# Cyclooctene epoxidation with $H_2O_2$ and single crystal X-ray determined crystal structures of new molybdenum and tungsten catalysts bearing the hydrophilic ligand hydroxymethyldiphenylphosphine oxide

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Dedicated to the memory of Professor F.A. Cotton. *Labor omnia vincit.*

## Abstract

The dioxo molybdenum and tungsten complexes $MoO_2Cl_2(OPPh_2CH_2OH)_2$ and $WO_2Cl_2(OPPh_2CH_2OH)_2$ have been synthesized and characterized by FT-IR, $^1H$ and $^{31}P$ NMR. Their structures, as determined by single crystal X-ray diffraction analysis, reveal distorted octahedral geometries with *cis* terminal oxygen atoms, *trans* Cl ligands and that the hydroxymethyldiphenylphosphine oxide ligands coordinate through the oxygen atom bonded to the P atom. Both of the compounds are studied as catalysts for the epoxidation of *cis*-cyclooctene in the presence of hydrogen peroxide as a source of oxygen. Both complexes showed good activity and very high selectivity for the formation of cyclooctene oxide.
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*Keywords:* Molybdenum oxide; Tungsten oxide; Olefin epoxidation; Hydrogen peroxide; Crystal structures; Catalysis
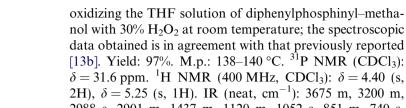
## 1. Introduction

Over the past decades, direct oxidation of olefins using oxidants such as hydrogen peroxide, oxygen and alkyl hydroperoxide in the presence of high-valent transition-metal catalysts have been used to produce epoxides [1]. Complexes of transition-metals such as rhenium [2], vanadium [3], molybdenum [2f,2g,4], manganese [5], tungsten [4e,6], selenium [7], platinum [8] and titanium [9] have been examined as catalysts for epoxidation. In particular, molybdenum and tungsten complexes have been widely investigated because of their demonstrated high activity for selective oxidation [4,6].

We have previously reported that molybdenum and tungsten compounds containing a series of phosphine oxides such as $MO_2Cl_2(OPR_3)_2$ (M = Mo or W; $OPR_3$ = $OPMePh_2$, $OPPh_3$), $MO_2Cl_2(dppmO_2)$ (M = Mo or W) are good catalysts for the epoxidation of olefins using *tert*-butyl hydroperoxide (TBHP) or hydrogen peroxide as the source for oxygen [4e,4k,4l,4m]. Hydrogen peroxide is constructive because of its unique features and advantages such as high atom-efficiency and that the byproduct ($H_2O$) is environmentally benign [10]. Consequently, metal-catalyzed epoxidation systems have been developed recently using hydrogen peroxide as oxidant [8,10b,10c, 10d,10e].

Hydroxymethyldiphenylphosphine oxide has been examined by X-ray crystallography to reveal a hydrogen bonded dimeric arrangement involving the hydrogen atom on the hydroxyl group of one molecule interacting with the P=O group on the adjacent molecule and vice versa [11]. One example of its coordinating capability is displayed in the crystal structure of the zirconium compound

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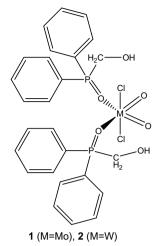
**1** (M=Mo), **2** (M=W)

Fig. 1. Representation of compounds synthesized.

$Cp_2Zr(C(SiMe_3)CHSiMe_3)(OCH_2P(O)Ph_2)$ where the ligand coordinates through the hydroxyl oxygen atom [12]. These type of ligands can be described as functionalized hydrophilic phosphines, for which related derivatives have been studied during the past decades [13]. They are expected to be good ligands for organometallic catalysts since they combine the bonding attributes of phosphine oxide ligands with the increased solubility in polar solvents of hydrophilic alcohols [14].

