Journal of Organometallic Chemistry, 340 (1988) 59–69
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

High oxidation state organometallics. Pentamethylcyclopentadienyloxo-molybdenum(VI) and -tungsten(VI) complexes

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(Received May 29th, 1987)

Abstract

The preparation, isolation, and characterization of $[(\eta^5\text{-}C_5Me_5)MoO_2]_2O$ (**1**) and $(\eta^5\text{-}C_5Me_5)MoO_2Cl$ (**2**) and their tungsten analogues (**1′** and **2′**) are described. A substantial improvement in stability, ease of preparation, and ease of separation from other reaction products are observed for these Cp* complexes compared to their cyclopentadienyl counterparts. The binuclear pentaoxo compound, **1**, crystallizes in the monoclinic space group $P2_1/c$ with one and a half molecules in the asymmetric unit, $Z = 6$, a 21.265(7), b 9.237(3), c 17.669(5) Å, β 101.78(3)°, and V 3398(4) Å^3. Anisotropic refinement of the molybdenum and isotropic refinement of the non-metal atoms with no hydrogen atoms included converged to the residuals $R_1 = 0.075$, $R_2 = 0.088$. Two independent μ-oxo complexes are represented in the cell: one is centrosymmetric having the bridging oxygen on a special position: and the other nearly centrosymmetric having a Mo–O–Mo angle of 177.9(5)°. Grignard addition to **2′** yields the air-stable alkyl, $(\eta^5\text{-}C_5Me_5)WO_2CH_2SiMe_3$.

Early studies of the hydrolysis of $(\eta^5\text{-}C_5H_5)MoBr_4$ provided a route to oxo-metal derivatives in which the cyclopentadienyl group was retained [1]. Variable quantities of different monomeric or dimeric complexes and/or mixtures were isolated depending upon the conditions. Evidently the anticipated problems with separation of mixtures and low solubility of some of the complexes discouraged other researchers from further investigation of the potentially fruitful area of cyclopentadienyloxometal complexes. However, recent developments in the preparation and characterization of diverse organometallic oxo complexes, such as $(\eta^5\text{-}C_5R_5)ReO_3$ for (R = Me or H) [2,3], $(\eta^5\text{-}C_5H_5)ReOMe_2$ [2b], $ReOI(MeCCMe)_2$ [4], $(\eta^5\text{-}C_5H_5)WO(C_2H_2)Me$ [5], $(\eta^5\text{-}C_5H_5)WO_2(CH_2SiMe_3)$ [6], $WO(C_2R_2)(S_2CNR_2)_2$ [7], R_2(2,2′-bipyridyl)-MoO_2 [8], $WOCl_2(CH_2{=}CH_2)(PMePh_2)$ [9], $(\eta^5\text{-}C_5H_5)VOCl_2$ [10], $MeReO_3$, Me_2ReO_3, $Re_2O_2(\mu\text{-}O)_2(CH_2CMePh_2)$ [11] are but the beginning stages in what promises to be the evolution of an extensive organometallic chemistry of higher oxidation state complexes. Owing to the high formal charge on the metal in oxo complexes, one might have previously anticipated a lack of stability in these high

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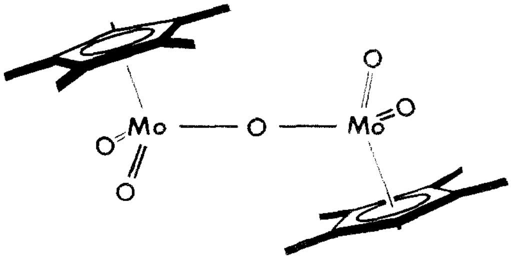
oxidation state organometallics. Nevertheless, the π-bonding of the oxo group, as well as the donor properties of $\eta^5\text{-}C_5H_5$, sufficiently decrease the charge on the metal such that even olefin [9] and acetylene [5] complexes are stable. We, as well as others [3], have found that the introduction of $\eta^5\text{-}C_5Me_5$ in place of the less electron-rich $\eta^5\text{-}C_5H_5$ group produces high oxidation state compounds which are even more tractable. Oxidations of nitrosyl complexes [6,12], such as $(\eta^5\text{-}C_5Me_5)M(CO)_2(NO)$, where M = Cr or Mo, have provided a new entry into the oxo-metal complexes and have recently yielded $[(\eta^5\text{-}C_5Me_5)CrO_2]_2$ and $[(\eta^5\text{-}C_5Me_5)MoO_2]_2O$ (**1**) [12]. Indeed, we have found that oxidation of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ and $[(\eta^5\text{-}C_5Me_5)W(CO)_2]_2$ gives products, the stabilities, solubility, and purification of which are substantially improved compared to their cyclopentadienyl analogues. The oxidation of multiply-bonded dimers provides straightforward alternative syntheses of $(\eta^5\text{-}C_5Me_5)MoO_2$ compounds and also provides a route to the tungsten analogues, which apparently are unavailable through the oxidation of $(\eta^5\text{-}C_5Me_5)W(CO)_2(NO)$ [12].

