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Investigation of the reaction of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ (M = Mo, W) with hydrogen peroxide and *tert*-butylhydroperoxide in MeCN; implications for olefin epoxidation catalyzed by organomolybdenum and organotungsten compounds

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Dedicated to Maria-José Calhorda on the occasion of her 65th birthday

Keywords: Molybdenum, Tungsten, Pentamethylcyclopentadienyl, Oxido ligands, Oxidation, Catalyst degradation

Abstract

Compounds $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ ($\text{M} = \text{Mo}, \text{W}$) react with stoichiometric amounts of H_2O_2 (as a 30% w/w solution in water) and *t*BuOOH (TBHP, as a 70% w/w solution in decane) in MeCN solution to yield a variety of products as shown by the ^1H NMR monitoring of the Cp^* resonance. The reaction rate increases in the order $\text{W} < \text{Mo}$ and $\text{TBHP} < \text{H}_2\text{O}_2$. While the total Cp^* intensity remains constant when using stoichiometric amounts of oxidant, use of excess oxidant results in the ultimate total Cp^* loss. From the decomposed solutions, crystals of $[\text{Cp}^*_2\text{Mo}_6\text{O}_{17}]$ (**1**), $(\text{C}_5\text{Me}_5\text{O})[\text{Cp}^*\text{M}_6\text{O}_{18}]$ ($\text{M} = \text{Mo}$, **2a**; W , **2b**), and $(\text{C}_5\text{Me}_5\text{O})_2[\text{Mo}_6\text{O}_{19}]$ (**3**) were recovered and analyzed by X-ray diffraction. Catalytic cyclooctene epoxidation experiments with $(n\text{Bu}_4\text{N})_2[\text{M}_6\text{O}_{19}]$ ($\text{M} = \text{Mo}, \text{W}$) in a 3:1 MeCN/toluene mixture at 55°C using either aqueous H_2O_2 or TBHP/decane as oxidant revealed that these are not the active forms of the catalyst which is generated under the same conditions from $[\text{Cp}^*_2\text{M}_2\text{O}_5]$, as reported in previous contributions from our group (*Chem. Eur. J.*, 2010, 16, 9572–9584; *Eur. J. Inorg. Chem.*, 2013, 2728–2735). Further catalytic studies using aged $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]/\text{TBHP}$ and $[\text{Cp}^*_2\text{W}_2\text{O}_5]/\text{H}_2\text{O}_2$ solutions show a small loss of activity (<50% in one week) attesting the robustness of the non-organometallic catalytically active species that is generated from the decomposition of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$. These results cast doubts on the role of cyclopentadienyl as a supporting ligand for stable olefin epoxidation catalysts.

1. Introduction

High oxidation state organometallic compounds are often thermally unstable and hydrolytically sensitive but exceptions are known [1] such as for instance methyltrioxorhenium (MTO), $[\text{MeReO}_3]$, which is air and water stable [2-4]. This compound is an active oxidation catalysts and its stoichiometric interaction with H_2O_2 yields a bis(peroxido) derivative $\text{MeReO}(\text{O}_2)_2$, which was isolated and fully characterized [5]. Another compound behaving similarly to MTO in terms of air and water stability, $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$, has attracted our attention for some time, particularly in terms of its behavior in an aqueous environment [6]. We have shown in early work that the compound resists hydrolytic cleavage of the $\text{Cp}^*\text{-Mo}$ bond even at the lowest pH, for at least a few days [7, 8]. Although the compound (and also its tungsten analogue $[\text{Cp}^*_2\text{W}_2\text{O}_5]$) maintains the dinuclear neutral structure in a variety of polar solvents including MeOH and MeCN [9], it displays an interesting speciation for the aqueous “ $\text{Cp}^*\text{Mo}^{\text{VI}}$ ” fragment: it behaves as an electrolyte in a water-rich environment with self-dissociation to $[\text{Cp}^*\text{MoO}_2(\text{H}_2\text{O})]^+$ and $[\text{Cp}^*\text{MoO}_3]^-$, each species becoming dominant at low and high pH, respectively. The neutral $[\text{Cp}^*\text{MoO}_2(\text{OH})]$ species is also present in solution in equilibrium with the charged complexes around pH 4. Partial loss of Cp^* , however, occurred over an extended period of time (months) from aqueous solutions upon standing at low pH in air to yield the organometallic polyoxometallate compound $[\text{Cp}^*_2\text{Mo}_6\text{O}_{17}]$ [10], which is isoelectronic and displays the same core structure as the Lindqvist anion $[\text{Mo}_6\text{O}_{19}]^{2-}$.

More recently, we have investigated $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ as a precatalyst for olefin epoxidation. The catalytic activity of $\text{Cp}^*\text{Mo}^{\text{VI}}$ derivatives in this reaction was first reported by Bergman, showing that compound $[\text{Cp}^*\text{MoO}_2\text{Cl}]$ has a high activity for the epoxidation of cyclooctene and a few other substrates by *tert*-butylhydroperoxide (TBHP) [11]. Stoichiometric oxidation of

[Cp*MoO₂Cl] by TBHP [11] or H₂O₂ [12] allowed isolation of a peroxido derivative, [Cp*MoO(O₂)Cl], which was however found inactive as an epoxidation catalyst. Kühn and Romão later showed that [Cp*MoO₂Cl] as well as analogues with differently substituted (η^5 -C₅R₅) ligands can be more conveniently generated *in situ* from the tricarbonyl complex [(η^5 -C₅R₅)MoCl(CO)₃] and TBHP [13]. This opened the way to the generation of alkylmolybdenum(VI) analogues by oxidation of a variety of [(η^5 -ring)Mo(R)(CO)₃] precursors and these compounds have been thoroughly investigated as olefin epoxidation catalysts [14-28].

We have initially tested the [Cp*₂Mo₂O₅] compound, as well as various analogues containing differently substituted cyclopentadienyl rings, (η^5 -C₅R₅), in the catalyzed cyclooctene epoxidation by TBHP in chloroform and found them to yield activities and kinetic profiles in close correspondence to those of the analogous [(η^5 -C₅R₅)MoO₂Cl] precatalysts [29]. Intrigued by the previously established stability of these compounds in an aqueous environment, we also tested [Cp*₂Mo₂O₅] in the cyclooctene epoxidation by TBHP/H₂O and by aqueous H₂O₂ resulting in lower or no epoxide yields, respectively. Subsequently, we have applied this compound as well as the tungsten analogue, [Cp*₂W₂O₅], for which we have meanwhile found a convenient and reproducible high-yield synthesis [30], to the catalytic oxidation of thiophene derivatives under different conditions (using aqueous H₂O₂ as oxidant in MeCN). We were pleased to find a clean catalytic process (well behaved first-order kinetics, high activities), with the W compound being much more active than the Mo compound ($k_W/k_{Mo} \sim 100$) [31]. Subsequent adaptation of the same conditions to cyclooctene epoxidation revealed the same phenomena: clean kinetics and greater activity for the W compound [32]. Theoretical calculations seemed to justify the greater activity of the W compound on the basis of a

mechanism closely related to one proposed by Thiel [33] and previously explored for the [Cp*MoO₂Cl] system [34].

