C}_5\text{Me}_5)\text{Mo}_6\text{O}_{18}] + 2(\text{C}_5\text{Me}_5)_2 \quad (1)$$

**Formation of *syn*-[(η-C$_5$Me$_5$)MoCl]$_2$(μ-Cl)(μ-CO$_3$H)(μ-O) and *syn*-[(η-C$_5$Me$_5$)MoCl]$_2$(μ-Cl)$_2$(μ-O) by Irradiation and Oxidation of [(η-C$_5$Me$_5$)Mo(CO)$_2$]$_2$.**

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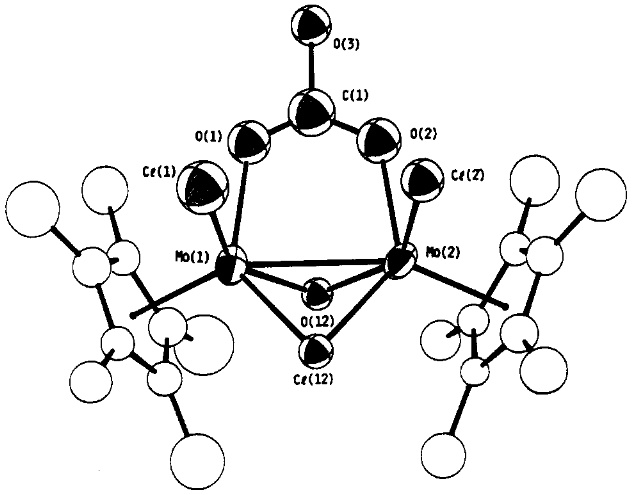

**Figure 3.** Structure of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ (hydrogen atoms omitted).

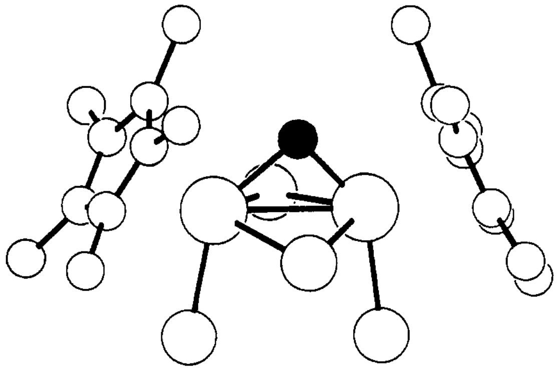

**Figure 4.** Structure of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$.

When a solution of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ in $CH_2Cl_2$ was irradiated with a 450-W lamp in the presence of a restricted supply of $O_2$ for 9 h, $CO_2$ was evolved and the solution turned from deep red to burgundy. Two products were obtained from this burgundy solution. The first was orange *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$. This was identified by infrared, NMR, and mass spectroscopy, as well as by X-ray diffraction (Figure 3). The second was green-blue *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$, which was identified by X-ray diffraction (Figure 4). Independent experiments showed that $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ reacted with $CH_2Cl_2$ to form $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$.

The irradiation of $[(\eta\text{-}C_5R_5)Mo(CO)_3]_2$ (R = H, Me) in inert solvents such as xylenes, and in the absence of $O_2$, has been investigated previously.[16-18] The only product was $[(\eta\text{-}C_5R_5)Mo(CO)_2]_2$, which must be assumed to be stable to irradiation under these conditions. Irradiation of $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ in the presence of an unlimited supply of $O_2$ gave $[(\eta\text{-}C_5H_5)Mo(O)(\mu\text{-}O)]_2$, $[(\eta\text{-}C_5H_5)Mo(O)_2]_2(\mu\text{-}O)$, and $(\eta\text{-}C_5H_5)MoCl(O)_2$.[8] It appears that the only investigation of the irradiation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ in the presence of $O_2$ was in a mixture with $Fe_2(CO)_9$. The product was the cluster $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2[Fe(CO)_3](\mu_3\text{-}O)$.[19] Irradiation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ in toluene containing water gave the cluster $[(\eta\text{-}C_5Me_5)Mo]_3(CO)_4(\mu\text{-}H)(\mu_3\text{-}O)$.[20] The related cluster $\{[(\eta\text{-}C_5H_5)Mo(CO)_2]_3(\mu_3\text{-}O)\}^+$ was obtained from $\{(\eta\text{-}C_5H_5)Mo(CO)_3\}^+$ and water.[21] These clusters all contain carbonyl ligands, which are readily identifiable by infrared spectroscopy. No carbonyl complexes were obtained under the conditions described in the present work.

**Table I. Important Average Distances (Å) and Angles (deg) in the $[(\eta\text{-}C_5Me_5)Mo_6O_{18}]^-$ Anion**

| | | | |
|---|---|---|---|
| Mo(1)[a]—Mo(2,4–6) | 3.263 (2, 16)[b] | Mo(3)—($\mu_6$-O) | 2.498 (9) |
| Mo(2–6)—Mo(3–6) | 3.314 (2, 15) | Mo(2,4–6)—($\mu_6$-O) | 2.343 (9, 15) |
| Mo(1)—($\mu_2$-O) | 1.967 (9, 58) | Mo(1)—Cp[c] | 2.091 (15) |
| Mo(2,4–6)—($\mu_2$-O) | 1.921 (10, 88) | Mo═O | 1.686 (11, 23) |
| Mo(1)—($\mu_6$-O) | 2.134 (9) | | |

| | |
|---|---|
| ($\mu_2$-O)–Mo(1)–($\mu_2$-O) | 153.1 (4, 2) |
| ($\mu_2$-O)–Mo(2,4–6)–($\mu_2$-O) | 152.0 (4, 20) |
| ($\mu_2$-O)–Mo(3)–($\mu_2$-O) | 149.9 (4) |
| Mo(1)–($\mu_2$-O)–Mo(2,4–6) | 116.5 (5, 16) |
| Mo(3)–($\mu_2$-O)–Mo(2,4–6) | 120.4 (5, 9) |
| Mo(2,4–6)–($\mu_2$-O)–Mo(2,4–6) | 117.7 (5, 36) |

[a] For the numbering scheme see Figure 1. [b] The first numeral in parentheses is the mean esd; the second numeral is the maximum deviation from the mean. [c] Cp is the centroid of the $C_5$ ring of $\eta\text{-}C_5Me_5$.

