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Reactions and properties of oxo and peroxo derivatives of (pentamethylcyclopentadienyl)-molybdenum and -tungsten

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Abstract

The characterization and reactivity of complexes $(\eta^5\text{-}C_5Me_5)M(=O)(\eta^2\text{-}O_2)Cl$ (M = Mo, W) and $(\eta^5\text{-}C_5Me_5)M(=O)Cl_3$ are described. In addition, the preparation and reactivity of some molybdenum-oxo alkyl complexes are discussed in this paper. The oxo-H_2O and oxo-peroxo exchange behavior of these systems was studied with infrared spectroscopy using ^{18}O isotope labeling techniques.

Introduction

The descriptions of a number of cyclopentadienylmolybdenum-oxo complexes by Green et al. [1] and the more recent developments in pentamethylcyclopentadienylrhenium-oxo chemistry by Hermann et al. [2] strongly suggest a potentially rich and diverse chemistry of molybdenum and tungsten oxo complexes containing the η^5-pentamethylcyclopentadienyl group. Although this chemistry has attracted wider attention, the number of complexes characterized in this category is still limited [3]. We have recently reported a series of pentamethylcyclopentadienylmolybdenum and -tungsten oxo and peroxo complexes (Scheme 1) [4]. We have now continued our investigation of the reactions of $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ with HCl and hydroperoxides. We report here the preparative details of $(\eta^5\text{-}C_5Me_5)M(=O)(\eta^2\text{-}O_2)Cl$ and $(\eta^5\text{-}C_5Me_5)M(=O)Cl_3$ and studies of their reactivity. We have extended the alkylation studies in Scheme 1 to provide preparations of the molybdenum-oxo alkyl complexes. Although the use of some of these molybdenum complexes as starting materials, prepared by an alternative route, was reported in a brief communication by Legzdins et al. [6], no detailed preparation is yet available in the literature. They have proven to be the very useful precursors in preparing some novel compounds [5,6], such as $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}S_2O)R$, $(\eta^5\text{-}C_5Me_5)M(=O)(=S)R$, and $(\eta^5\text{-}C_5Me_5)W(=S)_2R$, which have been reported elsewhere [5]. We

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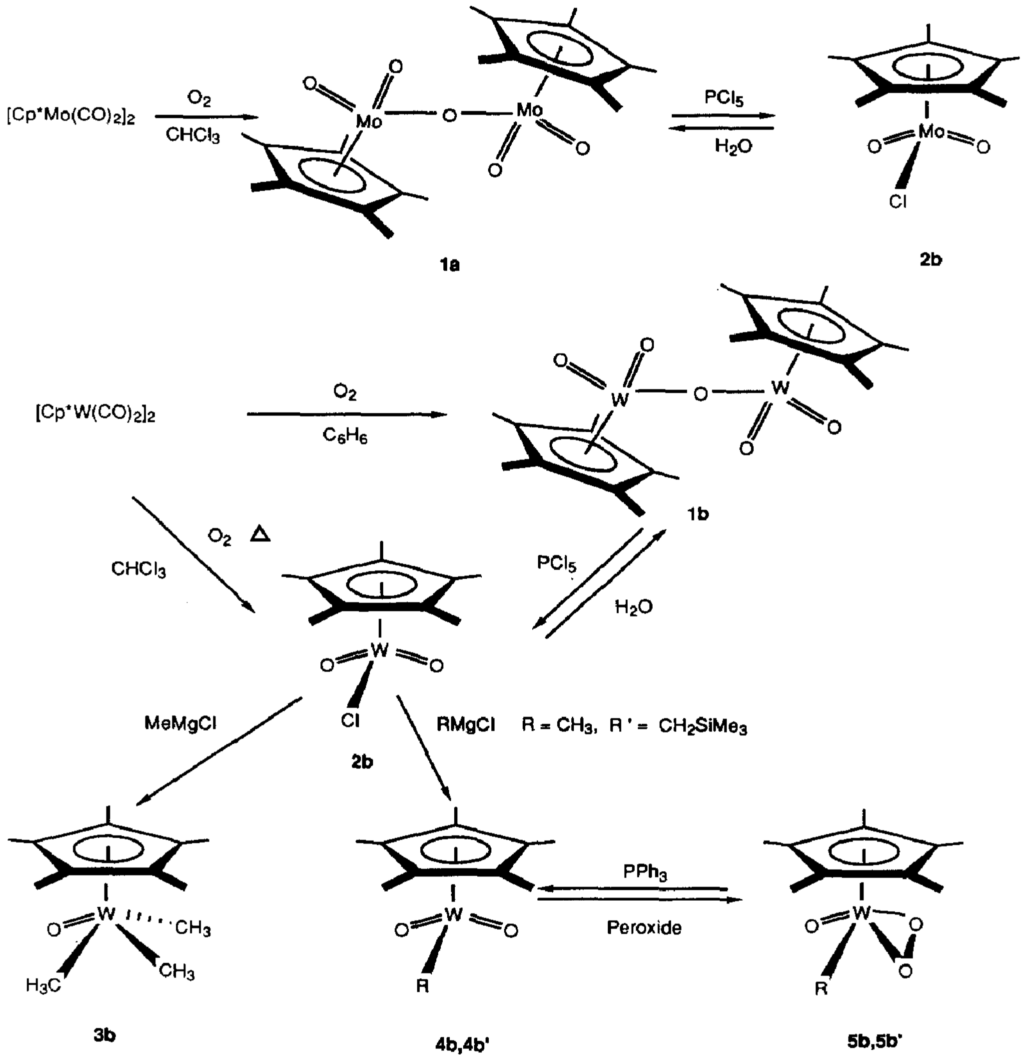


Scheme 1.

