EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe
FULL PAPER

DOI:10.1002/ejic.201500055

Dioxomolybdenum(VI) and -tungsten(VI) Complexes with Multidentate Aminobisphenol Ligands as Catalysts for Olefin Epoxidation

CLUSTER ISSUE

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Keywords: Molybdenum / Tungsten / Hydrogen bonds / Epoxidation / Green chemistry

The synthesis of four molybdenum and tungsten complexes bearing tetradentate tripodal amino bisphenolate ligands with either hydroxyethylene (**1a**) or hydroxyglycolene (**1b**) substituents is reported. The molybdenum dioxo complexes $[MoO_2L]$ (L = **2a**, **2b**) and tungsten complexes $[WO_2L]$ (**3a**, **3b**) were synthesized using $[MoO_2(acac)_2]$ and $[W(eg)_3]$ (eg = 1,2-ethanediolato, ethylene glycolate), respectively, as precursors. All complexes were characterized by spectroscopic means as well as by single-crystal X-ray diffraction analyses. The latter reveal, in all cases, hexacoordinate complexes in which the hydrogen atom of the hydroxy group is involved in hydrogen bonding with one of the metal oxo groups. In the case of the glycol substituent, the ether oxygen atom is coordinated to the metal whereas the hydroxy group remains uncoordinated. The complexes were tested as catalysts in the epoxidation of cyclooctene under eco-friendly conditions, using an aqueous solution of H_2O_2 as the oxidant and dimethyl carbonate (DMC) as solvent or neat conditions, as substitutes for chlorinated solvents. Molybdenum complexes **2a** and **2b** showed good catalytic activity using H_2O_2 without added solvent, and tungsten complexes **3a** and **3b** showed very high activity in the epoxidation of cyclooctene using H_2O_2 and DMC as solvents.

Introduction

High-valent molybdenum and tungsten oxides are found in a variety of metalloenzymes that take part in oxygen atom transfer (OAT) reactions, whereby an oxygen atom is transferred to or from a biologically relevant donor/acceptor molecule.[1] The molybdenum oxotransferase enzymes may be subdivided into three (structural) families that are named after prototypical enzymes: the xanthine oxidase, sulfite oxidase and DMSO reductase families.[2] Similarly, the tungsten enzymes can be divided into two families: the aldehyde oxidoreductases and the formate dehydrogenases.[3] A common feature of these proteins is a M(VI)=O moiety in the active site of the enzyme, which is bonded to the cofactor molybdopterin.[4] In view of these important biological functions, many examples of molybdenum and tungsten-containing model compounds for OAT are known.[5,6] Molybdenum-based catalysts for oxidation have been developed and used in important industrial processes such as alkene epoxidation.[7]

Tetradentate tripodal aminobisphenolate ligands have proven to be versatile ligands able to coordinate to a variety of metals.[8] A common type of complex with such ligands exhibits a trianionic $(O_3N)^{3-}$ donor atom motif around the metal center.[9–12,13] Because such a motif creates a coordination pocket around the metal atom resembling the active site of metalloenzymes, amino phenolate ligands have also been employed as structural and functional models of such metalloenzymes, for instance, the V^V-dependent haloperoxidases.[14] By varying the structure of one arm, along with the reaction conditions, a dianionic $(O_2NOR)^{2-}$ coordination motif can also be achieved. The corresponding complexes are useful catalysts for a broad range of reactions.[15,16] In our ongoing research into the coordination chemistry of dioxomolybdenum(VI) complexes,[17–19] we were interested in using amino bisphenolate ligands con-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500055.

