ELSEVIER

Improved syntheses of $[Cp_2^*Mo_2O_5]$ and $[Cp_2^*W_2O_5]$: Structural characterization of $Na[Cp^*MoO_3] \cdot 5H_2O$ and $[Cp_2^*W_2O_5]$

Chiara Dinoi [a], Gülnur Taban [b], Pelin Sözen [b], Funda Demirhan [b],
Jean-Claude Daran [a], Rinaldo Poli [a,*]

[a] Laboratoire de Chimie de Coordination, UPR CNRS 8241 liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 Route de Narbonne, 31077 Toulouse Cedex, France
[b] Celal Bayar University, Faculty of Sciences & Liberal Arts, Department of Chemistry, 45030 Muradiye-Manisa, Turkey

Abstract

Use of aqueous conditions and the ROOH (R = tBu or H) compounds as oxidizing agents affords a simple two-step, one-pot synthetic procedure leading to $[Cp_2^*M_2O_5]$ (M = Mo, W) from $[M(CO)_6]$ selectively and in high yields. The hexacarbonyl compounds are converted to $Na[Cp^*M(CO)_3]$ in refluxing THF, then the mixture is diluted with water (W) or aqueous NaOH (Mo) and directly treated with 6 equiv. of ROOH. Acidification of an aqueous solution of the $Na[Cp^*MO_3]$ product affords spectroscopically pure $[Cp_2^*M_2O_5]$ in high isolated yields (global yields from $[M(CO)_6]$, for R = tBu: Mo, 91%; W, 87%). The X-ray structures of $Na[Cp^*MoO_3] \cdot 5H_2O$ and $[Cp_2^*W_2O_5]$ are also reported.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Molybdenum; Tungsten; Aqueous organometallic chemistry; Oxo ligands; Pentamethylcyclopentadienyl ligands

1. Introduction

High oxidation state organometallic compounds have found useful applications in a variety of catalytic processes [1,2], mostly related but not limited to oxidations processes [3]. In particular, the catalytic activity of organometallic oxo molybdenum compounds in olefin epoxidation [4] has recently attracted renewed interest [5–12]. Together with other derivatives, compound $[Cp_2^*Mo_2O_5]$ was found an excellent catalytic precursor for the epoxidation of cyclooctene by tBuOOH in CHCl₃, even in the presence of water [12]. To the best of our knowledge, the analogous $[Cp_2^*W_2O_5]$ derivative has not been tested as an oxidation catalyst, although high oxidation state tungsten derivatives are often found to possess comparable or greater catalytic

activity than the molybdenum analogues [13]. The synthesis of these compounds, however, suffers from time investment and/or moderate global yields.

Compound $[Cp_2^*Mo_2O_5]$ was first obtained in 40% yields by aerial oxidation of $Cp^*Mo(CO)_2(NO)$, a precursor that must itself be prepared from commercially available starting materials [14]. Similar considerations apply to subsequently reported syntheses, starting from $[Cp^*Mo(CO)_2]_2$ (69% yields) [15,16], $[\{Cp^*Mo(CO)_2(OMe)\}_n]$ (7.5% yields) [17], and $[Cp^*MoBr(CH_3)(NO)]_2$ (unspecified yields) [18], again by aerial oxidation. The analogous aerial oxidation of $[Cp^*W(CO)_2]_2$ afforded $[Cp_2^*W_2O_5]$ in 14% yield [15]. Using a different strategy, basic (NaOH) hydrolysis of Cp^*MoCl_4 in air yields the product in two-steps via the Cp^*MoO_2Cl intermediate, the reported yield of each step being 78% and 82% [19]. The alternative hydrolysis using tBuNH₂ yields the same final product in two-steps via the $[t$BuNH₃][Cp^*MoO_3]$ intermediate, with yields of 68% and 58%, respectively (the tungsten analogue is similarly

* Corresponding author. Tel.: +33 561333173; fax: +33 561553003.
E-mail address: Rinaldo.Poli@lcc-toulouse.fr (R. Poli).

prepared via the [$tBuNH_3$][Cp^*WO_3] intermediate in 80% and 67% yields for the two-steps) [19]. An alternative hydrolytic approach by protonolysis of [$Cp^*M(NtBu)_2Cl$] (M = Mo, W) with aqueous HCl was reported by Sundermeyer [20]. The synthesis affords the final pentaoxo complex in high yield (98% yield for Mo or 81% yield for W) but requires again a preliminary synthetic effort to access the starting material (two-steps from commercially available starting materials) and the sacrificial use of $tBuNCO$.

Our current exploration of Cp^*Mo^{VI} aqueous chemistry [21–25] has required the frequent preparation of compound [$Cp_2^*Mo_2O_5$] in substantial amounts. Until now, we have opted for the hydrolytic approach via the [Cp^*MoCl_4] compound, which we have recently improved [26]. The synthesis of this starting material is high yield, but requires three steps from commercially available [$Mo(CO)_6$] [27,28] with isolation of the $Cp^*Mo(CO)_3(CH_3)$ intermediate. Furthermore, the oxidative hydrolysis step is delicate since the rates of oxidation and hydrolysis are similar; a complete hydrolysis before oxidation yields the dinuclear [$Cp_2^*Mo_2O_4$] by-product, which is relatively resistant to further oxidation and lowers the final yield [26]. This synthesis is summarized in Scheme 1. The considerable time investment required for this synthesis, in addition to the need of sacrificial reagents (MeI and PCl_5 or $PhICl_2$) has encouraged us to find a more direct and simpler preparative method.