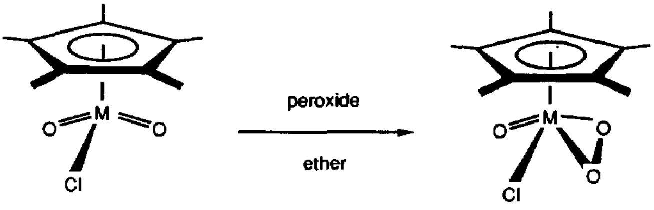
report here our studies of the reactivity of the oxo and peroxo complexes and the mechanism of peroxide formation.

Results and discussion

Reactions of $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ $(M = Mo, W)$ *with hydroperoxides: Formation and reactions of* $(\eta^5\text{-}C_5Me)M(=O)(\eta^2\text{-}O_2)Cl$

Peroxidized diethyl ether, which is made by exposing fresh diethyl ether to air for approximately a week, was used as both solvent and reagent in the preparations of peroxo complexes. For small scale reactions this unconventional reagent is mild, convenient, and avoids hydrolysis of the chloride to the μ-oxo dimer. Surprisingly t-butyl hydroperoxide does not readily effect the reaction. As the chlorides do not hydrolyze instantly, one can use 30% hydrogen peroxide to prepare the peroxo derivatives, but timing is essential to minimize hydrolysis. Compounds $(\eta^5$-

$C_5Me_5)Mo(=O)_2Cl$ (**2a**) or $(\eta^5\text{-}C_5Me_5)W(=O)_2Cl$ (**2b**) were dissolved in the hydroperoxide-containing diethyl ether and simply stirred for a prolonged period of time to give light yellow $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)Cl$ (**6a**) or white $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)Cl$ (**6b**), respectively (eq. 1). Chemical analyses are consistent with these

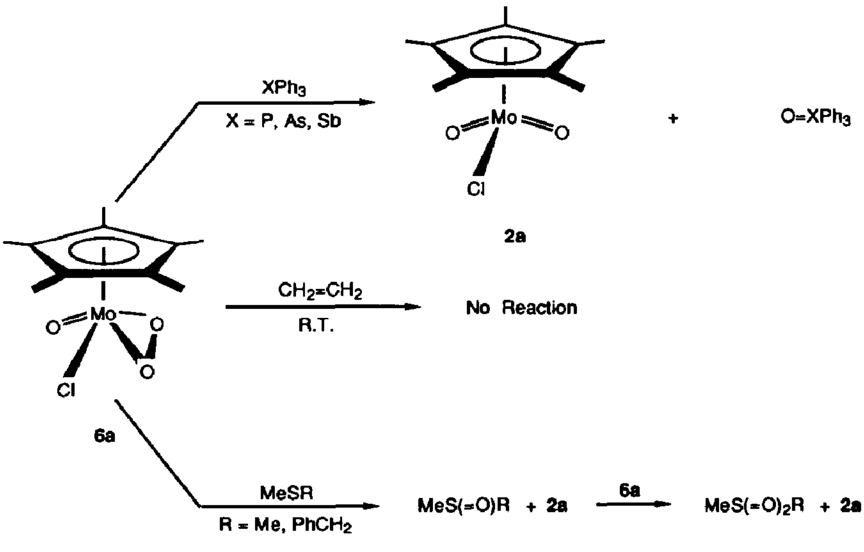


(1)

2a,b **6a,b**

formulae and the infrared spectra of both products display stretching bands typical of a $M(=O)(\eta^2\text{-}O_2)$ moiety (vide infra) [4b,7]. They presumably adopt a piano-stool structure similar to that of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)CH_2SiMe_3$, the structure of which we have determined by X-ray crystallography [4b]. In contrast to $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$, however, the reaction of $[(\eta^5\text{-}C_5Me_5)Mo(=O)_2]_2(\mu\text{-}O)$ with peroxide reagent did not give the expected bis peroxo compound. We were unable to identify the product, which appeared to be a polymeric molybdenum oxo and peroxo compound on the basis of the infrared spectrum.