μ-Oxo complexes

Although oxidation in a hydrocarbon solvent might be expected to provide the best route, we have found that the yellow crystalline pentaoxo dimer $[(\eta^5\text{-}C_5Me_5)MoO_2]_2O$ (**1**) can be readily prepared in higher yields by exposing a chloroform solution of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ to air. There is concomitant formation of $(\eta^5\text{-}C_5Me_5)MoO_2Cl$ (**2**) in this reaction, which represents an impurity of about 15–20% of the crude product. This contaminant, however, can be converted to **1** by stirring the crude product in acetone/water solution. Thus, a pure sample of **1** can readily be obtained in nearly 70% yield.

The IR of **1** showed terminal M=O stretching bands at 912 and 882 cm^{-1} and a bridging M–O–M band at 771 cm^{-1}, as expected for a formulation of $[(\eta^5\text{-}C_5Me_5)MoO_2]_2O$. Although we found that mass spectral measurements indicated the isotopic pattern characteristic of two molybdenum atoms and appropriate for $(\eta^5\text{-}C_5Me_5)_2Mo_2O_5^+$ as the very weak parent ion, a large peak attributable to $(\eta^5\text{-}C_5Me_5)_2Mo_2O_4^+$ was observed. The ready loss of one oxygen atom was unexpected and suggested, perhaps, that we may have overlooked a different structure consistent with the IR. In order to firmly establish the identity of the product, a single-crystal X-ray determination was undertaken and it showed that **1** was correctly formulated as a pentaoxo dimer with a single oxygen bridge. This result contrasts with the unpublished observations of Herrmann and coworkers [2d], which were briefly mentioned in a review after our work had been completed. In their hands, the air oxidation reportedly gives $(\eta^5\text{-}C_5Me_5)_2Mo_2O_4$. The tetraoxo compound can be obtained readily for the cyclopentadienyl [1] and trispyrazolylborate analogs [13]. We did not observe the tetraoxo compound in our procedure.



The unit cell contains six molecules: two of which are centrosymmetric with Mo–O–Mo angles of 180°; and four of which are approximately centrosymmetric with Mo–O–Mo angles of 177.9(5)°. The linearity of the Mo–O–Mo bond might at first appear surprising. Indeed, the brief communication describing the preparation of **1** by oxidation of $(\eta^5\text{-}C_5Me_5)Mo(CO)_2(NO)$ implied that the bond would be bent [12]. Anticipating whether the Mo–O–Mo bond should be straight or bent and rationalizing the factors controlling the angle are not straightforward.

Colinear bonds at an oxygen atom are well-known, having been first observed in 1935 for the pyrophosphate anion [14]. Colinear M–O–M bonds have been found in a number of $[(Cl_5M)_2O]^{4-}$ binuclear metal ions [15], as well as in $[(neopentyl)]_3$-$WO]_2O$ [16]. Recently, the crystal structure of the trispyrazolylborate complex, $[(HBpz_3)Mo(O)Cl]_2O$, firmly established precedent for the colinear M–O–M bond in a Mo^V analogue of **1** [13]. Force constant, ^{17}O NMR shift, and bond shortening correlations have been used to indicate the high π-bond character in Mo–O bonds [17,18]. In $[CpTiCl_2]_2O$ [19], for example, the effect of π-bonding has also been used to account for the linearity of the Ti–O–Ti bonds and the 0.14 Å shortening of the Ti–O bond relative to the sum of covalent radii. The relatively short bridging Mo–O bonds (< 1.90 Å) observed in **1** would also suggest that π-effects are dominant.

There are, however, times when steric arguments are of considerable merit [20,21]. For example, comparison of $[Ph_3Si]_2O$ and $[H_3Si]_2O$, which have bond angles at oxygen of 180 and 144° respectively [22], leads to the conclusion that steric repulsion accounts for the linearity. Thus, one might argue that non-bonded interactions might significantly influence the angle between the octahedral fragments in the $[(Cl_5M)_2O]^{4-}$ ions. In $[\eta^5\text{-}C_5R_5MX_2]_2O$ systems, for which the μ-O–M–X angles are substantially greater than 90° (i.e. averaging 106.7°), significantly less steric constraint should be involved. In $[CpTiCl_2]_2O$ with a O–Ti–Cl angle of $104 \pm 2°$ the linear Ti–O–Ti bridge bond was attributed to π-bonding after the possible consequences of steric interactions were considered [19].

