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Dioxomolybdenum(VI) and –tungsten(VI) amino bisphenolates as epoxidation catalysts

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ABSTRACT

Low-cost metallate salts $\text{Na}_2\text{MO}_4 \cdot 2\text{H}_2\text{O}$ (M = molybdenum, tungsten) react with a tridentate amine bisphenol bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)methylamine ($\text{H}_2\text{ONO}^{\text{tBu}}$) under ambient conditions in acidic methanol solutions. The reactions lead to the formation of isostructural dioxo complexes $[\text{MO}_2(\text{ONO}^{\text{tBu}})(\text{MeOH})] \cdot \text{MeOH}$ in convenient yields. Spectral data as well as X-ray analyses reveal these complexes to be isostructural. Both compounds were tested as catalysts for epoxidation of olefins using *cis*-cyclooctene, cyclohexene, norbornene and styrene as substrates and *tert*-butyl hydroperoxide and hydrogen peroxide as oxidants. The molybdenum complex catalyses selectively the oxidation of *cis*-cyclooctene and norbornene to corresponding epoxides, whereas oxidation of cyclohexene and styrene lead low yields as the epoxidations were associated with the formation of other oxidation products. Corresponding tungsten complex shows lower activity for epoxidation of norbornene and practically no activity for other olefins. Both complexes can also catalyse the conversion of benzoin to benzil using dimethyl sulphoxide as an oxidant, while the molybdenum complex shows higher activity.

KEYWORDS

Molybdenum complexes, tungsten complexes, tridentate ligands, epoxidation, catalysis

1 Introduction

Molybdenum and tungsten are found in nature as water-soluble and biologically available high-valent oxo species. These metals are found in a variety of metalloenzymes that take part in oxygen atom transfer (OAT) reactions. In such reactions, an oxygen atom is transferred from an oxygen donor to a biologically relevant acceptor molecule or vice versa [1-5]. Considering these important biological functions, many examples of molybdenum- and tungsten-containing model compounds for OAT have been studied [6-10]. Similarly, a number of artificial dioxomolybdenum(VI) and -tungsten(VI) complexes have been prepared for catalytic applications in important industrial processes, for example olefin epoxidation [11-13]. Such complexes can be also considered as soluble molecular models for metal oxide catalysts [14]. As group 6 d-block metals, Mo and W are rather similar elements in regard to their occurrence, metallurgy and physical properties [15]. In addition, they share many chemical properties and are able to form structurally identical compounds. However, there are also remarkable differences between these two metals, thus compounds of the same structural type may differ noticeably in their formation, reactions and biochemical function. This is clearly seen, for example, when comparing the properties of Mo-enzymes with those of their W-substituted analogues. For example, W can replace Mo in sulphite oxidase or nitrate reductase at the same coordination site but with remarkable differences in their behaviour, as these enzymes are less active or completely inactive upon the substitution of Mo by W [16-18]. Dioxomolybdenum(VI) complexes with amine bisphenol ligands have generally been prepared from stable and easily available $\text{MoO}_2(\text{acac})_2$ or MoO_2Cl_2 and relevant ligand precursors in high yields using simple ligand displacement reactions [19-26], whereas occasional examples employ the use of an acidic solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ [27-29]. Corresponding W compounds are made under dry conditions using $[\text{WO}_2\text{Cl}_2(\text{dme})]$ and ligands as free bases or sodium salts [30,31] or mixing free ligands and $[\text{W}(\text{eg})_3]$ (eg = ethylene glycol) in alcohol solutions in the presence of ambient moisture [19,32]. We have previously prepared a molybdenum complex $[\text{MoO}_2(\text{ONO}^{\text{tBu}})(\text{MeOH})]\cdot\text{MeOH}$ (**Mo1**) ($\text{H}_2\text{ONO}^{\text{tBu}}$ = bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)methylamine) using $\text{MoO}_2(\text{acac})_2$ as a starting material [19]. In the present study, stable and low-cost metallate salts, $\text{Na}_2\text{MO}_4\cdot 2\text{H}_2\text{O}$ (M = Mo, W) were used to prepare **Mo1** and its tungsten analogue $[\text{WO}_2(\text{ONO}^{\text{tBu}})(\text{MeOH})]\cdot\text{MeOH}$ **W1**. These complexes were tested as catalysts for epoxidation of olefins *cis*-cyclooctene, cyclohexene, norbornene and styrene using *tert*-butyl hydroperoxide (TBHP) as an oxidant.