More recently, however, we have discovered a puzzling change of relative activity when changing the oxidant from aqueous H₂O₂ to TBHP/decane, all other conditions and notably the reaction solvent remaining the same [35]. The relative catalytic activity of [Cp*₂M₂O₅] (M = Mo, W) for the cyclooctene epoxidation by TBHP/decane in MeCN becomes Mo >> W. This result has made us suspect that the catalyst is chemically transformed in different ways during the initial moments of the catalytic process, depending on the oxidant and metal nature. It is also relevant to mention that a study published by Colbran *et al.* [36], which focused on a bromide derivative with a bulky perarylcyclopentadienyl ligand, [(η⁵-C₅Ph₄{C₆H₃(OMe)_{2-2,5}})MoO₂Br], demonstrated that this complex catalyzes cyclooctene epoxidation by TBHP but decomposes to a much more active non-cyclopentadienyl containing catalyst as the reaction proceeds. We have therefore set out to investigate the stoichiometric reaction between [Cp*₂M₂O₅] and the oxidants used in the epoxidation process, H₂O₂ and TBHP, under our experimental conditions (MeCN solution) and report here the results of our findings.

2. Experimental section

General. All preparations and manipulations were carried out with Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures and distilled under argon prior to use. ¹H NMR spectra were recorded on a Bruker Avance 300. For the quantitative NMR analyses, the relaxation delay was incremented to 30 s (the use of the instrumental standard settings did not yield reliable quantitative intensities). Chemical shifts are expressed in ppm downfield from Me₄Si. The IR spectra were recorded on Perkin Elmer Spectrum 100 FT-IR

Spectrometer. The gas chromatographic analyses were completed by using Fisons 8130 instrument equipped with a DB-1MS capillary column (30 m × 0.32 mm × 0.25 μm) and with a flame ionization detector. The elemental analyses were carried out by the analytical service of the Laboratoire de Chimie de Coordination, Toulouse. Compounds [Cp*₂M₂O₅] (M = Mo, W) [30] and (nBu₄N)₂[M₆O₁₉] (M = Mo [37], W [38]) were prepared as described in the literature. Cyclooctene (Fluka), dodecane (Aldrich), ^tBuOOH solution in decane (5.5 M) and H₂O₂ (30 wt % in water) (Aldrich) were used as received.

Oxidation experiments monitored by ¹H NMR. The oxidation reactions of [Cp*₂M₂O₅] (M = Mo, W) were carried out in an NMR tube at room temperature. For each experiment the NMR tube was charged with 0.7 mL of the deuterated acetonitrile solvent. Subsequently the compound ([Cp*₂M₂O₅]; 10.5 μmol) was added and finally the oxidation reactions were started by the addition of oxidants and monitored by NMR with time. As examples, 1.1 μL of 30% aqueous H₂O₂ was used for the oxidation of the Mo compound 1 equivalent of with H₂O₂, whereas 3.8 μL of a 5.5 M TBHP solution in decane was used for the oxidation of the same compound with 2 equivalents of TBHP.

Isolation and characterization of metallic products.

(a) From the [Cp*₂Mo₂O₅]/H₂O₂ reaction. [Cp*₂Mo₂O₅] (50 mg; 0.092 mmol) was dissolved in 2.5 ml of MeCN. To this solution was added 18.43 μL of 30% aq. H₂O₂ (0.184 mmol) followed by stirring for 15 min and then standing undisturbed overnight. The color of the solution changed from yellow to orange-red and an orange precipitate formed along with a few well formed, diamond shaped orange-red crystals. A single crystal of **1** from this batch was analyzed by X-ray diffraction (see supporting information). From a second reaction run under identical conditions, the recovered orange solid was isolated by filtration, washed with MeCN

and dried under vacuum. Elem. anal. Found: C, 22.50; H, 2.44%. IR in the M-O stretching region (cm^{-1}): 957 s, 751 vs (br), 577 s (br).

(b) From the $[\text{Cp}^*_2\text{W}_2\text{O}_5]/\text{H}_2\text{O}_2$ reaction. $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ (75 mg; 0.105 mmol) was dissolved in 3.0 ml of MeCN. To this solution was added 52.5 μL (0.525 mmol) of 30% aq. H_2O_2 , followed by stirring for 30 min and then standing overnight. The color of the solution changed from colorless to yellow and a yellow precipitate formed along with a few crystals. Elem. anal. Found: C, 15.31; H, 1.73%. IR in the M-O stretching region (cm^{-1}): 974 s, 776 vs (br), 595 m, 556 m. A single crystal of **2b** from this batch was analyzed by X-ray diffraction (see supporting information).

(c) Reaction leading to $[\text{C}_5\text{Me}_5\text{O}]_2[\text{Cp}^*\text{Mo}_6\text{O}_{18}]$ crystals. $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ (28.9 mg, 5.33×10^{-5} mol) was dissolved in 4.0 mL of MeCN/Toluen (3:1) mixture. To this solution was added 0.1 mL (5.33×10^{-4} mol) TBHP (5.5M in decane). The solution was stirred at room temperature for 2 hours. After 2 days at room temperature in air, crystal formation was observed from yellow solution. A single crystal of **2a** from this batch was analyzed by X-ray diffraction (see supporting information).

(d) Reaction leading to $[\text{C}_5\text{Me}_5\text{O}]_2[\text{Mo}_6\text{O}_{19}]$ crystals. $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ (50 mg; 0.092 mmol) was dissolved in 2.5 ml of MeCN. To this solution was added 46.1 μL (0.46 mmol) of 30% aq. H_2O_2 followed by stirring for 15 min and then standing overnight. The color of the solution changed from yellow to red and led to the crystallization of deep-red colored, square shaped crystals, suitable for x-ray diffraction. A single crystal of **3** from this batch was analyzed by X-ray diffraction (see supporting information).

Catalytic epoxidation experiments with $[n\text{Bu}_4\text{N}]_2[\text{M}_6\text{O}_{19}]$. The epoxidation reactions were carried out under an argon atmosphere in Schlenk tubes equipped with a magnetic stirrer and immersed in a thermostatic bath set at 55°C. In a typical experiment, the tube was charged with cyclooctene (130 μL , 110 mg, 1.0 mmol), the internal standard dodecane (160 μL , 120 mg, 0.7 mmol), the catalyst ($[n\text{Bu}_4\text{N}]_2[\text{M}_6\text{O}_{19}]$; 10.0 μm) and the oxidant (TBHP, as a 5.5 M solution in decane, 0.4 mL, 2.2 mmol or 30 wt % aqueous H_2O_2 , 190 μL , 2.2 mmol) in 9.6 mL of acetonitrile/toluene (3:1). Aliquots of the reaction mixture (0.2 ml) were withdrawn at predetermined times, quenched by addition of manganese dioxide, diluted with 2 ml of diethyl ether and filtered through a Pasteur pipette filled up with silica to eliminate the residual MnO_2 . The silica was washed by 1 ml diethyl ether. The resulting organic phase was analyzed by gas chromatography.

Catalytic epoxidation experiments with aged solutions of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$. The epoxidation reactions were carried out under an argon atmosphere in Schlenk tubes equipped with a magnetic stirrer and immersed in a thermostatic bath set at the 55°C. In a typical experiment, the tube was charged with 4 ml stock solution and cyclooctene (157 μL , 132 mg, 1.2 mmol). The preparation of the stock solutions is described in the supporting information. Aliquots of the reaction mixture (0.2 ml), withdrawn at predetermined times, were worked-up and analyzed as described in the previous section.

