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Organometallic Oxides: Convenient, High-Yield Syntheses of the (Pentamethylcyclopentadienyl)molybdenum Oxo Complexes (η-C_5Me_5)$MoCl(O)_2$, *anti*-[(η-C_5Me_5)$MoCl(O)$]$_2$(μ-O), (η-C_5Me_5)$MoCl_2(O)$, and *syn*-[(η-C_5Me_5)Mo(O)(μ-O)]$_2$

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Convenient, high-yield syntheses of (pentamethylcyclopentadienyl)molybdenum oxo complexes are presented. Oxidation of [(η-C_5Me_5)$Mo(CO)_2$]$_2$ with H_2O_2/HCl in $CHCl_3$ solution gave (η-C_5Me_5)$MoCl(O)_2$. Oxygen abstraction from (η-C_5Me_5)$MoCl(O)_2$ with $P(OMe)_3$ gave *anti*-[(η-C_5Me_5)MoCl(O)]$_2$(μ-O), which was converted into (η-C_5Me_5)$MoCl_2(O)$ by treatment with Me_3SiCl. Hydrolysis of [(η-C_5Me_5)MoCl(O)]$_2$(μ-O) in toluene containing Et_3N gave *syn*-[(η-C_5Me_5)Mo(O)(μ-O)]$_2$. The physical properties of the oxo complexes are reported. It is noted that (η-C_5Me_5)$MoCl(O)_2$ is unstable both thermally and photochemically. X-ray diffraction showed that the Mo–O distance in (η-C_5Me_5)$MoCl_2(O)$ was very short (1.683(2) Å). Crystal data: triclinic, $P\bar{1}$, $a = 6.5752(4)$ Å, $b = 8.6699(7)$ Å, $c = 11.2425(8)$ Å, $\alpha = 85.937(8)°$, $\beta = 86.302(7)°$, $\gamma = 89.352(6)°$, $Z = 2$, $R = 0.031$ for 3476 observed reflections and 187 parameters.

Introduction

In continuation of our work on (cyclopentadienyl)metal oxides,[1] we have turned to molybdenum. The preparation of (cyclopentadienyl)molybdenum oxides poses special problems because the oxidative aggregation method used to prepare oxides such as [(η-C_5R_5)Cr(μ_3-O)]$_4$ from (η-C_5R_5)$_2$Cr (R = H,[2] Me[3]) requires the unknown (η-C_5R_5)$_2$Mo as starting material. The only readily available low-valent (cyclopentadienyl)molybdenum compounds are the carbonyls [(η-C_5R_5)$Mo(CO)_n$]$_2$ (n = 2, 3).[4,5] Oxidation of [(η-C_5Me_5)$Mo(CO)_2$]$_2$ with [$MeAsO$]$_4$ gave the oxide (η-C_5Me_5)$_6Mo_8O_{16}$,[6] and (η-C_5Me_5)$_4Mo_5O_{11}$ was formed when *syn*-[(η-C_5Me_5)Mo(O)(μ-O)]$_2$ was the reactant.[7] In general, however, oxidation of [(η-C_5R_5)$Mo(CO)_2$]$_2$ gave mono- or dinuclear oxo complexes.[8–11] We therefore wished to investigate reductive aggregation as a route to (cyclopentadienyl)molybdenum oxides.[12] However, this method of preparation requires reasonable quantities of suitable starting materials. The Mo(VI) complexes (η-C_5Me_5)$MoX(O)_2$ (X = Cl, R) and [(η-C_5Me_5)$Mo(O)_2$]$_2$(μ-O) were obtained previously by a variety of procedures,[8,13–18] but the yields were relatively low or the syntheses involved many steps. The dinuclear Mo(V) complexes *anti*-[(η-C_5Me_5)MoCl(O)]$_2$(μ-O), and *syn*-[(η-C_5Me_5)Mo(O)(μ-O)]$_2$ have been described also,[10,19] but again no useful syntheses are known. The most desirable starting material for reductive aggregation is (η-C_5Me_5)$MoCl_2(O)$,[12] but this complex does not appear to have been reported previously. We describe here convenient, high-yield syntheses of (η-C_5Me_5)$MoCl(O)_2$, *anti*-[(η-C_5Me_5)MoCl(O)]$_2$(μ-O), (η-C_5Me_5)$MoCl_2(O)$, and *syn*-[(η-C_5Me_5)Mo(O)(μ-O)]$_2$.