The reactions of compound **6a** with various substrates were investigated as shown in Scheme 2. The reaction between compound **6a** and thioethers showed a high degree of kinetic selectivity in the formation of sulfoxides in preference to sulfones. At room temperature, a 2/1 ratio of peroxo complex to thioether in benzene-d_6 reacted completely converting the thioether to a sulfoxide within 1 h with no observable formation of any sulfone. The subsequent oxidation of sulfoxide by the remaining equivalent of peroxo complex required approximately two days for



Scheme 2.

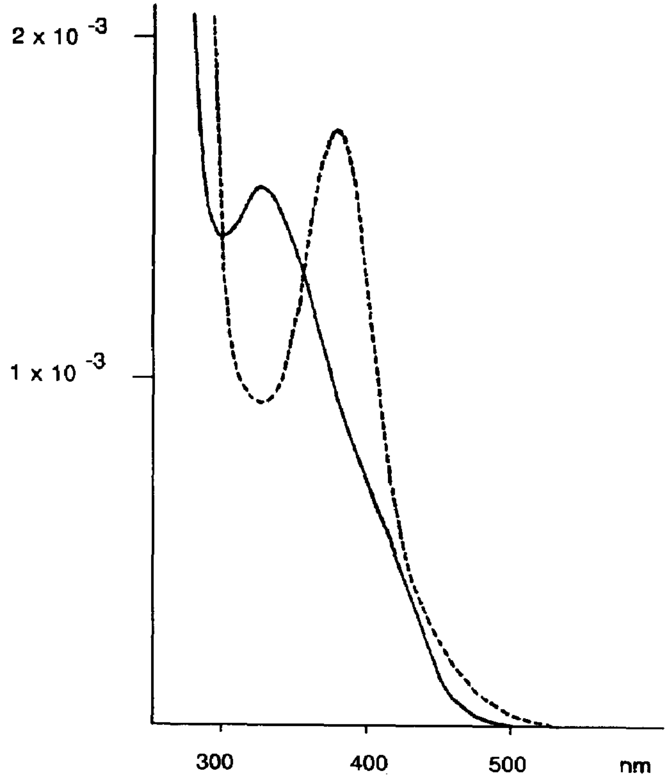


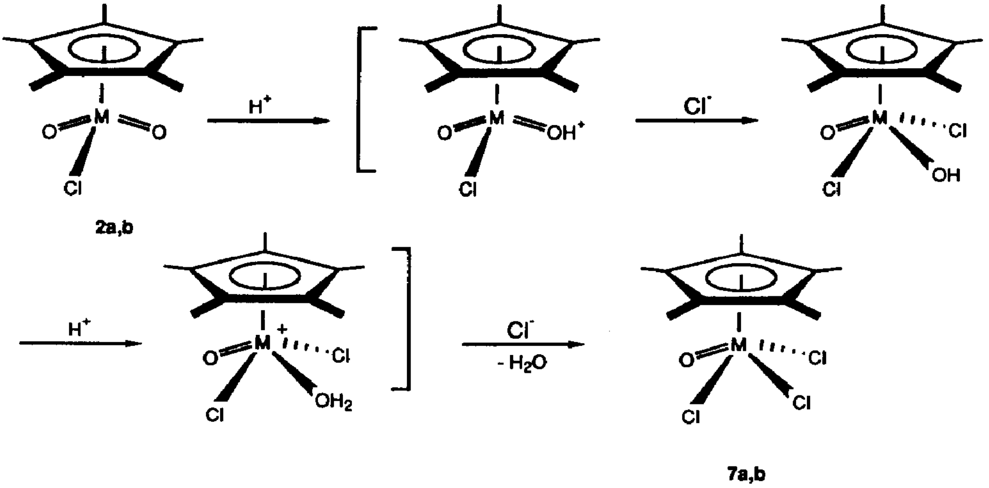
Fig. 1. The absorption spectrum of $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$ (------) and $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)Cl$ (———) in acetonitrile.

completion. Compound **6a** did not oxidize ethylene at ambient temperature. An attempt to carry out the reaction at elevated temperature only led to the thermal decomposition of the compound (**6a** begins to decompose at ~ 45 °C in benzene).

The electronic absorption spectra of $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$ and $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)Cl$ in acetonitrile (Fig. 1) show a relatively strong charge transfer band (($\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$: λ 379 nm, ϵ 1.73×10^3 cm^{-1} mol^{-1} l; $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)Cl$: λ 325 nm, ϵ 1.56×10^3 cm^{-1} mol^{-1} l), which is typical for Mo-oxo complexes and is responsible for the yellow color of both compounds. The blue-shift of the latter correlates with the stronger Mo=O bond resulting from the absence of a competing π-donating Mo=O group. This increased Mo=O strength is also suggested by the higher frequency Mo=O stretch in the IR in the peroxo compound.