A linear, centrosymmetric arrangement in a $\{(MoO_2)_2O\}^{2+}$ unit similar to that in **1** has been previously observed in the $\{[MoO_2(C_2O_4)(H_2O)]_2O\}^{2-}$ ion [23]. In this pseudooctahedral Mo system the μ-O–M–O angles involving the water and one of the oxalate oxygen atoms are less than 90°, suggesting the possibility of increased steric interactions between dimer halves relative to **1**. Nevertheless, the μ-O–Mo bond distance is 1.876(2) Å compared to 1.864(1) Å for the most accurately determined bond distance in **1**. This μ-O–Mo bond length is also comparable to the 1.861(1) Å distance found in the diamagnetic Mo^V complex, *meso*-$[(HBpz_3)Mo(O)Cl]_2O$ [13]. For **1** the closest intramolecular contact between a methyl carbon and a terminal oxygen in one-half of a dimer is 2.96 Å (see Fig. 1), whereas the closest contact between the halves is 3.36 Å. This suggests further that steric effects are minimal and that the π-effects are largely determining the straightening of the Mo–O–Mo bridge bond angle in **1**.

The IR spectrum of **1** in CS_2 shows three characteristic bands at 912, 882, and 771 cm^{-1} corresponding to the two Mo=O stretching modes and the antisymmetric Mo–O–Mo stretching mode. This contrasts with the bands at 960, 920, and 860 cm^{-1} for the oxalate complex anion [23] and the 930, 898, and 850 cm^{-1} bands for the $\eta^5\text{-}C_5H_5$ analogue of **1** [1]. The substantially lower Mo–O stretching frequencies in **1**, however, would not be reflected in crystallographically significant lengthening

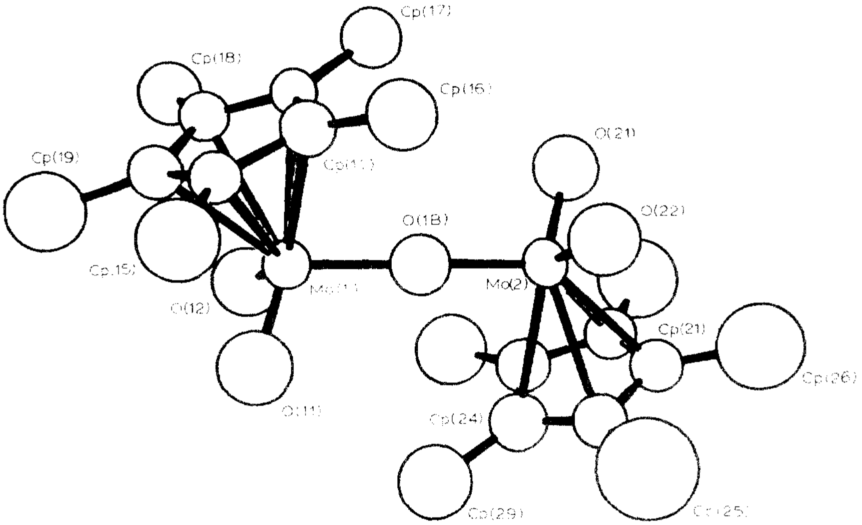


Fig. 1. An ORTEP diagram for **1** showing 50% probability ellipsoids for Mo and 50% spheres for the other atoms.

of the bonds as one might expect based on force constant–bond length correlations [17,18]. In fact, the terminal Mo=O distances for **1** are within experimental error (average 1.67 Å) of those for the $\{(MoO_2(C_2O_4)(H_2O))_2O\}^{2-}$ ion, which were reported as 1.69(2) Å [23]. The short bond lengths of terminal M=O bonds have been suggested to increase O–O repulsion and result in O–M–O angles larger than 90° in octahedral complexes [23]. For example, O_t–Mo–O_t angles of 106.51 ± 1.03° were found in the oxalate complex [23]. Smaller angles of 102.7(6), 100.6(6) and 99.2(7)°, however, were found for the independent angles in **1**.

The tungsten analogue, **1′**, which can be prepared in low yield by oxidation of the unsaturated carbonyl dimer, is isomorphous with **1**. It has metal–oxygen stretching frequencies of 942, 896, and 820 cm^{-1}, all of which are higher than those in **1**, as expected on the basis of the stronger bonding anticipated for tungsten [17].