In this contribution, we report a substantial improvement of the synthetic method, affording both [$Cp_2^*M_2O_5$] (M = Mo, W) compounds in excellent yields from the corresponding [$M(CO)_6$] starting material, in three simple steps without isolation of any intermediate and using inexpensive oxidants ($tBuOOH$ or H_2O_2). We also describe the molecular structures of Na[Cp^*MoO_3]·$5H_2O$ and [$Cp_2^*W_2O_5$].
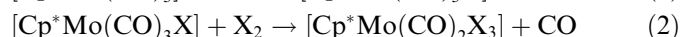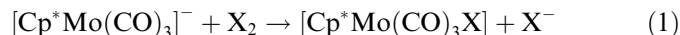
2. Results

2.1. Syntheses

We wondered whether compound Na[$Cp^*Mo(CO)_3$] could be transformed directly into Na[Cp^*MoO_3], therefore by-passing three steps and the isolation of two intermediates with respect to our traditional synthetic scheme outlined in Scheme 1. In addition, the Na salt of the trioxo-

molybdate(VI) complex, as obtained from the hydrolytic procedure from [Cp^*MoCl_4], can be converted to the final product by direct acidification of an aqueous solution without isolation. It is also possible to envisage a direct oxidation of the first intermediate, the sodium salt of the tricarbonylmolybdate(0) complex, without isolation. Therefore, the potential exists for a simple one-pot synthesis.

The new method that we report in this contribution has been inspired by the following considerations, partly extrapolated from previously published observations. The Cp^* tricarbonyl anion may be oxidized monoelectronically by $Fe_2(SO_4)_3$ (1 equiv.) to produce [$Cp_2^*Mo_2(CO)_6$] [29,30], and by $FeCl_3$ (2 equiv.) to afford the corresponding [$Cp^*Mo(CO)_3Cl$] [30]. Although a synthesis of the latter compound from [$Cp^*Mo(CO)_3$]⁻ and Cl_2 does not seem to have been described, the corresponding bromo compound has been prepared from [$Cp^*Mo(CO)_3$]⁻ and Br_2 (Eq. (1), X = Br) [31]. The Mo^{IV} compounds [$Cp^*Mo(CO)_2X_3$] (X = Cl, Br) have been prepared from [$Cp_2^*Mo_2(CO)_6$] and 3 equiv. of X_2 [32,33]. Thus, the stoichiometry of Eq. (2) can be deduced, as well as a possible direct synthesis of [$Cp^*Mo(CO)_2X_3$] from [$Cp^*Mo(CO)_3$]⁻. Further oxidation yields [Cp^*MoX_4] (Eq. (3)) [28]. An analogous process has also been described for the Cp system: stepwise generation of [$CpMoCl_4$] from [$Cp_2Mo_2(CO)_6$] via [$CpMo(CO)_3Cl$] and [$CpMo(CO)_2Cl_3$] [34].

$$[Cp^*Mo(CO)_3]^- + X_2 \rightarrow [Cp^*Mo(CO)_3X] + X^- \quad (1)$$

$$[Cp^*Mo(CO)_3X] + X_2 \rightarrow [Cp^*Mo(CO)_2X_3] + CO \quad (2)$$

$$[Cp^*Mo(CO)_2X_3]_2 + X_2 \rightarrow 2[Cp^*MoX_4] + 2CO \quad (3)$$
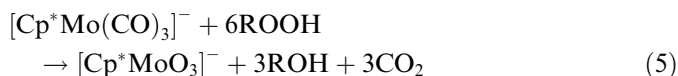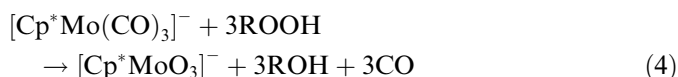
The halogen nature determines the maximum allowed oxidation state of the [Cp^*MoX_n] system ($n = 4$ for X = Cl and Br; 3 for X = I in the anionic complex [Cp^*MoI_4]⁻) [33]. The corresponding fluoride system has not been investigated for molybdenum, but Cp^*WF_5 (prepared by aerial oxidation from Cp^*WF_4) is a stable compound [35], whereas the highest oxidation state attainable for X = Cl appears to be the same as for the Mo system, [Cp^*WCl_4] [27]. On the other hand, the maximum oxidation state (+6) is reached once again with oxo ligands, [Cp^*MoO_3]⁻ (M = Mo, W). Since an oxo ligand is readily obtained from two hydroxo ligands by elimination of H_2O, we have imagined that a direct transformation of [$Cp^*M(CO)_3$]⁻ to [Cp^*MO_3]⁻ could be accomplished with X = OH, namely by using the easily available and inexpensive ROOH (R = tBu or H) compounds as oxidants. Further results suggesting that this idea has solid foundations are the good yield synthesis of [Cp^*MoO_2Cl] by oxidation of [$Cp^*Mo(CO)_3Cl$] with $tBuOOH$ [5], as well as that of [$Cp^*MoO_2(CH_3)$] and other similar cyclopentadienyl derivatives by oxidation of the corresponding tricarbonyl methyl precursors with the same oxidizing reagent [6].

A word of caution relates to a possible over-oxidation to afford peroxo derivatives. Indeed, excess $tBuOOH$ converts
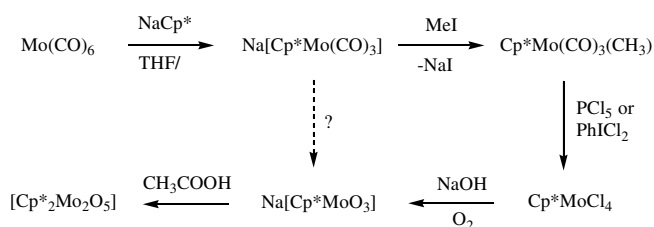
Scheme 1.