Reactions of $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ (M = Mo, W) with hydrogen chloride: preparation of $(\eta^5\text{-}C_5Me_5)M(=O)Cl_3$

Diethyl ether solutions of $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ were purged with a stream of HCl to produce a red crystalline precipitate of $(\eta^5\text{-}C_5Me_5)Mo(=O)Cl_3$ (**7a**) or a yellow crystalline precipitate of $(\eta^5\text{-}C_5Me_5)W(=O)Cl_3$ (**7b**) in good yield (eq. 2). Compounds **7a** and **7b** are moderately stable as solids and can be handled in air briefly without significant decomposition. They are insoluble in less polar organic solvents such as pentane, diethyl ether and benzene, but very soluble in polar



(2)

solvents such as methylene chloride and acetone. Upon dissolution, they can be readily hydrolyzed to give very pure samples of corresponding dioxo starting materials. As a result, the above reactions can be used as either a purification step or a means of isotopic labeling in preparations of respective dioxo chloride complexes (vide infra).

Like the formation of $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ with peroxide, in which only one oxo group was replaced to yield a mono-oxo species, $(\eta^5\text{-}C_5Me_5)M(=O)(\eta^2\text{-}O_2)Cl$, the trichlorides, $(\eta^5\text{-}C_5Me_5)M(=O)Cl_3$, did not undergo further reaction with HCl. This inertness of the M=O bond in the mono-oxo species may be attributed to the increased bond order of the M=O bond [8]. This reactivity difference is analogous to the comparison of C=C and C≡C toward electrophilic addition by HCl; the vinyl cation intermediate in the alkyne reaction is substantially less stable than an ordinary alkyl cation intermediate in the alkene reaction. For the M=O complexes, the second oxo-HCl exchange presumably involves the protonated intermediate $(\eta^5\text{-}C_5Me_5)M(=OH)Cl_3^+$, which has higher M–O multiple bond character and is relatively unstable in comparison with the intermediate $(\eta^5\text{-}C_5Me_5)M(=OH)(=O)Cl^+$ in the first exchange.

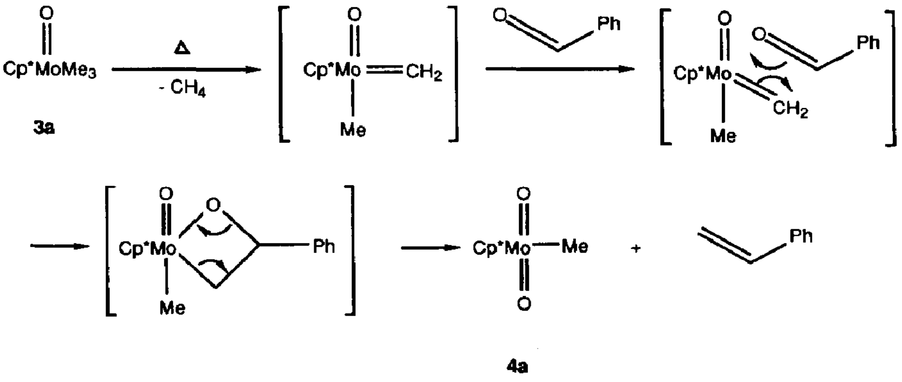
Alkylation of $(\eta^5\text{-}C_5Me_5)$Mo oxo complexes and formation of $(\eta^5\text{-}C_5Me_5)Mo(=O)Me_3$, $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Me$, and $(\eta^5\text{-}C_5Me_5)Mo(=O)_2CH_2SiMe_3$

The reactions of $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$, $(\eta^5\text{-}C_5Me_5)Mo(=O)Cl_3$ and $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)Cl$ with methylmagnesium chloride gave reasonable yields of a very pale yellow compound $(\eta^5\text{-}C_5Me_5)Mo(=O)Me_3$ (**3a**) and a small amount of the by-product $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Me$ (**4a**). However, the direct methylation of the dimer $[(\eta^5\text{-}C_5Me_5)Mo(=O)_2]_2(\mu\text{-}O)$ (**1a**) with Me_3Al appeared more advantageous, giving 50% yield of **3a**, while using more readily available **1a** as starting material. The reaction of Me_3SiCH_2MgCl with $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$ only resulted in compound $(\eta^5\text{-}C_5Me_5)Mo(=O)_2CH_2SiMe_3$ (**4a′**). Compounds **3a**, **4a** and **4a′** have been characterized by NMR, IR and microanalyses. Attempts to isolate ethyl analogues of **3a** and **4a** by employing Et_3Al and Et_2Zn in similar procedures were not successful.

Many methyl-stabilized high-oxidation-state transition metal complexes are known, and most of them also contain oxo ligands, for example $MeRe(=O)_3$ [9], $(\eta^5\text{-}C_5Me_5)Re(=O)Me_2$ [2b], $(\eta^5\text{-}C_5H_5)Nb(=O)Me$ [10], $(\eta^5\text{-}C_5Me_5)W(=O)Me_3$ [4b] and $(\eta^5\text{-}C_5Me_5)W(=O)_2Me$ [4b]. The thermodynamic stabilities of these complexes can be attributed to the weak agostic interactions between C–H bonds in methyl ligands and transition metal *d*-orbitals. In the previous communication we examined the tungsten-proton coupling constants of various methyl-oxo tungsten complexes. The magnitudes of the coupling constants show an interesting trend: they increase in the order of decreasing electron densities on the metal centers [4b]. We believe that this is a strong indication of weak agostic effects to stabilize the high oxidation state metal centers. On the other hand, the existence of extremely strong oxo–metal bonds restricts the fluxional behavior. Thus, the rearrangement of piano-stool structures which would normally average the NMR of the methyl groups does not occur rapidly [1] *. Like its tungsten analog **3b**, no exchange of the two different methyl groups of **3a** was observed at temperatures up to 85 °C in the variable temperature ^1H NMR experiment.