(η^5-C_5Me_5)MO_2X complexes

Besides forming as a by-product of the oxidation of $[\eta^5\text{-}C_5Me_5Mo(CO)_2]_2$, the chloride, **2**, can be obtained by treatment of **1** with PCl_5 in CS_2. The orange-yellow crystals of the pure complex are readily soluble in CS_2 and the solution exhibits terminal Mo=O stretching bands in the IR at 919 and 888 cm^{-1}. A single crystal X-ray determination has showed that it has the expected monomeric piano stool structure, but disorder between an oxygen and the chloride prevented us from obtaining accurate structural data. Disorder between oxygen and chloride in this type of complex occurs frequently and has also been observed in a Mo^V analogue, $(HBpz_3)MoOCl_2$ [13]. The chloride is a thermally stable compound which can be handled readily even in dry air. The bromide, however, is thermally unstable and decomposes rapidly. The analogous tungsten complexes are more stable and $(\eta^5\text{-}C_5Me_5)WO_2Cl$ (**2′**) can be prepared directly in ~30% yield by oxidizing $[(\eta^5\text{-}C_5Me_5)W(CO)_2]_2$ in chloroform or by treating **1′** with PCl_5. The chloride can be handled much more readily than the bromide in this system as well.

Treatment of $(\eta^5\text{-}C_5Me_5)MoO_2Cl$ (**2**) with Me_3SiCH_2MgCl did not yield a stable product; however, $(\eta^5\text{-}C_5Me_5)WO_2CH_2SiMe_3$ (**3′**) can be prepared by this route from the tungsten analogue **2′**. The relatively low yields in the preparation of $(\eta^5\text{-}C_5Me_5)WO_2Cl$ starting material do not presently make this procedure a more attractive route compared to that of Legzdins [6], but the high yield conversions of **2** may prove useful for other alkyloxo complexes [24]. For the moment, oxidation of complexes with the preformed metal alkyl bond appears to be a superior method [6]. The two terminal W=O stretching bands and the relatively large coupling (10.3 Hz in **3′**) of the α-protons to ^{183}W are characteristic of this $(\eta^5\text{-}C_5Me_5)WO_2$(alkyl)system. This J(W–H) is substantially larger than that observed in hexamethyltungsten (3.0 Hz) [25] or $(\eta^5\text{-}C_5Me_5)WMe_3O$ (6.0 Hz) [24].

The coupling of ^{29}Si to the α-protons is not significantly different from that to the methyl groups and furthermore the couplings to ^{183}W and ^{29}Si are not temperature dependent. Consequently, a major bonding interaction of an α-hydrogen with the tungsten, as in a methylene-hydride or a strongly agostic system, is not indicated. The W–C–Si bond angle is opened to 115.8° [6], however, which suggests a smaller W–C–H angle and a different hybridization at carbon. Comparisons with other alkyls will be necessary to rationalize the coupling constants and correlate them with bonding and structural considerations.

In contrast to the cyclopentadienyl complexes, which require meticulous care in the hydrolysis of halides to yield the pure analogues of **1** and **2** [1], the $\eta^5\text{-}C_5Me_5$ complexes are simply prepared and a single isomer is readily obtained. Several isomers with varying numbers of oxo groups were the typical products of the unsubstituted cyclopentadienyl preparations. Furthermore, the $\eta^5\text{-}C_5Me_5$ products are quite soluble in organic solvents and easily handled. The use of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ as a starting material provides a convenient entryway into $(\eta^5\text{-}C_5Me_5)Mo^{VI}$ chemistry, and further investigations of the reactivity and stability of this kind of complex are in progress.

Experimental

Reagent grade solvents were used as supplied by the manufacturers. Pentamethylcyclopentadiene was purchased from Aldrich. The dimers, $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ and $[(\eta^5\text{-}C_5Me_5)W(CO)_2]_2$, were prepared according to the method of King et al. [26], with the exception that an increased yield was obtained when ethylcyclohexane was used as solvent for the molybdenum complex.

Proton NMR spectra were recorded at 250 MHz with a Bruker spectrometer and are reported as ppm downfield from tetramethylsilane using the solvent resonance for calibration. Infrared spectra were obtained with a Nicolet 5SX FTIR spectrometer. Mass spectra were obtained with a Kratos MS-80 RFA mass spectrometer.

Syntheses

$[(\eta^5\text{-}C_5Me_5)MoO_2]_2O$ (1)

The $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ dimer (150 mg, 0.261 mmol) was dissolved in 50 ml chloroform and stirred for 2 d while exposed to air. The solvent was removed from the resulting yellow solution, and the residue was taken up in 50 ml of wet acetone. This solution was allowed to stir in air for 1 h in order to allow conversion of the

$(\eta^5\text{-}C_5Me_5)MoO_2Cl$ impurity to **1**. After removal of the solvent, the residue was extracted with 75 ml of Et_2O in three portions. The removal of the ether gave a crude product, which was recrystallized from ether/acetone to yield 99 mg of yellow crystalline **1** (69%). $[(\eta^5\text{-}C_5Me_5)MoO_2]_2O$: m.p. ~ 215 °C (dec): ^1H NMR ($CDCl_3$, 25 °C) δ 2.01 (C_5Me_5); IR (CS_2, M=O, M=O, M–O–M) 912s, 882s, 771br cm^{-1}; MS-EI (20 eV), m/z for $[C_{10}H_{15}{}^{98}MoO_2]_2O = 546$; MS-DCI, m/z $\{[C_{10}H_{15}{}^{98}MoO_2]_2O\}H = 547$. Analysis. Found: C, 44.21; H, 5.60. $Mo_2O_5C_{20}H_{30}$ calc: C, 44.29; H, 5.58%. The structure was established by a single crystal X-ray determination.