Herein, we report on the synthesis, characterization and catalytic capabilities of molybdenum and tungsten compounds **1** and **2** bearing the hydrophilic phosphine oxide ligand $Ph_2P(O)CH_2OH$ coordinated via the oxygen atom bonded to the phosphorus atom as represented in Fig. 1.

## 2. Experimental

### 2.1. General method

Infrared spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer. $^1H$ and $^{31}P$ NMR data were recorded on a Varian XL-400 spectrometer referenced to $CDCl_3$ or acetone-$d_6$ and 85% $H_3PO_4$, respectively. A Fisher–Johns melting point apparatus (Fisher Scientific Company) was used for the melting point determinations. A Shimadzu QP5050 GC–MS was used for the mass spectra determinations and quantitative analysis for the epoxidation reactions. The elemental analysis data were obtained from Galbraith Laboratories, Inc. Solvents were used as received from commercial suppliers. Most chemicals were purchased from Aldrich, and all chemicals were used as received.

### 2.2. Synthesis and characterization

#### 2.2.1. Synthesis and characterization of $Ph_2P(O)CH_2OH$

Diphenylphosphinyl–methanol was synthesized according to a previously published procedure [15]. Hydroxymethyldiphenylphosphine oxide was prepared by oxidizing the THF solution of diphenylphosphinyl–methanol with 30% $H_2O_2$ at room temperature; the spectroscopic data obtained is in agreement with that previously reported [13b]. Yield: 97%. M.p.: 138–140 °C. $^{31}P$ NMR ($CDCl_3$): $\delta = 31.6$ ppm. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 4.40$ (s, 2H), $\delta = 5.25$ (s, 1H). IR (neat, cm$^{-1}$): 3675 m, 3200 m, 2988 s, 2901 m, 1437 m, 1120 m, 1052 s, 851 m, 740 s, 718 s, 691 s.

#### 2.2.2. Synthesis and characterization of $MoO_2Cl_2(OPPh_2CH_2OH)_2$ (**1**)

Lead molybdate (0.92 g, 2.5 mmol) was moistened with 1.0 ml dichloromethane, and then acetyl chloride (2.3 ml) was added to the suspension. The mixture was stirred for 30 min. A brown solution was obtained after filtration. A solution of hydroxymethyldiphenylphosphine oxide (5.0 mmol, 0.80 g) in 5 ml dichloromethane was added to the above brown solution. The resulting gold yellow solution was stirred overnight at room temperature and then concentrated under vacuum. An oily product resulted after diethyl ether was added to the above solution. A yellow precipitate was subsequently obtained after the addition of benzene to the oily product. This yellow compound was separated by filtration and dried under vacuum at room temperature. Yield: 1.08 g (65%). Anal. Calc. for $C_{26}H_{26}Cl_2O_6P_2Mo \cdot 1.5C_6H_6$: C, 48.37; H, 4.06. Found: C, 48.60; H, 4.03%. M.p.: 113–115 °C. $^{31}P$ NMR ($CH_2Cl_2$): $\delta = 43.8$ ppm. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 3.57$ (s, 1H), $\delta = 4.61$ (s, 2H), $\delta = 7.34–7.81$ (m, 10H). IR (cm$^{-1}$): 3457 m, 1437 s, 1125 s, 998 m, 941 s (Mo=O), 901 s (Mo=O), 739 s, 725 s, 687 s.

