

# Preparation and structure of the 17-electron ( $\eta^5\text{-C}_5\text{R}_5$ )Mo(OH)<sub>2</sub>(dppe) (R = Me, Et) organometallic compounds containing two *gem*-terminal hydroxide ligands

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Dedicated to Al Cotton on the occasion of his 70th birthday for his outstanding contributions to chemistry.

## Abstract

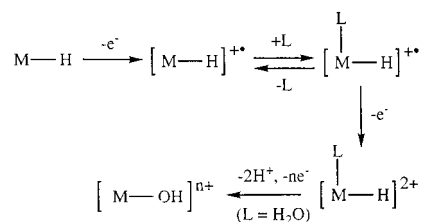
Oxidation of ( $\eta^5\text{-C}_5\text{R}_5$ )MoH<sub>3</sub>(dppe) (R = Me, Et) by Cp<sub>2</sub>Fe<sup>+</sup> in wet THF leads to the formation of the corresponding ( $\eta^5\text{-C}_5\text{R}_5$ )Mo(OH)<sub>2</sub>(dppe). These compounds show a low-potential reversible oxidation wave. The structure of the C<sub>5</sub>Et<sub>5</sub> complex has been confirmed by X-ray diffraction methods: triclinic; space group  $P\bar{1}$ ;  $a = 11.030(1)$ ;  $b = 12.533(1)$ ;  $c = 16.241(1)$  Å;  $\alpha = 68.585(7)$ ;  $\beta = 75.197(5)$ ;  $\gamma = 83.991(7)^\circ$ ;  $V = 2020.6(3)$  Å<sup>3</sup>;  $Z = 2$ ;  $D_{\text{calc}} = 1.324$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.441$  mm<sup>-1</sup>;  $R_1 = 0.0325$ ;  $wR_2 = 0.0875$  for 415 parameters and 6823 independent reflections [ $R_{\text{int}} = 0.0177$ ] with  $I = 2\sigma(I)$ . The molecule shows a four-legged piano-stool geometry with two terminal OH ligands in a relative *trans* configuration. The complex EPR properties indicate that an equilibrium mixture of various species is present in solution. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Half-sandwich complexes; Hydride complexes; Hydroxide complexes; Molybdenum; Oxidation

## 1. Introduction

There has been wide interest in organometallic hydroxide complexes, because of their role in catalysis and in materials chemistry [1–3]. In a recent review, it has been pointed out that these complexes often form adventitiously and that the understanding of these formation reactions is incomplete [3]. Recently, we have reported on a new method that leads to the formation of hydroxide complexes, namely the oxidation of hydride complexes in a wet, poorly coordinating organic solvent (see Scheme 1) [4]. One-electron oxidation renders the hydride species more acidic and susceptible to both deprotonation by an external base [5] and coordination by a two-electron donor ligand. Electron-donating and sterically protecting ligands, however, kinetically disfavor the deprotonation process and further

oxidation may occur, generating a doubly oxidized, even more acidic hydride complex. Under suitable conditions, water can act as a ligand (L), being the source of the hydroxide ligand for the metal center, and also as a Brønsted base [5,6]. Additional external bases, however, may also be used. In this process, both the hydride and one of the water H atoms are lost as protons. This method has allowed the preparation of [CpMo(OH)(PMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup> from CpMoH(PMe<sub>3</sub>)<sub>3</sub> in wet THF [4,7], while the use of dry MeCN as solvent leads



Scheme 1.

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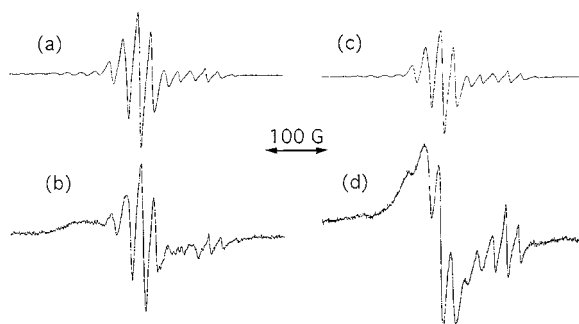


Fig. 1. EPR spectra in pentane solutions of compound **1** at room temperature (a) and at  $-40^{\circ}\text{C}$  (b), and of compound **2** at room temperature (c) and at  $-68^{\circ}\text{C}$  (d).

to the stable doubly oxidized complex  $[\text{CpMoH}(\text{MeCN})(\text{PMe}_3)]^{2+}$  [8].