**Table II. Important Distances (Å) and Angles (deg) in $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$**

| | | | |
|---|---|---|---|
| Mo(1)—Mo(2)[a] | 2.799 (4)[b] | Mo—O(1,2) | 2.124 (21, 3) |
| Mo—Cl(1,2) | 2.388 (16, 14) | Mo—Cp[c] | 2.04 (3) |
| Mo—Cl(12) | 2.420 (8, 1) | C(1)—O(1,2) | 1.22 (3, 2) |
| Mo—O(12) | 1.860 (20, 22) | C(1)—O(3) | 1.74 (4) |

| | |
|---|---|
| Mo(1)–Cl(12)–Mo(2) | 70.6 (2) |
| Mo(1)–O(12)–Mo(2) | 97.6 (12) |
| O(1)–C(1)–O(2) | 132 (3) |

[a] See Figure 3 for the numbering scheme. [b] Esd's in parentheses. [c] Cp is the centroid of the $C_5$ ring of $\eta\text{-}C_5Me_5$.

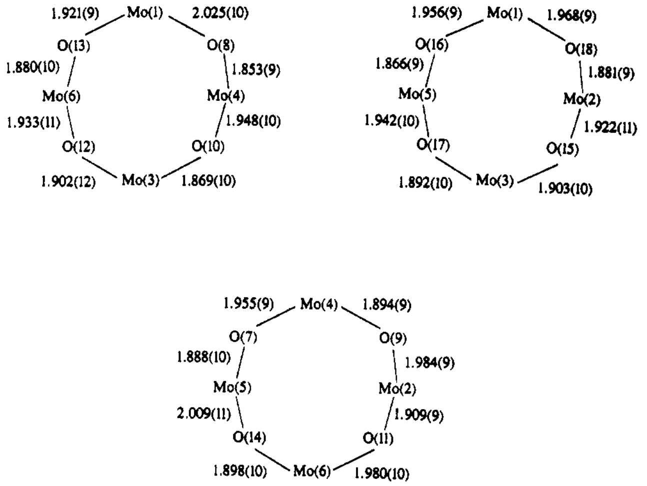

**Figure 5.** Alternating Mo—O bonds in $[(\eta\text{-}C_5Me_5)Mo_6O_{18}]^-$.

Both $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ and $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ formally contain Mo(IV). They are syn complexes and are related in that a $\mu\text{-}\eta^2\text{-}CO_3H^-$ ligand replaces a bridging $Cl^-$. The restricted supply of $O_2$ has clearly prevented the formation of Mo(V) or Mo(VI) compounds. It is also noteworthy that there is a greater abstraction of chlorine from $CH_2Cl_2$ under these conditions, compared to those of exhaustive oxidation, presumably because oxidative addition of low-valent $(\eta\text{-}C_5Me_5)Mo$ derivatives can still occur. The oxidation of CO to $CO_2$ and $CO_3^{2-}$ has been observed previously for cyclo-

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pentadienyltitanium[22,23] and -molybdenum[24] carbonyls.

**Structure of [(η-$C_5Me_5$)$Mo_6O_{18}$]$^-$.** The structure of the [(η-$C_5Me_5$)$Mo_6O_{18}$]$^-$ anion is shown in Figure 1, which also gives the necessary labels. Important distances and angles are listed in Table I and shown in Figure 5. The anion is an η-$C_5Me_5$ derivative of the polyoxometalate anion $Mo_6O_{19}^{2-}$ and is closely related to [(η-$C_5H_5$)Ti($Mo_5O_{18}$)]$^{3-}$[25-27] and (η-$C_5Me_5$)$_2W_6O_{17}$.[28] The $Mo_6$($\mu_2$-O)$_{12}$($\mu_6$-O) core of [(η-$C_5Me_5$)$Mo_6O_{18}$]$^-$ is distorted relative to that in $Mo_6O_{19}^{2-}$, partly because of the increased coordination number of Mo(1) (the molybdenum carrying the η-$C_5Me_5$ ligand) but mainly because of the very low trans influence of η-$C_5Me_5$ relative to that of a terminal oxygen ligand. This influence has been noted previously in mononuclear compounds such as (η-$C_5R_5$)$MCl_2$(O) (M = V,[29] Mo,[30] Re[31]) but appears here in a polynuclear derivative. In the parent $Mo_6O_{19}^{2-}$, the distances from the Mo atoms to the central oxygen (the $\mu_6$-O) average 2.319 (4, 7)[32] or 2.315 (1, 12) Å.[33] In [(η-$C_5Me_5$)$Mo_6O_{18}$]$^-$ the Mo(1)—($\mu_6$-O) distance is 2.134 (9) Å, but the distance between the molybdenum atom trans to Mo(1) in the octahedron (Mo(3)) and $\mu_6$-O is 2.498 (9) Å. The distances between the molybdenum atoms cis to Mo(1) and $\mu_6$-O average 2.343 (9, 15) Å. Thus, $\mu_6$-O is displaced considerably away from Mo(3) toward Mo(1). This must be due to the high trans influence of Mo=O versus Mo—(η-$C_5Me_5$). The Mo(1)—($\mu_2$-O) distances average 1.967 (9, 58) Å, the Mo(3)—($\mu_2$-O) distances 1.891 (10, 22) Å, and the *cis*-Mo—($\mu_2$-O) distances 1.921 (10, 88) Å. In $Mo_6O_{19}^{2-}$ the Mo—($\mu_2$-O) distances average 1.927 (4, 77)[32] or 1.916 (9, 35) Å,[33] in good agreement with the *cis*-Mo—($\mu_2$-O) distances in [(η-$C_5Me_5$)$Mo_6O_{18}$]$^-$. We believe that the relatively short Mo(3)—($\mu_2$-O) distances are due to the reduction in nonbonding O---O repulsions because of the long Mo(3)—($\mu_6$-O) distance. The long Mo(1)—($\mu_2$-O) distances are due to the increase in coordination number to 8 at Mo(1), combined with an increase in nonbonded O---O repulsion due to the short Mo(1)—($\mu_6$-O) distance. The analysis is supported by changes in the O–Mo–O and Mo–O–Mo bond angles (Table I), but these are relatively minor compared to the changes in the distances. The difference in the trans influence between Mo=O and Mo($NC_6H_4Me$) appears to produce a similar distortion in the $Mo_6$($\mu_2$-O)$_{12}$($\mu_6$-O) core of the recently prepared {($Mo_5O_{18}$)Mo($NC_6H_4Me$)}$^{2-}$.[34]