#### 2.2.3. Synthesis and characterization of $WO_2Cl_2(OPPh_2CH_2OH)_2$ (**2**)

A solution of $(Me_3Si)_2O$ (0.21 g, 1.25 mmol) in 2.5 ml of dichloromethane was added to a suspension of $WCl_6$ (0.50 g, 1.25 mmol) in 2.5 ml of dichloromethane. The resulting suspension was stirred vigorously at ambient temperatures for 1 h. A solution of $Ph_2P(O)CH_2OH$ (0.52 g, 3.25 mmol) in 2.0 ml dichloromethane was then added to the above solution and stirred for 30 min; the addition resulted in an immediate color change from orange to yellow. To this yellow solution 0.22 g $(Me_3Si)_2O$ in 2.0 ml dichloromethane was added and the mixture stirred overnight at room temperature resulting in a yellow green solution. The solution was concentrated under vacuum. A light blue precipitate formed after diethyl ether was added to the solution slowly. This product was obtained by filtration and dried under vacuum overnight. Yield: 0.70 g (75%). Anal. Calc. for $C_{26}H_{26}Cl_2O_6P_2W \cdot 0.25CH_2Cl_2$: C, 40.82; H, 3.46. Found: C, 40.98; H, 3.57%. M.p.: 158–160 °C. $^{31}P$ NMR ($CH_2Cl_2$) $\delta = 45.6$ ppm. $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta = 2.88$ (s, 1H), $\delta = 4.80$ (s, 2H), $\delta = 7.51–7.98$ (m, 10H). IR (cm$^{-1}$): 3372 w, 3278 w, 1437 s, 1123 s, 997 m, 951 s (W=O), 892 s (W=O), 849 m, 736 m, 722 s, 686 s.

## 2.3. Preparation of single crystals

X-ray quality crystals were obtained by the solvent layering method. Compound **1** was dissolved in dichloromethane in a crystallizing tube, and a layer of benzene was added carefully. The tube was sealed and left undisturbed at room temperature for about a week resulting in X-ray quality crystals around the boundary layer. Crystals of **2** were prepared in an identical manner except that diethyl ether was used as the upper solvent.

## 2.4. X-ray crystallography

Suitable crystals were selected, rolled in epoxy resin and mounted on glass fibers. An Enraf Nonius CAD-4 X-ray diffractometer was used to collect the data. Final cell constants and orientation matrix were obtained by collecting appropriate preliminary data, selecting 25 reflections, centering and refinement by a least squares fit. Mo Kα radiation ($\lambda = 0.71073$ Å) was used for data collection. The procedures used to collect the data, solve and refine the structure were as detailed previously for other complexes [16]. The Windows program WINGX was used as the interface for the solution and refinement of the models [17]. The data were solved using the program SIR97 [18]. The models, with H atoms at calculated positions with their thermal parameters constrained to be 1.2 or 1.5 times the isotropic equivalent of the C or O atoms respectively to which they are bonded, were refined to convergence using SHELXL97 [19]. Complex **1** contained disorder in the position of the hydroxy oxygen atom for one of the $OPPh_2CH_2OH$ ligands and in the occupancy and position of a benzene molecule of solvation. This was accounted for using standard refinement procedures [20]. Complex **2** was ordered.

## 2.5. Catalytic reactions using $H_2O_2$ as oxidant

The reactions were carried out under an open atmosphere using a two-necked 25 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 0.200 g (1.82 mmol) of *cis*-cyclooctene, 1 mol% catalyst ($1.82 \times 10^{-2}$ mmol) in 2.0 mL ethanol, 0.28 ml of 30% $H_2O_2$ (2.72 mmol, 1.5 equiv) and 0.100 g *n*-decane (0.703 mmol) as internal standard were added to initiate the reaction. The reaction was then heated to 70 °C for a specific time. Samples were taken periodically and analyzed by a Shimadzu QP5050 GC–MS. The conversion of cyclooctene and the selectivity to cyclooctene oxide were calculated using calibration curves recorded prior to the reaction.

## 3. Results and discussion

### 3.1. Synthesis and spectroscopic characterization of dioxomolybdenum and dioxotungsten compounds

We have previously reported on the syntheses and characterization of dioxomolybdenum and dioxotungsten compounds bearing diphenylmethylphosphine oxide, triphenylphosphine oxide and $dppmO_2$ ligands [4e,4k,4l,4m,21]. We have now extended this to Mo and W compounds containing the hydroxymethyldiphenylphosphine oxide ligand. This ligand may afford a higher catalytic property for olefin epoxidation in polar solvents which is important if we are to take advantage of using hydrogen peroxide. It is also noteworthy that in the studies of the mechanism of olefin epoxidation, of the two mechanisms proposed, i.e., prior binding of the olefin to the metal followed by oxygen transfer [22] and direct transfer of the distal oxygen atom in a bonded peroxide group to the olefin [23], recent studies point out that while the latter mechanism is favored, intermediates, which involve binding of the olefin to the metal center, may well be formed, even though they do not contribute to the epoxidation reaction directly [24]. With these considerations in mind, a catalyst which has more solubility in ethanol should be able to function more effectively irrespective of which mechanism accomplishes the oxygen transfer.