In the above example, only one open coordination site is made available by the two-electron oxidation process. In parallel studies, we have recently discovered that oxidation of the trihydride complex  $\text{Cp}^*\text{MoH}_3(\text{dppe})$  induces the reductive elimination of  $\text{H}_2$  to produce the solvated complexes  $[\text{Cp}^*\text{MoH}(\text{dppe})(\text{S})]^+$  [9,10]. This process, therefore, makes available two potential coordination sites to the intervention of water as a ligand, with the possibility of obtaining a *gem*-terminal bis(hydroxo) or an oxo complex. In this contribution, we describe the extension of our oxidation studies in wet THF to the  $(\eta\text{-C}_5\text{R}_5)\text{MoH}_3(\text{dppe})$  ( $\text{R} = \text{Me}, \text{Et}$ ) systems, which indeed proves the validity of this concept.

## 2. Experimental

### 2.1. General procedures

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of dinitrogen or argon by the use of Schlenk-line or glove-box techniques. Solvents were dried by conventional methods and distilled under dinitrogen prior to use.  $\text{NEt}_3$  was distilled under dinitrogen prior to use. Deuterated solvents were dried over molecular sieves and degassed by three freeze–pump–thaw cycles prior to use. EPR measurements were carried out at the X-band microwave frequency on a Bruker ESP300 spectrometer. The spectrometer frequency was calibrated with DPPH ( $g = 2.0037$ ). Cyclic voltammograms were carried out at  $20^{\circ}\text{C}$  with an EG&G 283 analogue potentiostat connected to a Macintosh computer via a MacLab analogue–digital converter. The electrochemical cell was fitted with a  $\text{Ag}|\text{AgCl}$  reference electrode, a platinum disk working electrode and a Pt wire counterelectrode.  $\text{Bu}_4\text{NPF}_6$  (ca. 0.1 M) was used as supporting electrolyte. All potentials are reported relative to the fer-

rocene standard, which was added to each solution and measured at the end of the experiments. The elemental analyses were carried out by the analytical service of the Laboratoire de Synthèse et d'Electrosynthèse Organométalliques with a Fisons Instruments EA1108 analyzer. Compound  $\text{Cp}^*\text{MoH}_3(\text{dppe})$  was prepared as described elsewhere [10], while compound  $(\text{C}_5\text{Et}_5)\text{MoH}_3(\text{dppe})$  was prepared by an extension of this procedure from  $(\text{C}_5\text{Et}_5)\text{MoCl}_4$ , dppe and  $\text{LiAlH}_4$  [11]. In turn,  $(\text{C}_5\text{Et}_5)\text{MoCl}_4$  was obtained from  $(\text{C}_5\text{Et}_5)\text{Mo}(\text{CO})_3\text{CH}_3$  [12] and  $\text{PCl}_5$  by the same procedure reported for the  $\text{Cp}^*$  analogue [13].

### 2.2. Preparation of compounds $(\eta\text{-C}_5\text{R}_5)\text{Mo}(\text{OH})_2(\text{dppe})$ ( $\text{R} = \text{Me}, \mathbf{1}; \text{Et}, \mathbf{2}$ )