The Mo—($\mu_2$-O) distances are in agreement with the trans-bond alternating mechanism discussed by Klemperer and co-workers.[25] This is clear from the three [Mo($\mu_2$-O)]$_4$ rings of [(η-$C_5Me_5$)$Mo_6O_{18}$]$^-$ depicted in Figure 5.

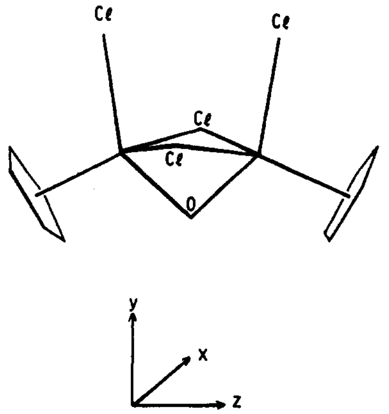

**Figure 6.** Geometry and axes for the model compound [(η-$C_5H_5$)$MoCl$]$_2$($\mu$-Cl)$_2$($\mu$-O), of idealized $C_{2v}$ symmetry.

**Structure of *syn*-[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)$_2$($\mu$-O).** The crystals of this compound were of very poor quality, and the data could only be refined to R = 0.20. The analysis clearly established that the dinuclear complex adopted the syn (eclipsed) configuration (Figure 4); the Cl(terminal)–Mo–Mo–Cl(terminal) torsion angle was 0 within the limits of error. The Mo–Mo distance was 2.72 (1) Å.

**Structure of *syn*-[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_3H$)($\mu$-O).** Crystals of this compound decomposed rapidly in the X-ray beam (they were also light-sensitive). A full data set could not be obtained. The X-ray analysis unequivocally defined the *syn*-{[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_2$)($\mu$-O)}$^+$ fragment of the molecule, with a Mo—Mo distance of 2.799 (4) Å. This fragment was also the peak of highest mass in the electron ionization mass spectrum. The method of preparation of the compound, its diamagnetism and infrared spectrum, and its chemical properties allow three formulations: {[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_2$)($\mu$-O)}$^+${OH}$^-$, [(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_3H$)($\mu$-O), and {H}$^+${[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_3$)($\mu$-O)}$^-$. Isotropic refinement of the {[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_2$)($\mu$-O)}$^+$ fragment proceeded to R = 0.10. A difference Fourier synthesis showed, as the highest peak, a region of electron density corresponding to atom O(3) of Figure 3. Refinement of this atom as oxygen gave R = 0.08 but resulted in a large thermal parameter (U = 0.18 Å$^2$) and a long C(1)—O(3) distance (1.78 Å). A difference Fourier revealed two regions of electron density: X(1), of height 0.85 e Å$^{-3}$, 1.75 Å from O(3) and X(2), of height 0.66 e Å$^{-3}$, 1.50 Å from O(3). The C(1)–O(3)–X(1) angle was 98° and the C(1)–O(3)–X(2) angle 111°. The X(1)O(3)X(2) plane made an angle of 22° with the plane of the {$Mo_2$($O_2C$)} fragment. The peaks X(1) and X(2) were too intense to be hydrogen atoms. We believe that a true description of the crystal would require contributions from all three formulations. However, the data were not of sufficient quality for a detailed analysis. For simplicity the formula [(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_3H$)($\mu$-O) is used here.

**Bonding in *syn*-[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)$_2$($\mu$-O) and *syn*-[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_3H$)($\mu$-O).** Both dinuclear complexes were diamagnetic, and both contained two formally Mo(IV) ($d^2$) ions. Conventionally the complexes would be assigned a Mo=Mo double bond to give an 18-electron configuration about each molybdenum atom. However, such an assignment is not in agreement with the Mo—Mo distances of 2.72 (1) Å in *syn*-[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)$_2$($\mu$-O) and 2.799 (4) Å in *syn*-[(η-$C_5Me_5$)MoCl]$_2$($\mu$-Cl)($\mu$-$CO_3H$)($\mu$-O). These distances may be compared to the Mo—Mo single bond in [(η-$C_5H_4Pr^i$)Mo($\mu$-Cl)$_2$]$_2$ (2.607 (1) Å[35,36]), *syn*-[(η-$C_5H_5$)Mo-

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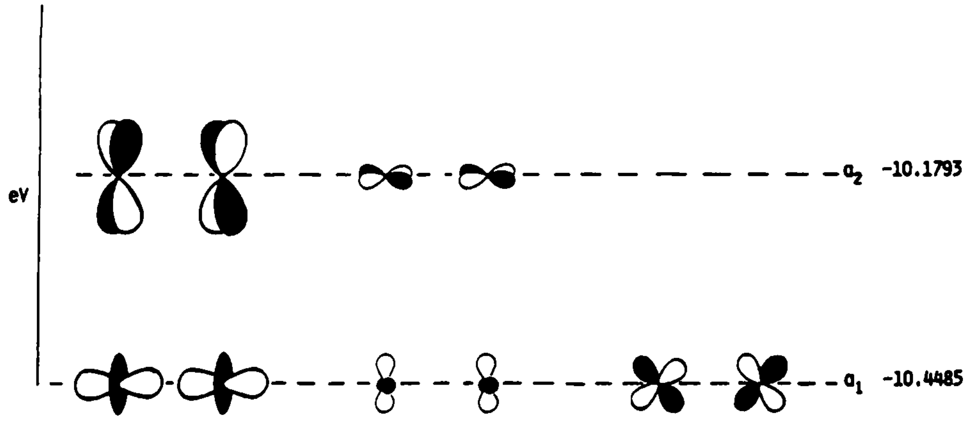

**Figure 7.** Energies, compositions, and symmetries of the two highest occupied molecular orbitals of $[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$.