An analogous preparation involving oxidation of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ in benzene gave only a 55% yield of **1**.

$[(\eta^5\text{-}C_5Me_5)WO_2]_2O$ (*1′*)

The $[(\eta^5\text{-}C_5Me_5)W(CO)_2]_2$ dimer (500 mg, 0.667 mmol) was dissolved in 100 ml of benzene and exposed to air for 18 h with stirring. The solvent was removed from the resulting yellow solution and the yellow residue extracted with 150 ml Et_2O in three portions. The combined extracts were evaporated to yield a pale yellow residue which was washed with 3 ml Et_2O. Recrystallization from acetone gave 66 mg (14%) of pale yellow crystals of **1′**. ^1H NMR ($CDCl_3$, 25 °C) δ 2.16 (C_5Me_5); IR (CS_2, W=O, W=O, W–O–W) 942s, 896s, 820br and 799sh cm^{-1}. Determination of the unit cell by X-ray diffraction showed that it was isomorphous with the molybdenum analog **1** and therefore has effectively the analogous composition and structure. Cell parameters (23 °C): *a* 21.203(11), *b* 9.213(6), *c* 17.678(10) Å, β 101.76(4)°. Analysis. Found: C, 33.19; H, 4.17. $W_2O_5C_{20}H_{30}$ calc: C, 33.45; H, 4.21%.

Attempts to improve the yield of 1′

Oxidation of $[(\eta^5\text{-}C_5Me_5)W(CO)_2]_2$ in chloroform produces predominantly the chloride, **2′**, which can be hydrolyzed to yield **1′** in overall yield of ~ 27% from the dimer.

Low yields of **1′** are produced by oxidation in benzene owing to the formation of a substantial amount of another product which remains in the yellow residue after the extraction with ether. This other product has not been identified; however, it has a low carbon content [C, 15.88; H, 2.04%]. Attempts to prepare **1′** via peroxide oxidations led to the observation that the compound(s) in this residue catalyzes the production of ketone peroxides. ***Caution***! Solutions of any $(\eta^5\text{-}C_5Me_5)W$ derivatives containing hydrogen peroxide and ketones may form cyclic peroxides; e.g. acetone yields $(Me_2CO_2)_3$ and cyclopentanone yields $(C_5H_8O_2)_2$. Although these colorless crystals of peroxides are fairly stable, the potential of detonation demands caution.

$(\eta^5\text{-}C_5Me_5)MoO_2Cl$ (*2*)

A solution of 627 mg (1.16 mmol) of **1** in 50 ml CS_2 was treated with 250 mg (1.20 mmol) PCl_5 under an atmosphere of dry nitrogen. After stirring for 2 h, a dark orange supernatant was decanted and evaporated to yield a residue, which was extracted with 75 ml Et_2O in three portions. Evaporation and recrystallization from Et_2O yielded 540 mg (80%) of air-stable yellow-orange crystalline **2**. ^1H NMR ($CDCl_3$, 25 °C) δ 2.09 (C_5Me_5); IR (CS_2, Mo=O, Mo=O) 919s, 888s cm^{-1}; MS-EI (20 eV), m/z for $C_{10}H_{15}{}^{98}MoO_2{}^{35}Cl = 300$. A single crystal X-ray determination established the structure, although accurate determination of structural parameters was prevented by disorder. X-Ray: space group $P\bar{1}$, a 6.166(1), b 8.577(2), c 11.296(2) Å, α 85.65(1), β 87.55(2), γ 88.40(2)°, V 595.0(3) Å^3, ρ_{obs} 1.66, ρ_{calc} 1.667 g/cm^3 ($Z = 2$), $R_1 = 0.077$. Analysis. Found: C, 40.14; H, 5.07. $MoClO_2C_{10}H_{15}$ calc: C, 40.22; H, 5.06%.

The attempted preparation and isolation of (η^5-C_5Me_5)MoO_2Br

A solution of **1** in CS_2 was treated with equimolar Br_2 in CS_2 (1 *M*). The reaction mixture was stirred for 1.5 h under dry nitrogen to yield a reddish-brown precipitate and a yellow-orange solution. The air-sensitive precipitate was not identified. The IR of the solution showed two strong M=O stretching bands at 918 and 887 cm^{-1}. A ^{1}H resonance was observed at δ 2.12 in $CDCl_3$. Although this complex can be obtained as red-orange crystals upon evaporation of the solvent, the complex is extremely air-sensitive and thermally unstable. We presume it was (η^5-C_5Me_5)MoO_2Br, but were unable to obtain elemental analyses.