#### 2.2.1. $\text{R} = \text{Et}$

A solution of  $(\text{C}_5\text{Et}_5)\text{MoH}_3(\text{dppe})$  (0.420 g, 0.59 mmol) in 10 ml of THF at  $-78^{\circ}\text{C}$  was transferred to a suspension of  $\text{Cp}_2\text{FeBF}_4$  (0.246 g, 0.885 mmol). The violet solution exhibited a triplet of quartets in the EPR spectrum ( $g = 2.016$ ,  $a_{\text{P}}(t) = 28.9 \text{ G}$ ,  $a_{\text{H}}(q) = 11.6 \text{ G}$ ) attributable to  $[(\text{C}_5\text{Et}_5)\text{MoH}_3(\text{dppe})]^+$  [11]. This solution was stirred at room temperature (r.t.) for ca. 15 min. The solvent was evaporated in vacuo and the residue was washed with pentane ( $5 \times 10 \text{ ml}$ ) in order to eliminate the  $\text{Cp}_2\text{Fe}$ . The residue was redissolved in 20 ml of THF and  $\text{NEt}_3$  (246  $\mu\text{l}$ , 1.77 mmol) was added. The brown–yellow solution was stirred for 90 min, followed by evaporation to dryness. The residue was extracted with pentane (ca. 150 ml) and the resulting suspension was filtered through Celite. The solution was concentrated in vacuo to ca. 10 ml and placed at  $-12^{\circ}\text{C}$  overnight, resulting in the formation of **2** as a yellow–green microcrystalline solid: yield: 0.239 g, 55%. The sample used for the elemental analysis had been thoroughly dried under vacuum. Anal. Calc. for  $\text{C}_{41}\text{H}_{51}\text{MoO}_2\text{P}_2$ : C, 67.11; H, 7.01; Found: C, 67.43, H, 7.15. Single crystals were obtained by slow evaporation (12 h) at r.t. of a pentane solution under argon and contained an interstitial pentane molecule (see below). The product is stable as a solid in air for days. It is very soluble in all common organic solvents and stable in MeCN or MeCN–water mixtures. The addition of a large excess of water only induces the reprecipitation of **2**. The compound is also stable in  $\text{CH}_2\text{Cl}_2$  under an inert atmosphere for a short period of time but decomposes rapidly in  $\text{CHCl}_3$  to afford an EPR silent solution. EPR (THF, r.t.):  $g = 1.997$  (apparent quintet, with Mo satellites,  $a_{\text{P}} = 19.7 \text{ G}$ ,  $a_{\text{Mo}} = 44.8 \text{ G}$ , see Fig. 1). Cyclic voltammetry (THF, r.t.): reversible oxidation at  $E_{1/2} = -0.64 \text{ V}$ .

Compound **2** was also obtained by an alternative procedure where an excess of water was used in place of triethylamine.  $\text{Cp}_2\text{FeBF}_4$  (0.012 g, 0.043 mmol) was

added to a stirred solution of  $(C_5Et_5)MoH_3(dppe)$  (0.020 g, 0.029 mmol) in 4 ml of THF at  $-80^\circ C$ . The

Table 1  
Crystal data and refinement parameters for  $(\eta-C_5Et_5)Mo(OH)_2(dppe)$

Formula	$C_{41}H_{51}O_2P_2MoC_5H_{12}$
<i>M</i>	805.84
<i>T</i> (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	11.030(1)
<i>b</i> (Å)	12.533(1)
<i>c</i> (Å)	16.241(1)
$\alpha$ (°)	68.585(7)
$\beta$ (°)	75.197(5)
$\gamma$ (°)	83.991(7)
<i>V</i> (Å <sup>3</sup> )	2020.6(3)
<i>Z</i>	2
<i>F</i> (000)	854
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.324
$\lambda$ (Å)	0.71073
$\mu$ (mm <sup>-1</sup> )	0.441
Crystal size (mm <sup>3</sup> )	0.3 × 0.2 × 0.2
$\sin(\theta)/\lambda$ max (Å <sup>-1</sup> )	0.62
<i>Index ranges</i>	
<i>H</i>	–13, 0
<i>K</i>	–15, 15
<i>L</i>	–20, 19
Decay (%)	0
Absorption correction	psi scan
Solvent correction	PLATON (see text)
RC = reflections collected	8582
IRC = independent RC	8135 [ <i>R</i> <sub>int</sub> = 0.0177]
IRCGT = IRC and [ <i>I</i> > 2σ( <i>I</i> )]	6823
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	8135/0/415
<i>R</i> for IRCGT	<i>R</i> <sub>1</sub> = 0.0325 <sup>a</sup> , <i>wR</i> <sub>2</sub> = 0.0875 <sup>b</sup>
<i>R</i> for IRC	<i>R</i> <sub>1</sub> = 0.0464 <sup>a</sup> , <i>wR</i> <sub>2</sub> = 0.0914 <sup>b</sup>
Goodness-of-fit <sup>c</sup>	1.037
Largest difference peak and hole (e Å <sup>-3</sup> )	0.624 and –0.364

$$^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2} \quad \text{where} \quad w = 1 / [\sigma^2(F_o^2) + (0.0512 * P)^2 + 0.75 * P] \quad \text{where} \quad P = (\max(F_o^2, 0) + 2 * F_c^2) / 3$$

$$^c \text{Goodness-of-fit} = [\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_c)]^{1/2}$$