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 dried over $LiAlH_4$ (THF), Na (toluene, hexane), or P_2O_5 (CH_2Cl_2, $CHCl_3$). The procedure was adopted even when water was to be added as a reagent, since the concentration of water was often crucial to the synthesis. The starting material [(η-C_5Me_5)$Mo(CO)_2$]$_2$ was prepared by the literature method.[4]

Instruments used were as follows: Varian XL-200 for ^{1}H and ^{13}C NMR spectra; Perkin-Elmer 683 for infrared spectra; Kratos MS50 for mass spectra. Microanalyses were performed by Beller Laboratorium, Göttingen, Germany.

Preparation of (η-C_5Me_5)$MoCl(O)_2$. To a vigorously stirred solution of [(η-C_5Me_5)$Mo(CO)_2$]$_2$ (2.0 g, 3.5 mmol) in chloroform (200 cm^3) was added a 30% aqueous solution of H_2O_2 (3.5 cm^3), followed immediately by concentrated hydrochloric acid (1.5 cm^3). Normally, within 1 h the solution changed color from red to orange. If the color change did not occur, further portions of

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H_2O_2 and HCl were added. Stirring was continued, in air, until the color became bright yellow (approximately 6 h). The aqueous layer was separated and extracted with portions of chloroform (20 cm^3) until the chloroform extract was colorless. All chloroform solutions were combined, washed with water (150 cm^3), and then treated with an aqueous solution of $FeSO_4$ (5%, 150 cm^3) to remove residual H_2O_2, followed by saturated aqueous NaCl (150 cm^3) to assist in the drying process. The chloroform layer was separated and dried over Na_2SO_4 for 1 h. Na_2SO_4 was removed by filtration and washed with chloroform. Chloroform was removed from the combined washings by rotary evaporation to give a yellow solid. This was recrystallized by dissolving in THF (10 cm^3) at 50 °C and adding hexane (100 cm^3). Yield of (η-C_5Me_5)MoCl(O)$_2$: 1.78 g, 86%. Anal. Calcd for $C_{10}H_{15}ClMoO_2$: C, 40.2; H, 5.1; Cl, 11.9. Found: C, 38.9; H, 4.85; Cl, 11.3. The microanalysis is inaccurate because of the decomposition detailed in the Results and Discussion. ^{1}H NMR (200 MHz, C^{2}HCl$_3$ solution): 2.09 ppm. ^{13}C NMR (50 MHz): 30.2 ($C_5(CH_3)_5$), 122.3 ppm ($C_5(CH_3)_5$). Infrared (KBr pellet): 927 (vs, (ν(Mo=O)), 879 (vs, ν(Mo=O)), 568 cm^{-1} (s, ϑ(O=Mo=O)). Mass spectrum (EI): m/e 300, relative intensity 13%, {(C_5Me_5)-^{98}Mo^{35}ClO$_2$}$^+$; 282, 29%, {M-H_2O}$^+$ (with the appropriate isotope patterns). The spectral data are consistent with those reported by Faller and Ma.[8]

Preparation of *anti*-[(η-C_5Me_5)MoCl(O)]$_2$(μ-O). To an ice-cold solution of (η-C_5Me_5)MoCl(O)$_2$ (1.25 g, 4.19 mmol) in tetrahydrofuran (20 cm^3) was added P(OMe)$_3$ (1.10 cm^3, 9.33 mmol). The mixture was stirred for 12 h, while it was warmed to room temperature. The color changed from bright yellow to wine red. Tetrahydrofuran was removed completely under vacuum, giving a red-brown solid. This was dried under vacuum overnight and recrystallized from THF/hexane (60 cm^3, 1/5) at -30 °C to give wine red crystals of [(η-C_5Me_5)MoCl(O)]$_2$(μ-O). Yield: 1.06 g, 87%. Anal. Calcd for $C_{20}H_{30}Cl_2Mo_2O_3$: C, 41.3; H, 5.2; Cl, 12.2. Found: C, 41.0; H, 5.2; Cl, 12.1. ^{1}H NMR (200 MHz, C$_6{}^2$H$_6$ solution): 1.85 ppm (s). Infrared (KBr pellet): 930 cm^{-1} (s, ν(Mo=O)). Mass spectrum (EI): m/e 584, relative intensity 26%, {(η-C_5Me_5)$_2$^{98}Mo$_2$^{35}Cl$_2$O$_3$}$^+$ (with the appropriate isotope pattern and fragments). Crystal data: monoclinic; space group $P2_1/n$; a = 10.608(3), b = 14.351(4), c = 7.670(2) Å; β = 93.29(2)°; D_c = 1.66 Mg m^{-3} for Z = 2 (lit.:[19] monoclinic, $P2_1/n$, a = 10.621(1) Å, b = 14.371(3) Å, c = 7.689(1) Å, β = 93.24(2)°, D_c = 1.65 Mg m^{-3} for Z = 2).