$[CpMo(CO)_3(CH_3)]$ to $[CpMoO(O_2)(CH_3)]$, although the intermediacy of $[CpMoO_2(CH_3)]$ in this reaction was established [6]. It has also been reported that the reaction of $[Cp^*MoO_2Cl]$ with tBuOOH leads to the corresponding peroxo derivative, $[Cp^*MoO(O_2)Cl]$ [4]. Another point to be clarified concerns the release of the three CO ligands as either CO or CO_2, the two extreme cases requiring the use of either 3 or 6 equiv. of ROOH ($R = t$Bu or H) according to the stoichiometries shown in Eqs. (4) and (5), respectively. Obviously, an intermediate stoichiometry may also be followed. Finally, the pH is also to be considered as a variable. At neutral pH, both starting material and reaction product are present in anionic form, whereas at lower pH the tricarbonyl anion is protonated to $[Cp^*Mo(CO)_3H]$ ($pK_a = 17.1$ in MeCN [36], from which the aqueous pK_a may be estimated [37] as ∼9), whereas the trioxo anion affords the unstable complex $[Cp^*MoO_2(OH)]$ ($pK_a = 3.65$) [38], followed by rearrangement to $[Cp_2^*Mo_2O_5]$. Although protons are not directly consumed during the oxidation process, the reaction may be catalyzed by acids or bases

$$[Cp^*Mo(CO)_3]^- + 3ROOH$$
$$\rightarrow [Cp^*MoO_3]^- + 3ROH + 3CO \qquad (4)$$
$$[Cp^*Mo(CO)_3]^- + 6ROOH$$
$$\rightarrow [Cp^*MoO_3]^- + 3ROH + 3CO_2 \qquad (5)$$

Because of the above-mentioned precedents of the $[Cp^*Mo(CO)_3X]$ oxidation ($X = Cl$, CH_3) with tBuOOH [5,6], this oxidizing agent was selected for our initial synthetic studies. The synthetic procedure was carried out several times at various tBuOOH/Mo ratios and pH values. The optimized conditions are given in the experimental section. First, we have observed the need of 6 equiv. of oxidant to complete the reaction. A MnO_2 test on the final reaction mixture did not show any gas evolution, indicating the complete consumption of the oxidant. On the other hand, we did not observe any evidence for the formation of peroxo derivatives. It must be remarked that we have not tested the reaction with >6 equiv. of oxidant and that a complex having the stoichiometry $[Cp^*MoO_2(O_2)]^-$ has not been described. The ^{1}H NMR spectrum of the crude reaction mixture only showed the resonance of the $[Cp^*MoO_3]^-$ ion when 6 equiv. of oxidant were used, whereas impure mixtures were obtained when using lower tBuOOH/Mo ratios. The reaction worked best (selective oxidation and cleaner product) under basic conditions, although the product was also formed upon working at neutral pH. It is interesting to note, however, that the oxidation of $[Cp_2^*Mo_2O_4]$ (as a pure starting compound, prepared separately) with tBuOOH does not occur at a significant rate at neutral pH (no observable oxidation overnight at room temperature; slow oxidation upon heating). Oxidation to $Na[Cp^*MoO_3]$, on the other hand, takes place under basic (NaOH) conditions (this is the predominant species after stirring overnight at room temperature). At acidic pH, compound $[Cp_2^*Mo_2O_4]$ did react with

tBuOOH, but the colour changed to orange-brown instead of the known [38] bright yellow colour of $[Cp^*MoO_2(H_2O)]^+$ (the stable acidic form of "Cp^*Mo^{VI}") and an ^{1}H NMR analysis indicated that a different product was obtained.

Using the optimized procedure, the final $[Cp_2^*Mo_2O_5]$ product was recovered in high yields and in a spectroscopically pure form, notably without any sign of contamination by the tetraoxo Mo^V derivative, $[Cp^*MoO_2]_2$, which systematically accompanies our previously reported synthetic protocol [26]. After the tBuOOH addition, an immediate colour change occurs from orange to red, followed by slow bleaching to the final yellow colour of $[Cp^*MoO_3]^-$ over 3 days. The intermediate red colour is due to $[Cp^*Mo(CO)_3]_2$, as verified by its isolation and spectroscopic (IR, ^{1}H NMR) characterization when the reaction was stopped at earlier conversions. During the entire synthetic procedure, no isolation of intermediates is required because water and tBuOOH can be added directly to the THF solution of $Na[Cp^*Mo(CO)_3]$ that results from the first step. However, the solvents must be completely removed after the oxidation step and replaced with neat water in order to optimize the precipitation of $[Cp_2^*Mo_2O_5]$.

We have also tested the same synthetic protocol using the "greener" hydrogen peroxide as oxidant. Formation of the desired product was observed under the same conditions used for the tBuOOH oxidation (6 equiv., high pH). In fact, the transformation is faster, the observed colour bleaching indicating that a complete conversion required only a few minutes, rather than 3 days. Conversely, the yields of isolated product were lower and less reproducible. The best yield (66.3%) is reported in the experimental section but much lower yields have also been occasionally obtained. We therefore recommend use of the tBuOOH oxidant for reliable results.