3. Results and Discussion

(a) Oxidations of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ by aqueous H_2O_2

Compounds $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ react within seconds at room temperature with aqueous H_2O_2 in CD_3CN under conditions similar to those previously used in catalytic cyclooctene epoxidation

(oxidant:M = 50:1), except for the absence of cyclooctene, to yield clear solutions that no longer revealed ^1H NMR resonances attributable to a metal coordinated Cp* ligand. For the Mo compound, the ^1H NMR spectrum did not reveal any resonances except for that of water at ca. δ 2.0 and the 1:2:3:2:1 solvent multiplet. For the W compound, on the other hand, the spectrum revealed the immediate formation of a main Cp*-derived product where the ring is desymmetrized (three uncoupled Me resonances in a 2:2:1 ratio at δ 1.28, 1.13 and 0.96, see Figure 1), while the water peak is dramatically shifted downfield to ca. δ 5.0, suggesting a significant alteration of the water hydrogen bonding network. This product, however, has limited stability in the strongly oxidizing environment because the observed resonances disappeared at longer reaction times. The possible nature of this species will be clarified below.

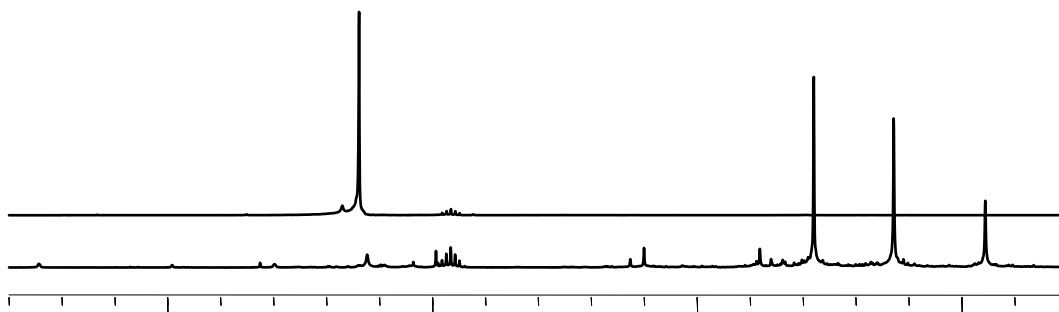


Figure 1. ^1H NMR of the CD_3CN solution of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ before (a) and after (b) the addition of H_2O_2 (100 equiv).

When using a lower amounts of oxidant, the formation of several Cp* containing species could be evidenced by ^1H NMR for both $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ compounds (M = Mo or W). For the Mo compound, the results obtained with a molar $\text{H}_2\text{O}_2/\text{Cp}^*_2\text{Mo}_2\text{O}_5$ ratio of 1:1 are summarized in Figure 2 whereas Figure 3 shows the results obtained with a 2:1 molar ratio.

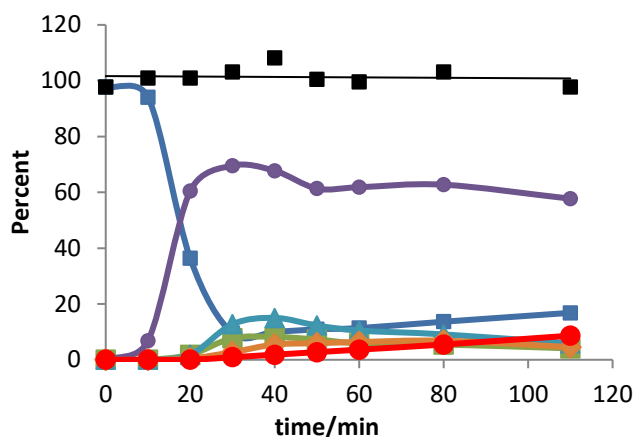


Figure 2. Time evolution of various resonances in the ¹H NMR spectrum of the CD₃CN solution resulting from the reaction of [Cp*₂Mo₂O₅] with H₂O₂ (1 equiv). Blue squares, δ 1.994 (starting material); purple circles, δ 2.007 and 2.054 (1:1 resonances); green squares, δ 2.039; light blue triangles, δ 2.078; orange diamonds, δ 2.099; red circles, δ 2.112. The black squares correspond to the total integrated intensity of the above resonances.

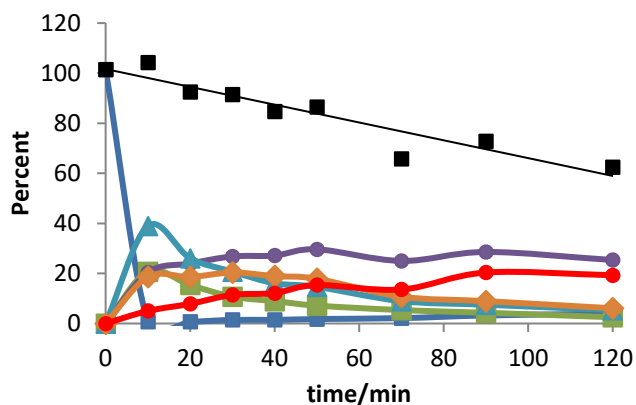


Figure 3. Time evolution of various resonances in the ¹H NMR spectrum of the CD₃CN solution resulting from the reaction of [Cp*₂Mo₂O₅] with H₂O₂ (2 equiv). The used symbols are as in Figure 2.

It can be immediately observed that the total Cp* intensity remains constant for the 1:1 experiment (while the solution remained homogeneous), whereas it is slowly eroded over time for the 2:1 reaction (accompanied by the formation of a precipitate). The starting material resonance at δ 1.994 disappears faster for the experiment with the 2:1 ratio. In the 1:1 experiment the intensity initially decreases to a minimum of ca. 10% of the initial value after 30 min, but then it increases again to reach ca. 17% of the initial amount after 110 min. Simultaneously, an intermediate compound which is characterized by two resonances at δ 2.007 and 2.054 in a 1:1 ratio grows to a maximum amount of 70% of the total Cp* intensity after 30 min and then slowly decreases. The combination of these two trends suggests that this intermediate partially reverts back to starting material. Starting at ca. 20-30 min, a number of other products, each one being characterized by a single Cp* resonance, also become visible in the ^1H NMR spectrum. Notably three products with resonances at δ 2.039, 2.078 and 2.099 reach a maximum intensity of ca. 8, 15 and 7% respectively after 40, 40 and 80 min before decreasing again, whereas a last product with a resonance at δ 2.112 continues to accumulate. In the 2:1 experiment, the starting material resonance also regains a bit of intensity after essentially disappearing (<1%) after 10 min, but to a much lesser extent relative to the 1:1 experiment. The intermediate with the two 1:1 resonances at δ 2.007 and 2.054 accumulates to a smaller extent (ca. 30% after 40 min) and then remains approximately constant. The three intermediates with resonances at δ 2.039, 2.078 and 2.099 reach a greater maximum intensity (21, 39 and 20%) on a shorter time scale (10, 10 and 30 min, respectively), before decreasing. Finally, the last product with the resonance at δ 2.112 increases to a greater relative amount (ca. 20% after 2 h). Figure 4 shows a representative spectrum in the Cp* region taken for the 2:1 reaction after 50 min. When repeating the same reaction with 5 equiv of H_2O_2 , there was an immediate precipitation and all the Cp* resonances were already lost

in the first spectrum collected after 10 min. The precipitate formed under these conditions was isolated and investigated by IR spectroscopy and elemental analysis. In addition, three compounds could be crystallized out of these solutions (with or without quenching the excess H₂O₂ by MnO₂ at a preset reaction time) and investigated by X-ray diffraction, revealing their identity as polyoxometallates, see details in section (c).