The dioxomolybdenum compound **1** was synthesized by slight modifications to the procedure for the synthesis of the related complex $MoO_2Cl_2(OPPh_2Me)_2$ [21]. Complex **1** can be isolated as a yellow precipitate if the sticky product obtained upon removal of reaction solvent is stirred in benzene at room temperature. We also attempted to make the dioxotungsten compound **2** using the published procedure [21] for $WO_2Cl_2(OPPh_2Me)_2$ but this was not successful. A mixture of products believed to consist of $WO_2Cl_2(OPPh_2CH_2OH)_2$ and $WO(O)_2Cl_2(OPPh_2CH_2OH)_2$ was obtained in low yields. The dioxotungsten compound **2** was made by modification to the procedure for $WO_2Cl_2(DME)$ [25]. A pale light blue precipitate was obtained upon the addition of diethyl ether to the reaction mixture in dichloromethane which was further purified into white crystals after filtration and recrystallization from a dichloromethane/ether solvent mixture.

The spectroscopic data for compounds **1** and **2** were assessed by FT-IR and NMR spectroscopy ($^1H$, $^{31}P$). Compound **1** contained two strong $v(Mo{=}O)$ absorption bands at 941 cm$^{-1}$ and 901 cm$^{-1}$. The equivalent to this for complex **2** was shifted to 951 cm$^{-1}$ and 892 cm$^{-1}$. These absorptions are in the same range for related compounds of the form $MO_2Cl_2(OPR_3)_2$, M = Mo or W [4e], and similarly located strong absorptions were previously assigned to the symmetric and asymmetric stretching vibrations for the metal oxygen double bonds [26]. The $v(P{=}O)$ absorption bands shifts to higher frequencies at 1125 cm$^{-1}$ and 1123 cm$^{-1}$ for the compounds **1** and **2**, respectively compared to 1120 cm$^{-1}$ for the free ligand. Interestingly, complexes containing the $OPPh_2Me$ ligand revealed a shift to lower frequencies, i.e., 1171 cm$^{-1}$ in the free ligand compared to 1155–1152 cm$^{-1}$ in the Mo and W analogues [4e]. The difference in the initial shifts of the free ligands, i.e., $v(P{=}O)$ in $O{=}PPh_2CH_2OH$ at 1120 cm$^{-1}$ compared to $v(PO)$ in $O{=}PPh_2CH_3$ at 1171 cm$^{-1}$, is due to the existence of $O{=}PPh_2CH_2OH$ as

a hydrogen bonded dimer [11] which would lower the stretching frequency of the P=O bond.

The H atoms on the OH and $CH_2$ groups in the free ligand appear as broad singlets at 5.25 and 4.40 ppm, respectively. The resonance for the H atom in the OH moiety for compound **1** and **2** was observed shifted upfield greatly to 3.57 and 2.88 ppm, respectively. This increased shielding is probably due to the removal of the H-bonded interactions as the free ligand may also exist in solution as a dimer. In contrast, the resonance for the $CH_2$ group in compounds **1** and **2** shifted downfield only slightly to 4.61 and 4.81 ppm, respectively.