We have subsequently adapted the same procedure to the preparation of $[Cp_2^*W_2O_5]$. The oxidation step works much the same way as for the molybdenum analogue (6 equiv. of oxidant are required). However, in this case the best results were obtained by working at neutral pH, whereas the use of basic conditions led to less satisfactory and erratic results. Dissolution of an authentic sample of $[Cp_2^*W_2O_5]$ in basic MeOH–H_2O (presumably yielding $[Cp^*WO_3]^-$) and monitoring by ^{1}H NMR against an internal standard showed a slow decomposition (ca. 50% over 2 days). This decomposition may be pH dependent, explaining the erratic results in synthesis, but we have not pursued a study of this decomposition process any further.

We should also underline two additional and subtle differences between the W and the Mo systems, not clearly described in the previous literature. The $[Cp_2^*W_2O_5]$ compound has a non negligible solubility in water, whereas the Mo analogue is essentially insoluble. On the other hand, whereas $[Cp_2^*Mo_2O_5]$ is relatively soluble in diethyl ether, the W analogue is not. Therefore, extraction of the neutral precipitate with ether, which constitutes a convenient work-up procedure for the Mo compound, cannot

be used for the W analogue. Another noticeable difference is the precipitation of the W product in the form of a very fine colloidal suspension, which does not settle even upon heating. Increasing the solution ionic strength did not show any apparent beneficial effect. Thus, the most effective procedure, though a bit more tedious, consists of dissolving the Na[Cp*WO$_3$] residue into the minimum amount of water, followed by acidification and extraction of the resulting [Cp$_2^*$W$_2$O$_5$] product with CH$_2$Cl$_2$, in which the compound is readily soluble. Like for the synthesis of the Mo compound, the oxidation of Na[Cp*W(CO)$_3$] also occurs when using 6 equiv. of H$_2$O$_2$, though once again the overall yield is less satisfactory and not always reproducible.

We would also like to briefly mention a few attempts to synthesize [Cp$_2^*$M$_2$O$_5$] from Na[Cp*M(CO)$_3$] using bleach (ClO$^-$) as oxidant. Although this reagent is not as "green" as H$_2$O$_2$, its ready availability and low cost made it an interesting candidate for our study. The Mo system was investigated more in detail. Use of just 1 equiv. of the reagent led rather selectively to Cp*Mo(CO)$_3$Cl (as indicated by comparing the IR spectrum with the literature [39]; the compound was not isolated). Use of a higher amount of ClO$^-$ led (after acidification with CH$_3$COOH as described above) to a mixture of the expected [Cp$_2^*$Mo$_2$O$_5$] product and significant amounts of [Cp$_2^*$Mo$_2$O$_4$] and [Cp*MoO$_2$Cl] (^{1}H NMR signals at δ 2.02 [19], 1.99 [26] and 2.09 [19], respectively, in CDCl$_3$), the chloro derivative being the major product. A separate procedure starting from pure [Cp$_2^*$Mo$_2$O$_4$] shows that this is oxidized by bleach in THF, but once again both [Cp$_2^*$Mo$_2$O$_5$] and [Cp*MoO$_2$Cl] are obtained and the tetra-oxo starting compound was not completely consumed, even when using a large excess of oxidant. Analogous results (several products according to the ^{1}H NMR spectrum) were obtained for the W system. Therefore, this reagent was abandoned in favour of tBuOOH.

2.2. Molecular structures

Compound Na[Cp*MoO$_3$], obtained as a crude product from the oxidation procedure under basic conditions, could be crystallized from hot THF. The structure of the related [Cp*WO$_3$]$^-$ ion has already been described in three different salts, [tBu(EtC{O}CH$_2$CH$_2$)NH$_2$][Cp*WO$_3$], [tBuN-H$_3$][Cp*WO$_3$] · 1/2[tBuNH$_3$]Cl, and [(Ph$_3$P)$_2$N][Cp*WO$_3$] · 2H$_2$O [19], but no salts of the [Cp*MoO$_3$]$^-$ has previously been structurally characterized to the best of our knowledge. The compound crystallizes with two independent [Cp*MoO$_3$]$^-$ ions in the asymmetric unit. The corresponding Na$^+$ ions are octahedrally surrounded by water molecules, three of which (defined by atoms O1, O3 and O5) are shared by the two Na atoms in a face-sharing bioctahedral (FSBO) arrangement. In addition, the sodium atoms Na1 and Na1^i of two different asymmetric units, related to each other by an inversion center, share two additional water molecules (those defined by O2 and O2^i), forming a
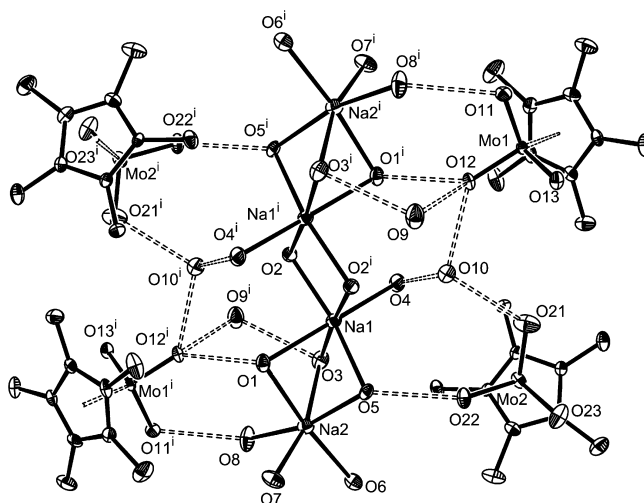

Fig. 1. ORTEP view showing two asymmetric units of the structure of Na[Cp*MoO$_3$] · 5H$_2$O. The aqua ligand and interstitial water H atoms have been omitted for clarity.