It appears reasonable to assign the two 1:1 resonances at δ 2.007 and 2.054 to an asymmetric dinuclear compound where only one terminal oxido ligand has been transformed to a peroxido ligand, which could be produced by an oxygen transfer process from H₂O₂ (or from peroxyacetimidic acid, CD₃C(OOH)=NH, which is known to form from H₂O₂ and acetonitrile)[39, 40] (Scheme 1(a), M = Mo). The asymmetric peroxido compound could then undergo a slow ligand redistribution to regenerate starting material plus a bis(peroxido) compound (Scheme 1(b)), thus rationalizing why the starting material increases again at longer reaction times and why this phenomenon is more evident in the 1:1 experiment. The putative bis(peroxido) compound may be associated with the resonance at δ 2.112, since this resonance increases in parallel with the reappearance of starting material in the 1:1 experiment and it increases to a greater extent in the 2:1 experiment. Candidates for the other unassigned resonances are dinuclear symmetric compounds such as Cp*(O)₂Mo-O-O-Mo(O)₂Cp* or Cp*(O)(O₂)Mo-O-O-Mo(O)(O₂)Cp*, and mononuclear compounds such as Cp*MoO₂(OH), Cp*MoO₂(OOH), Cp*MoO(O₂)(OH), etc.

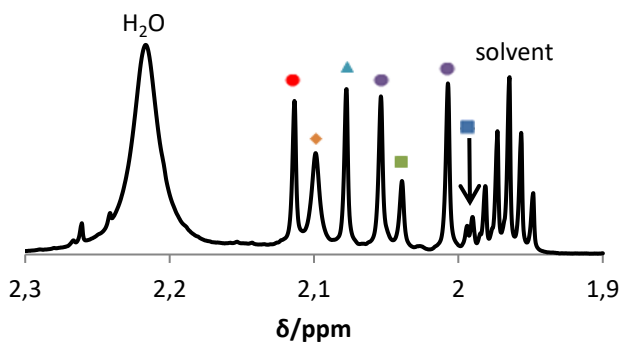
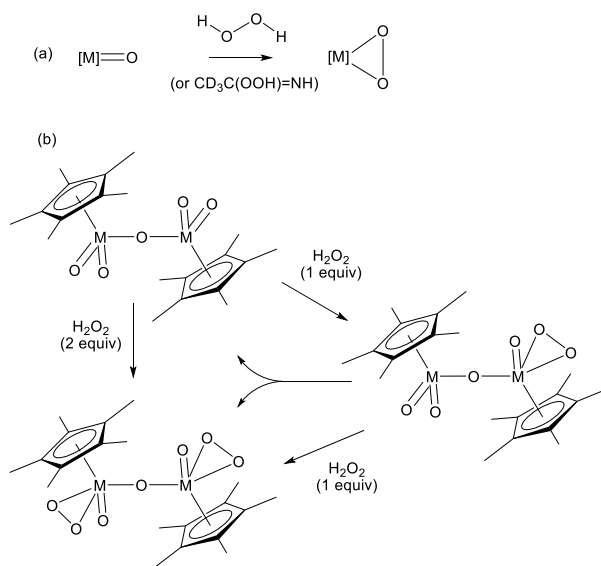


Figure 4. ^1H NMR spectrum of the CD_3CN solution resulting from the reaction of $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ with H_2O_2 (2 equiv) after 50 min. The symbols correspond to those of the marks in Figure 2 and Figure 4.



Scheme 1

The same experiment conducted on the W compound gave similar results, shown in Figure 5 for the 1:1 experiment and in Figure 6 for the 2:1 experiment. The number of observed products is smaller and the chemical transformations are slower, however. For the 1:1 experiment, a slight initial decrease of the total integrated Cp^* intensity is followed by stability beyond 1 h. The main

product (ca. 80% of the initial Cp* amount) is again an asymmetric dinuclear intermediate as for the Mo experiment, characterized in this case by two 1:1 resonances at δ 2.175 and 2.160. The only other observed product in minor amounts (< 3%) shows a resonance at δ 2.112. The starting material (δ 2.140) is not completely consumed with ca. 10% remaining after 90 min, probably because of an imperfect stoichiometry. In comparison with the Mo system, it seems that this asymmetric W intermediate does not decompose as rapidly by a ligand redistribution process (e.g. according to Scheme 1). The reaction carried out in a 2:1 ratio, like in the Mo case, resulted in a progressive degradation of the total Cp* intensity with >35% being lost after 3 h and in the formation of a precipitate. The starting material was consumed faster relative to the 1:1 reaction (30 min instead of ca. 80 min) and yielded a lower amount of the asymmetric dinuclear intermediate (maximum amount of ca. 65% at 30 min, instead of 80%). After 30 min, the amount of this intermediate decreased to ca. 40% while a new resonance at δ 2.180 increased. The latter resonance appears therefore attributable to a double oxygenation product such as that proposed in Scheme 1. The minor product with resonance at δ 2.112 is also observable in this case, its relative amount being greater relative to the 1:1 experiment, but always remaining the minor product in the spectrum (maximum of 7% after 40 min). A representative spectrum of this experiment is shown in Figure 7.

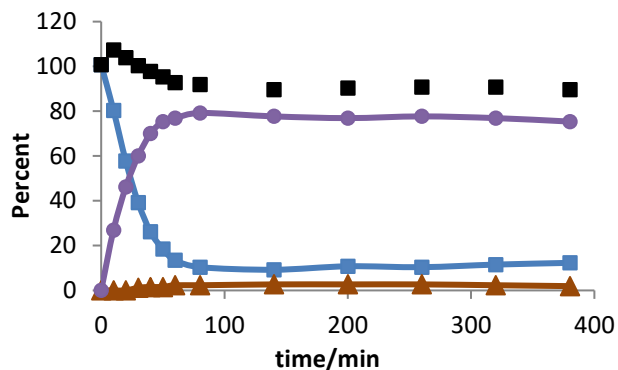


Figure 5. Time evolution of various resonances in the ^1H NMR spectrum of the CD_3CN solution resulting from the reaction of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ with H_2O_2 (1 equiv). Blue squares, δ 2.140 (starting material); purple circles, δ 2.175 and 2.160 (1:1 resonances); brown triangles, δ 2.112. The black squares correspond to the total integrated intensity of the above resonances.

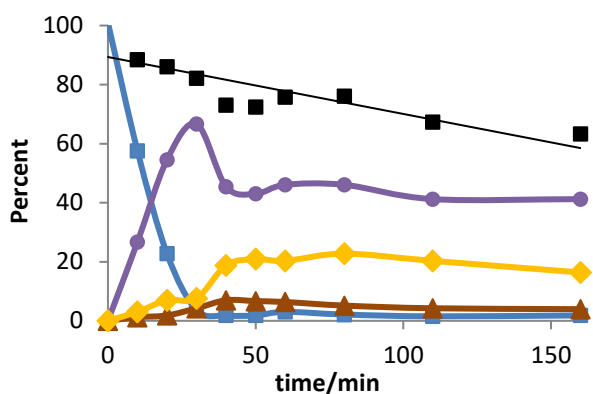


Figure 6. Time evolution of various resonances in the ^1H NMR spectrum of the CD_3CN solution resulting from the reaction of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ with H_2O_2 (2 equiv). The used symbols are as in Figure 5, plus orange diamonds for the resonance at δ 2.180.