Treatment of **1** with PBr_5 also yielded a yellow-orange solution showing the same spectral features, but this route did not give a more stable product.

(η^5-C_5Me_5)WO_2Cl (2′)

Method 1. A solution of 30 mg (0.042 mmol) of **1′** in 50 ml CS_2 was treated with PCl_5 (9 mg, 0.043 mmol) under an atmosphere of dry nitrogen for 2 h. The pale yellow solution was evaporated to yield a residue which was extracted with 50 ml Et_2O in three portions. Evaporation and recrystallization from Et_2O yielded 32 mg (99%) of air-stable pale yellow crystals of **2′** melting at 172° C. ^{1}H NMR ($CDCl_3$, 25° C) δ 2.23 (C_5Me_5); IR (CS_2, 2 W=O) 905s, 945s cm^{-1}. Analysis. Found: C, 31.16; H, 3.96. $WClO_2C_{10}H_{15}$ calc: C, 31.07; H, 3.91%.

Method 2. A solution of 1.54 g (0.21 mmol) of [(η^5-C_5Me_5)$W(CO)_2]_2$ in 120 ml chloroform was heated under reflux under an atmosphere of oxygen for 24 h. The brown solution was evaporated to yield a brown oily residue which was extracted with 250 ml Et_2O in five portions. Evaporation of the combined extracts and recrystallization of the residue gave 432 mg (27%) of **2′**.

Attempted preparation and isolation of (η^5-C_5Me_5)WO_2Br

A solution of 19 mg (0.026 mmol) of **3** in 50 ml CS_2 was treated with PBr_5 (11 mg, 0.026 mmol) under an atmosphere of dry nitrogen for 2 h. The yellow solution was evaporated to yield a residue which gave an unstable yellow-orange crystalline compound presumed to be the bromo analogue of **2′**. ^{1}H NMR ($CDCl_3$, 25° C) δ 2.26 (C_5Me_5); IR (CS_2, 2 W=O) 944s, 904s cm^{-1}.

(η^5-C_5Me_5)$WO_2CH_2SiMe_3$ (3′)

A solution of 16 mg of **2′** in 10 ml Et_2O was treated with 0.1 ml of 1 *M* Me_3SiCH_2MgCl in Et_2O at 0° C. The reaction mixture was stirred and allowed to warm to room temperature over a period of 1.5 h. The reaction mixture was filtered and the solvent removed from the filtrate. Extraction of the residue with 25 ml of Et_2O in three portions, evaporation, and recrystallization from Et_2O produced 14.7 mg (80%) of an air stable white compound. ^{1}H NMR ($CDCl_3$, 25° C, 90 MHz) δ 2.07 (s, C_5Me_5, 15H), δ 0.48 (s, CH_2, 2H, $J(^{183}W\text{-}H)$ 10.3 Hz, $J(^{29}Si\text{-}H)$ 6.4 Hz), δ 0.09 (s, $SiMe_3$, 9H, $J(^{29}Si\text{-}H)$ 6.4 Hz); IR (CS_2, W=O, W=O) 903s, 943s cm^{-1}; MS-EI (20 eV), m/z for $C_5(CH_3)_5{}^{184}WO_2CH_2Si(CH_3)_3 = 438$. Analysis. Found: C, 38.44; H, 6.02. $WSiO_2C_{14}H_{26}$ calc: C, 38.37; H, 5.98%.

Crystallographic analyses

Crystals suitable for diffraction analysis were obtained from acetone/ether solutions by slow evaporation of solvent. A crystal was mounted in a thin-walled glass capillary. Diffraction measurements were carried out on an Enraf–Nonius CAD-4 fully automated four circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index and least-squares routines. Data processing was performed on a Digital PDP 11/23 computer using the Enraf–Nonius SDP program library (Version 18). Absorption corrections were not performed owing to the low absorption coefficients. Neutral atom scattering factors were calculated by standard procedures [27a]. Anomalous dispersion corrections were applied to all atoms [27b]. Full-matrix least-squares refinements minimized the function $\Sigma_{hkl} w(|F_o| - |F_c|)^2$.

