Notes

First Structurally Characterized Organometallic Chloro Oxo−Peroxo Compounds of Molybdenum and Tungsten

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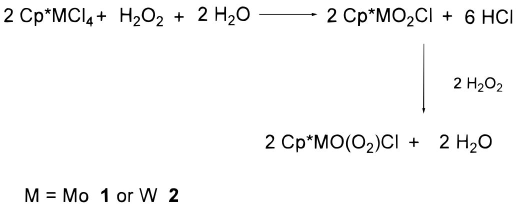
*Summary: Reactions of H_2O_2 with Cp^*MoCl_4 and Cp^*WCl_4 ($Cp^* = C_5Me_5$) yield chloro oxo−peroxo complexes of the type $Cp^*MoO(O_2)Cl$ (**1**) and $Cp^*WO(O_2)Cl$ (**2**) in high yields. The compounds have been characterized using X-ray structural analysis.*

Introduction

In the recent years there has been considerable interest in the chemistry of transition metal peroxo compounds.[1] This is in view of their relevance in biological systems as well as their utility in organic synthesis.[1] Among the organometallic peroxo systems known is the species $[MeReO(O_2)_2(H_2O)]$, which has been implicated as the active site compound in the methyl trioxo rhenium catalyzed epoxidation.[2] This species has also been synthesized independently starting from $MeReO_3$ and H_2O_2. $[MeReO(O_2)_2(H_2O)]$ has been characterized by single-crystal X-ray structural analysis.[3] Other organometallic peroxides known include molybdenum and tungsten peroxo compounds of the type $Cp'MO(O_2)R$ ($Cp' = C_5H_5$ or C_5Me_5; M = Mo or W; R = Me or CH_2SiMe_3 or Cl).[4−6] One of the major objectives in this area is facile synthetic methods for the assembly of these compounds. Unlike the $MeReO_3$-derived peroxide, other organometallic peroxides have to be prepared by a multistep synthesis.[4−6] Also, it may be noted that reports on halogen-containing transition metal peroxides are scant in the literature because of the difficulty involved in the synthesis of such compounds.[1c] To the best of our knowledge there have also been few reports involving the structural characterization of organometallic halo peroxides. In the following account we describe a one-step synthesis of the mixed organometallic oxo−peroxo chlorides and also report on the X-ray structural characterization of $Cp^*MoO(O_2)Cl$ (**1**) and $Cp^*WO(O_2)Cl$ (**2**).

Scheme 1



Results and Discussion

To obtain the mixed halo oxo−peroxo compounds we reasoned that the half-sandwich organometallic halides Cp^*MCl_4 (M = Mo, W) would serve as ideal precursors. It may be noted that the literature method[6] for the synthesis of **1** and **2** involves the reaction of Cp^*MO_2Cl with peroxidized ether. The compound Cp^*MO_2Cl has to be obtained from the reaction of PCl_5 with $[Cp^*MO_2]_2O$. The latter compound itself has to be prepared in a multistep synthesis starting from $[Cp^*M(CO)_2]_2$. In contrast to the above cumbersome and lengthy procedure our strategy involved a direct reaction of Cp^*MCl_4 with 30% H_2O_2 in ether, so that the intermediate Cp^*MO_2Cl would be generated *in situ*, which on further reaction with H_2O_2 would give the desired products. Our expectations were realized by the high-yield synthesis of compounds **1** and **2** as outlined in Scheme 1.

The compounds can be isolated in the solid state. However, they decompose on standing at room temperature both in the solid state and in solution. In solvents such as acetonitrile, THF, or trichloromethane the decomposition is particularly rapid, as indicated by the formation of a blue-colored residue. We were unable to characterize the blue-colored solid due to its insolubility. However, the decomposed products on treatment with an excess of H_2O_2 afforded the parent compounds again in high yield. The IR spectra of the compounds **1** and **2** recorded immediately after their isolation show characteristic bands due to ν(M=O), ν(O−O) [ν_1], and ν(M−

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Table 1. Crystal Data and Structure Refinement Details for 1 and 2