^{31}P NMR spectroscopy is very useful in assessing the composition and purity of compounds bearing phosphorus atoms [27]. Similar to $OPPh_2Me$ at 30 ppm [4e], the resonance for the P atom in the free ligand, i.e., $O=PPh_2CH_2OH$, was found at 31.6 ppm (relative to 85% $H_3PO_4$). This resonance for the P atom in compounds **1** and **2** shifts downfield to 43.8 and 45.6 ppm, respectively due to coordination via the O atom (bonded to the P atom) to the metal. A similar downfield shift was also observed for the related $MO_2Cl_2(OPPh_2Me)_2$, M = Mo or W compounds [4e]. The single resonance suggests that the P atoms are magnetically equivalent in these compounds at least in solution.

## 3.2. X-ray crystallographic data

Crystals were grown as described in the experimental section. Crystal data and details of structural refinement are listed in Table 1. Selected bond lengths and angles of compound **1** and **2** are given in Table 2.

### 3.2.1. Crystal structure of $MoO_2Cl_2(OPPh_2CH_2OH)_2$ (1)

An ORTEP-3 [29] drawing of **1** is shown as Fig. 2. This crystal contains a disordered benzene molecule of crystallization that was slowly evaporating out of the crystal lattice as evident by the reduction in the intensity standards to 95%. The geometry about the molybdenum atom is distorted octahedral with two Cl-atoms *trans* to each other (Cl1–Mo1–Cl2 = 166.43(3)°) and the two oxo-oxygen atoms (O1, O2 or $O_{oxo}$) *cis* to each other. The two oxygen atoms of the hydroxymethyldiphenylphosphine oxide ligands ($O_{lig}$) are thus also *cis* to each other with an O3–Mo1–O4 angle of 78.58(8)°. These four oxygen atoms are located in a distorted equatorial plane. The bond distance for Mo=$O_{oxo}$ is within the expected range of 1.66–1.76 Å [30]. The P–O bond lengths and P–O–Mo angles are also similar to that measured for other phosphine oxide ligands binding to Mo atoms [4e,4k,4m].

The molecule also contained disorder in the position of one OH group on one ligand which refined to a 50:50 ratio and P1–C11–O6 and P1–C11–O61 angles of 116.8(3)° and 110.6(4)°, see Fig. 2. There appeared to be two intramolecular H-bonds within the molecule. One of these involves the disordered O atom O61 and the terminal oxo O2 atom with a O61–O2 distance of 3.140(7) Å and an H61–O2 dis-

Table 1
Details of the structural refinement for **1** and **2**

| | 1 | 2 |
|---|---|---|
| Formula | $(C_{13}H_{13}O_2P)_2O_2Cl_2$-$Mo0.5C_6H_6$ | $(C_{13}H_{13}O_2P)_2$-$O_2Cl_2W$ |
| Formula weight | 702.3 | 751.16 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *P21/n* | *P21/c* |
| Radiation (Mo) (Å) | 0.71069 | 0.71069 |
| $a$ (Å) | 9.248(3) | 9.494(3) |
| $b$ (Å) | 15.562(4) | 14.467(2) |
| $c$ (Å) | 21.490(6) | 20.805(8) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 96.66(2) | 99.22(3) |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 3071.9(15) | 2820.6(15) |
| $Z$ | 4 | 4 |
| Reflections collected/unique [$R_{int}$] | 4664/3995 [0.0159] | 3939/3677 [0.0108] |
| Data/restraints/parameters | 3995/0/395 | 3677/0/334 |
| Completeness to theta = 22.47 (%) | 100.0 | 100.0 |
| Absorption correction | $\psi$-scan[a] | $\psi$-scan[a] |
| $d_{calc}$ (g/cm$^3$) | 1.519 | 1.769 |
| $\mu$ (mm$^{-1}$) | 0.745 | 4.437 |
| $\theta$ (°) | 1.62–22.48 | 1.72–22.47 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| $T$ (K) | 293(2) | 293(2) |
| Goodness-of-fit | 1.054 | 1.050 |
| $R_1$,[b] $wR_2$ ($I > 2\sigma(I)$)[c] | 0.0262, 0.0687[d] | 0.0204, 0.0437[e] |