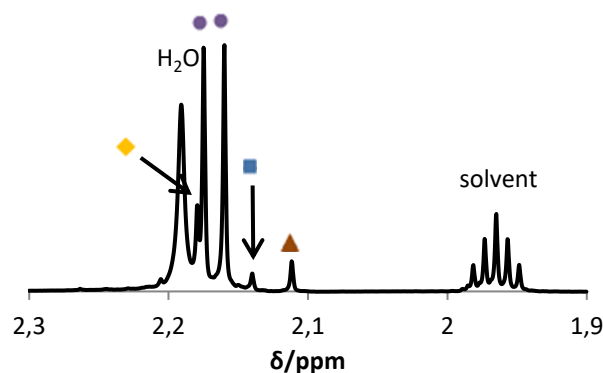


Figure 7. ^1H NMR spectrum of the CD_3CN solution resulting from the reaction of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ with H_2O_2 (2 equiv) after 30 min. The symbols correspond to those of the marks in Figure 5 and Figure 6.

Note that all resonances in the W experiment are downfield shifted relative to those in the Mo experiment (*cf.* Figure 4 and Figure 7), thus additional products for the W reaction could remain undetected because of overlap with the strong water peak at δ 2.2. Using 5 equiv of H_2O_2 , the starting material was completely consumed within 10 min while the solution became slightly turbid. No trace of the asymmetric dimer was found in this case, the only observed product resonances being that at δ 2.180 attributed to the doubly oxygenated dimer (24% of the initial Cp^* intensity after 10 min), and a less intense one at δ 2.204 (13%) which is now clearly visible because the water resonance is shifted further downfield (δ 2.75) and broadened in this experiment, see Figure 8. However, both these resonances decreased rapidly in intensity and completely disappeared from the spectrum after 40 min. Thus, relative to the experiment on the Mo compound, the intermediates formed from the W compound show greater resistance to the oxidative decomposition but complete Cp^* loss still eventually takes place. As for the experiments run with $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$, we could not succeed in crystallizing any of the soluble intermediates generated in these reactions. However, the precipitate that formed under these

conditions was analyzed by IR spectroscopy and elemental analysis, and a single crystal of a polyoxometallate obtained from these solutions was studied by X-ray diffraction, see section (c).

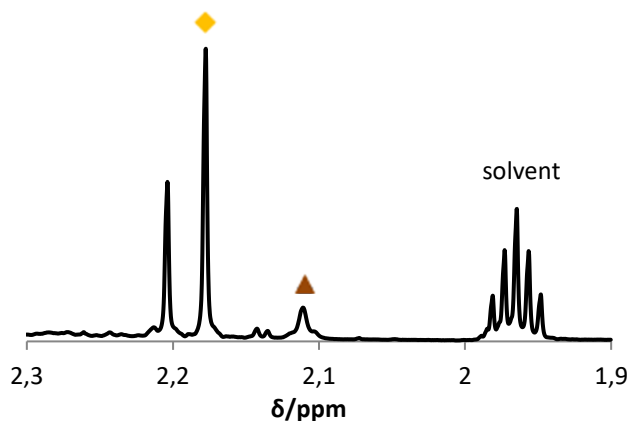


Figure 8. ^1H NMR spectrum of the CD_3CN solution resulting from the reaction of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ with H_2O_2 (5 equiv) after 10 min. The symbols corresponds to those of the marks in Figure 5 and Figure 6. The new resonance at δ 2.204 could not be observed in the experiments with 1 or 2 equiv of H_2O_2 because masked by the H_2O resonance.

(b) Oxidations of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ by TBHP/decane.

Additional NMR experiments were conducted using a decane solution of TBHP as oxidant in CD_3CN . For the Mo compound, a slow reaction could be monitored when using 2 equiv of TBHP, as shown in Figure 9. The starting material resonance at δ 1.994 decreased to ca. 65% of the initial intensity after 0.5 h and was no longer present in the final spectrum take after 18 h. The decay of this resonance followed a first order rate law with $k = 2.6 \cdot 10^{-4} \text{ s}^{-1}$ (based on 5 points; $t_{1/2} \sim 45 \text{ min}$). After 0.5 h from the TBHP addition, the spectrum showed a major intermediate characterized by a single resonance at δ 2.025 (29% of the initial Cp^* intensity), plus other minor resonances at δ 2.112 and 2.261. The broader resonance observed at δ 2.173 is

due to the water impurity that is present in the solvent and/or in the oxidant solution. While the δ 2.025 and 2.261 signals disappear from the final spectrum, the signal at δ 2.112 further grew and remained by far the major signal in the spectrum after 18 h, with an intensity corresponding to 23% of the initial Cp* intensity. Therefore, although the reaction of $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ with TBHP/decane is slower than that with aqueous H_2O_2 , it also results in loss of Cp*.

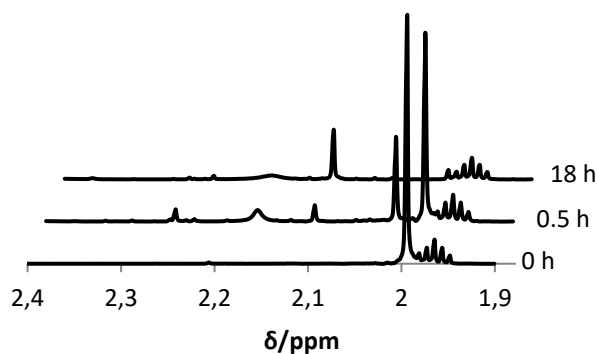
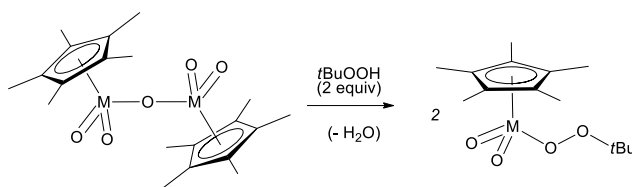


Figure 9. Representative ^1H NMR spectra of the CD_3CN solution resulting from the reaction of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ with TBHP/decane (2 equiv).

The major intermediate at δ 2.025 does not correspond to any of the compounds observed for the oxidation with H_2O_2 , whereas the minor intermediate at δ 2.261 and the signal at δ 2.112 which is assigned to the dinuclear symmetric peroxido complex $[\{\text{Cp}^*\text{MoO}(\text{O}_2)\}_2(\mu\text{-O})]$ are also observed at the same positions in the H_2O_2 experiment (*cf.* Figure 4). The new intermediate, therefore, likely contains the TBHP reagent, as confirmed by the appearance of a new *t*Bu resonance at δ 1.236 integrating correctly for 9 protons vs the 15 protons of the Cp* resonance at δ 2.025. Furthermore, these two resonances initially increase and then decrease proportionally. This intermediate is therefore interpreted as the *tert*-butylperoxido derivative $[\text{Cp}^*\text{MoO}_2(\text{OO}t\text{Bu})]$, as shown in Scheme 2. The *t*Bu region of the ^1H NMR spectrum also

shows the TBHP resonance at δ 1.204, decreasing with time, and another resonance at δ 1.195, assigned to *t*BuOH, which continuously increases. Note that this experiment does not produce any asymmetric dinuclear intermediate, confirming the tentative assignment made in Scheme 1 because only H₂O₂ could produce the proposed peroxido ligand by a fast proton transfer process.