central edge-sharing bioctahedral (ESBO) unit. This arrangement gives rise to an overall tetraoctahedral [Na$_4$(H$_2$O)$_{16}$]$^{4+}$ cluster, see Fig. 1. Similar chains of aqua-bridged sodium cations have been described before [40–43], but a discrete tetranuclear unit with a FSBO-ESBO-FSBO arrangement, as observed in the present structure, is unprecedented according to the Cambridge Crystallographic Data Centre's database. This cluster is hydrogen bonded to additional, symmetry related Na$_4$ clusters to form a one-dimensional infinite sodium chain, which is linked to other chains by additional hydrogen bonding to form two-dimensional sheets (two views are provided in the Supporting Information). The two-dimensional sheets are separated from each other by two hydrophobic layers of organometallic anions. The anion layers are linked to the cation layers by hydrogen bonds, both directly (e.g. O11···O8′, O12···O1′, O22···O5) and indirectly via two additional interstitial water molecules in each asymmetric unit, O9 and O10. All H atoms of the water molecules have been directly located from the difference Fourier map, unambiguously establishing the chemical composition as a sodium salt of the [Cp*MoO$_3$]$^-$ ion, rather than a co-crystallized hydrated NaOH network and neutral Cp*MoO$_2$(OH). Note that, although the crystallization solvent is neat THF, only water molecules from the oxidation reaction medium are retained for sodium coordination and for networking (see Fig. 1).

Significant distances and angles are shown in Table 1. The Mo–O distances average 1.752(12) and 1.747(30) Å for the two crystallographically independent anions (cf. 1.751, 1.746 and 1.758 Å in the three above-mentioned salts of [Cp*WO$_3$]$^-$). As discussed in that contribution [19], hydrogen bonding is probably responsible for the significant lengthening relative to a typical Mo–O double bond (for instance, 1.69(2) Å in [Cp$_2^*$Mo$_2$O$_5$], average over three different polymorphs [16]). The average O–Mo–O angles
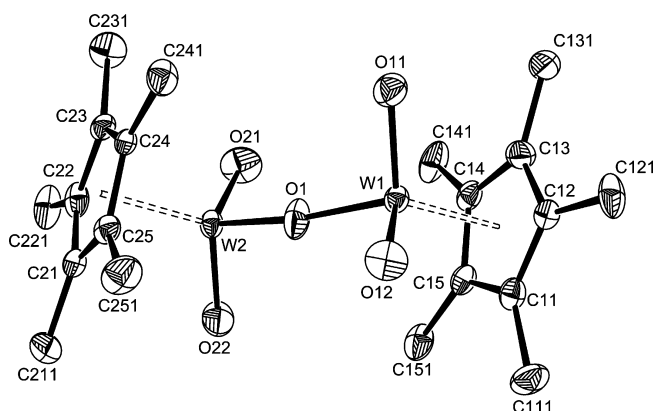
Fig. 2. ORTEP view of compound $[Cp_2^*W_2O_5]$.

Table 1
Selected bond distances (Å) and angles (°) for compound Na[Cp*MoO₃] · 5H₂O[a]

Mo(1)–O(11)	1.749(4)	Mo(2)–O(21)	1.714(5)
Mo(1)–O(12)	1.765(4)	Mo(2)–O(22)	1.751(4)
Mo(1)–O(13)	1.742(4)	Mo(2)–O(23)	1.775(5)
Mo(1)–CT01	2.1166(5)	Mo(2)–CT02	2.1011(6)
O(11)–Mo(1)–O(12)	105.8(2)	O(21)–Mo(2)–O(22)	106.9(3)
O(13)–Mo(1)–O(11)	106.2(2)	O(21)–Mo(2)–O(23)	106.7(3)
O(13)–Mo(1)–O(12)	106.1(2)	O(22)–Mo(2)–O(23)	102.4(2)
O(11)–Mo(1)–CT01	111.74(14)	O(21)–Mo(2)–CT02	115.35(18)
O(12)–Mo(1)–CT01	113.64(14)	O(22)–Mo(2)–CT02	113.50(15)
O(13)–Mo(1)–CT01	112.71(14)	O(23)–Mo(2)–CT02	110.97(16)

[a] CT01 and CT02 are the ring centroids of the Cp* ligands bonded to atoms Mo1 (C11–C15) and Mo2 (C21–C25), respectively.

(106.0(2)° and 105.3(25)°, respectively) are also close to those observed in the three $[Cp^*WO_3]^-$ salts (105.2°, 104.6° and 105.3°) [19].

The structure of compound $[Cp_2^*W_2O_5]$ has already been reported, although this also contains an interstitial $C_6F_5NH_2$ molecule [44]. Here, we describe a crystal structure that is devoid of any co-crystallized foreign molecule, see Fig. 2. This structure is isomorphous with that of $[Cp_2^*Mo_2O_5]$ (polymorph **II**) described by Rheingold and Harper [16]. The relevant metric parameters (see Table 2) are close to those of the previously reported structure [44]: average W=O, 1.725(9) Å (cf. 1.722); average W–O (bridg-

Table 2
Selected bond distances (Å) and angles (°) for compound $[Cp_2^*W_2O_5]$[a]

W(1)–O(1)	1.881(6)	O(1)–W(2)	1.892(6)
W(1)–O(11)	1.729(6)	W(2)–O(21)	1.711(7)
W(1)–O(12)	1.727(6)	W(2)–O(22)	1.732(7)
W(1)–CT1	2.0993(3)	W(2)–CT2	2.0957(3)
O(12)–W(1)–O(11)	105.2(3)	O(21)–W(2)–O(22)	105.7(4)
O(12)–W(1)–O(1)	105.5(3)	O(21)–W(2)–O(1)	105.7(3)
O(11)–W(1)–O(1)	104.6(3)	O(22)–W(2)–O(1)	104.2(3)
O(12)–W(1)–CT1	115.3(2)	O(21)–W(2)–CT2	114.3(3)
O(11)–W(1)–CT1	113.8(2)	O(22)–W(2)–CT2	115.3(2)
O(1)–W(1)–CT1	111.4(2)	O(1)–W(2)–CT2	110.7(2)
W(1)–O(1)–W(2)	170.1(4)		

[a] CT1 and CT2 are the ring centroids of the Cp* ligands bonded to atoms W1 (C11–C15) and W2 (C21–C25), respectively.