[a] Ref. [28].
[b] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.
[d] $w = 1/[^2(F_o^2) + (0.0338P)^2 + 2.5648P]$, where $P = (F_o^2 + 2F_c^2)/3$.
[e] $w = 1/[^2(F_o^2) + (0.0212P)^2 + 2.6767P]$, where $P = (F_o^2 + 2F_c^2)/3$.

tance of 2.358(3) Å. This interaction may be responsible for the significantly longer bond length in Mo1–O2 of 1.764(2) Å as compared to a Mo1–O1 bond distance of 1.732(2) Å. The second intramolecular H-bond consists of the OH group on the adjacent phosphine oxide ligand and one of the terminal Cl ligands resulting in an O5–Cl2 distance of 3.157(3) Å and a H5–Cl2 distance of 2.378(1) Å, see Fig. 2. This interaction may also be responsible for the significantly longer Mo1–Cl2 distance of 2.4263(11) Å compared to the Mo1–Cl1 distance of 2.3875(11) Å. An inspection of the crystal packing does not reveal any intermolecular bonding interactions. It is possible that the presence of the benzene molecules of solvation within the crystal hinder this development as these interactions were observed in the structure of the related compound **2**, see below.

### 3.2.2. Crystal structure of $WO_2Cl_2(OPPh_2CH_2OH)_2$ (2)

An ORTEP-3 [29] representation of **2** is shown in Fig. 3. The tungsten atom is in a distorted octahedral environment in which the two chlorides are in *trans* positions and the two terminal oxygen atoms are *cis* to each other. The inner core arrangement of **2** is similar to **1** except that there is no disorder in the structure of **2** and the phosphine oxide ligand exhibits a slightly different rotational conformation.

Table 2
Selected bond length (Å) and angles (°) for **1** and **2**

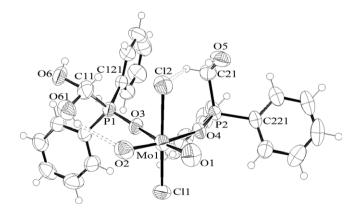| | 1 | 2 |
|---|---|---|
| M1–Cl1 | 2.3875(11) | 2.3646(12) |
| M1–Cl2 | 2.4263(11) | 2.3661(12) |
| M1–O1 | 1.732(2) | 1.698(3) |
| M1–O2 | 1.764(2) | 1.724(3) |
| M1–O3 | 2.198(2) | 2.230(3) |
| M1–O4 | 2.154(2) | 2.118(3) |
| P1–O3 | 1.505(2) | 1.503(3) |
| P1–C11 | 1.847(3) | 1.821(5) |
| P1–C111 | 1.794(3) | 1.790(5) |
| P1–C121 | 1.799(3) | 1.793(5) |
| P2–O4 | 1.508(2) | 1.503(3) |
| P2–C21 | 1.816(4) | 1.819(4) |
| P2–C211 | 1.795(3) | 1.788(4) |
| P2–C221 | 1.795(3) | 1.794(4) |
| O5–C21 | 1.411(4) | 1.418(5) |
| O6–C11 | 1.317(5) | 1.408(6) |
| O61–C11 | 1.288(7) | |
| Cl1–M1–Cl2 | 166.43(3) | 162.83(4) |
| Cl1–M1–O1 | 95.08(10) | 96.53(11) |
| Cl1–M1–O2 | 94.85(9) | 94.36(11) |
| Cl1–M1–O3 | 84.42(6) | 84.61(8) |
| Cl1–M1–O4 | 85.04(6) | 82.73(8) |
| Cl2–M1–O1 | 94.49(10) | 94.97(11) |
| Cl2–M1–O2 | 92.66(9) | 95.89(11) |
| Cl2–M1–O3 | 84.37(6) | 82.30(8) |
| Cl2–M1–O4 | 85.26(6) | 83.60(8) |
| O1–M1–O2 | 101.46(12) | 101.09(16) |
| O1–M1–O3 | 169.12(10) | 172.17(13) |
| O1–M1–O4 | 90.55(10) | 95.05(13) |
| O2–M1–O3 | 89.40(10) | 86.52(13) |
| O2–M1–O4 | 167.94(10) | 163.83(13) |
| O3–M1–O4 | 78.58(8) | 77.39(10) |
| M1–O3–P1 | 147.19(13) | 141.74(16) |
| M1–O4–P2 | 157.56(13) | 163.37(18) |
| P1–C11–O6 | 116.8(3) | 110.8(3) |
| P1–C11–O61 | 110.6(4) | |
| O61–C11–O6 | 86.6(4) | |
| P2–C21–O5 | 111.4(2) | 110.4(3) |