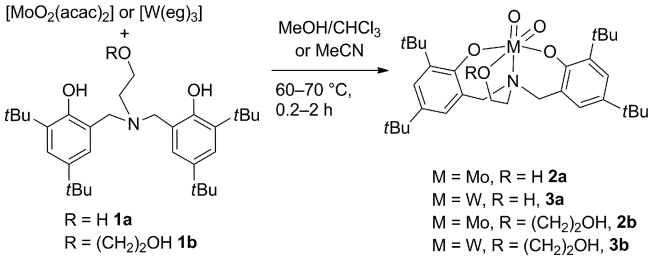
taining an aliphatic alcohol as a third arm donor moiety, to generate a tetradentate dianionic ligand $(O_2NOH)^{2-}$ with the hydroxy moiety remaining intact. The presence of such a neutral hydroxy group in proximity to the molybdenum center might allow for hydrogen bonding with incoming oxidants like *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide (H_2O_2). Such hydrogen bonds have been identified as important contributors to the activation of OAT reactions from peroxides to olefins during catalytic epoxidations.[20]

The catalytic epoxidation of alkenes by dioxomolybdenum(VI)[6,17–19,21] and dioxotungsten(VI)[22,23] complexes has been intensively investigated. Amino bisphenolate complexes have also been tested as epoxidation catalysts using *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) as oxidants.[9,10,24] One major issue when considering catalytic reactions involves the question of how to limit their environmental impact by establishing optimal reaction conditions (i.e. low catalyst loading, reduction of side-product formation and substitution of chlorinated or hazardous solvents by non-toxic solvents or neat conditions). Within this paper the synthesis and characterization of dioxomolybdenum(VI) and dioxotungsten(VI) complexes equipped with dianionic amino bisphenolate ligands $(O_2NOH)^{2-}$ with a pendant hydroxy donor arm are described. These novel complexes show high catalytic activity in the epoxidation of cyclooctene with either TBHP or H_2O_2 in dimethyl carbonate (DMC)[25] and even under neat reaction conditions, using 1 mol-% catalyst.

Results and Discussion

Ligands **1a** and **1b** were synthesized under neat conditions in a fashion analogous to published procedures.[26] Yields, relative to published reports, were improved by purifying **1a** and **1b** via column chromatography (gradient mixtures of EtOAc and cyclohexane as eluent) affording **1a** in 75% and **1b** in 67% yields. Both compounds, isolated as white solids, are highly soluble in common organic solvents such as chlorinated solvents and hot methanol. Analytical data for **1a** and **1b** are consistent with previously published data.[11,27]

For the synthesis of the molybdenum complexes, a solution of 1 equiv. **1a** or **1b**, respectively, in acetonitrile was added to a suspension of 1 equiv. of $[MoO_2(acac)_2]$ in acetonitrile. The orange mixtures were heated at 70 °C, whereupon corresponding molybdenum complexes **2a** and **2b** rapidly precipitated as yellow solids (Scheme 1). After filtration, **2a** and **2b** were isolated in good yields. The complexes are soluble in common chlorinated and aromatic solvents. Proton NMR analyses in deuterated chloroform confirmed the coordination of the ligands to each metal center as indicated by the disappearance of the broad signals from each phenol OH proton, and by splitting of respective singlets corresponding to the four CH_2 protons bound to the aromatic groups into two doublets with large coupling constants, as is typical for C_s-symmetric amino bisphenolate complexes. Only one set of resonances is visible (only two aromatic and two *t*Bu signals), consistent with formation of symmetric *O,O-trans* species. The proton of the hydroxy group, not visible in the spectrum of the free ligand, appears as a triplet at δ = 3.33 ppm in the spectrum of **2b**, arising from coupling (J = 6.2 Hz) to the methylene group directly bound to the hydroxy group, which appears as a multiplet at δ = 4.10 ppm. This indicates slow or non-existent exchange of the alcohol proton, suggesting hydrogen interaction between this proton (hydrogen) and the oxo group (as also observed by X-ray crystallography, see below). After several days, it was noticed that the NMR sample of **2a** turned purple, indicating degradation of the complex to a possible chlorinated species. A new measurement of this sample showed multiple new sets of peaks that could not be assigned.



Scheme 1. Amino bisphenolate ligands **1a** and **1b**, complexes **2a** and **2b** (M = Mo) and **3a** and **3b** (M = W).