Table 3
Selected crystallographic and refinement parameters for compounds

Identification code	2{Na[Cp*MoO₃]} · 10H₂O	$[Cp_2^*W_2O_5]$
Empirical formula	C₂₀H₅₀Mo₂Na₂O₁₆	C₂₀H₃₀O₅W₂
Formula weight	784.46	718.14
Temperature (K)	180(2)	160(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.7340(9)	9.3219(3)
b (Å)	12.5507(11)	16.7198(5)
c (Å)	15.5984(16)	13.8918(5)
α (°)	78.673(8)	90.0
β (°)	78.370(9)	98.568(3)
γ (°)	85.901(8)	90.0
V (Å³)	1641.2(3)	2141.02(12)
Z	4	4
D_{calc} (Mg/m³)	1.587	2.228
μ (mm⁻¹)	0.855	10.763
F(000)	808	1352
Crystal size (mm³)	0.58 × 0.112 × 0.045	0.498 × 0.101 × 0.071
θ°, range	2.90–26.31	2.85–28.28
Reflections collected	12944	18790
Independent reflections [R_{int}]	6702 [0.0371]	5299 [0.0504]
Absorption correction	Multi-scan	Multi-scan
Maximum and minimum transmission	0.9997 and 0.7370	1.00000 and 0.18984
Refinement method	F^2	F^2
Data/restraints/ parameters	6702/0/371	5299/0/254
Goodness-of-fit on F^2	1.050	1.053
R_1, wR_2 [$I > 2\sigma(I)$]	0.0586, 0.1485	0.0369, 0.0966
R_1, wR_2 (all data)	0.0885, 0.1640	0.0583, 0.1072
Largest difference in peak and hole	3.757 and −2.679	4.163 and −1.722

ing), 1.886(7) Å (cf. 1.882(7) Å). These values are also close to those of the same polymorph of $[Cp_2^*Mo_2O_5]$: Mo=O, 1.708(9) Å and Mo–O (bridging), 1.882(12) Å. Although there is no imposed symmetry in this dinuclear molecule, the W–O–W moiety is close to linear (linearity is symmetry-imposed in the previously reported structure [44]).

3. Conclusion

We have developed rapid, high yield, and simple one-pot synthetic procedures to access $[Cp_2^*M_2O_5]$ (M = Mo, W) from commercially available $[M(CO)_6]$, needing only Cp*Na, tBuOOH (or H₂O₂), and CH₃COOH reagents. With minor adaptations, taking solubility differences into account, these procedures should be applicable to other cyclopentadienyl derivatives, the only provision being that the compounds are stable in water. This is not the case, for instance, for compound $[Cp_2Mo_2O_5]$ [26]. We expect that these new syntheses will give further impulse to the development of high oxidation state organomolybdenum and -tungsten chemistry and catalysis in water.

4. Experimental

4.1. General procedures

Unless otherwise stated, all preparations and manipulations were carried out with Schlenk techniques under an oxygen-free argon atmosphere. All glassware was oven-dried at 120 °C. Solvents were dried by standard procedures and distilled under dinitrogen prior to use. ^1H NMR spectra were recorded on a Bruker AM 250, operating at 250 MHz. Chemical shifts are expressed in ppm downfield from Me_4Si. Coupling constants are given in Hertz. Compound $[M(CO)_6]$ (Aldrich), a 70% aqueous solutions of tBuOOH (Aldrich) and 30% aqueous solutions of H_2O_2 (Fluka) were used as received. Pentamethylcyclopentadiene (Cp^*H, Acros) was converted to the Na salt by reaction with $NaNH_2$ in refluxing THF.

4.2. Tetraoxo-μ-oxobis(pentamethylcyclopentadienyl) dimolybdenum(VI), $[Cp^*_2Mo_2O_5]$

(a) By oxidation of $[Cp^*Mo(CO)_3]Na$ with tBuOOH. In a flask containing $NaCp^*$ (0.521 g, 3.3 mmol) was added a solution of $[Mo(CO)_6]$ (0.792 g, 3 mmol) in THF (60 mL). The resulting solution was stirred at reflux during 24 h affording the deep orange solution of the corresponding $Na[Cp^*Mo(CO)_3]$ salt (IR strong peaks at 1886, 1784, 1733 cm^{-1}). To this solution, after cooling to room temperature, was added 40 mL of previously degassed 0.4 M NaOH, then 2.5 mL of a 70% aqueous tBuOOH solution (18 mmol), resulting in a colour change to red with vigorous gas evolution. The mixture was stirred at room temperature for 3 days, turning orange and then pale yellow, and finally evaporated to dryness to yield $[Cp^*MoO_3]Na$ as a white solid. ^1H NMR (D_2O): $\delta = 1.89$ (Cp^*). This solid was then extracted with 40 mL of distilled water and filtered. The pale yellow filtrate was acidified with diluted glacial acetic acid, causing precipitation of a yellow solid at pH 3.8–4.0. The acetic acid addition was stopped when the addition of one further drop did not cause any additional precipitation. The precipitate was extracted with 4×100 mL portions of ether, the last extract being colorless. The combined organic layers were washed with distilled water and dried over $MgSO_4$ overnight. Evaporation of the solvent yielded $Cp^*_2Mo_2O_5$ as a yellow solid (0.742 g, 1.37 mmol, 91.2% yield). The ^1H NMR spectrum of this compound (singlet at $\delta = 2.01$ in $CDCl_3$) corresponds to that described in the literature [19].