Decomposition pathways

Decomposition of **3a** began at about 70 °C and the major organic products were methane and ethane. The release of methane suggests the formation of a molybdenum–carbene complex via α-hydride elimination. No carbenes were detected in the proton NMR spectrum of either **3a** or its tungsten analogue, $(\eta^5\text{-}C_5Me_5)W(=O)(Me)_3$ on heating [4b]. Nevertheless, the potential existence of such a compound as $(\eta^5\text{-}C_5Me_5)Mo(=CH_2)(=O)Me$ is suggested by the recently isolated oxo tungsten–alkylidene complex $(\eta^5\text{-}C_5H_5)W(=CHR)(=O)CH_2R$ ($R = SiMe_3$) by Legzdins et al. [3b]. A greater stability for the trimethylsilylmethyl derivative, however, is expected owing to stabilization of the metal–carbon double bond by the bulky trimethylsilyl group. To test for the possibility of α-elimination and carbene formation, benzaldehyde and **3a** were held at elevated temperature (70 °C) and yielded styrene. This strongly suggests that the oxo metal–carbene species suggested



Scheme 3.

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* High barriers to rearrangement can also be found in high oxidation state organometallics without oxo groups, but with bulky ligands. This has been attributed to steric interactions [11].

above might be the unstable intermediate in the thermal decomposition of compound **3a**. The reaction probably proceeds via the mechanism shown in Scheme 3. Unlike its molybdenum analog, (η^5-C_5Me_5)W(=O)Me_3 (**3b**) does not decompose in boiling toluene. Consequently, no transformation similar to that shown in Scheme 3 was observed after prolonged heating of the reaction mixture at 110 ° C.

Exchange between metal-oxo groups and $H_2{}^{18}O$

The infrared spectrum of **6a** in diethyl ether treated with $H_2{}^{18}O$ revealed a decrease in the Mo=O band at 934 cm^{-1} and an emerging new band at 891 cm^{-1}, which arises from shift of ν(M=O) to lower frequency upon replacement of ^{16}O by ^{18}O (Fig. 2). The absence of any ^{18}O shifts in the absorptions attributable to the characteristic peroxo stretching bands at 883, 590 and 571 cm^{-1} indicates that there is no incorporation of ^{18}O into the peroxo group. On standing in solution for several days, the mixture of (η^5-C_5Me_5)Mo(=O)(η^2-O_2)Cl and (η^5-C_5Me_5)Mo(=^{18}O)(η^2-O_2)Cl still showed no incorporation of ^{18}O into the η^2-O_2. Thus there is no facile intramolecular or intermolecular O transfer between the oxo and the η^2-O_2 in the compound.

With this information on the stability of η^2-O_2, we are in a position to examine the pathway for formation of the peroxo complex. In particular, we wish to determine whether an O atom is transferred to an existing Mo=O or if the O–O bond in the reagent is maintained. To demonstrate that ^{18}O was not inadvertently exchanged out of the complex by adventitious water, the solution was saturated with $H_2{}^{18}O$ in the following experiment. This assures that any exchangeable oxygen will

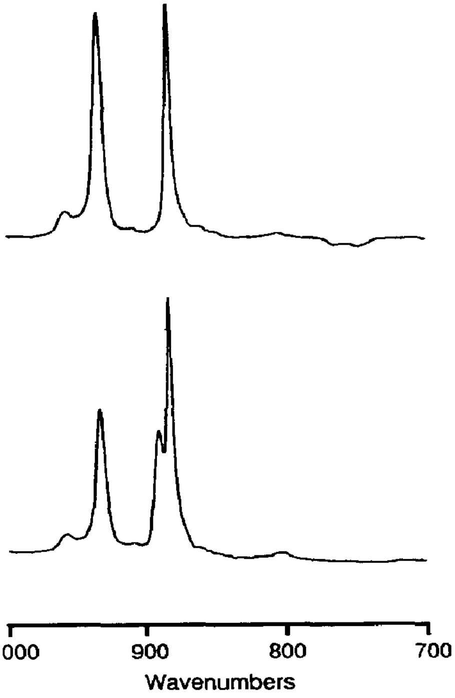


Fig. 2. The infrared spectrum of (η^5-C_5Me_5)Mo(=O)(η^2-O_2)Cl in CS_2 before (upper) and after (lower) exchange with $H_2{}^{18}O$.