Preparation of (η-C_5Me_5)MoCl$_2$(O). To an ice-cold solution of [(η-C_5Me_5)MoCl(O)]$_2$(μ-O) (0.503 g, 0.84 mmol) in toluene (100 cm^3) was added Me$_3$SiCl (0.25 cm^3, 1.9 mmol). The mixture was stirred at room temperature under argon for 12 h, during which time the color changed from wine red to brick red. The solvent and excess Me$_3$SiCl were reduced to a volume of 35 cm^3 under vacuum and then layered with hexane (40 cm^3), producing brick red crystals of (η-C_5Me_5)MoCl$_2$(O). These were collected by filtration, washed with cold hexane (10 cm^3), and recrystallized by dissolving in CH_2Cl_2 (65 cm^3), filtering, and reducing the volume to 20 cm^3. Layering with hexane (30 cm^3) gave crystals of (η-C_5Me_5)MoCl$_2$(O). Yield: 0.40 g, 75%. Anal. Calcd for $C_{10}H_{15}Cl_2MoO$: C, 37.8; H, 4.75; Cl, 22.3. Found: C, 37.4; H, 4.85; Cl, 22.0. ^{1}H NMR (200 MHz, C^{2}HCl$_3$ solution): 1.99 ppm, very broad. Infrared: 932 cm^{-1} (vs, ν(Mo=O)). Mass spectrum (EI): m/e 319, 33% relative intensity, {(C_5Me_5)^{98}Mo^{35}Cl$_2$O}$^+$; 283, 61%, {(C_5Me_5)^{98}Mo^{35}ClO}$^+$ (with the appropriate isotope patterns). The crystals were also characterized as (η-C_5Me_5)-MoCl$_2$(O) by X-ray crystallography. Crystal and refinement data: $C_{10}H_{15}Cl_2MoO$; M_r = 318.07; triclinic; space group $P\bar{1}$; a = 6.5752(4), b = 8.6699(7), c = 11.2425(8) Å; α = 85.937(8), β = 86.302(7), γ = 89.352(6)°; V = 637.94(8) Å^3; Z = 2; D_c = 1.66 Mg m^{-3}; crystal dimensions 0.44 × 0.40 × 0.12 mm; T = 293 K; 24 reflections for cell in 2θ range 40–47°; 2θ limits for data collection 2–60°; 7390 reflections measured, averaged to 3695 unique and 3476 observed ($I > 0.5\sigma(I)$); data empirically corrected for absorption using ψ scans; final $R(F)$ = 0.031; $R_w(F)$ = 0.036; GOF = 2.88; 187 refined parameters; maximum Δ 0.93 e Å^{-3}; N_o/N_v = 18.59; weight modifier 1 × 10^{-5}. The atomic coordinates are given in Table 1 and important distances and angles in Table 2. The numbering scheme is shown in Figure 1.

Table 1. Atomic Parameters x, y, z, and B_{iso} for (η-C_5Me_5)MoCℓ_2(O)

	x	y	z	B_{iso},[a] Å^2
Mo	0.05435(3)[b]	0.72950(2)	0.21107(2)	3.180(7)
Cℓ(1)	0.2240(1)	0.49503(9)	0.25356(7)	4.89(3)
Cℓ(2)	0.2215(1)	0.8555(1)	0.35205(9)	6.87(4)
O	0.1407(3)	0.7983(2)	0.0736(2)	5.02(8)
C(1)	–0.2521(3)	0.6079(2)	0.1827(2)	2.99(7)
C(2)	–0.2472(3)	0.6048(2)	0.3111(2)	3.06(7)
C(3)	–0.2515(3)	0.7571(3)	0.3435(2)	3.19(7)
C(4)	–0.2582(3)	0.8575(2)	0.2368(2)	3.48(8)
C(5)	–0.2718(3)	0.7645(2)	0.1387(2)	3.26(7)
C(6)	–0.2591(5)	0.4684(3)	0.1117(3)	4.1(1)
C(7)	–0.2488(5)	0.4598(3)	0.3923(3)	4.3(1)
C(8)	–0.2576(5)	0.8099(4)	0.4675(3)	4.7(1)
C(9)	–0.2734(6)	1.0309(3)	0.2317(4)	5.3(1)
C(10)	–0.2964(6)	0.8186(4)	0.0111(3)	4.9(1)