In a separate procedure, the isolated white $Na[Cp^*MoO_3]$ intermediate was recrystallized by slowly cooling a hot saturated THF solution to room temperature, yielding suitable single crystals for the X-ray analysis.

(a) By oxidation of $[Cp^*Mo(CO)_3]Na$ with H_2O_2. This procedure is identical to that described above, except for the use of a 35% aqueous H_2O_2 solution (1.6 mL, 18 mmol) in place of the tBuOOH solution. The same color changes described above were observed. However, these took place within a few minutes rather than over 3 days. Treatment of a small aliquot of this solution with MnO_2 showed no gas evolution, indicating that complete consumption of H_2O_2 had taken place. The isolated white $[Cp^*MoO_3]Na$ intermediate had the same ^1H NMR properties described above. Using this procedure, 0.539 g of spectroscopically (^1H NMR) pure $[Cp^*_2Mo_2O_5]$ product (0.99 mmol; 66.3% yield) were recovered.

4.3. Tetraoxo-μ-oxobis(pentamethylcyclopentadienyl) ditungsten(VI), $[Cp^*_2W_2O_5]$

(a) By oxidation of $[Cp^*W(CO)_3]Na$ with tBuOOH. In a flask containing $NaCp^*$ (0.521 g, 3.3 mmol) was added a solution of $[W(CO)_6]$ (1.053 g, 3 mmol) in THF (80 mL). The resulting solution was stirred at reflux during 24 h affording the dark orange solution of the corresponding $Na[Cp^*W(CO)_3]$ salt (IR strong peaks at 1881, 1780, 1729 cm^{-1}). To this solution, after cooling to room temperature, was added 40 mL of degassed water, then 2.5 mL of a 70% aqueous tBuOOH solution (18 mmol), resulting in a colour change to red with vigorous gas evolution. The solution was stirred at room temperature for 3 days, turning orange, then yellow, and finally colourless. The solution was then evaporated to dryness to yield $[Cp^*WO_3]Na$ as a white solid. ^1H NMR (D_2O): $\delta = 2.04$ (Cp^*). This solid was then extracted with the minimum amount of distilled water and then acidified with diluted glacial acetic acid, causing a colour change from colourless to yellow with precipitation of a very fine pale yellow solid (pH around 4), which did not settle. The acetic acid addition was alternated by extractions of the product into CH_2Cl_2, until further addition of one further drop did not cause any additional precipitation. The combined organic layers (total: 150 mL) were washed with distilled water and dried over $MgSO_4$ overnight. Evaporation of the solvent yielded $Cp^*_2W_2O_5$ as a yellow solid (0.93 g, 1.30 mmol, 87% yield). The ^1H NMR spectrum of this compound (singlet at $\delta = 2.18$ in $CDCl_3$) corresponded to that described in the literature [19].

(b) By oxidation of $[Cp^*W(CO)_3]Na$ with H_2O_2. This procedure is identical to that described above, except for the use of a 30% aqueous H_2O_2 solution (2 mL, 18 mmol) in place of the tBuOOH solution. The same color changes described above were observed. The isolated white $[Cp^*WO_3]Na$ intermediate had the same ^1H NMR properties described above. Using this procedure, 0.50 g of spectroscopically (^1H NMR) pure $[Cp^*_2W_2O_5]$ (0.696 mmol; 46.4% yield) were recovered. Suitable single crystals were grown by layering a saturated CH_2Cl_2 solution with pentane at 0 °C.

4.4. X-ray diffraction studies

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of the Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using the

monochromatic Mo Kα radiation ($\lambda = 0.71073$). The structures were solved by direct methods (SIR97) [45] and refined by least-squares procedures on F^2 using SHELXL-97 [46]. All H atoms attached to carbon atoms were introduced in calculations in idealized positions and treated as riding models. The H atoms attached to oxygen atoms were located in the difference Fourier synthesis but they were treated as riding on their parent O atoms. The drawing of the molecules was realized with the help of ORTEP32 [47]. Crystal data and refinement parameters are shown in Table 3.

Acknowledgements

Appendix A. Supplementary material

CCDC 644159 and 644160 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.021.