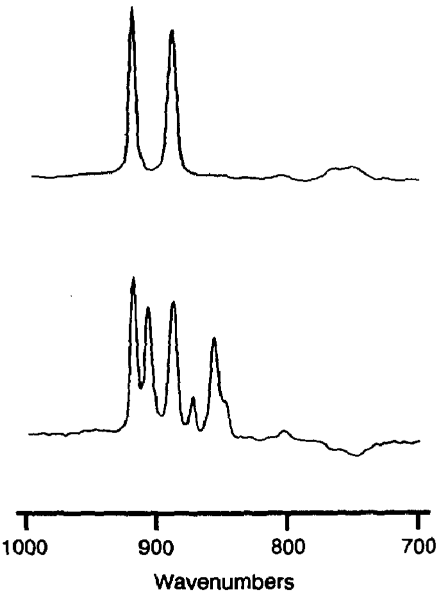


Fig. 3. The infrared spectrum of $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$ in CS_2 before (upper) and after (lower) exchange with $H_2{}^{18}O$.

retain ^{18}O. The reaction of ^{18}O-labeled compound **2a**, which is a statistical mixture of doubly-labeled, singly-labeled and unlabeled $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$ (vide infra), was treated with peroxide containing diethyl ether saturated with 50% $H_2{}^{18}O$. This did not yield any isotopomer of **6a** with ^{18}O incorporated into the peroxy group. The IR spectrum of the product showed that compound $(\eta^5\text{-}C_5Me_5)Mo(={}^{18}O)(\eta^2\text{-}O_2)Cl$ was the only isotopically labeled isomer. This clearly demonstrates that the O–O bond of the organoperoxide remains intact during formation of the metal peroxide.

$$(\eta^5\text{-}C_5Me_5)Mo(=^{\star}O)_2Cl + RO\text{-}OH \rightarrow (\eta^5\text{-}C_5Me_5)Mo(=^{\star}O)(\eta^2\text{-}O_2)Cl \qquad (5)$$

Thus, the reaction does not occur by oxygen atom transfer from the peroxide reagent with an original Mo=O retained, but both oxygens in the $Mo(\eta^2\text{-}O_2)$ group come from the peroxide reagent. This result is in agreement with the observation made by Sharpless and Mimoun on similar transformations on different types of Mo=O complexes which form $Mo(\eta^2\text{-}O_2)$ using H_2O_2 [12,13].

Statistical mixtures (unlabeled, singly-labeled and doubly-labeled dioxo) of dioxochlorides of both tungsten and molybdenum complexes were most conveniently observed by stirring the corresponding oxotrichloro metal complexes in methylene chloride with a large excess of 50% $H_2{}^{18}O$ for ~ 10 min. A considerably longer time was needed to achieve the statistical mixture of isotopically labeled $[(\eta^5\text{-}C_5Me_5)M(=O)]_2(\mu\text{-}O)$ than of $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ ($t_{1/2}$ ~ 120 min for the μ-oxo complex verses $t_{1/2}$ ~ 30 min for the chloro complex). The resulting IR spectra are shown in Figs. 3 and 4. The analogous alkyl complexes exchange with $H_2{}^{18}O$ extremely slowly and no isotopomers were observed after the complexes had been treated with 50% $H_2{}^{18}O$ for several days.

Perhaps the simplest mechanism for oxygen exchange involves the formation of a dihydroxy intermediate, as proposed for $(\eta^5\text{-}C_5Me_5)_2W(=O)$ (Scheme 4) [14].

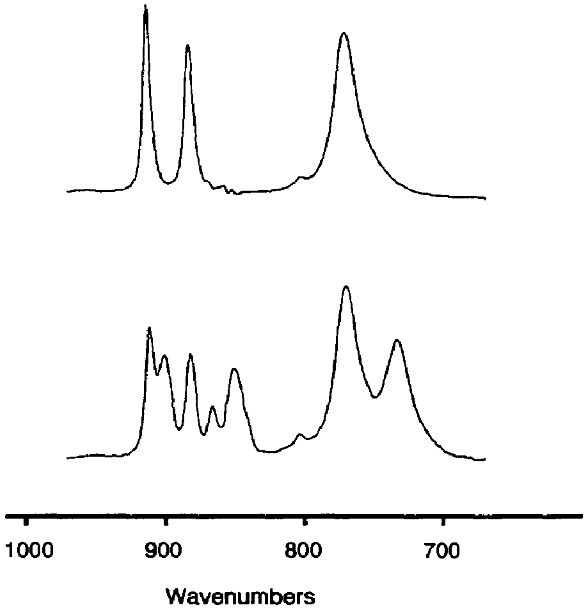
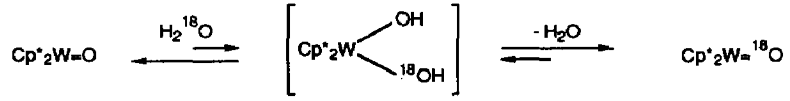
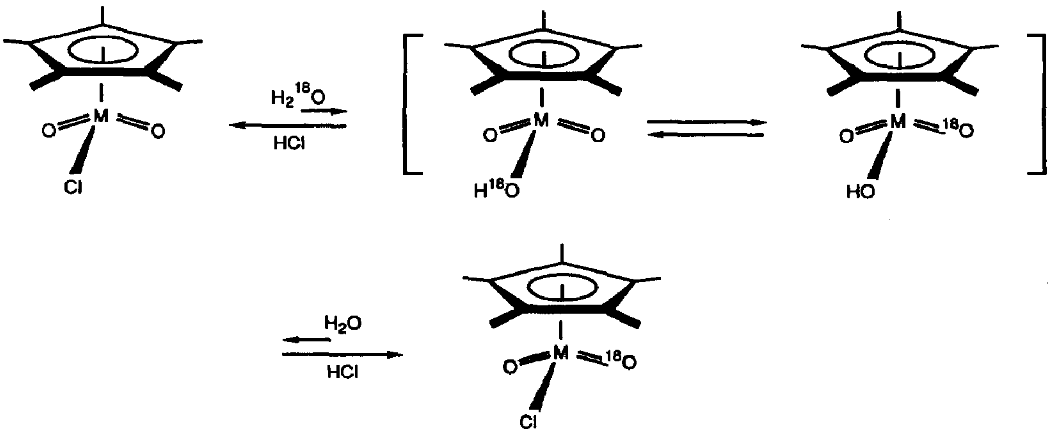