Table 2  
Selected bond lengths [Å] and angles (°) for  $(\eta-C_5Et_5)Mo(OH)_2(dppe)^{at}$

<i>Bond lengths</i>			
Mo–CNT	2.020(2)	Mo–O(1)	1.984(2)
Mo–P(1)	2.4954(6)	Mo–O(2)	2.0111(14)
Mo–P(2)	2.4951(5)		
<i>Bond angles</i>			
O(1)–Mo–O(2)	148.28(6)	O(2)–Mo–P(2)	80.76(4)
O(1)–Mo–P(1)	79.56(5)	O(2)–Mo–CNT	105.6(2)
O(1)–Mo–P(2)	77.26(5)	P(1)–Mo–P(2)	80.05(2)
O(1)–Mo–CNT	106.0(2)	P(1)–Mo–CNT	142.9(3)
O(2)–Mo–P(1)	74.31(4)	P(2)–Mo–CNT	137.0(2)

<sup>a</sup> CNT is the centroid of the cyclopentadienyl ring.

solution showed the spectrum corresponding to  $[(C_5Et_5)MoH_3(dppe)]BF_4$ . This solution was stirred for 15 min at r.t., followed by the addition of distilled and deoxygenated water (10 μl, 0.55 mmol) and stirring was continued for 45 min. The EPR properties of the resulting yellow–brown solution matched those described above for compound **2**.

### 2.2.2. *R* = *Me*

By an identical procedure to that described above for *R* = Et, compound **1** (71 mg, 30% yield) was prepared from  $Cp^*MoH_3(dppe)$  (0.23 g; 0.36 mmol) and  $Cp_2FePF_6$  (0.12 g, 0.36 mmol). EPR ( $C_6H_6$ , r.t.): *g* = 1.999 (apparent quintet, with Mo satellites, *a*<sub>P</sub> = 21.0 G, *a*<sub>Mo</sub> = 38.0 G, see Fig. 1). Cyclic voltammetry (THF, room temperature): reversible oxidation at *E*<sub>1/2</sub> = –0.72 V.

### 2.3. X-ray crystallography for compound $(\eta-C_5Et_5)Mo(OH)_2(dppe)$ (**2**)

Crystals for the X-ray structure analysis were grown by a slow evaporation at 0°C from a pentane solution. A green crystal (0.3 × 0.2 × 0.2 mm<sup>3</sup>) was mounted in the presence of solvent vapours in a capillary on an Enraf–Nonius CAD4 diffractometer. A total of 8563 reflections (8122 unique) were collected at r.t. up to  $\sin(\theta)/\lambda = 0.62 \text{ \AA}^{-1}$ . The data were corrected for Lorentz and polarization effects and for absorption (psi-scan method) [14]. No decay was observed. The structure was solved via a Patterson search program [15] and refined (space group  $P\bar{1}$ ) with full-matrix least-squares methods [15] based on  $|F^2|$ . All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the complex, except for those of the hydroxyl groups, were included in their calculated positions and refined with a riding model. Any attempt to locate the hydrogen atoms of the hydroxyl groups failed. At the end of this refinement the agreement indices were *wR*<sub>2</sub> = 0.145 for all data and *R*<sub>1</sub> = 0.0394 for intensities with *I* = 2σ(*I*). The final difference electron density map exhibited peaks near the oxygen atoms (ca. 0.6 e Å<sup>-3</sup>) but also in a region far from the model (ca. 1 e Å<sup>-3</sup>). A PLATON [14] run indicated a potential solvent region of 280 Å<sup>3</sup>. The electron difference density map was not sufficiently clear to successfully model a badly disordered solvent molecule and the BYPASS procedure, implemented in the PLATON program [16] was used to handle this problem. In this procedure the contribution of the solvent (one molecule of pentane) electron density is subtracted to the structure factors. The refinement with the solvent-corrected data set led to the final agreement indices: *wR*<sub>2</sub> = 0.0914 for all data, *R*<sub>1</sub> = 0.0325 for 6823 data with *I* = 2σ(*I*) and GoF = 1.037. Crystal data are reported in Table 1, while selected bond distances and angles are listed in Table 2.