2 Experimental

All syntheses and manipulations were done under an ambient atmosphere. Solvents (HPCL grade) were used as received. Ligand precursor $\text{H}_3\text{ONO}^{\text{tBu}}$ was synthesised applying slight modification of a published procedure [33].

TBHP was purified by vacuum distillation prior to use. CAUTION: a mixture of TBHP with organic compounds is potentially explosive. All other chemicals and solvents were reagent grade, available commercially and used as received. The IR spectra were measured with Bruker Optics, Vertex 70 device with a diamond ATR setup. The ^1H spectra were recorded with Bruker Avance 500 (^1H : 500.13 MHz) NMR spectrometer.

Preparation of complexes: Metal precursors $\text{Na}_2\text{MO}_4 \cdot 2\text{H}_2\text{O}$ (1.0 mmol, M = Mo: 0.29 g; W: 0.38 g) and ligand (1.0 mmol, 0.38 g) were dissolved in 20 ml of MeOH and 0.2 ml of acetic acid was added. The reaction mixtures were refluxed for two hours, cooled and then kept overnight at room temperature (**Mo1**) or at 5 °C (**W1**). The products were isolated as large crystals by filtration and washed with a small amount of cold methanol.

$[\text{MoO}_2(\text{ONO}^{\text{tBu}})(\text{MeOH})] \cdot \text{MeOH}$ **Mo1**: 380 mg (63 %) of yellow crystals. IR: 3333m, 3147w, 2951m, 2907w, 2860w, 1607w, 1550w, 1530w, 1513w, 1478m, 1469m, 1445m, 1414m, 1389m, 1358w, 1313w, 1288w, 1252m, 1240s, 1229s, 1211m, 1146m, 1096m, 1028m, 1018s, 987w, 940m, 916w, 887s, 862s, 837vs, 798w, 770w, 762m, 681w, 596w, 569vs, 559s, 538w, 513w, 492w, 474w. ^1H NMR (DMSO-d_6): δ_{H} 6.97 (d, $J = 1.8$ Hz, 2H, ArH), 6.82 (d, $J = 1.8$ Hz, 2H, ArH), 4.39 (d, $J = 12.1$ Hz, 2H, NCH_2), 3.17 (s, 6 H, CH_3OH), 2.91 (d, $J = 14.0$, 2H, NCH_2), 2.20 (s, 6H, Ar CH_3), 2.08 (s, 3H, NCH_3), 1.35 (s, 18H, $\text{C}(\text{CH}_3)_3$). Anal. calcd. for $\text{C}_{27}\text{H}_{43}\text{MoNO}_6$ (MW = 573.60 $\text{g}\cdot\text{mol}^{-1}$): C 56.54; H 7.56; N 2.44; found: C 56.15; H 7.50; N 2.43. IR and NMR spectra were essentially identical to those reported earlier by us [19].

$[\text{WO}_2(\text{ONO}^{\text{tBu}})(\text{MeOH})] \cdot \text{MeOH}$ **W1**: 0.35 g (53 %) of colourless crystals. IR: 3221m, 3086w, 2953m, 2908w, 2868w, 2814w, 1604w, 1550w, 1530w, 1512w, 1478m, 1469m, 1445m, 1416m, 1391m, 1358w, 1315w, 1290w, 1254m, 1240s, 1229s, 1211m, 1146m, 1092w, 1032m, 1013s, 987w, 957m, 937w, 916w, 893s, 860s, 839vs, 798w, 770w, 760m, 681w, 596w, 569vs, 559s, 536w, 513w, 494w, 478w. ^1H NMR (DMSO-d_6): δ_{H} 7.02 (d, $J = 1.8$ Hz, 2H, ArH), 6.83 (d, $J = 1.8$ Hz, 2H, ArH), 4.44 (d, $J = 12.4$ Hz, 2H, NCH_2), 3.16 (s, 6H, CH_3OH), 3.01 (d, $J = 12.0$, 2H, NCH_2), 2.22 (s, 6H, Ar CH_3), 2.14 (s, 3H, NCH_3), 1.35 (s, 18H, $\text{C}(\text{CH}_3)_3$). Anal. calcd. for $\text{C}_{27}\text{H}_{43}\text{WNO}_6$ (MW = 661.48 $\text{g}\cdot\text{mol}^{-1}$): C 49.03; H 6.55; N 2.12; found: C 48.88; H 6.84; N 2.11.