Table 1

Crystallographic data for X-ray diffraction studies of $[(\eta^5\text{-}Me_5C_5)MoO_2]_2O$

(A) Crystal data	
Formula	$Mo_2O_5C_{20}H_{30}$
Temp. (±2°C)	23
Space group	$P2_1/c$, No. 14
a (Å)	21.265(7)
b (Å)	9.237(3)
c (Å)	17.669(5)
β (°)	101.78(3)
V (Å^3)	3398(4)
M	542.34
ρ_{calcd} (g/cm^3)	1.59 ($Z = 6$)
(B) Measurement of intensity data	
Radiation	Mo-K_α (0.71073 Å)
Monochromator	graphite
Reflctns measd.	$+h, +k, \pm l$
max. 2θ (°)	44
Scan type	moving crystal-stationary counter
ω-scan width (°)	$(1.00 + 0.347\tan\theta)$
Background	1/4 additional at each end of scan
ω-scan rate (variable)	
max. deg/min	10.0
min. deg/min	1.3
No. of reflctns measd.	4382 including absences
Data used $\{F^2 \geq 3\sigma(F^2)\}$	1765
(C) Treatment of data	
Abs. correctn.	not applied
Abs. coeff. (cm^{-1})	11.1
p factor	0.02
Final residuals	
R_1, R_2	0.075, 0.088
e.s.d. of unit weight	3.45
largest shift/error value on final cycle	0.30
largest peak in final difference Fourier (e/Å^3)	0.83

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

For **1**, the space group $P2_1/c$ was established by the systematic absences. The structure was solved by a combination of Patterson and difference Fourier techniques. One and one-half molecules were found in the asymmetric unit, $Z = 6$, *a* 21.275(5), *b* 9.240(2), *c* 17.658(4) Å, β 101.83(2)°, and *V* 3398(3) Å^3. Anisotropic refinement of the molybdenum and isotropic refinement of the non-metal atoms with no hydrogen atoms included in the structure factor calculation converged to

Table 2

Positional and thermal parameters for $[Cp^{\star}MoO_2]_2O$

Atom	x/a	y/b	z/c	B
Mo(1)	0.3377(1)	−0.0123(2)	0.7407(1)	4.47(5) [a]
Mo(2)	0.3300(1)	0.0258(2)	0.9491(1)	4.33(5) [a]
O(11)	0.2800(9)	−0.127(2)	0.7026(11)	8.5(6)
O(12)	0.4025(9)	−0.111(2)	0.7367(11)	8.6(6)
O(21)	0.3937(9)	0.137(2)	0.9918(11)	7.9(5)
O(22)	0.2668(8)	0.128(2)	0.9505(10)	7.7(5)
O(1B)	0.3322(7)	0.008(2)	0.8460(8)	6.1(4)
Cp(10)	0.278(1)	0.169(2)	0.655(1)	3.7(5)
Cp(11)	0.299(1)	0.237(2)	0.726(1)	4.4(6)
Cp(12)	0.368(1)	0.241(2)	0.741(1)	3.3(5)
Cp(13)	0.389(1)	0.176(3)	0.681(1)	4.0(6)
Cp(14)	0.335(1)	0.122(3)	0.631(1)	4.3(6)
Cp(15)	0.211(1)	0.134(3)	0.611(2)	8.1(9)
Cp(16)	0.254(1)	0.300(3)	0.771(2)	6.5(7)
Cp(17)	0.407(1)	0.314(3)	0.815(1)	6.1(7)
Cp(18)	0.459(1)	0.158(3)	0.676(2)	7.1(8)
Cp(19)	0.339(1)	0.044(4)	0.553(2)	9.4(9)
Cp(20)	0.276(1)	−0.186(3)	0.987(1)	4.9(6)
Cp(21)	0.307(1)	−0.119(3)	1.049(1)	4.9(6)
Cp(22)	0.373(1)	−0.137(3)	1.051(1)	5.2(6)
Cp(23)	0.379(1)	−0.211(3)	0.981(1)	5.8(7)
Cp(24)	0.312(1)	−0.240(3)	0.942(1)	6.0(7)
Cp(25)	0.205(2)	−0.176(6)	0.982(2)	15.7(16)
Cp(26)	0.284(2)	−0.049(5)	1.117(2)	13.0(13)
Cp(27)	0.434(2)	−0.090(5)	1.110(2)	13.5(13)
Cp(28)	0.436(2)	−0.252(4)	0.945(2)	10.8(11)
Cp(29)	0.287(2)	−0.322(4)	0.865(2)	9.4(10)
Mo(3)	−0.0160(1)	0.5201(3)	0.3928(1)	5.52(6) [a]
O(3B)	0.0000	0.500	0.5000	5.3(5)
O(31)	0.0276(10)	0.652(2)	0.3741(12)	9.6(6)
O(32)	−0.0886(11)	0.599(3)	0.3683(13)	11.1(7)
Cp(30)	0.038(1)	0.366(3)	0.316(1)	6.0(7)
Cp(31)	0.046(1)	0.296(3)	0.385(1)	5.4(6)
Cp(32)	−0.028(1)	0.260(2)	0.387(1)	2.9(5)
Cp(33)	−0.064(1)	0.317(3)	0.324(1)	3.8(5)
Cp(34)	−0.026(1)	0.388(3)	0.280(1)	4.7(6)
Cp(35)	0.099(2)	0.426(4)	0.294(2)	10.1(10)
Cp(36)	0.095(1)	0.247(3)	0.448(2)	7.9(9)
Cp(37)	−0.051(1)	0.175(4)	0.450(2)	8.1(9)
Cp(38)	−0.138(1)	0.301(4)	0.298(2)	8.8(9)
Cp(39)	−0.052(1)	0.465(4)	0.203(2)	8.6(9)