$(O)(\mu\text{-}O)]_2$ (2.602 (1) Å[37]), *anti*-$[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ (2.647 (3) Å[38]), and *anti*-$[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}S)]_2$ (2.904 (1) Å[39]). The Mo—Mo distance in *syn*-$[(\eta\text{-}C_5H_4Me)Mo(O)(\mu\text{-}S)]_2$ is 2.873 (1) Å, whereas in the anti isomer it is 2.885 (1) Å.[40] The molecular and electronic structures of $[(\eta\text{-}C_5R_5)MCl_2]_2$ (M = Mo, W with a formal M≡M triple bond) have been analyzed.[36] The tungsten–tungsten distance in $[(\eta\text{-}C_5H_4Pr^i)WCl_2]_2$ was 2.368 (1) Å,[41] and in the related $\{[(\eta\text{-}C_5H_5)MoCl_2]_2(\mu\text{-}Cl)\}^-$ the Mo—Mo distance was 2.413 (1) Å.[42] It appears that $[(\eta\text{-}C_5R_5)MoX]_2$ derivatives with a formal Mo═Mo double bond have not been structurally characterized previous to the present work.

An extended Hückel molecular orbital analysis of the model compound $[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$, with idealized $C_{2v}$ symmetry, was performed using the axis system shown in Figure 6. The analysis showed that the two occupied orbitals of highest energy were $a_1$ at -10.4485 eV and $a_2$ at -10.1793 eV (see Figure 7). The $a_1$ orbital contained contributions of approximately 48% from $d_{z^2}$, 17% from $d_{x^2-y^2}$ and 22% from $d_{yz}$; the $a_2$ orbital contained 76% $d_{xy}$ and 17% $d_{xz}$. As is clear from Figure 7, the $a_1$ orbital is symmetric with respect to the plane which reflects the molybdenum atoms. There was a net Mo—Mo overlap integral of 0.118 for the three major contributors to this orbital. Thus, the electrons in the $a_1$ orbital represent considerable direct bonding between the molybdenum atoms. The $a_2$ orbital, on the other hand, is antisymmetric with respect to the plane which reflects the molybdenum atoms. There was a net overlap integral of -0.046 for the two main contributors to this $a_2$ orbital, and the electrons in this orbital have an antibonding effect on the two molybdenum atoms. The net bonding between the two molybdenum atoms is thus small (net Mo—Mo overlap population of 0.062, which may be compared to a value of 0.270 for the Mo—Cl(terminal) interaction). This is clearly considerably less than a single bond, let alone the double bond implied by the conventional representation.

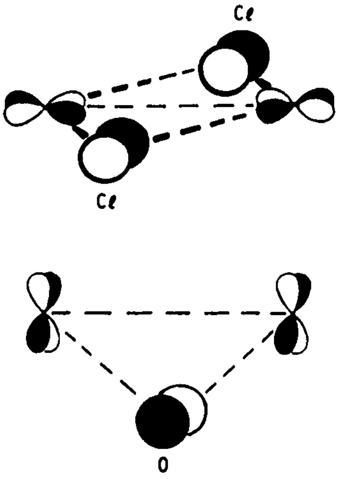

**Figure 8.** Contributors to the $\pi$ bonding in the bridging unit of $[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$.

The reason the $a_2$ orbital is antisymmetric and antibonding with respect to the Mo—Mo interaction is that the $d_{xy}$ orbital, which is the major contributor to $a_2$, is also involved in $\pi$ bonding to the bridging oxygen. This occurs in an orbital of $b_1$ symmetry at -15.7133 eV and requires that this $b_1$ orbital be symmetric with respect to the molybdenum atoms (Figure 8). The $a_2$ orbital is the Mo—O $\pi$-antibonding counterpart of $b_1$. The $d_{xz}$ orbital, which is the minor contributor to the $a_2$ orbital, is involved in the Mo—Cl(bridge) $\sigma$ bond, as shown also in Figure 8. Again, this requires that the $b_1$ orbital be symmetric and that the $a_2$ orbital (which is Mo—Cl(bridge) $\sigma$ antibonding) be antisymmetric with respect to the Mo—Mo interaction. The major contributor to the destruction of M—M bonding is the M—O $\pi$ bonding. As in other cases,[36,43] the Mo—Mo distance is determined primarily by M—O $\pi$ bonding and the geometry at the bridging O and Cl ligands, not by the Mo—Mo interaction.

It should be noted that the LUMO orbital, of $b_1$ symmetry, is the direct counterpart to the HOMO $a_2$; i.e., it is symmetric with respect to the Mo—Mo interaction, with the $d_{xy}$ contribution being 76% and $d_{xz}$ 17%. Therefore, it is predicted that occupation of this orbital by two electrons (e.g. on reduction of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$) will increase the Mo—Mo bonding interaction.

Calculations showed that the syn (eclipsed) form of $[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ had a significantly lower total energy than the anti (staggered) form. No particular orbital was responsible for this difference. A possible reason

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is intramolecular nonbonded interactions. In the idealized *syn*-$[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$, the closest approach of the hydrogen atoms on the $\eta$-$C_5H_5$ rings is 4.7 Å. This distance can be increased by cogwheel rotation of the rings. In *anti*-$[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ the H---Cl distance across the dinuclear bridge is 4.3 Å. This distance cannot be increased by rotation. The nonbonded $C_{methyl}$---$C_{methyl}$ distance in *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ is 4.2 Å. In *anti*-$[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ the nonbonded $C_{methyl}$---Cl distance is 3.6 Å.[38] The Mo—Mo distances are longer for the anti isomers of $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}A)]_2$ (A = O,[38] S[39,40]) than for the syn forms. These differences must be due to the nonbonded interactions.