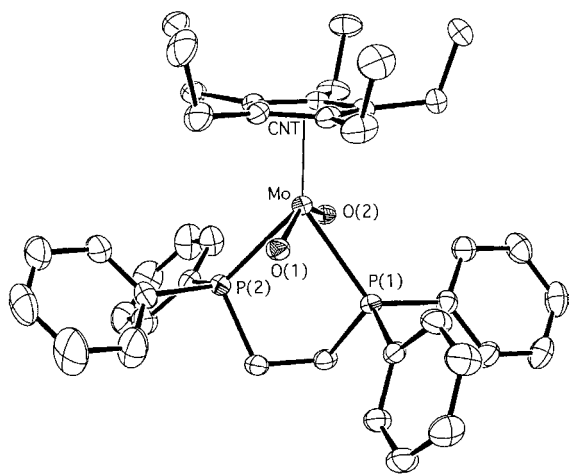


Fig. 2. An ORTEP [33] view of compound **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

### 3. Results and discussion

We have recently reported [10] that the oxidation of compound  $\text{Cp}^*\text{MoH}_3(\text{dppe})$  in dry THF,  $\text{CH}_2\text{Cl}_2$  or MeCN affords the one-electron oxidation product,  $[\text{Cp}^*\text{MoH}_3(\text{dppe})]^+$ , which is characterized by a triplet of quartets signal in the EPR spectrum. This coupling pattern is due to two equivalent phosphorus donors and three rapidly exchanging hydride ligands. This paramagnetic trihydride complex decomposes by  $\text{H}_2$  reductive elimination in the first two solvents and by a combination of proton transfer and disproportionation mechanisms in the last one [10]. We now report that, when the oxidation is carried out in wet THF, the solution evolves to a product which is characterized by an EPR signal having the apparent shape of a quintet (Fig. 1). Work-up of the solution affords a pentane-soluble fraction from which the bis-hydroxo product  $\text{Cp}^*\text{Mo}(\text{OH})_2(\text{dppe})$ , **1**, is recovered by crystallization from pentane at low temperature. The product was initially obtained from procedures carried out in 'dry' THF, the hydroxo ligands presumably originating from small amounts of adventitious water which also acts as a deprotonating base (see Section 1) [17]. We find, however, that the use of  $\text{NEt}_3$  as an additional external base as described in Section 2 affords more satisfactory results. The mechanism of formation of **1** must involve a number of electron and proton transfer and water coordination processes. Any attempt to analyze this mechanism in greater detail would be wildly speculative. The product of the first one-electron transfer,  $[\text{Cp}^*\text{MoH}_3(\text{dppe})]^+$ , decomposes by  $\text{H}_2$  reductive elimination in dry solvents, but the presence of water may well trigger alternative reaction pathways.

In spite of several attempts, we were not able to grow single crystals of compound **1**. We have therefore devel-

oped the analogous  $\text{C}_5\text{Et}_5$  derivative. Oxidation of compound  $(\eta\text{-C}_5\text{Et}_5)\text{MoH}_3(\text{dppe})$  in dry THF,  $\text{CH}_2\text{Cl}_2$ , or MeCN follows the same pattern already described for the  $\text{Cp}^*$  analogue. The EPR spectrum of  $[(\eta\text{-C}_5\text{Et}_5)\text{MoH}_3(\text{dppe})]^+$  shows a triplet of quartets at  $g = 2.016$ ,  $a_{\text{P}}(t) = 28.9$  G,  $a_{\text{H}}(q) = 11.6$  G, and thus compares very closely to the spectrum of the  $\text{Cp}^*$  analogue [10]. The ferrocenium oxidation of  $(\eta\text{-C}_5\text{Et}_5)\text{MoH}_3(\text{dppe})$  in wet THF parallels the pattern described above for the  $\text{Cp}^*$  species, affording again an apparent quintet resonance in the EPR spectrum (Fig. 1). By an analogous work-up procedure, compound  $(\eta\text{-C}_5\text{Et}_5)\text{Mo}(\text{OH})_2(\text{dppe})$ , **2**, was isolated in 55% yields. Thus, the oxidation of the  $\text{C}_5\text{Me}_5$  and  $\text{C}_5\text{Et}_5$  parent trihydride species is identical in all respects. However, the  $\text{C}_5\text{Et}_5$  product **2** readily afforded single crystals which were suitable for an X-ray investigation.