For the synthesis of tungsten complexes **3a** and **3b**, $[W(eg)_3]$ (eg, 1,2-ethanediolato)[28] was used as a precursor and dissolved in methanol. A solution of the corresponding ligand **1a** or **1b** in chloroform was added and the mixture heated at 60 °C until precipitation of the product occurred. Complex **3a** was isolated as a white solid albeit in poor yield (34%). By using $[WO_2(acac)_2]$ as the starting material, **3a** could be alternatively prepared in acetonitrile in significantly higher yield (69%). IR spectroscopy and EI mass spectrometry confirm the formation of **3a**, with characteristic resonances in IR at 948 and 918 cm^{-1} for the W=O stretching (925 and 917 cm^{-1} for Mo=O in **2a**), and a molecular ion peak corresponding to 711.6 g mol^{-1}. The compound is poorly soluble in common organic solvents such as methanol, toluene or THF, and slightly more soluble in chlorinated solvents. However, as observed for **2a**, upon dissolution of the solid in $CDCl_3$, slow degradation becomes evident. Despite its poor solubility, **3a** was partially dissolved in $[D_4]$MeOH allowing acquisition of NMR data. The NMR spectrum obtained shows a set of resonances consistent with a symmetric species. Determination of the molecular structure (vide infra) points to a six-coordinate species with a coordinated hydroxy group. Similarly, **3b** was prepared using $[W(eg)_3]$ as the starting material and isolated as a white solid in 53% yield. Like **2b**, NMR spectroscopic data of **3b** in deuterated chloroform revealed only one set of signals corresponding to the symmetric *O,O-trans* complex and the hydrogen form the hydroxy group appeared as a triplet at δ = 2.86 ppm (J = 5.8 Hz).

Molecular Structures of Complexes 2a, 2b, 3a and 3b

The molecular structures, determined by single-crystal X-ray diffraction analyses, are displayed in Figures 1 and 2; selected bond lengths and angles are given in Table 1. Selected details pertaining to data collection and refinement are given in Table 4; full details are given in the Supporting Information. For all four complexes, the positions of the H atoms of all OH groups could be found in difference Fourier maps. The O–H distances were fixed at 0.84 Å.

Table 1. Selected bond lengths [Å] and angles [°] for **2a**, **2b**, **3a** and **3b**.

	2a	2b	3a	3b
M1–O1	1.7305(14)	1.7004(9)	1.7457(13)	1.7408(16)
M1–O2	1.6952(14)	1.7204(8)	1.7204(13)	1.7162(16)
M1–O3	2.2867(10)	2.3321(9)	2.2357(13)	2.3128(16)
M1–O11	1.9403(14)	1.9543(9)	1.9449(13)	1.9493(16)
M1–O31	1.9337(14)	1.9360(9)	1.9393(13)	1.9349(17)
M1–N1	2.3697(16)	2.3628(10)	2.3682(15)	2.3573(19)
O1–M1–N1	156.99(6)	155.00(4)	159.43(6)	155.42(7)

Single crystals of **2a** and **2b** were obtained by slow evaporation from concentrated acetonitrile solutions at room temperature. Both complexes display a distorted octahedral coordination environment around the Mo atom. For both complexes, the amino bisphenolate ligand coordinates in a dianionic, tetradentate fashion, with the hydroxy group of the pendant arm still protonated (H3 in **2a**, H6 in **2b**), resulting in an overall neutral dioxomolybdenum(VI) complex. The coordination of the hydroxy group as a neutral donor in **2a** can be deduced from the long Mo1–O3 bond length [2.2867(10) Å].[29] Both solid-state structures indicate hydrogen bonding from the hydroxy hydrogen atom to the metal oxo group. Short distances between the hydroxy oxygen atom and the oxo group are observed [2.6680(19) Å in **2a** and 2.7516(17) Å in **2b**]. For the latter, NMR spectroscopy confirms this interaction. The bond lengths of the oxo ligands O1 and O2 [1.7305(14) and 1.6952(14) Å resp.] and of the phenolate ligands O11 and O31 [1.9403(14) Å and 1.9337(14) Å, respectively] to the Mo center are within the expected range for such complexes.[10,12,16,30]