Single crystals of **W1** were obtained from a reaction mixture and the X-ray data was collected and analysed according to the procedure reported earlier by our group [34]. Crystallographic data for **W1**: formula $\text{C}_{27}\text{H}_{43}\text{NO}_6\text{W}$, Mr = 661.47, monoclinic, space group $\text{P}2_1/\text{c}$, $a = 12.6357(3)$, $b = 14.7758(4)$, $c = 15.7124(3)$ Å, $\beta = 101.2346(12)^\circ$, $Z = 4$, $V = 2877.33(12)$ Å 3 , $T = 170$ K, $\rho_{\text{c}} = 1.527$ $\text{g}\cdot\text{cm}^{-3}$, $F(000) = 1336.0$, $\mu(\text{Mo-K}\alpha) = 4.053$ mm^{-1} , 15396 data, 5621 unique ($R_{\text{int}} = 0.0326$), 333 parameters, final $R_1(I > 2\sigma(I)) = 0.0344$, $wR_2 = 0.0682$, GOF = 1.069. CCDC 1431928 contains the supplementary crystallographic data for **W1**. 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.

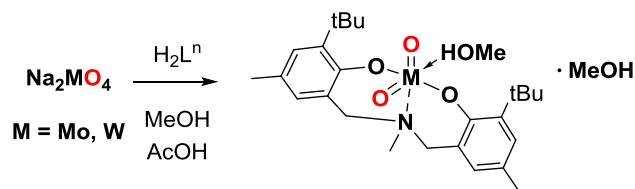
Catalytic activities. The epoxidations of *cis*-cyclooctene (**S1**), cyclohexene (**S2**), norbornene (**S3**) and styrene (**S4**) were run in the screw-cap vials under ambient atmosphere. A sample of a catalyst (7.1 μmol , **Mo1**: 4.1 mg or **W1**: 4.7 mg) was suspended in a mixture of TBHP (3.0 mmol, 0.29 ml), olefin (1.5 mmol, **S1**: 0.20 ml; **S2**: 0.15 ml; **S3**: 0.14 g; **S4**: 0.17 ml) and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ (0.2 ml) to have an oxidant:olefin:catalyst ratio of 420:210:1. The reaction mixtures were kept at 60 °C for 2 hours and subsequently analysed by ^1H NMR. In some experiments, the epoxidations of *cis*-cyclooctene and norbornene were studied using corresponding amounts of H_2O_2 (3.0 mmol, 0.34 ml of 30 % solution in water) as an oxygen source. The epoxidations of *cis*-cyclooctene and norbornene were also followed by ^1H NMR spectroscopy at various temperatures (40, 50 and 60 °C for *cis*-cyclooctene; 50 and 60 °C for norbornene) using a five-minute interval. Samples of catalysts (1.7×10^{-3} mmol, 1.0 mg of **Mo1** or 1.2 mg of **W1**) were mixed in solutions of TBHP (0.40 mmol, 39 μl) and substrate (0.20 mmol, 26 μl of **S1** or 18.8 mg of **S3**) in 0.6 ml of CDCl_3 . 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ (10 μl) was used as an internal standard. The oxidant:olefin:catalyst ratio was 210:110:1. In all experiments, the yields were calculated upon the integrated intensities of substrate olefin and product epoxide spectra. The control experiments were carried out without any catalyst in which case no reaction was observed. In the oxotransfer reactions, 0.20 mmol (42 mg) of benzoin was dissolved in 0.6 ml of DMSO-d_6 in a NMR tube and then treated with catalyst (1.7×10^{-3} mmol, **Mo1**: 1.0 mg; **W1**: 1.2 mg). The reaction mixtures were kept at 100 °C for 20 h and subsequently cooled to the room temperature. 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ (10 μl) was added as an internal standard and conversion of benzoin to benzil was detected by ^1H NMR. Detected yield of benzil was 60 % for **Mo1** and 26 % for **W1**.