[a] B_{iso} is the mean of the principal axes of the anisotropic displacement tensor. [b] Esd's (in parentheses) refer to the last significant digit.

Table 2. Important Distances (Å) and Angles (deg) in (η-C_5Me_5)MoCℓ_2(O)

Mo–O	1.683(2)[a]	Mo–C(2)	2.440(2)
Mo–Cℓ(1)[b]	2.3420(7)	Mo–C(3)	2.444(2)
Mo–Cℓ(2)	2.3260(8)	Mo–C(4)	2.336(2)
Mo–C(1)	2.335(2)	Mo–C(5)	2.351(2)
O–Mo–Cℓ(1)	107.33(7)	Cℓ(1)–Mo–Cℓ(2)	93.07(3)
O–Mo–Cℓ(2)	108.84(8)		

[a] Esd's in parentheses. [b] For the numbering scheme, see Figure 1.

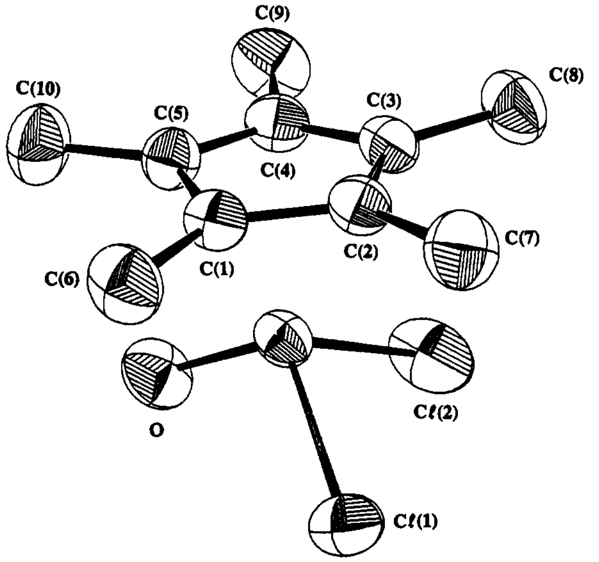

Figure 1. Structure of (η-C_5Me_5)MoCl$_2$(O).

Preparation of *syn*-[(η-C_5Me_5)Mo(O)(μ-O)]$_2$. A mixture of [(η-C_5Me_5)MoCl(O)]$_2$(μ-O) (1.62 g, 2.19 mmol), water (3 cm^3), and Et$_3$N (2 cm^3) in toluene (150 cm^3) was stirred at room temperature for 5 days. The color changed from wine red to orange. The organic layer was separated, washed twice with water (100 cm^3), and then dried over Na_2SO_4 for 1 h. The mixture was filtered and the solvent removed under vacuum, giving 1.22 g (83%) of crude product. This was recrystallized by dissolving in THF (80 cm^3), adding hexane (400 cm^3), and concentrating the mixed solvents to 250 cm^3 under vacuum. When this solution was set aside at -30 °C, crystals of [(η-C_5Me_5)Mo(O)(μ-O)]$_2$ formed. Yield: 0.75 g, 51%. Anal. Calcd for $C_{20}H_{30}Mo_2O_4$: C, 45.6; H, 5.7. Found: C, 45.4; H, 5.7. ^{1}H NMR (200 MHz, C^{2}HCl$_3$ solution): 1.97 ppm (lit.[10] 1.93). Infrared (KBr pellet): 904 cm^{-1} (vs, ν(Mo=O); lit.[10] 914). Mass spectrum (EI): m/e 530, relative intensity 30%, {(C_5Me_5)$_2$^{98}Mo$_2$O$_4$}$^+$ (with the appropriate isotope pattern). Crystal data: tetragonal space group $P\bar{4}2_1c$; a = 11.671-

(4), $c = 15.482(6)$ Å; $D_c = 1.658$ Mg m^{-3} for $Z = 4$ (lit.:[10] $P\bar{4}2_1c$; $a = 11.681(5)$, $c = 15.470(9)$ Å; $D_c = 1.656$ Mg m^{-3} for $Z = 4$).