The Mo—Mo distance in $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ (2.799 (4) Å) is longer than that in $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ (2.72 (1) Å). An extended Hückel calculation on the model compound $\{[(\eta\text{-}C_5H_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3)(\mu\text{-}O)\}^-$ revealed no significant differences between the two highest occupied orbitals of the bicarbonate-bridged complex compared to those of the chloro-bridged one. Three reasons may be advanced for the difference in the Mo—Mo distances. The first is simply that the data for $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ were so poor that the Mo—Mo distance may be in error. The second is that the $(\eta\text{-}C_5Me_5)MoCl$ units are forced further apart by the increased bite angle of the carbonate ligand and its steric bulk, compared to chloride. The third reason is that the involvement of the coordinating oxygen atoms of the carbonate ligand in $\pi$ bonding to carbon reduces their ability to $\pi$ bond to molybdenum; $\pi$ bonding across the bridging ligands is a major contributor to the magnitude of the metal–metal separation. In any event, the Mo—Mo distance in $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ reinforces the conclusion that there is little Mo—Mo bonding in these dinuclear compounds.

## Experimental Section

**General Considerations.** A standard double-manifold vacuum line was used for the manipulation of air-sensitive compounds. Solvents were predried over molecular sieves and distilled over $LiAlH_4$ (ether, THF) or Na (toluene, hexane). Dichloromethane was dried over $P_2O_5$. Chloroform and acetone were used as received. $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ was prepared by the literature method.[44]

Instruments used in this work were as follows: Varian XL-200 for $^1H$ NMR spectra; Perkin-Elmer 683 for infrared spectra, as KBr pellets or Nujol mulls; Kratos MS50 for mass spectra, using EI or FAB ionization. Microanalyses (C, H, Cl) were performed by the Beller Laboratorium, Göttingen, Germany.

**Preparation of $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$. (a) By Oxidation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$.** A solution of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ (3.90 g, 6.8 mmol) in chloroform (270 $cm^3$) was stirred at room temperature in air for 9 days. Chloroform was added occasionally to keep the volume constant. The chloroform was removed under vacuum, leaving an oily brown residue. This was extracted with acetone (3 × 100 $cm^3$) to give a yellow-brown solution. Layering of the solution with chloroform gave red-orange crystals of $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ (yield 0.50 g, 19% based on molybdenum). Anal. Calcd for $C_{20}H_{30}Mo_6O_{19}$: C, 20.9; H, 2.6. Found: C, 21.1; H, 2.7. NMR ($^1H$, $(C^2H_3)_2CO$ solution; $\delta$): 2.97 (s, 6 H), 2.51 (s, 3 H), 2.29 (s, 6 H), assigned to the protons of the 2,6-, 4-, and 3,5-methyl groups of $[C_5Me_5O]^+$, respectively; 2.20 (s, 15 H), assigned to the $\eta$-$C_5Me_5$ ligand. Infrared ($cm^{-1}$): 983 (s) and 957 (vs), assigned to $\nu$(Mo=O); 795 (vs) and 780 (vs), assigned to an antitranslation mode of the $Mo_6(\mu_6\text{-}O)(\mu_2\text{-}O)_{12}$ unit. The compound was also characterized by X-ray diffraction (see Table III).

After removal of $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$, the acetone–chloroform mixture was evaporated under vacuum, leaving a mixture of $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ and $(\eta\text{-}C_5Me_5)MoCl(O)_2$. These were separated and identified as described by Faller and Ma.[10]

**Table III. Crystal and Refinement Data for $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ and $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$**

| | $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ | $[(\eta\text{-}C_5Me_5)MoCl]_2\text{-}(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ |
|---|---|---|
| mol formula | $C_{20}H_{30}Mo_6O_{19}$ | $C_{21}H_{31}Cl_3Mo_2O_4$ |
| fw | 1150.09 | 645.93 |
| cryst syst | orthorhombic | monoclinic |
| space group | *Pcab* | $P2_1/c$ |
| $a$, Å | 15.971 (1) | 8.451 (8) |
| $b$, Å | 16.825 (1) | 28.771 (16) |
| $c$, Å | 23.597 (1) | 10.925 (14) |
| $\alpha$, deg | 90 | 90 |
| $\beta$, deg | 90 | 107.2 (10) |
| $\gamma$, deg | 90 | 90 |
| $V$, Å$^3$ | 6340.8 (6) | 2538 (4) |
| $Z$ | 8 | 4 |
| $D$(calcd), Mg m$^{-3}$ | 2.41 | 1.69 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 2.33 | 1.78 |
| temp, K | 293 | 293 |
| cryst size, mm | 0.40 × 0.28 × 0.20 | 0.80 × 0.20 × 0.04 |
| $2\theta$ limits, deg | 2–50 | 2–40[a] |
| no. of rflns for cell | 23 | 24 |
| $2\theta$ limits for cell, deg | 40–50 | 16–21 |
| no. of rflns collcd | 5239 | 1690[a] |
| no. of unique rflns | 5223 | 1450 |
| no. of obsd rflns | 3458 | 829 |
| criteria for observn | $I > 2.5\sigma(I)$ | $I > 1.0\sigma(I)$ |
| $R(F')$ | 0.051 | 0.067 |
| $R_w(F')$ | 0.062 | 0.069 |
| GOF | 3.00 | 1.84 |
| no. of refined params | 382 | 131 |
| max $\Delta/\sigma$ | 0.125 | 0.002 |
| max $\Delta$, e Å$^{-3}$ | 1.03 | 0.84 |
| $N_o/N_v$ | 9.05 | 6.33 |
| $K$ (weight modifier) | 0.0001 | 0.0005 |

[a] The maximum number of reflections is 2461. Because of crystal decomposition (see text) only a partial data set was collected. This data set did not represent a complete quadrant.