3 Results and discussions

3.1. Catalyst preparation and characterisation

In this study, simple metallate salts were used as inexpensive starting materials for epoxidation catalyst. The stoichiometric amounts of metal precursors $\text{Na}_2\text{MO}_4 \cdot 2\text{H}_2\text{O}$ (M = Mo, W) and amine bisphenol $\text{H}_2\text{ONO}^{\text{iBu}}$ were mixed in MeOH in the presence of acetic acid, the reaction mixtures were allowed to reflux for two hours and then cooled to the room temperature. Yellow **Mo1** crystallised in a 63 % yield at room temperature, whereas colourless **W1** crystallised in a 53 % yield at 5 °C. The crystalline products are made of distinct complex units $[\text{MO}_2(\text{ONO}^{\text{iBu}})(\text{MeOH})]$, which crystallise together with one molecule of methanol. The IR and ^1H NMR spectra of **Mo1** were identical to those found earlier by us [19], whereas the spectra of **W1** and **Mo1** were closely related

as expected for an isostructural compound. The main differences are seen in the IR spectra, which show two distinctive absorption maxima for MO_2^{2+} moiety in the expected region. The symmetric and asymmetric stretches are observed at 940 and 887 cm^{-1} for **Mo1** and at 957 and 893 cm^{-1} for **W1**, respectively.



Scheme 1. Preparation of the catalysts.

The X-ray single crystal analysis of **W1** reveal that the solid complex is formed of mononuclear units, in which the aminobis(phenolate) is coordinated to the dioxotungsten(VI) ion as a tridentate ligand. A methanol molecule *trans* to the oxo group completes the distorted octahedral coordination sphere (see Fig. 1). Another methanol molecule is attached to the complex unit by a hydrogen bond. Uncoordinated MeOH molecule forms an H-bond with terminal oxygen atoms O1 ($\text{H}\cdots\text{O}$ distance is 1.935 \AA , see Figure S1), therefore the $\text{W}-\text{O1}$ bond is slightly longer than the $\text{W}-\text{O2}$ bond. The $\text{O}=\text{W}=\text{O}$ angles and the $\text{W}=\text{O}$ bonds are typical for cis-dioxotungsten(VI) complexes. Similarly, the $\text{W}-\text{Oaryloxyde}$, $\text{W}-\text{N}$ and $\text{W}-\text{OMeOH}$ distances are comparable with previous results.[13,20,29,30] In general, **W1** is isostructural with the equivalent molybdenum compound with only negligible differences in the bonding parameters [19].

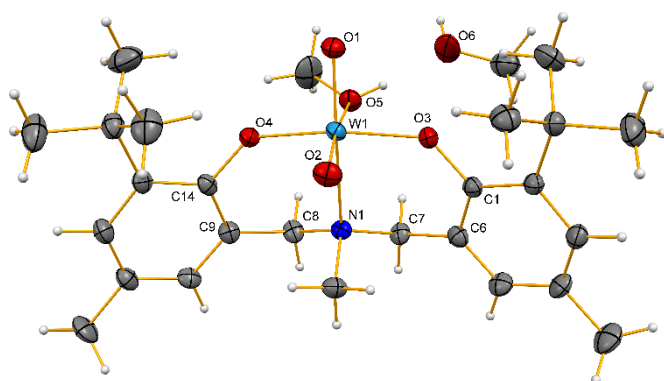
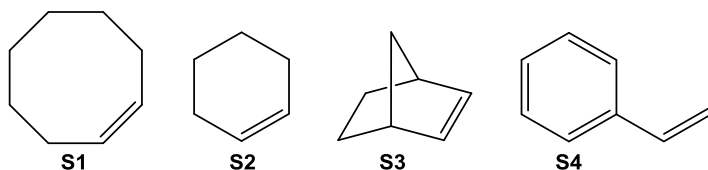


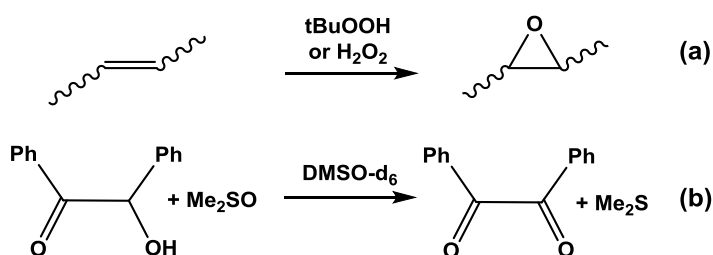
Figure 1. Molecular structure of **W1**. Selected bond lengths (\AA) and angles ($^\circ$): $\text{W1}-\text{O1}$: $1.733(3)$; $\text{W1}-\text{O2}$: $1.705(3)$; $\text{W1}-\text{O3}$: $1.928(3)$; $\text{W1}-\text{O4}$: $1.928(3)$; $\text{W1}-\text{O5}$: $2.320(3)$; $\text{W1}-\text{N1}$: $2.419(4)$; $\text{O1}-\text{W1}-\text{O2}$: $104.26(17)$; $\text{O3}-\text{W1}-\text{O4}$: $153.50(14)$; $\text{O1}-\text{W1}-\text{N1}$: $166.06(15)$; $\text{O2}-\text{W1}-\text{O5}$: $167.79(15)$