X-ray Crystallography. X-ray diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer. The radiation was Mo Kα_1 ($\lambda = 0.709\,30$ Å). Data were collected using the $\omega/2\theta$ scan method. Refinement used the NRCVAX suite of programs.[20] The weighting scheme was of the form $w = 1/(\sigma^2(F)^2 + kF^2)$. Scattering factors for the neutral atoms were taken from the program. Crystal data are given with the appropriate compound.

Results and Discussion

The primary objective of the present work was to prepare the complexes $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$, $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$, and $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_2\text{(O)}$ in high yield and by convenient methods. This has been achieved. The use of the powerful oxidizing agent H_2O_2/HCl in chloroform solution effects an essentially quantitative oxidation of $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(CO)}_2]_2$ to give $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$. Faller and Ma found that oxidation of $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(CO)}_2]_2$ with air gave a mixture of $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ and $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$ and that the latter was converted into the former on treatment with PCl_5.[8] We have reported that $[\text{C}_5\text{Me}_5\text{O}][\eta\text{-C}_5\text{Me}_5)\text{Mo}_6\text{O}_{18}]$ and $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl}]_2(\mu\text{-CO}_3\text{H})(\mu\text{-Cl})(\mu\text{-O})$ could be obtained in addition to $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ and $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$.[9] We also found that scaling the oxidation of $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(CO)}_2]_2$ by O_2 beyond milligram quantities increased the complexity of the mixture of products, which also varied with the solvent used in the oxidation. Faller and Ma apparently attempted oxidation of $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(CO)}_2]_2$ with peroxides, but in acetone solution, which did not give a unique product.[8] It is of interest that the most efficient preparation of $(\eta\text{-C}_5\text{Me}_5)\text{Re(O)}_3$ is via oxidation of $(\eta\text{-C}_5\text{Me}_5)\text{Re(CO)}_3$ with acidic H_2O_2 in benzene.[21]

The complex $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ decomposed easily in our hands, giving a blue material. The decomposition was thermal but was accelerated by light and inhibited by dry O_2. It appeared that a radical reaction involving loss of $\eta\text{-C}_5\text{Me}_5$ and/or Cl resulted in the formation of an intractable "molybdenum blue".[22] Hydrolysis of $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ was also facile (see below). Thus, $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ is unstable under normal conditions and must be used immediately in further reactions.

The ultimate objective of the research is the preparation of (cyclopentadienyl)molybdenum oxides by reductive aggregation of $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_m\text{O}_n$ complexes. The number of electrons which can be introduced by a metallic reducing agent such as sodium is a direct function of the number of Cl ligands in the starting material. Thus, we wished to increase the number of chloride ligands or reduce the molybdenum oxidation state, while retaining the chloride ligand, of $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$. Faller and Ma showed that $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_3\text{(O)}$ was readily obtained from $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ on treatment with dry HCl.[23] However, this Mo(VI) complex proved to be no more stable than $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$, and the advantage of the larger number of chloride ligands was thereby lost. We therefore turned to reduction by deoxygenation and found that quantitative removal of oxygen from $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ could be achieved with $P(OMe)_3$ (eq 1). Treatment of

$$2(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2 + \text{P(OMe)}_3 \rightarrow [(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O}) + \text{OP(OMe)}_3 \quad (1)$$

$[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$ with Me_3SiCl produced $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_2\text{(O)}$, again essentially quantitatively (eq 2). The

$$[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O}) + 2\text{Me}_3\text{SiCl} \rightarrow 2(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_2\text{(O)} + (\text{Me}_3\text{Si})_2(\mu\text{-O}) \quad (2)$$

molybdenum(V) complexes $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$ and $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_2\text{(O)}$ are stable indefinitely at room temperature in the absence of dioxygen and water in the solid state. They are therefore excellent starting materials.