The structure of compound **2** exhibits individual molecules of the bis-hydroxo complex (see Fig. 2) in general positions without any intermolecular hydrogen bonding interactions (shortest  $\text{O}\cdots\text{O}$  separation = 5.073 Å). The absence of these interactions may be attributed to steric encumbrance. A space-filling model shows that the hydroxide ligands are sterically protected by a shield of the dppe phenyl groups and the  $\text{C}_5\text{Et}_5$  ligand. The conformation adopted by the  $\text{C}_5\text{Et}_5$  ligand has all five substituents bent toward the same side of the ring and away from the metal. According to the Cambridge Crystallographic Database, this ligand has only been previously investigated in the decaethylferrocenium cation (with two different counterions, namely the 7,7',8,8'-tetracyano-*p*-quinodimethanide at two different temperatures [18,19], and the 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyano-*p*-quinodimethanide [20]). In all cases, the same conformation of the  $\text{C}_5\text{Et}_5$  ligand was observed.

The four-legged piano-stool geometry around the central metal atom is characteristic of the wide class of 17-electron half-sandwich Mo(III) derivatives [21]. In particular, the *trans* relative arrangement of the OH ligands and the phosphorus donors is identical with that observed for the related complex  $\text{Cp}^*\text{MoCl}_2(\text{dppe})$  [22]. The metric parameters of compound **2** (distances and angles) are indeed quite close to those of the  $\text{Cp}^*$ -dichloride analogue, confirming the metal oxidation state assignment as a bis(hydroxo) derivative, even though the H atoms on the hydroxide ligands could not be located from the X-ray diffraction data. In terms of bond distances, the Mo–CNT separation (CNT =  $\text{C}_5\text{R}_5$  ring centroid) is 2.020(2) Å for **2** and 2.046(3) Å for  $\text{Cp}^*\text{MoCl}_2(\text{dppe})$ , while the average Mo–P distance is 2.4952(6) for **2** and 2.499(3) for the dichloride complex. In terms of bond angles, the CNT–Mo–X angles also show a remarkable similarity: X = P, 142.9(3) and 137.0(2)° for **2**, 140.1(1) and 139.3(1)° for the dichloride complex; X = O/Cl, 106.0(2) and 105.6(2)° for **2**,

107.2(1) and 104.9(1)° for the dichloride complex. As previously shown [23], these angular parameters are quite sensitive to the metal electronic configuration. The identity of the hydroxide ligands is further ascertained by the Mo–O distances (average 1.998(13) Å) which favorably compare with that of the previously reported [CpMo(OH)(PMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup> (2.080(3) Å) [4]. A related distance in a terminal Mo(IV)–OH organometallic complex is 2.050(5) Å for complex [Cp<sub>2</sub>Mo(NH<sub>2</sub>Me)(OH)]PF<sub>6</sub> [24], while Mo–oxo distances are much shorter, for instance 1.674(13) Å in [CpMoO(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> or 1.710(3) Å for [CH<sub>3</sub>C(CH<sub>2</sub>-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>MoO]<sup>+</sup> [4,25].