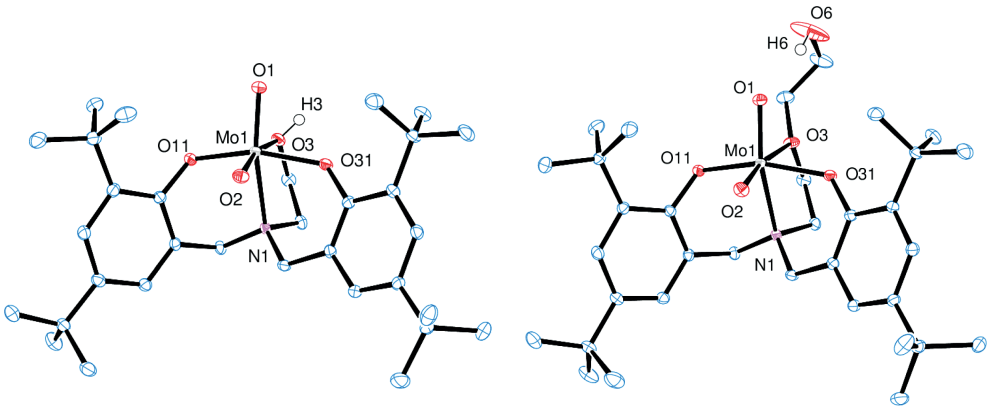


Figure 1. Molecular views (50% probability level) of complexes **2a** (left) and **2b** (right) (solvent molecules and hydrogen atoms except for hydroxy group are omitted for clarity). Complex **2a** shows two independent molecules in the unit cell with very similar conformations; only one molecule is shown here. The hydroxyethyl group in **2b** was disordered over two orientations and refined with site occupation factors of 0.813(4) and 0.187(4), respectively. The less occupied 2-hydroxyethoxy orientation has been omitted for clarity reasons.

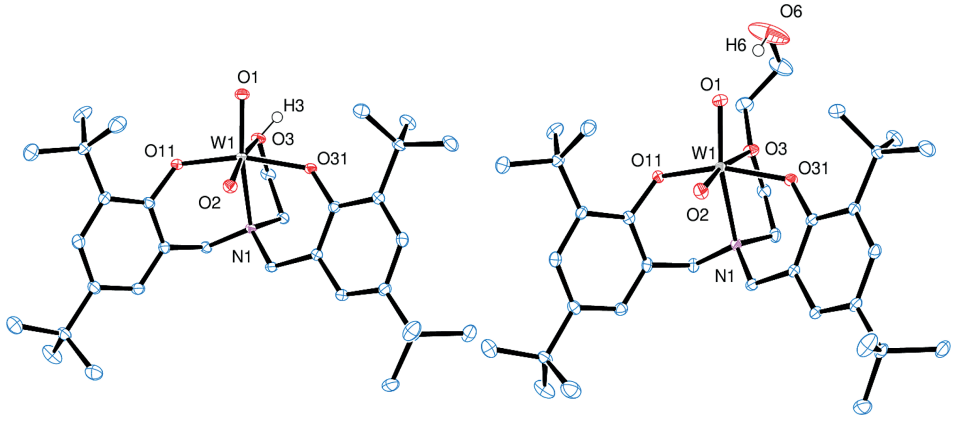


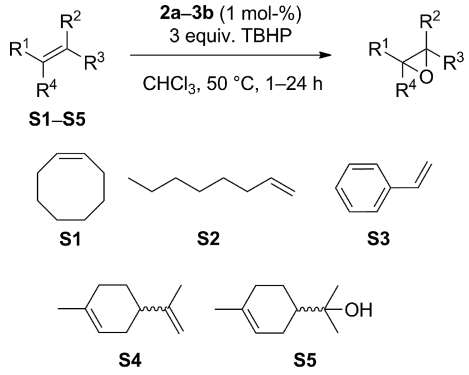
Figure 2. Molecular views (50% probability level) of complexes **3a** (left) and **3b** (right) (solvent molecules and hydrogen atoms except for hydroxy group are omitted for clarity).