References

[1] W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 27 (1988) 1297.
[2] W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 30 (1997) 169.
[3] P.M. Reis, C.C. Romão, B. Royo, J. Chem. Soc., Dalton Trans. (2006) 1842.
[4] M.B. Trost, R.G. Bergman, Organometallics 10 (1991) 1172.
[5] M. Abrantes, A. Santos, J. Mink, F. Kühn, C. Romão, Organometallics 22 (2003) 2112.
[6] J. Zhao, A.M. Santos, E. Herdtweck, F.E. Kühn, J. Mol. Catal. A 222 (2004) 265.
[7] J. Zhao, E. Herdtweck, F.E. Kühn, J. Organomet. Chem. 691 (2006) 2199.
[8] L.F. Veiros, A. Prazeres, P.J. Costa, C.C. Romão, F.E. Kühn, M.J. Calhorda, J. Chem. Soc., Dalton Trans. (2006) 1383.
[9] C. Freund, M. Abrantes, F.E. Kühn, J. Organomet. Chem. 691 (2006) 3718.
[10] M. Abrantes, A. Sakthivel, C.C. Romão, F.E. Kühn, J. Organomet. Chem. 691 (2006) 3137.
[11] F.E. Kühn, A.M. Santos, M. Abrantes, Chem. Rev. 106 (2006) 2455.
[12] A.M. Martins, C.C. Romão, M. Abrantes, M.C. Azevedo, J. Cui, A.R. Dias, M.T. Duarte, M.A. Lemos, T. Lourenço, R. Poli, Organometallics 24 (2005) 2582.
[13] B. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457.
[14] M. Herberhold, W. Kremnitz, A. Razavi, H. Schöllhorn, U. Thewalt, Angew. Chem., Int. Ed. Eng. 24 (1985) 601.
[15] J.W. Faller, Y. Ma, J. Organometal. Chem. 340 (1988) 59.
[16] A.L. Rheingold, J.R. Harper, J. Organometal. Chem. 403 (1991) 335.
[17] P. Leoni, M. Pasquali, L. Salsini, C. Di Bugno, D. Braga, P. Sabatino, J. Chem. Soc., Dalton Trans. (1989) 155.
[18] P. Gomez-Sal, E. De Jesus, P. Royo, A. Vazquez De Miguel, S. Martinez-Carrera, S. Garcia-Blanco, J. Organometal. Chem. 353 (1988) 191.
[19] M.S. Rau, C.M. Kretz, G.L. Geoffroy, A.L. Rheingold, Organometallics 12 (1993) 3447.
[20] J. Sundermeyer, U. Radius, C. Burschka, Chem. Ber. 125 (1992) 2379.
[21] R. Poli, Chem. Eur. J. 10 (2004) 332, and references therein.
[22] E. Collange, L. Metteau, P. Richard, R. Poli, Polyhedron 23 (2004) 2605.
[23] F. Demirhan, G. Taban, M. Baya, C. Dinoi, J.-C. Daran, R. Poli, J. Organometal. Chem. 691 (2006) 648.
[24] F. Demirhan, B. Çagatay, D. Demir, M. Baya, J.-C. Daran, R. Poli, Eur. J. Inorg. Chem. (2006) 757.
[25] J.-E. Jee, A. Comas-Vives, C. Dinoi, G. Ujaque, R. Van Eldik, A. Lledós, R. Poli, Inorg. Chem. 46 (2007) 4103.
[26] D. Saurenz, F. Demirhan, P. Richard, R. Poli, H. Sitzmann, Eur. J. Inorg. Chem. (2002) 1415.
[27] R.C. Murray, L. Blum, A.H. Liu, R.R. Schrock, Organometallics 4 (1985) 953.
[28] D.W. Keogh, R. Poli, in: W.A. Herrmann (Ed.), Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer), Georg Thieme Verlag, Stuttgart, 1997.
[29] R. Birdwhistell, P. Hackett, A.R. Manning, J. Organometal. Chem. 157 (1978) 239.
[30] A. Asdar, M.-J. Tudoret, C. Lapinte, J. Organometal. Chem. 349 (1988) 353.
[31] T. Straub, M. Haukka, T.A. Pakkanen, J. Organomet. Chem. 612 (2000) 106.
[32] F. Abugideiri, G.A. Brewer, J.U. Desai, J.C. Gordon, R. Poli, Inorg. Chem. 33 (1994) 3745.
[33] J.U. Desai, J.C. Gordon, H.-B. Kraatz, V.T. Lee, B.E. Owens-Waltermire, R. Poli, A.L. Rheingold, C.B. White, Inorg. Chem. 33 (1994) 3752.
[34] J.C. Gordon, V.T. Lee, R. Poli, Inorg. Chem. 32 (1993) 4460.
[35] K. Köhler, A. Herzog, A. Steiner, H.W. Roesky, Angew. Chem., Int. Ed. Engl. 35 (1996) 295.
[36] E.J. Moore, J.M. Sullivan, J.R. Norton, J. Am. Chem. Soc. 108 (1986) 2257.
[37] K. Abdur-Rashid, T.P. Fong, B. Greaves, D.G. Gusev, J.G. Hinman, S.E. Landau, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 122 (2000) 9155.
[38] E. Collange, J. Garcia, R. Poli, New J. Chem. 26 (2002) 1249.
[39] D.S. Ginley, M.S. Wrighton, J. Am. Chem. Soc. 97 (1975) 3533.
[40] X.-Y. Yi, B. Liu, R. Jimenez-Aparicio, F.A. Urbanos, S. Gao, W. Xu, J.-S. Chen, Y. Song, L.-M. Zheng, Inorg. Chem. 44 (2005) 4309.
[41] L.C. Nathan, T.D. Mai, J. Chem. Cryst. 30 (2000) 509.
[42] S. Samanta, S. Mukhopadhyay, D. Mandal, R.J. Butcher, M. Chaudhury, Inorg. Chem. 42 (2003) 6284.
[43] W.J. Dressick, C. George, S.L. Brandow, T.L. Schull, D.A. Knight, J. Org. Chem. 65 (2000) 5059.
[44] K. Köhler, H.W. Roesky, A. Herzog, H. Gornitzka, A. Steiner, I. Usón, Inorg. Chem. 35 (1996) 1773.
[45] A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 32 (1999) 115.
[46] G.M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
[47] L.J. Farrugia, J. Appl. Crystallogr. 32 (1997) 565.