	1	**2**
empirical formula	$C_{10}H_{15}ClMoO_3$	$C_{10}H_{15}ClO_3W$
fw	314.61	402.52
temp	133(2) K	133(2) K
λ	0.71073 Å	0.71073 Å
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens	$a = 6.391(10)$ Å	$a = 6.369(1)$ Å
	$b = 8.565(2)$ Å	$b = 8.574(2)$ Å
	$c = 10.939(2)$ Å	$c = 10.985(2)$ Å
	$\alpha = 84.83(3)°$	$\alpha = 84.95(3)°$
	$\beta = 86.79(3)°$	$\beta = 86.86(3)°$
	$\gamma = 89.04(3)°$	$\gamma = 88.86(3)°$
Z	2	2
cell volume	595.4(2) $Å^3$	596.6(2) $Å^3$
ρ_{calc}	1.755 Mg m^{-3}	2.241 Mg m^{-3}
μ	1.310 mm^{-1}	9.889 mm^{-1}
$F(000)$	316	380
cryst dimens	0.20 × 0.10 × 0.10 mm	0.20 × 0.20 × 0.10 mm
θ range	1.87−26.00°	2.38−27.54°
index range	$-7 \leq h \leq 7$	$-8 \leq h \leq 8$
	$-10 \leq k \leq 10$	$-11 \leq k \leq 11$
	$0 \leq l \leq 13$	$-14 \leq l \leq 14$
total no. of reflns	8349	14 359
no. of ind reflns	2329 ($R_{int} = 0.0474$)	2731($R_{int} = 0.0759$)
completeness to θ	= 26.00; 99.8%	= 27.54; 99.1%
max and min transmission	0.8802 and 0.7796	0.4380 and 0.2424
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/parameters	2329/220/168	2731/232/168
goodness-of-fit on F^2	0.980	0.987
R1, R2 [$I > 2\sigma(I)$]	R1 = 0.0379, wR2 = 0.0873	R1 = 0.0433, wR2 = 0.1003
R1, R2 (all data)	R1 = 0.0586, wR2 = 0.0928	R1 = 0.0619, wR2 = 0.1069
largest diff peak and hole	0.916 and −1.495 e $Å^3$	2.608 and −3.587 e $Å^3$

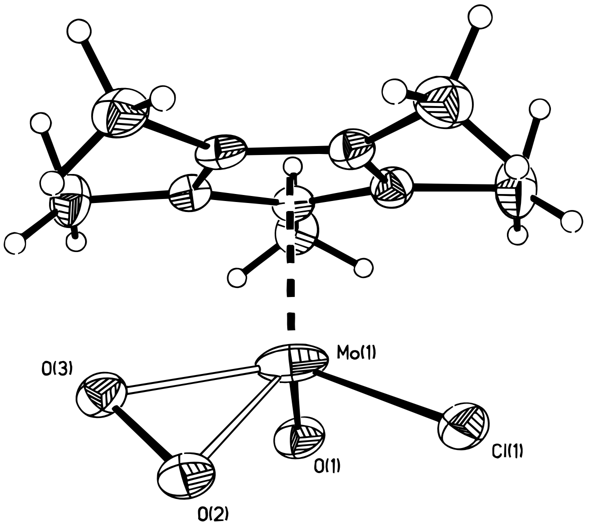

Figure 1. Molecular structure of $Cp^*MoO(O_2)Cl$.

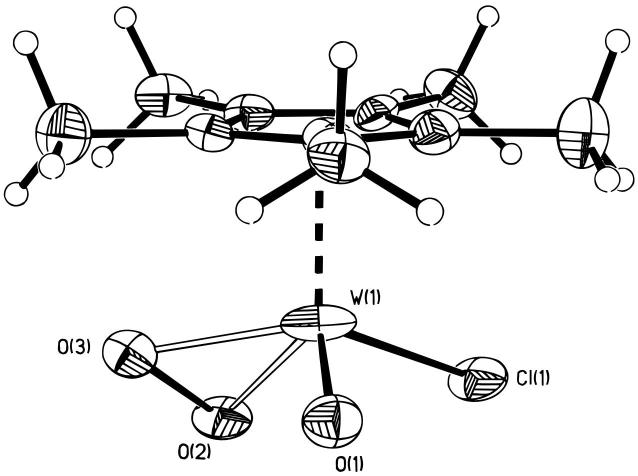

Figure 2. Molecular structure of $Cp^*WO(O_2)Cl$.