Fig. 4. The infrared spectrum of $[(\eta^5\text{-}C_5Me_5)Mo(=O)_2]_2$ in CS_2 before (upper) and after (lower) exchange with $H_2{}^{18}O$.



Scheme 4.

Although exchange via a dihydroxy compound probably occurs, the variation of rates among the chloro, μ-oxo, and alkyl derivatives would appear to be too great. Furthermore, in the μ-oxo complex, the bridging oxo group appears to exchange at a rate comparable to that of the terminal oxo groups. These results may be rationalized by considering a secondary route involving partial hydrolysis to yield a dioxohydroxy intermediate, as shown for the chloride in Scheme 5.



Scheme 5.

For this mechanism, the relative rates for the dimer and the chloride would reflect differences in hydrolysis rates of Mo–Cl verses Mo–OMo, as well as potential acid catalysis. For the alkyl analogues Mo–C cleavage would not be anticipated; hence, the most plausible route for exchange with $H_2{}^{18}O$ is via the formation of a dihydroxy intermediate. This intermediate is formed as a result of protonation of the M=O bond, which opens a site for hydroxide addition to the metal.

Exchange of $H_2{}^{18}O$ with $(\eta^5\text{-}C_5Me_5)_2W(=O)$ is rapid at room temperature [14], whereas that for the $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ complex is extremely slow. We attribute this to the greater ease of protonation of the oxygen in $(\eta^5\text{-}C_5Me_5)_2W(=O)$ owing to the higher oxygen lone pair availability in this 18 e^- complex compared to the formally 16 e^- $(\eta^5\text{-}C_5Me_5)W(=O)_2R$. The weaker π-donation from the oxygen to the metal in the former is reflected in the lower $\nu(W{=}O)$ frequency of 860 cm^{-1} compared to the average of 910 cm^{-1} in the latter.

Experimental

Reagent grade solvents and hydrogen chloride gas were used as supplied by the manufacturers. The preparation of compounds $(\eta^5\text{-}C_5Me_5)M(=O)_2Cl$ and $[(\eta^5\text{-}C_5Me_5)M(=O)_2]_2(\mu\text{-}O)$ were published elsewhere [4]. For small scale preparations, "peroxidized" diethyl ether was used to prepare peroxo complexes. After being opened to the air and standing for approximately one week, diethyl ether usually contains sufficient hydroperoxide for these reactions. The addition of 1 ml of ether to a solution of 100 mg NaI in 1 ml acetone gives a yellow solution when appropriate concentrations of hydroperoxide are present.

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 HP 5985 GC/MS mass spectrometer (using direct injection). UV spectra were recorded with a Varian Cary 219 spectrophotometer.

*Preparation of $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)Cl$ (**6a**)*

Upon stirring 120 mg of $(\eta^5\text{-}C_5Me_5)Mo(=O)_2Cl$ (**2a**) (0.40 mmol) in 150 ml of peroxidized diethyl ether for 10 h, the solution changed from yellow to bright yellow. After removing solvent on a rotary evaporator to near dryness, the bright yellow residue was washed with 5 ml of fresh diethyl ether to give 112 mg of compound **6a** (89%). Compound **6a**: ^1H NMR (C_6D_6, 25 °C, 250 MHz) δ 1.53 (s, 15H, C_5Me_5); IR (CS_2, $\nu(Mo{=}O)$) 934s, ($\nu(O{-}O)$) 883s, ($\nu(Mo{-}O)$) 590w and 571 cm^{-1}; MS-EI (20 eV), m/z for $C_{10}H_{15}{}^{98}MoO_3{}^{35}Cl = 316$; Analysis. Found: C, 38.27; H, 4.84. $MoClO_3C_{10}H_{15}$ calc: C, 38.18; H, 4.81%.