Scheme 2

When the above experiment was repeated in the presence of 100 equivalents of TBHP, the starting material resonance decayed very rapidly and disappeared after 15 min. The [Cp*MoO₂(OO*t*Bu)] intermediate at δ 2.025 was again formed, in this case up to a maximum intensity of 56% after 15 min, then rapidly decaying. Several other minor resonances were observed at δ 2.268, 2.252, 2.243, 2.229, 2.121, 2.106, 2.089 and 2.019, only those at δ 2.121 and 2.106 ever reaching a notable intensity of ca. 12% of the initial Cp* intensity, whereas the others had a maximum of 2% of the intensity. After 430 min, the highest residual Cp* resonance was that at δ 2.121 with 9% of the initial intensity. This resonance was still present with approximately the same intensity after one week. Figure in SI?

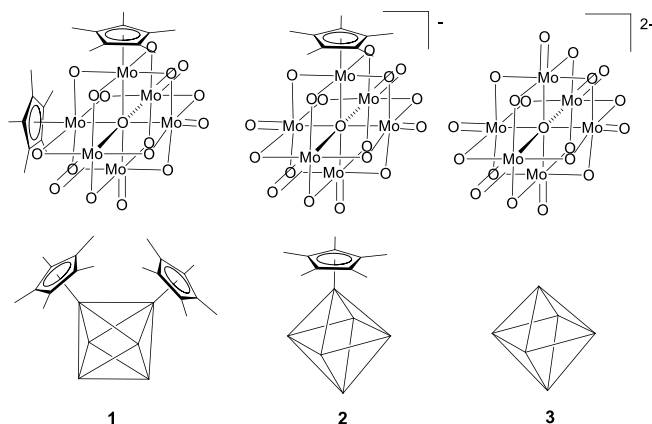
For the W compound, no change was evident in the NMR spectrum over a 24 h range at room temperature in the presence of only 2 equiv of the oxidant. When 100 equivalents of TBHP were used, the starting material resonance decreased slowly according to a first order decay (based on 7 points, $k = 6.3 \cdot 10^{-4} \text{ s}^{-1}$, $t_{1/2} \sim 18 \text{ min}$) and numerous small Cp* resonances were produced. The

main ones were observed at δ 2.167, 2.161, 2.121 and 2.090, none of them corresponding to those observed for the H_2O_2 reaction (Figure 7 and Figure 8) and none ever having greater than 5% of the initial Cp^* intensity. The first two resonances eventually disappeared, whereas the other two remained with approximately constant intensity (4.5% and 1.5%) after 6 h. Thus, a decay process with Cp^* loss also occurred in this case. Figure in SI?

In conclusion of the NMR investigation of sections (a) and (b), the stoichiometric reaction between $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ and ROOH in CD_3CN ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{H}$, aqueous solution; $\text{R} = t\text{Bu}$, decane solution) shows that the Mo complex reacts faster than the W complex and that aqueous H_2O_2 reacts faster than TBHP/decane. Several Cp^* -containing intermediates were generated in all cases, these being relatively stable when no more than 1 equivalent of oxidant per dimer was used, but Cp^* loss (faster for greater oxidant/complex ratios) eventually took place in every case and this loss was complete when aqueous H_2O_2 was used as oxidant.

(c) Analysis of the isolated decomposition products

Different crystallization attempts from solutions generated by oxidation of $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ yielded three different crystals under different conditions. The reaction with two equiv of H_2O_2 in MeCN followed by standing for three days at room temperature generated crystals of $[\text{Cp}^*_2\text{Mo}_6\text{O}_{17}]$ (**1**), identified by comparison of its unit cell parameters with those previously published for the same compound [10]. Under very similar conditions single crystals corresponding to compound $[\text{C}_5\text{Me}_5\text{O}][\text{Cp}^*\text{Mo}_6\text{O}_{18}]$ (**2a**) were also isolated and characterized. Finally, another solution containing the Mo complex and 5 equiv of TBHP/decane in MeCN led to the formation of crystals of compound $[\text{C}_5\text{Me}_5\text{O}]_2[\text{Mo}_6\text{O}_{19}]$ (**3**). Under similar conditions, the solution generated by oxidation of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ yielded crystals corresponding to compound $[\text{C}_5\text{Me}_5\text{O}][\text{Cp}^*\text{W}_6\text{O}_{18}]$ (**2b**).



Scheme 3

The three polyoxometallates constitute an isoelectronic series because of the isolobality of the Cp^{*-} and O^{2-} ligands (see Scheme 3). The structures of the two charged polyoxometallates in compounds **2** and **3** are completed by the pentamethylpyrilium cation, $[\text{C}_5\text{Me}_5\text{O}]^+$, which obviously derives from the Cp^{*-} ligand by an oxidative process as outlined in the formal stoichiometry of equation 1, with the oxide ion being consumed in the production of the anionic polyoxometallates. The five Me groups of the Cp^{*-} ligand are desymmetrized upon oxidation to the pyrilium ion, to yield three chemically distinct groups in a 2:2:1 ratio. Therefore, the resonances described above in Figure 1 for the oxidation of $[\text{Cp}^{*}_2\text{W}_2\text{O}_5]$ probably correspond to this ion. The pentamethylpyrilium ion is already reported in the literature for the crystallographically characterized salts $[\text{C}_5\text{Me}_5\text{O}]\text{I}_3$ [41] and $[\text{C}_5\text{Me}_5\text{O}][\text{Cp}^*\text{Mo}_6\text{O}_{18}]$ [42], the latter being the same compound described here, although previously obtained (from the aerial oxidation of $[\text{Cp}^*\text{Mo}(\text{CO})_2]_2$) in a different crystal habit. The metric parameters of the cation in our new structure of **2a** are similar to those previously reported in the above mentioned salts. The single crystals of the tungsten analogue **2b** were of very poor quality, but the unit cell was

isomorphous with that of **2a**. The data set was sufficient to identify the hexagonal W_6 array but did not warrant a full structural refinement (see more details in the Supporting Information). However, these results make the identity of this crystal completely unambiguous. The structure of **3** is affected by severe disorder and no reliable structural information beyond confirmation of the chemical constitution may be inferred. The Lindqvist anion $[Mo_6O_{19}]^{2-}$ is reported in another > 130 structurally characterized salts according to the Cambridge structural database, whereas the $[Cp^*Mo_6O_{18}]^{2-}$ ion is already reported for the above mentioned polymorph of the $[C_5Me_5O]^+$ salt [42], for the nBu_4N^+ salt [43] and for the Ph_4P^+ salt [44]. A detailed discussion of these structures is not warranted. Figures and relevant metric parameters can be found in the Supporting Information.