O_2) [ν_2 and ν_3] (925−945, 855−880, and at 585−600 and 565−570 cm^{-1}, respectively). The observed IR spectra are in accordance with literature precedents.[5,6] The mass spectra of **1** and **2** give molecular ion peaks as well as peaks due to [$M^+ - O$] and [$M^+ - Cl$] moieties, showing that the compounds retain their integrity under EI conditions. In the ^1H NMR spectra one signal (2.1 ppm for **1** and 2.2 ppm for **2**) is seen due to the methyl protons attached to the cyclopentadienyl group. The equivalence of the methyl resonances shows that the penta-hapto nature of the cylopentadienyl ligand remains unchanged in the peroxo complexes. Analytical and spectroscopic characterization of **1** and **2** was found to be difficult due to slow decomposition at room temperature. These structural conclusions were corroborated by the single-crystal X-ray analysis of both **1** and **2**.

Figures 1 and 2 show the molecular structure of **1** and **2**. Table 1 gives the metric parameters for these compounds. **1** and **2** are isostructural and can be described as adopting distorted piano stool structures, the midpoint of the peroxo ligand being one of the legs of the piano stool. Two other structurally characterized oxo−peroxo compounds known in the literature, [Cp′WO(O_2)(CH_2SiMe_3)] (Cp′ = C_5H_5 or C_5Me_5), also have a similar structural arrangement.[5,6] The M═O bond lengths in **1** and **2** [Mo(1)−O(1) 1.683(3) Å, W(1)−O(1) 1.703(5) Å] are unexceptional and indicate the continued presence of M═O in these compounds. The O−O distances in **1** and **2** are similar [O(2)−O(3) distance in **1** is 1.445(7) Å and in **2** is 1.478(12) Å] and are comparable to those in [$CpWO(O_2)(CH_2SiMe_3)$] [1.44(3) Å] and other reported compounds.[5,6]

We have attempted to use compounds **1** and **2** as catalysts for the epoxidation of some olefins. These compounds cannot be considered as catalysts for olefin epoxidation. It may be pointed that earlier studies by Bergman and co-workers[7] in this regards also are consistent with the present observation.

Experimental Section

General Information. All the experimental manipulations involving the synthesis of the concerned starting materials were carried out under a dry prepurified argon atmosphere, using Schlenk techniques rigorously excluding moisture and air. All ^{1}H NMR spectra were recorded on a Bruker AS 200 instrument. The chemical shifts are reported in ppm with reference to $SiMe_4$ as an external standard. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 mass spectrometer. Melting points were obtained on a HWS-SG 3000 instrument and are reported uncorrected. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Starting Materials. Cp^*MoCl_4 and Cp^*WCl_4 were prepared using literature procedures.[8]

Preparation of $Cp^*MO(O_2)Cl$ 1 and 2. Since the methods of preparation of **1** and **2** are the same, only a general method is described below.

To a stirred suspension of Cp^*MCl_4 (1 mmol) in ether (50 mL) at −40 °C was added very slowly H_2O_2 (0.5 mL, 30%). The suspension was slowly allowed to attain a temperature of −5 °C and maintained at this temperature for a period of 12 h. A yellow to light yellow solution was obtained, which was dried over sodium sulfate and then filtered. The above-mentioned operations were carried out at −5 °C. The solvent was removed *in vacuo* to yield the products. The compounds were recrystallized from a mixture of ether (10 mL) and toluene (3 mL).

Anal. Calcd for $C_{10}H_{15}ClMoO_3$ (314.62): C, 38.2 H; 4.8; Cl, 11.3. Found: C, 37.6; H, 4.7; Cl, 11.7. MS (EI, 70 eV): *m*/*e* 316 (4, M^+), 134 (100, Cp*). IR (KBr): 928 (s), 878 (s), 585 (m), 567 (m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 2.1 (s). Yield: 0.26 g (85%). Mp: 70 °C (dec).

Anal. Calcd for $C_{10}H_{15}ClO_3W$(402.52): C, 29.8; H, 3.8; Cl, 8.8. Found: C, 29.4; H, 3.9; Cl, 9.0. MS (EI, 70 eV): *m*/*e* 402 (6, M^+), 134 (100, Cp*). IR (KBr): 944 (s), 859 (s), 599 (m), 565 (m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 2.2 (s). Yield: 0.32 g (80%). Mp: 77 °C (dec).

Warning: **1** and **2** have the potential of spontaneous detonation due to sudden temperature variations or mechanical shock. Hence, large-scale preparations are not recommended.