3.2. Catalytic activities

Complexes **Mo1** and **W1** were screened in the catalytic epoxidation of four different olefinic substrates *i.e.* *cis*-cyclooctene (**S1**), cyclohexene (**S2**), norbornene (**S3**) and styrene (**S4**) (Scheme 2) using two equivalents of TBHP (Table 1, entries 1 - 8) or H₂O₂ (Table 1, entries 9 -12) as oxidants (Scheme 3a). The reaction mixtures were analysed by ¹H NMR while the yields were calculated upon the integrated intensities of substrate olefin and product epoxide spectra (Table 2, entries 13 -17). Only selectivity towards epoxide formation is reported and attempts to identify other products were not made.



Scheme 2. Substrates for the oxidation reactions



Scheme 3. Studied epoxidation (a) and oxo transfer (b) reactions.

Table 1. Catalytic activities of **Mo1** and **W1**.

Entry ^a	catalyst	substrate	oxidant	conversion (selectivity) [%] ^b	TON ^c
1	Mo1	S1	TBHP	51 (100)	107
2	Mo1	S2	TBHP	45 (38)	36
3	Mo1	S3	TBHP	42 (90)	80
4	Mo1	S4	TBHP	5 (60)	6
5	W1	S1	TBHP	2 (100)	4
6	W1	S2	TBHP	-	-
7	W1	S3	TBHP	12 (100)	25
8	W1	S4	TBHP	-	-
9	Mo1	S1	H ₂ O ₂	15 (100)	32
10	Mo1	S3	H ₂ O ₂	4 (100)	4

11	W1	S1	H ₂ O ₂	11 (100)	23
12	W1	S3	H ₂ O ₂	3 (100)	6

^aThe reaction conditions: 60 °C, 2 h, 3.0 mmol of TBHP, 1.5 mmol of olefin, 0.2 ml of 1,2-C₂H₄Cl₂. The oxidant:olefin:catalyst ratio = 420:210:1.

^b Conversion (based on olefin consumption) and selectivity to the epoxide determined by ¹H NMR analysis on the crude reaction mixture (1,2-C₂H₄Cl₂ as an internal standard).

^c TON calculated as (mol epoxide)·(mol catalyst)⁻¹

The epoxidation of cyclooctene **S1** using TBHP as oxidant was accomplished by **Mo1** (51 % conversion, the turn-over number TON = 107) with high selectivity. Moreover, **Mo1** catalysed the oxidation of norbornene **S3** to corresponding epoxide with TON of 80. The oxidations of the more challenging substrates cyclohexene and styrene gave the desired epoxides in low yields as the epoxidations were associated with the formation of other oxidation products. In contrast, **W1** showed less activity as only 2 % of *cis*-cyclooctene **S1** was converted to the corresponding epoxide. **W1** had some activity for the selective epoxidation of **S3** but practically no activity for other olefins. The selectivity with substrates **S1** and **S3** using structurally related catalysts equals with the earlier studies by us [13] as well as other groups.[21,35,36] **Mo1** and **W1** were also tested as catalysts for epoxidation of **S1** and **S3** using aqueous hydrogen peroxide as oxidant instead of TBHP solutions. The reaction was carried out in a two-phase mixture (H₂O-C₂H₄Cl₂) and the organic phase was analysed after a two hour reaction. Both complexes showed some activity, whereas no differences between **Mo1** and **W1** were seen. The activities were lower than in reactions using TBHP, which is possible due to the slow diffusion in a two-phase system. In all epoxidation experiments, the colour of the solutions turned from yellow (**Mo1**) or colourless (**W1**) to orange-red during the reaction, which indicates the formation of new metal species or occurrence of redox reactions of the metal centres.