**(b) From a Mixture of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ and $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$.** A mixture of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ (0.219 g, 0.77 mmol) and $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ (0.197 g, 0.37 mmol) was dissolved in a 1:1 mixture of acetone and chloroform (15 $cm^3$). The mixture was stirred, open to the air, for 10 days. The solvent mixture was removed in vacuo; the residue was washed with hexane (20 $cm^3$) and then extracted three times with $CHCl_3$ (20-$cm^3$ portions) until the $CHCl_3$ extracts were colorless. These operations removed unreacted $(\eta\text{-}C_5Me_5)MoCl(O)_2$ and $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$, leaving a light brown residue. This was recrystallized from acetone (20 $cm^3$), giving orange crystals (0.038 g, 84% based on the molybdenum consumed). The product was identified by comparison of its spectroscopic properties and cell dimensions with those of a sample prepared as in (a).

**Preparation of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ and $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$.** A solution of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ (6.00 g, 10.4 mmol) in $CH_2Cl_2$ (1000 $cm^3$) was placed in a photolysis cell, which was then evacuated. To the cell was attached a gas bulb containing $O_2$ (100 mmol). A side arm covered by a balloon was attached to the gas bulb to contain the pressure of CO and $CO_2$ produced on photolysis. The mixture was irradiated using a Hanovia 679A medium-pressure mercury lamp for 22 h, giving a very air-sensitive burgundy solution. The gases evolved were determined to be a mixture of CO and $CO_2$ by infrared spectroscopy. The burgundy solution was filtered and the solvent evaporated from the filtrate under vacuum, giving a red-brown residue. The residue was extracted with toluene (3 × 80 $cm^3$), giving a burgundy solution, which was concentrated to 30 $cm^3$. Addition of hexane (30 $cm^3$) gave orange crystals of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ (yield 3.52 g, 52% based on molybdenum). Anal. Calcd for $C_{21}H_{31}Mo_2Cl_3O_4$: C, 39.1; H, 4.8; Cl, 16.5. Found: C, 39.5; H, 4.8; Cl, 19.1. $^1H$ NMR ($C^2H_2Cl_2$

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[44] King, R. B.; Iqbal, M. Z.; King, A. D. *J. Organomet. Chem.* **1979**, *171*, 53.

**Table IV. Atomic Parameters $x$, $y$, $z$, and $B_{iso}$ for $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$**

| | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 0.07752 (7)[b] | 0.56971 (7) | 0.19100 (5) | 1.91 (5) |
| Mo(2) | 0.14022 (8) | 0.57021 (8) | 0.05980 (5) | 2.65 (6) |
| Mo(3) | 0.32189 (9) | 0.64661 (9) | 0.10061 (6) | 3.61 (7) |
| Mo(4) | 0.14298 (9) | 0.73634 (7) | 0.13408 (5) | 2.84 (6) |
| Mo(5) | 0.25398 (9) | 0.64701 (9) | 0.23332 (6) | 3.29 (6) |
| Mo(6) | 0.25193 (9) | 0.47955 (8) | 0.15904 (6) | 3.36 (7) |
| O(1) | 0.1904 (6) | 0.6047 (5) | 0.1493 (4) | 2.8 (4) |
| O(2) | 0.1002 (7) | 0.5465 (6) | −0.0038 (4) | 3.8 (5) |
| O(3) | 0.4103 (7) | 0.6734 (8) | 0.0681 (5) | 5.4 (6) |
| O(4) | 0.1073 (8) | 0.8317 (6) | 0.1261 (4) | 4.6 (6) |
| O(5) | 0.2987 (7) | 0.6723 (6) | 0.2958 (4) | 4.3 (5) |
| O(6) | 0.2914 (7) | 0.3876 (7) | 0.1648 (5) | 5.7 (7) |
| O(7) | 0.2027 (6) | 0.7406 (6) | 0.2065 (4) | 3.2 (4) |
| O(8) | 0.0584 (6) | 0.6865 (6) | 0.1745 (4) | 2.9 (4) |
| O(9) | 0.1105 (6) | 0.6842 (6) | 0.0664 (4) | 2.9 (5) |
| O(10) | 0.2560 (6) | 0.7382 (5) | 0.1028 (4) | 3.2 (4) |
| O(11) | 0.1925 (6) | 0.4748 (5) | 0.0855 (4) | 3.1 (5) |
| O(12) | 0.3375 (6) | 0.5376 (8) | 0.1183 (5) | 5.4 (7) |
| O(13) | 0.1429 (6) | 0.4740 (5) | 0.1887 (4) | 2.7 (4) |
| O(14) | 0.2864 (6) | 0.5323 (7) | 0.2263 (4) | 4.0 (5) |
| O(15) | 0.2502 (7) | 0.6094 (6) | 0.0420 (4) | 3.8 (5) |
| O(16) | 0.1482 (6) | 0.6088 (5) | 0.2527 (4) | 2.6 (4) |
| O(17) | 0.3426 (6) | 0.6649 (5) | 0.1788 (4) | 3.6 (5) |
| O(18) | 0.0520 (6) | 0.5504 (5) | 0.1106 (4) | 2.5 (4) |
| C(11) | 0.9660 (10) | 0.6004 (9) | 0.2540 (8) | 3.9 (8) |
| C(12) | 1.0027 (9) | 0.5294 (10) | 0.2764 (7) | 3.6 (8) |
| C(13) | 0.9912 (9) | 0.4685 (8) | 0.2359 (7) | 3.1 (7) |
| C(14) | 0.9442 (10) | 0.4996 (10) | 0.1913 (6) | 3.5 (7) |
| C(15) | 0.9306 (9) | 0.5803 (9) | 0.2019 (8) | 4.2 (9) |
| C(111) | 0.9639 (13) | 0.6769 (13) | 0.2862 (9) | 6.8 (5) |
| C(121) | 1.0473 (12) | 0.5203 (11) | 0.3316 (8) | 5.0 (4) |
| C(131) | 1.0189 (11) | 0.3843 (12) | 0.2428 (8) | 5.4 (4) |
| C(141) | 0.9136 (13) | 0.4586 (12) | 0.1404 (9) | 6.7 (5) |
| C(151) | 0.8765 (12) | 0.6326 (11) | 0.1684 (8) | 5.4 (4) |
| O(101) | 0.7032 (8) | 0.1079 (7) | −0.0216 (5) | 4.0 (6) |
| C(102) | 0.6659 (11) | 0.1641 (9) | 0.0098 (8) | 3.6 (9) |
| C(103) | 0.7111 (11) | 0.2139 (10) | 0.0421 (7) | 3.6 (8) |
| C(104) | 0.7985 (13) | 0.2044 (10) | 0.0426 (6) | 4.2 (9) |
| C(105) | 0.8379 (10) | 0.1427 (11) | 0.0123 (7) | 3.9 (8) |
| C(106) | 0.7866 (11) | 0.0946 (9) | −0.0202 (7) | 3.6 (8) |
| C(1021) | 0.5716 (12) | 0.1580 (12) | 0.0039 (9) | 6.1 (11) |
| C(1031) | 0.6653 (13) | 0.2764 (11) | 0.0765 (9) | 6.5 (11) |
| C(1041) | 0.8550 (12) | 0.2621 (11) | 0.0749 (7) | 5.5 (10) |
| C(1051) | 0.9306 (12) | 0.1218 (14) | 0.0189 (11) | 8.6 (14) |
| C(1061) | 0.8073 (13) | 0.0248 (11) | −0.0562 (8) | 6.1 (11) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid. [b] Esd's in parentheses refer to the last digit printed.