The precipitates that were isolated from the controlled decomposition of $[Cp^*_2M_2O_5]$ with a small excess of aqueous H_2O_2 have been analyzed by IR spectroscopy and by elemental analysis. The C,H analyses gave results in slight excess relative to the expected values for the formulations determined by X-ray diffraction (C/H for Mo: 22.50/2.44 vs. 21.28/2.70 for **1**, 20.88/2.62 for **2** and 20.32/2.56 for **3**; for W: 15.31/1.73 vs. 14.60/1.84 for **1**, 14.32/1.80 for **2** and 14.05/1.77 for **3**) but much closer to these formulations than to those of compounds with a 1:1 Cp^*/M ratio (e.g. for the starting material $[Cp^*_2M_2O_5]$: 44.29/5.58 for Mo and 33.45/4.21 for W). The IR spectra (shown in the Supporting Information) clearly display the typical M-O vibrational pattern of the Lindqvist type polyoxometallates. The solid derived from the $[Cp^*_2Mo_2O_5]$ decomposition shows a sharp absorption centered at 957 cm^{-1} for Mo=O and two

broader bands centered at 751 and 577 cm^{-1} for Mo-O-Mo. The frequency of the former is close, though a bit higher, to that measured for $[\text{nBu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ (949 cm^{-1} , also reported in SI). It is closer to those reported for the $[\text{Cp}^*\text{Mo}_6\text{O}_{18}]^-$ salts (957 cm^{-1} for the nBu_4N^+ salt, 967 cm^{-1} for the nBu_4P^+ and Ph_4P^+ salts, and 962 cm^{-1} for the *n*-butylpyridinium salt [44]) and for **1** (966 cm^{-1} [10]). The IR pattern of the solid isolated from the controlled decomposition of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ is similar, with a sharp band centered at 974 cm^{-1} and a broader band centered at 776 cm^{-1} . The former is close to those observed for $[\text{nBu}_4\text{N}]_2[\text{W}_6\text{O}_{19}]$ (966 cm^{-1}), for different salts of $[\text{Cp}^*\text{W}_6\text{O}_{18}]^-$ (960 cm^{-1} for the nBu_4N^+ , nBu_4P^+ and Ph_4P^+ salts), and for the W analogue of **1**, $[\text{Cp}^*_2\text{W}_6\text{O}_{17}]$ (984 cm^{-1} [45]).

The combined evidence from these isolation and characterization studies, in combination with the NMR studies outlined in the previous sections, is that while a small excess of oxidant generates soluble products that are still characterized by a Cp^*/M ratio of 1, larger and larger amounts lead to oxidation of the Cp^* rings, initially to the pyrilium cation $[\text{C}_5\text{Me}_5\text{O}]^+$, with formation of insoluble polyoxometallate salts. The analysis of the solids obtained with a moderate excess of H_2O_2 are rather consistent with the presence of **1** for the Mo sample (and its analogue for the W sample) but the presence of small amounts of other intermediates with a Cp^*/Mo ratio $> 2:6$ is not to be excluded. Obviously, after precipitation, further oxidation of the solid material becomes slower. Thus, with a moderate excess of oxidant, less extensive Cp^* removal has resulted in the crystallization of neutral **1**, whereas use of a greater excess has resulted in faster and more extensive Cp^* removal with formation of anionic polyoxometallates that are probably more soluble and more slowly crystallize as **2** and ultimately **3**. Therefore, use of a much larger excess of oxidant (*e.g.* 100 equivalents of more as under catalytic conditions) likely leads to $[\text{M}_6\text{O}_{19}]^{2-}$ as the only polyoxometallate species, which do not precipitate under

catalytic conditions given their greater solubility and the lower concentration relative to the conditions used for crystallization. It is interesting to mention in this respect that the oxidative decarbonylation by TBHP of the tris(pyrazolyl)methane complexes of molybdenum, [$\{\text{HC}(3,5\text{-Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_3$], also leads to the generation of a salt of the Lindqvist polyoxometallate, [$\{\text{HC}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mo}_2\text{O}_5$][Mo_6O_{19}], which was completely characterized and found to be an active catalyst in olefin epoxidation [46].

(d) Epoxidation catalysis with the $[\text{M}_6\text{O}_{19}]^{2-}$ complexes

On the basis of the considerations outlined in the above section, we considered it possible that all the $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ pre-catalyst is converted *in situ* to the Lindqvist structure during the catalytic experiments. In order to establish whether this species could correspond to the real epoxidation catalyst, we proceeded to verify the catalytic activity of the $n\text{Bu}_4\text{N}^+$ salts of the $[\text{M}_6\text{O}_{19}]^{2-}$ ions, which are completely soluble under the chosen experimental conditions. The tests were carried out under the same conditions previously employed for $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ (MeCN/toluene 3:1 as solvent, [cyclooctene] \sim 0.1 M; oxidant/cyclooctene = 2, cyclooctene/metal = 50, T = 55°C) [32, 35].

The catalytic tests revealed very poor activity and selectivity relative to the previously reported ones run with the $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ precursors. When using H_2O_2 as oxidant and the $[\text{Mo}_6\text{O}_{19}]^{2-}$ salt as catalyst, the conversion was only 56% (32% epoxide yield) after 28 h. This performance is not dramatically poorer in terms of activity, though the selectivity is worse, relative to that of $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ (63% conversion and 63% epoxide yield after 24 h) [32]. On the other hand, the H_2O_2 oxidation catalyzed by the $[\text{W}_6\text{O}_{19}]^{2-}$ salt gave only 6% conversion (0% epoxide yield) after 4 h, vs. a quantitative conversion and epoxide yield after only 2 h for $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ [32]. For the epoxidation reactions with the TBHP/decane reagent, a conversion of only 13% (2% epoxide

yield) was recorded after 3.5 h with the $[\text{Mo}_6\text{O}_{19}]^{2-}$ catalyst (*cf.* quantitative conversion and epoxide yield in less than 1 h in the presence of $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$) [35], whereas a conversion of only 10% (2% epoxide yield) was recorded after 2.5 h with the $[\text{W}_6\text{O}_{19}]^{2-}$ catalyst (*cf.* > 20% epoxide yield after 4 h in the presence of $[\text{Cp}^*_2\text{W}_2\text{O}_5]$) [35]. Plots of cyclooctene conversion and epoxide yield for the epoxidations catalyzed by $[\text{nBu}_4\text{N}]_2[\text{M}_6\text{O}_{19}]$ (M = Mo, W) are shown in the Supporting Information. Clearly, the oxidative decomposition of the $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ (M = Mo, W) compounds must produce also other species which are the real active and selective epoxidation catalyst, particularly for $[\text{Cp}^*_2\text{W}_2\text{O}_5]$ in the presence of H_2O_2 and for $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ in the presence of TBHP.

(e) Catalysis with aged solutions of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$

Since the results presented above establish quite clearly that both $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ (M = Mo, W) compounds are more or less rapidly decomposed with Cp^* loss by a large excess of oxidant, it is important to verify the catalytic activity of aged solutions. The most interesting cases pertain to the $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]/\text{TBHP}$ and $[\text{Cp}^*_2\text{W}_2\text{O}_5]/\text{H}_2\text{O}_2$ combinations which show the highest activities. In each case, a stock solution containing the oxidant and the precatalyst in a 200:1 ratio was prepared and kept at room temperature, as in the NMR monitoring experiments described above. Then, aliquots of this solution were used for cyclooctene epoxidation experiments started at different times (immediately after preparation and after 18 h, 24 h and 7 days) and run under conditions of concentrations and temperature similar to those previously reported (3:1 MeCN/toluene, 55%, oxidant/substrate = 2, *i.e.* the final catalytic solution contained a substrate/precatalyst ratio of 100, or 2% metal loading) [32, 35]. The catalytic activity was

evaluated by the initial rate method and the results are reported in Table 1. Graphs of the time evolution of the concentrations monitored by GC are available in the SI.