The dinuclear molybdenum(V) complex $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}(\mu\text{-O})]_2$ was obtained in high yield by hydrolysis of $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$ in the presence of Et_3N (eq 3). The product was very soluble in THF, and thus the

$$[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O}) + \text{H}_2\text{O} + 2\text{Et}_3\text{N} \rightarrow [(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}(\mu\text{-O})]_2 + 2\text{Et}_3\text{NHCl} \quad (3)$$

yield of recrystallized material is relatively low (51%). However, the crude product (yield 83%) is sufficiently pure that it can be used directly as a starting material.

Although the molybdenum(VI) complex $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$ would not be a useful starting material for reductive aggregation, a convenient synthesis of this compound would complete the series. We attempted to hydrolyze $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ in toluene containing Et_3N, a procedure which was successful for $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$ (eq 3). However, a complicated mixture of products was obtained, with $(\text{C}_5\text{Me}_5)_2$ as a prominent constituent. Hydrolysis of $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ under a variety of other conditions always gave a mixture. The instability of $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ to light and heat probably plays a role in the decomposition on hydrolysis. Faller and Ma obtained $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$ in 69% yield by first oxidizing $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(CO)}_2]_2$ with O_2 in $CHCl_3$ and then hydrolyzing the resultant mixture in wet acetone.[8] The oxidation product which hydrolyzed was presumed to be $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$, but our results suggest that this cannot be the case. Oxidation of $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(CO)}_2]_2$ with O_2 in benzene gave $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$ in 55% yield.[8] This preparation represents the most convenient and reproducible synthesis of $[(\eta\text{-C}_5\text{Me}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$.

The various reactions are summarized in Scheme 1.

Structure of $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$. Umakoshi and Isobe reported four absorption bands in the ν(Mo=O) region for $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$ (959, 933, 910, and 879 cm^{-1}).[19] We found only one such band at 930 cm^{-1} (spectrum of the KBr pellet). Because of the discrepancy, a complete structural determination was performed on the crystals of $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$ obtained as described in the Experimental Section, even though the crystal data were very similar to those given by Umakoshi and Isobe[19] for *anti*-$[(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}]_2(\mu\text{-O})$. Although the determination was more accurate than that described previously,[19] the final metrical parameters were not significantly different. There was no evidence of positional disorder between the O and Cl atoms, as is sometimes

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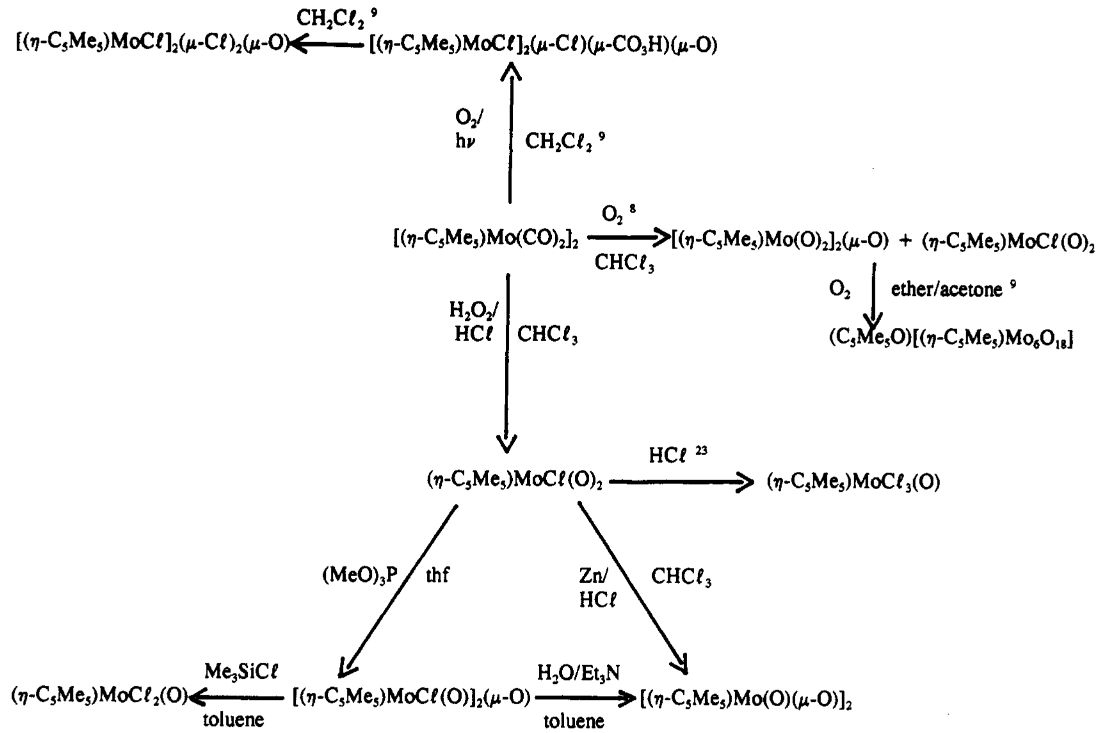
Scheme 1