**Table V. Atomic Parameters $x$, $y$, $z$, and $B_{iso}$ for $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$**

| | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 0.5153 (6)[b] | 0.34147 (8) | 0.36712 (21) | 2.4 (3) |
| Mo(2) | 0.3581 (5) | 0.39785 (8) | 0.15769 (23) | 2.5 (3) |
| Cl(1) | 0.7618 (20) | 0.3249 (3) | 0.3131 (9) | 6.8 (3) |
| Cl(2) | 0.5649 (17) | 0.3972 (3) | 0.0470 (7) | 4.25 (20) |
| Cl(12) | 0.3722 (15) | 0.31391 (22) | 0.1536 (6) | 3.20 (17) |
| O(1) | 0.648 (3) | 0.4037 (7) | 0.4342 (16) | 4.7 (5) |
| O(2) | 0.519 (4) | 0.4486 (6) | 0.2698 (18) | 4.8 (5) |
| O(3) | 0.714 (6) | 0.4881 (11) | 0.452 (3) | 13.9 (11) |
| O(12) | 0.332 (3) | 0.3791 (5) | 0.3154 (14) | 2.9 (4) |
| C(1) | 0.604 (5) | 0.4397 (10) | 0.379 (3) | 4.0 (8) |
| C(11) | 0.637 (6) | 0.2960 (10) | 0.552 (3) | 3.9 (8) |
| C(12) | 0.563 (6) | 0.3308 (9) | 0.5906 (23) | 2.8 (7) |
| C(13) | 0.380 (6) | 0.3262 (10) | 0.527 (3) | 3.8 (8) |
| C(14) | 0.373 (6) | 0.2899 (11) | 0.452 (3) | 3.7 (8) |
| C(15) | 0.524 (6) | 0.2681 (9) | 0.4599 (23) | 2.9 (7) |
| C(16) | 0.817 (7) | 0.2829 (12) | 0.598 (3) | 7.8 (12) |
| C(17) | 0.641 (6) | 0.3686 (11) | 0.690 (3) | 6.5 (10) |
| C(18) | 0.279 (6) | 0.3567 (13) | 0.556 (3) | 7.5 (11) |
| C(19) | 0.218 (6) | 0.2678 (11) | 0.375 (3) | 6.3 (10) |
| C(20) | 0.556 (5) | 0.2251 (10) | 0.400 (3) | 5.1 (9) |
| C(21) | 0.068 (6) | 0.3922 (8) | 0.0567 (24) | 2.8 (7) |
| C(22) | 0.096 (5) | 0.4322 (9) | 0.1366 (24) | 3.2 (7) |
| C(23) | 0.190 (5) | 0.4662 (8) | 0.0931 (22) | 2.6 (6) |
| C(24) | 0.216 (5) | 0.4480 (9) | −0.013 (3) | 3.2 (7) |
| C(25) | 0.153 (5) | 0.4040 (9) | −0.0377 (24) | 3.0 (6) |
| C(26) | −0.020 (5) | 0.3503 (10) | 0.062 (3) | 5.6 (9) |
| C(27) | 0.026 (6) | 0.4355 (8) | 0.245 (3) | 3.8 (7) |
| C(28) | 0.228 (6) | 0.5144 (10) | 0.146 (3) | 5.5 (9) |
| C(29) | 0.294 (6) | 0.4732 (10) | −0.105 (3) | 5.8 (9) |
| C(30) | 0.158 (5) | 0.3717 (9) | −0.147 (3) | 4.4 (8) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid. [b] Esd's in parentheses refer to the last digit printed.

solution, 200 MHz; $\delta$): 2.10 ($C_5(CH_3)_5$). Infrared (cm$^{-1}$): 1724 (w), 1542 (m), 932 (vs), 911 (s), and 880 (s), assigned to the bridging $CO_3H$ group; 1512 (m), 1445 (m), 1376 (m), and 1023 (m), assigned to $C_5Me_5$; 802 (m), assigned to the Mo—O—Mo unit. Mass spectrum (EI; $m/e$): 628 ($\{[(C_5Me_5)MoCl]_2Cl(CO_2)O\}^+$, with the appropriate fragmentation and isotope pattern). Crystals grown from $CH_2Cl_2$/hexane (1:3 volume ratio) were used to characterized the compound by X-ray crystallography (Table III).

When a $CH_2Cl_2$ solution of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ was set aside, it slowly became green-blue and deposited crystals. These were shown by X-ray crystallography to be $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$. This compound was also obtained by extracting the residue, after extraction with toluene, with $CH_2Cl_2$ (30 cm$^3$) and adding hexane (50 cm$^3$) (yield 0.69 g, 10% based on molybdenum). Anal. Calcd for $C_{20}H_{30}Mo_2Cl_4O$: C, 38.7; H, 4.9; Cl, 22.9. Found: C, 38.3; H, 4.4; Cl, 21.0. $^1$H NMR ($C^2H_2Cl_2$ solution, 200 MHz; $\delta$): 2.28 ($C_5(CH_3)_5$). Infrared (cm$^{-1}$): 1517 (s), 1480 (s), 1437 (m), 1370 (m), and 1025 (m) assigned to $C_5Me_5$; 702 (m) assigned to the Mo—O—Mo unit.