The epoxidation reactions of **S1** and **S3** with catalyst **Mo1** were studied in detail by monitoring the reactions via ¹H NMR spectroscopy with a five-minute interval (Table 2). The catalyst was mixed in solutions of TBHP and substrate (**S1** or **S3**) in CDCl₃. The control experiments were carried out without any catalyst in which case no reactions occurred. Conversely, the catalytic reactions started immediately without notable induction times and after 24 hour reactions, the conversions of olefins were practically quantitative in all experiments. The activities of **Mo1** for the epoxidation of **S1** (Turn-over frequency, TOF = 120, 330 and 660 h⁻¹ at 40, 50 and 60 °C, respectively) are comparable to those of a number of dioxomolybdenum(VI) complexes under related conditions, e.g. [MoO₂(OSiPh₃)(2,2'-bipyridine)] [35], [MoO₂Cl(HC(bim)₃)]Cl (HC(bim)₃ = tris(benzimidazolyl)methan) [36] and [MoO₂(acac)(^RN,O)] (^RN,OH = imino-alcohol derivative of α -pinene) [37]. The epoxidation activities for

S3 were (TOF = 210 and 410 h⁻¹ at 50 and 60 °C, respectively) were slightly lower than for **S1**. The kinetic profiles for these epoxidation reactions are presented in a supplementary material.

Table 2. Catalytic activity of **Mo1** for the epoxidations of *cis*-cyclooctene and norbornene.

Entry ^a	substrate	catalyst	T [°C]	t _{1/2} [min]	TOF [h ⁻¹] ^b
1	S1	Mo1	40	-	120
2	S1	Mo1	50	20	330
3	S1	Mo1	60	13	660
4	S3	Mo1	50	49	210
5	S3	Mo1	60	30	410

^aThe oxidant:olefin:catalyst ratio of 210:110:1.

^bTOF calculated at 10 min reaction as (mol epoxide)·(mol catalyst)⁻¹·(t/h)⁻¹. Conversion and yield of the epoxide were determined by ¹H NMR analysis on the reaction mixture (1,2-C₂H₄Cl₂ as an internal standard).

Dioxomolybdenum(VI) and tungsten(VI) complexes are known to catalyse oxotransfer reactions from DMSO to organic substrates or phosphines. [23, 24, 27-29, 38]. Generally, molybdenum-based catalysts are more active in these reactions than their tungsten counterparts. In the present study, the ability of **Mo1** and **W1** to catalyse oxotransfer reactions was investigated in DMSO solutions using benzoin as the substrate wherein the conversion of benzoin to benzil was monitored by ¹H NMR spectroscopy (Scheme 3b). As anticipated, both complexes catalysed oxotransfer from DMSO to benzoin, though the reactions were slow at low temperatures and no reactions were seen at room temperature. The detected yields of oxidized products after 20 h heating at 100 °C were 60 % for **Mo1** and 26 % for **W1** using 1 mol-% catalyst loading. On the grounds of structurally comparable molybdenum- and tungsten-based catalyst systems, we can assume that the dioxometal(VI) complexes react with benzoin to yield oxometal(IV) complexes and benzil. The central metal ions are then rapidly oxidized back to the initial dioxocompounds with DMSO to complete the catalytic cycle [23, 24]. Although reduced molybdenum and tungsten species are expected to be strongly coloured, only rather weak colour changes were observed during these catalytic reactions indicating that the re-oxidation process of metal is very rapid and/or only small parts of the complexes are actually reacting.

Conclusions

In conclusion, Na₂MO₄·2H₂O (M = Mo, W) can react with a tridentate O₂N-type ligand precursor (H₂ONO^{tBu}) to form isostructural dioxometal(VI) complexes [MO₂(ONO^{tBu})(MeOH)]·MeOH. The Mo complex catalyses selectively the epoxidation reactions of *cis*-cyclooctene and norbornene with *tert*-butyl hydroperoxide and H₂O₂, whereas the W analogue showed lower activities. The Mo complex compares well with a number of

dioxomolybdenum(VI) complexes used as catalysts for the epoxidation of cyclooctene. Both complexes catalyse also oxygen atom transfer reaction between benzoin and DMSO. These results show the possibility of using aminobisphenolate molybdenum complexes as epoxidation catalysts as well as using molybdenum and tungsten-based catalysts for oxygen atom transfer reactions.

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