No O–H stretching vibration could be identified in the IR spectrum, presumably because these are masked by the stronger aromatic C–H stretching bands. The cyclic voltammetric studies show a facile and reversible one-electron oxidation process ( $E_{1/2} = -0.72$  V for **1** and  $-0.64$  V for **2**). A comparison of these values shows similar electron-donating properties for C<sub>5</sub>Et<sub>5</sub> and C<sub>5</sub>Me<sub>5</sub>. Most half-sandwich, 17-electron Mo(III) complexes undergo a reversible one-electron oxidation process, for instance at  $E_{1/2} = -0.33$ ,  $-0.26$  and  $-0.20$  V for CpMoX<sub>2</sub>(dppe) (X = Cl, Br, and I, respectively) [26], and at  $E_{1/2} = -0.58$  V for Cp\*MoCl<sub>2</sub>(dppe) [27]. The low  $E_{1/2}$  values for **1** and **2**, relative to the dihalide analogues, may seem unusual because the higher electronegativity of oxygen would be expected to lead to a greater effective positive charge on the metal center and consequently to higher oxidation potentials. However, as previously discussed [26], the HOMO for this system has a relatively strong Mo–X π antibonding component. Thus, a stronger π donor such as the hydroxide will result in a higher HOMO energy, compensating for the energetically stabilizing σ effect. Furthermore, the  $E_{1/2}$  value also reflect the stabilization of the Mo(IV) oxidation product, which is greater for the more strongly π-donating OH ligand.

The deceiving EPR spectra deserve a brief discussion, although we cannot offer an unambiguous rationalization. Both compounds **1** and **2** show a pattern which resembles a binomial quintet. This pattern could be accounted for by accidental degeneracy of the hyperfine coupling to the two equivalent P nuclei and the two equivalent hydroxo H nuclei. In order to probe for this possibility, an H/D exchange experiment with D<sub>2</sub>O was attempted. The addition of excess D<sub>2</sub>O to a THF solution of **2** did not affect the shape nor the intensity of the EPR spectrum over 30 min, until addition of a larger excess induced the reprecipitation of the compound. We cannot rule out, however, that H/D exchange is too slow under our conditions. The observed patterns may also result from the overlap of different resonances due to isomers of the compounds. In this respect, we note that the presence of different isomers in solution has been established for Cp\*MoCl<sub>2</sub>(dppe)

[22] and CpMoCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub> [28], while the closely related complexes CpMoBr<sub>2</sub>(dppe) and Cp\*MoCl<sub>2</sub>(dppe) adopt *cis* and *trans* structures in the solid state, respectively [22,26]. A closer look at the room-temperature spectra of the two complexes (Fig. 1(a) and (c)), reveals that the satellites on the right-hand side of the main resonance have a greater intensity relative to those on the left hand side. This was reproducibly observed on recrystallized samples of both compounds. Cooling the samples (Fig. 1(b) and (d)) permits the right-hand side features to be distinguished more clearly as new signals with the apparent shape of binomial triplets ( $g = 1.948$ ,  $a_p = 18.7$  G for **1**;  $g = 1.943$ ,  $a_p = 18.8$  G for **2**). The low-temperature spectra also show the appearance of yet another broad signal, which is located to the left of the main ‘quintet’ signal. This is more evident for compound **1** (Fig. 1(b)) but can also be noticed for compound **2** (Fig. 1(d)). All these temperature-dependent spectral changes are fully reversible, consistent with reversible equilibria between different species. It is to be noticed that similar temperature-dependent spectral characteristics were previously observed for Cp\*MoCl<sub>2</sub>(dppe) [22], whose solid-state structure is related to that described here for **2**. The EPR properties of compounds **1** and **2** may also be complicated by solution equilibria between a bis(hydroxo) form and an oxo form. In fact, bis(hydroxo) compounds are often unstable species with respect to loss of water [29,30]. The room-temperature spectrum of **2** obtained in the presence of a large excess of D<sub>2</sub>O shows a slight increase of the triplet resonance at  $g = 1.943$ , but this change is not sufficiently pronounced to be considered significant.

In conclusion, we have extended a new method for obtaining organometallic hydroxo complexes, which involves the oxidation of hydride precursor complexes in wet THF, to the formation of geminal bis(hydroxo) derivatives. It is to be remarked that the complexes described here join a very limited family of terminal *gem*-M(OH)<sub>2</sub> compounds. Cp\*W(OH)<sub>2</sub>Cl<sub>2</sub> [31] seems to constitute the only precedent for organometallic derivatives of the Group 6 metals. The only other structurally characterized organometallic terminal *gem*-bis(hydroxo) complex appears to be Cp\*Zr(OH)<sub>2</sub> [32].

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 132464. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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