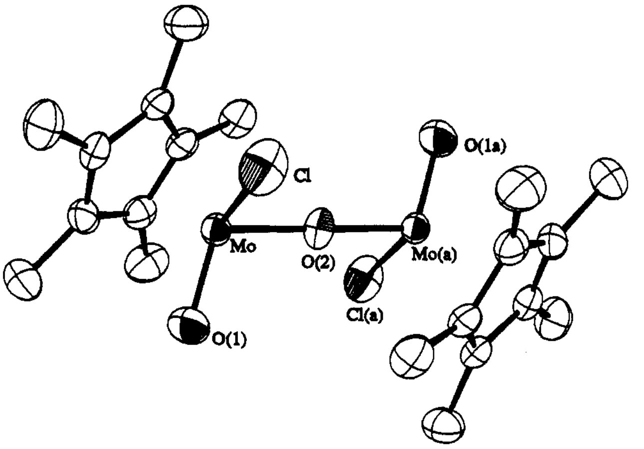


Figure 2. Structure of *anti*-$[(\eta\text{-}C_5Me_5)MoCl(O)]_2(\mu\text{-}O)$.

observed in compounds of this type.[24] The structure is shown in Figure 2. We conclude that the bulk material obtained by Umakoshi and Isobe was a mixture of isomers, one of which crystallized. The single band in the infrared spectrum of the bulk material described in the present work showed that only one isomer of $[(\eta\text{-}C_5Me_5)MoCl(O)]_2(\mu\text{-}O)$, with the *anti* arrangement of C_5Me_5, Cl, and O ligands shown in Figure 2, had been obtained.

Structure of $(\eta\text{-}C_5Me_5)MoCl_2(O)$. The molecular structure of $(\eta\text{-}C_5Me_5)MoCl_2(O)$ is shown in Figure 1 and a list of important distances and angles in Table 2. The complex has the familiar distorted-piano-stool geometry found previously for $(\eta\text{-}C_5Me_5)VCl_2(O)$[25] and $(\eta\text{-}C_5Me_5)ReCl_2(O)$,[26] with the strong *trans* influence of the terminal oxygen atom manifested in the unequal Mo–C distances to the $\eta\text{-}C_5Me_5$ ring. There was no disorder in the crystal, unlike the situation with $(\eta\text{-}C_5H_5)MoCl_2(O)$.[12] We have previously ascribed the variation in the X–M–X angle with the number of d electrons (d^0, ~105°; d^1, ~95°; d^2 ~85°) to the effect of M–X π-bonding in $(\eta\text{-}C_5R_5)MX_2(O)$ compounds.[12] The argument still holds, since the Cl–Mo–Cl angle in $(\eta\text{-}C_5Me_5)MoCl_2(O)$ (93.07(3)°) is identical with that in $(\eta\text{-}C_5H_5)MoCl_2(O)$ (93.4(1)°). We also note that the Br–Cr–Br angle in $(\eta\text{-}C_5Me_5)CrBr_2(O)$ (96.4(2)°[27]) and the Me–Cr–Me angle in $(\eta\text{-}C_5Me_5)CrMe_2(O)$ (90.0(2)°[28]) fall in the expected range for d^1 complexes. Bursten and Cayton have pointed out the relationship between $(\eta\text{-}C_5R_5)MX_2(O)$ and $(\eta\text{-}C_5R_5)MX_2(NO)$ complexes.[29] A d^0 oxo complex is electronically equivalent to a d^4 nitrosyl, and in agreement with this the R–W–R angle in $(\eta\text{-}C_5H_5)WR_2(NO)$ (R = CH_2SiMe_3) is 109.6(4)°.[30]

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Supplementary Material Available: Tables of hydrogen atom positions, anisotropic thermal parameters, and distances and angles for $(\eta\text{-}C_5Me_5)MoCl_2(O)$ (5 pages). Ordering information is given on any current masthead page.

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