*Preparation of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)Cl$ (**6b**)*

This synthesis was analogous to the procedure described for **6a**. Compound **6b** was obtained in 60% yield after stirring $(\eta^5\text{-}C_5Me_5)W(=O)_2Cl$ (**2b**) with the peroxide in diethyl ether for 24 h.

Compound **6b**: ^1H NMR (C_6D_6, 25 °C, 250 MHz) δ 1.73 (s, 15H, C_5Me_5); IR (CS_2, $\nu(W{=}O)$) 960sh and 949s, ($\nu(O{-}O)$) 864, ($\nu(W{-}O)$) 605w and 571 cm^{-1};

MS-EI (20 eV), m/z for $C_{10}H_{15}{}^{184}WO_3{}^{35}Cl = 402$; Analysis. Found: C, 29.96; H, 3.80. $WClO_3C_{10}H_{15}$ calc: C, 29.84; H, 3.76%.

Preparation of $(\eta^5$-$C_5Me_5)Mo(=O)Cl_3$ (7a)

Compound **2a** (23 mg, 0.077 mmol) was dissolved in 5 ml of dry diethyl ether and a stream of hydrogen chloride was passed through the solution until no further precipitation occurred. After filtration, the red microcrystalline solid was dried in vacuo to give 20 mg of analytically pure compound **7a** (80%).

Compound **7a**: IR (Nujol, ν(Mo=O)) 916s; Analysis. Found: C, 34.04; H, 4.29. $MoCl_3OC_{10}H_{15}$ calc: C, 33.97; H, 4.28%.

Preparation of $(\eta^5$-$C_5Me_5)W(=O)Cl_3$ (7b)

Analogous to the procedure described for **7a**, compound **2b** (32 mg, 0.083 mmol) reacted with HCl to give 31 mg of compound **7b** in 85% yield.

Compound **7b**: IR (Nujol, ν(W=O)) 937s; Analysis. Found: C, 27.32; H, 3.47. $WCl_3OC_{10}H_{15}$ calc: C, 27.21; H, 3.43%.

Preparation of $(\eta^5$-$C_5Me_5)Mo(=O)Me_3$ (3a)

Compound **1a** (26.3 mg, 0.048 mmol) was dissolved in 50 ml of dry diethyl ether and treated with 0.1 ml of 2 M trimethylaluminum in hexane at −70 °C. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and solvent was removed on a rotary evaporator. The residue was extracted with 100 ml of diethyl ether in three portions. The combined extracts were concentrated to give a yellow residue and this was purified by means of thin layer chromatography on a 0.25 mm silica gel plate with diethyl ether as a eluant. The pale yellow crystalline solid collected from the light yellow band near the solvent front was dried in vacuo to give 14.3 mg of $(\eta^5$-$C_5Me_5)Mo(=O)Me_3$ (**3a**) in 50% yield. A minor product was also isolated from TLC in less than 5% yield. This compound was characterized as $(\eta^5$-$C_5Me_5)Mo(=O)_2Me$ (**4a**) by comparison of its IR and NMR spectra with the corresponding spectra of its tungsten analogue $(\eta^5$-$C_5Me_5)W(=O)_2Me$ (**4b**).

Compound **3a**: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 1.76 (s, 15H, C_5Me_5), δ 1.27 (s, 6H, *cis*-methyl), δ 0.13 (s, 3H, *trans*-methyl); IR (CS_2, ν(Mo=O)) 993s; Analysis. Found: C, 53.32; H, 8.37. $MoOC_{13}H_{24}$ calc: C, 53.42; H, 8.28%.

Compound **4a**: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 1.98 (s, 15H, C_5Me_5), δ 0.98 (s, 3H, methyl); IR (CS_2, ν(Mo=O)) 920s and 894s; Analysis. Found: C, 47.59; H, 6.53. $MoOC_{11}H_{18}$ calc: C, 47.49; H, 6.52%.

Preparation of $(\eta^5$-$C_5Me_5)Mo(=O)_2(CH_2SiMe_3)$ (4a′)

A solution of 100 mg of **2a** in 20 ml diethyl ether was treated with 1.4 ml of 1 *M* Me_3SiCH_2MgCl in diethyl ether at −70 °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 through a short alumina column and the concentrated filtrate was then purified by thin layer chromatography on a 0.25 mm silica gel plate with diethyl ether as an eluant, yielding 57 mg (48%) of an air-stable pale yellow compound. ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 1.93 (s, 15H, C_5Me_5), 0.66 (s, CH_2, 2H), 0.05 (s, $SiMe_3$, 9H); IR (CS_2, ν(W=O)) 919s, 890s cm^{-1}; Analysis. Found: C, 48.08; H, 7.57. $MoSiO_2C_{14}H_{26}$: C, 47.99; H, 7.48%.

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