Fig. 3. ORTEP-3 [29] representation of **2** with selected atom numbering. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented by circles of arbitrary radii. The H-bonded interaction is illustrated by dashed lines.

The bond distances for W=O, W–Cl and W–O atoms are similar to those reported previously for related complexes [4e,4k,25,30,31].

Complex **2** exhibits one intramolecular H-bonded interaction between one OH moiety (i.e., O6) and the terminal oxo O2 with an O6–O2 distance of 2.755(5) Å and an H6–O2 distance of 1.982(3) Å, see Fig. 3. As was the case with complex **1**, this interaction also results in a significantly longer W1–O2 distance of 1.724(3) Å compared to W1–O1 of 1.698(3) Å. The absence of any H-bonded interactions with the terminal Cl atoms affords W–Cl distances of W1–Cl1 = 2.3646(12) and W1–Cl2 = 2.3661(12) Å that are not significantly different. The other hydroxy ligand is involved in an intermolecular H-bond to the O atom in the hydroxy group of an adjacent molecule that is linked up intramolecularly to the terminal oxo ligand with O5–O6′ distances of 2.788(4) Å and an H5–O6′ distance of 2.177(3) Å. This results in long parallel chains within the crystal lattice with the more hydrophobic part of the chains, i.e., the phenyl ligands on adjacent chains, oriented towards one another, see Fig. 4.

### 3.3. Application in epoxidation catalysis

Dioxotungsten compounds such as $WO_2Cl_2(OPPh_2Me)_2$, $WO_2Cl_2dppmO_2$ have been previously assessed as catalysts for the epoxidation of olefins and they have displayed high activity and selectivity [4e]. An oxo-tungsten cluster was also reported to show very good activity for olefin epoxidation using $H_2O_2$ as oxidant [6c,10e,32]. The catalytic reaction was believed to have proceeded through an oxo-peroxo-tungsten active species [33]; however, the active oxygen transfer specie has not so far been clarified [6c]. We examined the ability of compounds **1** and **2** to effect the epoxidation of cis-cyclooctene, and, in order to compare the catalytic attributes of these new dioxomolybdenum and dioxotungsten compounds with that of related



Fig. 2. ORTEP-3 [29] representation of **1** with selected atom numbering. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented by circles of arbitrary radii. H-bonded interactions are illustrated by dashed lines and both disordered OH atoms (O6 and O61) are illustrated. The benzene molecule of solvation is not included.
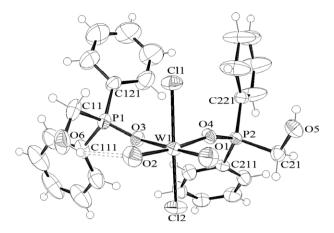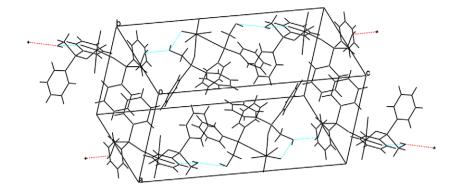
Fig. 4. Packing diagram depicting intra- and intermolecular H-bonding (dashed lines) and the orientation of the phenyl ligands on adjacent chains in **2**.