[a] Refinied anisotropically, B_{eq} is given.

Table 3

Selected interatomic distances (Å) for $[Cp^{*}MoO_2]_2O$

Mo(1)–Mo(2)	3.736(2)	Mo(2)–Cp(21)	2.35(1)
Mo(1)–O(11)	1.66(1)	Mo(2)–Cp(22)	2.38(1)
Mo(1)–O(12)	1.67(1)	Mo(2)–Cp(23)	2.44(2)
Mo(1)–O(1B)	1.89(1)	Mo(2)–Cp(24)	2.48(2)
Mo(1)–Cp(10)	2.43(1)	Mo(3)–Mo(3)	3.728(1)
Mo(1)–Cp(11)	2.44(1)	Mo(3)–O(3B)	1.864(1)
Mo(1)–Cp(12)	2.43(1)	Mo(3)–O(31)	1.60(1)
Mo(1)–Cp(13)	2.40(1)	Mo(3)–O(32)	1.68(1)
Mo(1)–Cp(14)	2.29(1)	Mo(3)–Cp(30)	2.42(2)
Mo(2)–O(21)	1.74(1)	Mo(3)–Cp(31)	2.48(2)
Mo(2)–O(22)	1.65(1)	Mo(3)–Cp(32)	2.42(1)
Mo(2)–O(1B)	1.84(1)	Mo(3)–Cp(33)	2.35(1)
Mo(2)–Cp(20)	2.43(2)	Mo(3)–Cp(34)	2.30(1)

the residuals $R_1 = 0.075$, $R_2 = 0.088$. It was difficult to locate a crystal of acceptable, but not high quality. The presence of more than one molecule in the asymmetric unit exacerbated the problem with the limited quantity of data and an anisotropic refinement of all atoms did not appear to be justified. As it was difficult to locate any hydrogen atoms on some of the methyl groups and since the conformation of the methyl groups cannot be idealized without one reference H atom, hydrogen atoms were not included in the structure factor calculations. Two independent μ-oxo complexes are represented in the cell: one is centrosymmetric having the bridging oxygen on a special position; and the other is nearly centrosymmetric having a Mo–O–Mo angle of 177.9(5)°. The data collection parameters, coordinates, interatomic distances and angles are given in Tables 1 through 4. Tables of anisotropic thermal parameters, structure factor amplitudes, and non-essential bond distance and angle parameters are available from the authors (J.W.F.).

The chloride, **2**, crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, a 6.166(1), b 8.577(2), c 11.296(2) Å, α 85.65(1), β 87.55(2), γ 88.40(2)°, V 595.0(3) Å^3. Anisotropic refinement of the molybdenum and isotropic refinement of the nonmetal atoms with no hydrogen atoms included converged to the residual $R_1 = 0.077$, $R_2 = 0.090$. A ~ 3/2 population of two conformations of the MoO_2Cl differing by ~ 21° was required to account for the electron density distribution. As the disorder would have prevented a reliable determination of bond lengths and only a qualitative verification of the structure was desired, the refinement was not carried further.

Table 4

Selected interatomic angles (°) for $[Cp^{*}MoO_2]_2O$

O(11)–Mo(1)–O(12)	100.6(6)	O(3B)–Mo(3)–O(31)	107.0(5)
O(11)–Mo(1)–O(1B)	105.8(5)	O(3B)–Mo(3)–O(32)	105.8(5)
O(12)–Mo(1)–O(1B)	108.3(5)	O(31)–Mo(3)–O(32)	99.2(7)
O(21)–Mo(2)–O(22)	102.7(5)	Mo(3)–O(3B)–Mo(3)′	180.0
O(21)–Mo(2)–O(1B)	107.8(5)		
O(22)–Mo(2)–O(1B)	104.6(5)		
Mo(1)–O(1B)–Mo(2)	177.9(5)		

The data collection parameters, tables of coordinates, anisotropic thermal parameters, structure factor amplitudes, bond distance and angle parameters are available from the authors (J.W.F.).

Acknowledgement

We wish to thank the National Science Foundation for support of this work.

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