Table 1. Initial rates for the epoxidation of cyclooctene with aged solutions of the catalyst in the presence of oxidant.

$t/h^{[a]}$	$r_{(Mo-TBHP)}/M \cdot s^{-1}$ [b,c]	$r_{(W-H_2O_2)}/M \cdot s^{-1}$ [b,d]
0	$3.0 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$
18	$2.3 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$
24	$2.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$
192	$1.7 \cdot 10^{-5}$	$0.8 \cdot 10^{-4}$

[a] Time of the beginning of the catalytic run from the preparation of the catalyst/oxidant solution. [b] The rate was measured from the amount of cyclooctene oxide produced in the first 20 min. [c] Conditions: $[Cp^*_2Mo_2O_5]_0 = 2.5 \cdot 10^{-3}$ M; $[TBHP]_0 = 0.5$ M; $[cyclooctene]_0 = 0.25$ M. [d] Conditions: $[Cp^*_2W_2O_5]_0 = 2.6 \cdot 10^{-3}$ M; $[H_2O_2]_0 = 0.5$ M; $[cyclooctene]_0 = 0.25$ M.

For the TBHP reaction, the initial rate method for the evaluation of the catalytic activity is rendered necessary by the fact that this reaction is affected by product inhibition [35], the reaction rate being negatively affected by the *tert*-butanol product and a data fit to an integrated rate law being therefore impossible. For the H_2O_2 reaction, the established first order decay makes it possible in principle to make use of the integrated rate law [32]. However, the experiments carried out with the solution aged for 24 and 192 hours showed that the reaction stopped after only a partial conversion of cyclooctene (ca. 70% and 55%, respectively), suggesting that the H_2O_2 concentration has decreased by a slow catalase process during the ageing in such a way that the amount is substoichiometric during the catalytic experiment. Thus, the initial rate provides a simpler and direct way to measure the catalytic activity. Note that the

rate law for the catalyzed epoxidation by aqueous H_2O_2 was shown to be zero order in H_2O_2 [32], hence the initial rate should in principle be independent on the actual starting H_2O_2 concentration.

As shown in Table 1, the initial rate decreases with increase ageing of the catalyst solution, but the degree of activity loss is rather small (less than 50% over one week) for both catalytic solutions. This attests to the relative robustness of the catalytically active species. On the other hand, the organometallic precatalysts are totally consumed on a much shorter timescale (within minutes for the W compound in the presence of H_2O_2 at the concentrations of the catalytic experiments). For the oxidations with H_2O_2 , no Cp^* -containing soluble compounds remained in solution, whereas only a minor amount of a Cp^* -containing complex remained in solution for the oxidation with TBHP.

4. Conclusions

We have clearly established herein that compounds $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ ($\text{M} = \text{Mo}, \text{W}$), previously shown to be efficient epoxidation catalysts and particularly the Mo compound when the oxidizing agent is TBHP/decane in CHCl_3 [29] or in MeCN [35] or the W compound when the oxidizing agent is aqueous H_2O_2 in acetonitrile [32], are rapidly decomposed under catalytic conditions to species that are devoid of the Cp^* ligand. A number of Cp^* -containing intermediates have been detected when using a small excess of oxidizing agent but full loss of the Cp^* resonance occurs in the presence of H_2O_2 , the process being faster in the order $\text{W} < \text{Mo}$. TBHP/decane reacts more slowly than $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ in CD_3CN , but still leads to extensive (though not quite complete) loss of the Cp^* resonance. The fate of the Cp^* ring was not studied in great detail. However, the formation of the pentamethyl pyrilium cation, $\text{C}_5\text{Me}_5\text{O}^+$, at least as an

intermediate, was demonstrated by the crystallographic study of two minor products and was also suggested by an ^1H NMR investigation.

The Cp* loss for the reaction of the W precatalyst with H_2O_2 was complete in a very short time (with respect to the time required for a complete catalytic epoxidation). For the reaction of the Mo precatalyst with TBHP/decane extensive loss of the Cp* resonance (>90%) occurred within a few hours. However, the initial reaction rate measured for epoxidation experiments run with differently aged solutions of both $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]/\text{TBHP}$ and $[\text{Cp}^*_2\text{W}_2\text{O}_5]/\text{H}_2\text{O}_2$ combinations decrease by less than a factor of 2 over 1 week. This clearly demonstrates that the active catalyst for the epoxidation by at least H_2O_2 and probably also TBHP must be a non-organometallic species, which is relatively stable under the catalytic conditions. For the $[\text{Cp}^*_2\text{W}_2\text{O}_5]/\text{H}_2\text{O}_2$ system, it is quite clear that the catalyzed transformation must entirely be promoted by a non-organometallic species. For the $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]/\text{TBHP}$ system, on the other hand, it cannot be completely excluded that the organometallic intermediates generated in the initial stages of the $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ oxidative degradation process continues to be responsible for part of the catalytic activity of the aged solutions, but it seems more likely that the predominant non-organometallic degradation products are also at least in part responsible for the catalytic effect. These results are closely related to those reported by Colbran *et al.* [36], as already mentioned in the Introduction, and hint to the possible intervention or even dominant contribution of non-organometallic degradation products also in the previously published catalytic studies making use of organometallic precatalysts [13-28], most of which were carried out with compounds of molybdenum and with TBHP/decane as oxidant.

The exact nature of the catalytically active non organometallic species that form after a very short time in the presence of a large excess of H_2O_2 (few min) or at longer times in the presence

of a large excess of TBHP (few h) is not yet elucidated. The identification of the Lindqvist polyoxomolybdate, $[\text{Mo}_6\text{O}_{19}]^{2-}$, as the ultimate product of Cp^* loss from the precatalysts made us initially suspect that this could be an active species, but experiments reported here allowed us to exclude this hypothesis. In this respect, the recently reported $[\{\text{HC}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mo}_2\text{O}_5][\text{Mo}_6\text{O}_{19}]$ compound, produced by the oxidative decarbonylation of $[\{\text{HC}(3,5\text{-Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_3]$ by TBHP [46], was shown to be an active, stable, and recyclable catalyst. These results, in combination with the results reported herein on the poor performance of the Lindqvist anion (although the catalytic conditions are different), suggest the intriguing possibility that the catalytic activity is associated with the cationic species and that related cationic complexes are also formed during the oxidative degradation of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$. Further work is ongoing in our laboratory to identify these species and to understand why the catalytic activity is greater for the epoxidation with H_2O_2 when $\text{M} = \text{W}$ and for the epoxidation with TBHP when $\text{M} = \text{Mo}$ under otherwise identical conditions.

5. Supporting Information

Infrared spectra of the solids isolated from the controlled oxidative decomposition of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$, experimental details of the data collection and structural refinement for compounds **2a** and **3**, results of the cyclooctene epoxidation by aqueous H_2O_2 and by TBHP/decane catalyzed by $[\text{nBu}_4\text{N}]_2[\text{M}_6\text{O}_{19}]$ ($\text{M} = \text{Mo}, \text{W}$), and results of the cyclooctene epoxidation with aged solutions of $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]/\text{TBHP}$ and $[\text{Cp}^*_2\text{W}_2\text{O}_5]/\text{H}_2\text{O}_2$ (12 pages).

6. Acknowledgements.

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