Decomposition Studies of $Cp^*MoO(O_2)Cl$. A solution of $Cp^*MoO(O_2)Cl$ (0.130 g, 0.4 mmol) in acetonitrile (20 mL) was stirred overnight, upon which a blue suspension was produced. H_2O_2 (1 mL, 30%) was added to the system at −5 °C. An immediate color change was noticed from blue to yellow. The solvent was removed *in vacuo*. The residue was washed with cold ether (5 mL) to yield 122 mg (0.39 mmol) of $Cp^*MoO(O_2)Cl$. Anal. Calcd for $C_{10}H_{15}ClMoO_3$ (314.62): C, 38.2; H, 4.8; Cl, 11.3. Found: C, 37.4; H, 4.7; Cl, 11.6. ^{1}H NMR (200 MHz, $CDCl_3$): 2.1 (s).

The tungsten compound shows a similar behavior during the studies of decomposition.

X-ray Structure Determination. Yellow crystals of **1** and colorless crystals of **2** suitable for single-crystal X-ray diffraction were obtained from a 3:1 ether/toluene mixture at a temperature of −6 °C over a period of 4 days. A 0.2 × 0.1 × 0.1 mm^3 sized crystal of **1** (0.2 × 0.2 × 0.1 mm^3 sized crystal of **2**) was mounted on a glass fiber in a rapidly cooled perfluoropolyether. Diffraction data were collected on a Siemens-Stoe-Huber four-cycle instrument coupled to a CCD detector at 133(2) K, with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). φ and ω scans were performed. Crystal data for **1**: Triclinic, $P\bar{1}$, unit cell dimensions $a = 6.391(1)$ Å, $b = 8.565(2)$ Å, $c = 10.939(2)$ Å, $\alpha = 84.83(3)°$, $\beta = 86.79(3)°$, $\gamma = 89.04(3)°$, unit cell volume 595.4(2) Å^3, $\rho_{calc} = 1.755$ Mg m^{-3}, $\mu = 1.31$ mm^{-1}, total number of reflections measured 8349, unique 2329 ($R_{int} = 0.0474$), $3.8° < 2\theta < 52°$. Crystal data for **2**: Triclinic, $P\bar{1}$, unit cell dimensions $a = 6.369(1)$ Å, $b = 8.574(2)$ Å, $c = 10.985(2)$ Å, $\alpha = 84.95(3)°$, $\beta = 86.86(3)°$, $\gamma = 88.86(3)°$, unit cell volume 596.6 (2) Å^3, $\rho_{calc} = 2.241$ Mg m^{-3}, $\mu = 9.89$ mm^{-1}, total number of reflections measured 14 359, unique 2731 ($R_{int} = 0.0759$), $4.8° < 2\theta < 55°$. Both structures are disordered in such a way that the chloro and the peroxo ligands exchange positions in the metal coordination sphere, each partially occupying both alternative sites. The site occupation factor was refined and eventually fixed at a convergence value of 0.54 (0.46 for the alternative site) for **1** and 0.55 (0.45 for the other disordered site) for **2**. The disordered peroxo groups, the Cl atoms, and, in case of **2**, the Cp* ring were refined using similarity restraints for 1−2 and 1−3 interatomic distances (bond length and angles) and isotropic displacement parameters. Rigid bond restraints were applied for the anisotropic displacement parameters. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

The structures were solved by direct methods using SHELXS-97[9] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[9] Refinement data for **1**: No. of data/restraint/parameters = 2329/220/168. Final *R* indices with $I > 2\sigma(I)$: R1 = 0.038, wR2 = 0.087. *R* indices on all data: R1 = 0.058, wR2 = 0.093. Goodness-of-fit on F^2: $S = 0.980$. Largest difference peak and hole: 0.92 and −1.50 e Å^3. For **2**: No. of data/restraints/parameters = 2731/232/168. Final *R* indices with $I > 2\sigma(I)$: R1 = 0.043, wR2 = 0.10. *R* indices on all data: R1 = 0.062, wR2 = 0.11. Goodness-of-fit on F^2: $S = 0.987$. Largest difference peak and hole: 2.61 and −3.59 e Å^3. $R = \|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = [[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]]^{1/2}$; $S = [[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma(n-p)]]^{1/2}$. The final fractional atomic coordinates are given in the Supporting Information.

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Supporting Information Available: X-ray structural data for **1** and **2**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (10 pages). See any current masthead page for ordering and Internet access instructions.

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