**X-ray Crystallography.** X-ray diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer operating under the control of the NRCCAD software.[45] The radiation was Mo K$\alpha$ ($\lambda$ = 0.71073 Å). Data were collected using the $\omega/2\theta$ scan method. Refinement used the NRCVAX suite of programs.[46] The weighting scheme was of the form $w = 1/(\sigma(F)^2 + kF^2)$. Scattering factors for the neutral atoms were taken from the program. Hydrogen atoms were included, where appropriate, as fixed contributors (C—H = 0.96 Å, isotropic $U$ equal to 0.01 plus the $U$ value of the C atom to which they were attached). Crystal and refinement data for $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ and $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ are given in Table III. The structure determination of $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ was uneventful. Atomic positions are given in Table IV. As outlined above, there was some problem in assigning the structure of the $CO_3H$ portion of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$, but the crystallography was in general straightforward. Atomic positions are given in Table V.

**Crystal Data for $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$.** All attempts to obtain crystals of $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ which would be suitable for X-ray diffraction gave thin plates of marginally acceptable quality. Moreover, these crystals decomposed fairly rapidly in the X-ray beam. The structure was ultimately obtained by combining data from two crystals, giving a total of 3390 intensities which could be regarded as observed by the criteria that $I > \sigma(I)$ (out of 6045 unique reflections). Because of the poor data the final $R$ was 0.198. The analysis proved the identity of the compound beyond doubt, and the Mo—Mo distance (2.720 (8) Å) is of significance. However, the other parameters are not of sufficient accuracy to warrant listing. Therefore, full details are given in the supplementary material. Crystal data: $C_{20}H_{30}Cl_4Mo_2O$, $M_r$ = 620.2, orthorhombic, $a$ = 8.581 (7) Å, $b$ = 39.610 (6) Å, $c$ = 56.650 (8) Å, space group $F2dd$, $Z$ = 32 (2 independent molecules per unit cell).

**Molecular Orbital Calculations.** The extended Hückel calculations used the programs of Hoffmann and co-workers,[47] with the exponents for molybdenum taken from the literature.[6,48]

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*Organometallics* 1992, *11*, 3411-3417

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**Supplementary Material Available:** Figures with numbering schemes and tables of hydrogen atom positions, anisotropic and isotropic thermal parameters, and comprehensive bond distances and angles for $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ and $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ and figures with numbering schemes and tables of crystal and refinement data, atomic positions, thermal parameters, and bond distances and angles for $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ (22 pages). Ordering information is given on any current masthead page.

OM920270T

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# Structure of the [1.1]Metallocenophanes of Fe and Ru: Single-Crystal X-ray Diffraction Analysis of $(C_5H_4\text{-}CH_2\text{-}C_5H_4)_2Fe_2$, $(C_5H_4\text{-}CH_2\text{-}C_5H_4)_2FeRu$, and $(C_5H_4\text{-}CH_2\text{-}C_5H_4)_2Ru_2$

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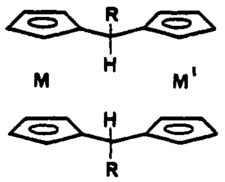
Single-crystal X-ray diffraction studies of the [1.1]metallocenophanes of Fe and Ru $[(Cp\text{-}CH_2\text{-}Cp)_2MM'$, 1, M = M′ = Fe; 2, M = Fe,M′ = Ru; and 3, M = M′ = Ru] clearly document that all three compounds exist only in a syn conformation which, in twisting by angles between 10° and 28°, can relieve the steric crowding of the inner $\alpha$-Cp protons. The anti conformation, in which such strain relief is not possible because of structural rigidity, does not exist. The structures indicate the presence of two fully independent metallocenes in each of these systems and give no obvious indication of any metal–metal bonding: the metallocene halves show now sign of distortion, and the Cp rings in them are coplanar. However, the larger twist in [1.1]ruthenocenophane indicates a metal–metal interaction which, while leading to a net nonbonding situation for the Ru atoms, drastically lowers the redox potential of this compound. Crystal data: compounds 1–3 crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$; (1) $C_{20}H_{20}Fe_2$, $a = 7.894$ (3) Å, $b = 10.530$ (3) Å, $c = 19.402$ (6) Å, $\beta = 94.57$ (3)°; (2) $C_{20}H_{20}FeRu$, $a = 7.980$ (2) Å, $b = 10.724$ (3) Å, $c = 19.112$ (5) Å, $\beta = 95.76$ (2)°; (3) $C_{20}H_{20}Ru_2$, $a = 6.003$ (3) Å, $b = 19.472$ (7) Å, $c = 14.196$ (5) Å, $\beta = 92.55$ (4)°.

## Introduction

The [1.1]metallocenophanes 1–3 of Fe and Ru are an intensively studied trio. We here communicate the full structural characterization of the three parent systems. Although mention, without details, of the structures of 1 and 2 has already been made in a review of metallocenophanes,[3] it has only been possible to complete this series of structural investigations through an improvement[4] in the synthesis of 3.



1: R = H, M = M′ = Fe
2: R = H, M = Fe, M′ = Ru
3: R = H, M = M′ = Ru
4: R = $CH_3$, M = M′ = Fe

Much interest has centered on the possible interactions between the two metals (a) in the neutral species, (b) in their monocations, and (c) in the dications or trications obtained by chemical or electrochemical means. One aim of this work has been to establish and use the structural information on the neutral compounds to provide a link to the differences in their redox properties, especially regarding metal–metal interactions which might facilitate the oxidation and lead to more stable oxidized species.

## Background Information: [1.1]Metallocenophanes

**[1.1]Ferrocenophane (1) and Its Derivatives.** Until we started the present work, the only structurally characterized [1.1]metallocenophanes were the bridge substituted exo,exo-1,12-dimethyl[1.1]ferrocenophane (4) and

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