Table 3
Epoxidation of *cis*-cyclooctene with catalysts in the presence of $H_2O_2$ in ethanol solvent[a]

| Catalysts | Conversion (%)[b] | | Selectivity (%)[c] | |
|---|---|---|---|---|
| | 6 h | 24 h | 6 h | 24 h |
| $MoO_2Cl_2(OPPh_2CH_2OH)_2$ (**1**) | $36.5 \pm 0.7$ | $67.7 \pm 1.3$ | >99 | >99 |
| $WO_2Cl_2(OPPh_2CH_2OH)_2$ (**2**) | $82.0 \pm 1.4$ | $83.7 \pm 0.7$ | >99 | >99 |
| $MoO_2Cl_2(OPPh_2CH_3)_2$ | | 35[d] | Ref. [4e] | |
| $WO_2Cl_2(OPPh_2CH_3)_2$ | | 70[d] | Ref. [4e] | |
| $MoO_2Cl_2(OPPh_2CH_3)_2$ | 43[e] | | Ref. [4e] | |
| $WO_2Cl_2(OPPh_2CH_3)_2$ | 90[e] | 100[f] | Ref. [4e] | |

[a] *Experiment condition:* catalyst/*cis*-cyclooctene/$H_2O_2$ mole ratio equals 1:100:150. $T = 70$ °C. GC–MS quantitative analysis using decane as internal standard.
[b] Conversion = {1 − [remaining mole of olefin]/$\sum$[initial mole of olefin]} × 100%.
[c] Selectivity = {[mole of olefin epoxide]/$\sum$[mole of oxo products]} × 100%. All of these data are based on at least three trials.
[d] $H_2O_2$ and $CH_3CN$ as solvent.
[e] Identical experimental conditions, $H_2O_2$ in ethanol.
[f] 78 °C, 24 h.

compounds made before, the reactions were carried out using conditions identical to those utilized previously [4e].

The results for the epoxidation of *cis*-cyclooctene with the ethanol/$H_2O_2$ system and complexes **1** and **2** and previously published selected data are summarized in Table 3. It is clear from the data in Table 3 that both of the catalysts display good activity and very high selectivity to form cyclooctene oxide. Within a 6 h reaction time period, the tungsten compound **2** displayed much better conversion than the molybdenum analogue **1**, which is comparable with what was found for related compounds [4e] as listed in Table 3. This may be related to the increased stability of complex **2** under these catalytic conditions [4e]. These catalysts show better activity than their related $OPPh_2CH_3$ analogs when the solvent used was acetonitrile, Table 3. However, in ethanol, the $OPPh_2CH_3$ derived catalysts appear more functional which may be reflective of the fact that a less polar catalyst may interact better with the cyclooctene substrate as suggested in the Sharpless et al. proposed mechanism for epoxidation [23].

Extending the time of reaction to 24 h revealed that while **2** did not complete further epoxidation of remaining substrate, **1** still displayed activity and almost achieved double the conversion. Interestingly, the transformation with both catalysts was very selective as cyclooctene oxide is the only product detected. ^{31}P NMR measurements after 24 h of reaction indicate the presence of the unattached phosphine oxide ligand suggesting that the starting catalytic material had decomposed in both cases.

## 4. Conclusion

Two new molybdenum and tungsten complexes containing hydrophilic phosphine oxide ligands have been synthesized and characterized using FT-IR and NMR spectroscopic methods. Their structures were assessed by single crystal X-ray diffraction methods and both displayed intramolecular H-bonded interactions. The tungsten compound also contained intermolecular H-bonds resulting in long polymeric stacked chains. The catalytic property of these compounds for the epoxidation of *cis*-cyclooctene was assessed using $H_2O_2$ as the source of oxygen. Both of them showed very high selectivity for the cyclooctene oxide with the tungsten compound **2** displaying an initial higher catalytic activity than the molybdenum complex **1**. The presence of the more polar $OPPh_2CH_2OH$ ligand did not confer any advantage (over related complexes containing $OPPh_2CH_3$) in the epoxidation reaction under the conditions of our experiment with ethanol as the solvent. Reactions with **1** and **2** using more polar substrates are envisaged.

## 5. Supplementary material

CCDC 660951 and 660952 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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