Single crystals of **3a** and **3b** were obtained by slow evaporation from methanol/chloroform mixtures (1:1 v/v) at ambient temperature. Both complexes display a distorted octahedral coordination environment around the W atom, similar to the Mo complexes **2a** and **2b**. Again, for both complexes the amino bisphenolate ligand coordinates in a dianionic, tetradentate fashion, with the hydroxy group of the pendant arm still protonated (H3 in **3a**, H6 in **3b**), resulting in an overall neutral dioxotungsten(VI) complex. In the solid-state structure of **3b**, the pendant hydroxy group is orientated towards the oxo ligand O1, and once again the short distance between O6 and O1 [2.717(3) Å] confirms formation of a hydrogen bond. The coordination of the hydroxy group in **3a** can again be deduced from the long W1–O3 bond length, and hydrogen bonding is confirmed by the short O3–O1 distance [2.5401(19) Å]. The bond lengths of the oxo ligands O1 and O2 [1.7457(13) and 1.7204(13) Å resp.] and of the phenolate ligands O11 and O31 [1.9449(13) Å and 1.9393(13) Å resp.] to the W centre are within the expected range for similar complexes.[16,31] In contrast, the W1–O3 distance is much longer at 2.2357(13) Å, consistent with a neutral hydroxy group.[29] In general, the structure of **3b** displays geometric parameters very similar to those of **2b**.

Catalytic Epoxidation

As a benchmark experiment to assess catalytic activities, complexes **2a**, **2b**, **3a** and **3b** were screened in the catalytic epoxidation of five different olefinic substrates **S1**–**S5** using TBHP (5.5 M in decane) as the oxygen source (Scheme 2) under standard experimental conditions (0.5 mL of $CHCl_3$ with 1 mol-% of catalyst and 3 equiv. of TBHP at 50 °C) as summarized in Table 2. The five olefin substrates used were cyclooctene **S1**, 1-octene **S2**, styrene **S3**, limonene **S4** and α-terpineol **S5**. In the case of **S4** and **S5**, racemic mixtures of the D- and L-enantiomers were used.

Products were identified by gas chromatography. Only selectivity towards epoxide formation is reported and attempts to identify enantiomers/diastereomers were not made. As expected, the epoxidation of cyclooctene **S1** with TBHP was achieved using all four complexes, with high selectivities. Alternatively, reactions with Mo complexes **2a** and **2b** afforded high yields of epoxide (>99%) relatively rapidly – after 2 h and 1 h, respectively but the W complexes **3a** and **3b** exerted less activity; the reaction with **3b** afforded a yield of only 70% after 24 h. For more challenging substrates **S2**–**S5**, activities as well as selectivities, dropped significantly for all four catalysts. Mo complexes **2a** and **2b** showed catalytic activity for all four substrates **S2**–**S5**. For the epoxidation of **S2**, high selectivities for epoxide formation with moderate yields were obtained. For styrene **S3**, low yields (17 and 14%, respectively) with diminished epoxidation selectivities (43 and 30%, respectively) were observed for **2a** and **2b**, with benzaldehyde and benzacetaldehyde being the main side products. For substrate **S4**, complexes **2a** and **2b** showed high regioselectivity as only the endocyclic double bond underwent epoxidation. However, no selectivity for *cis* or *trans* epoxidation was observed; both epoxides were detected by GC in a about 1:1 ratio. One of the side products formed could be identified as a mixture of D- and L-carvone, the cyclohexanone oxidation product of limonene. Finally, a catalytic profile similar to that found with **S4** was obtained for α-terpinol **S5**, demonstrating a functional group tolerance of **2a** and **2b** for hydroxy groups, as expected. Tungsten complexes **3a** and **3b** were less effective at catalyzing epoxidations with TBHP oxidant compared to Mo complexes **2a** and **2b**. This observation agrees well with previous reports.[23,32,33] No catalytic activity (<5% yield of epoxide) for 1-octene **S2**, styrene **S3** and α-terpinol **S5** could be detected with **3a** and **3b**. Good yields and high selectivities were obtained only in epoxidations of cyclooctene **S1** (Table 2). Low yields and selectivities for epoxide were observed for limonene **S4**. Interestingly, in all catalytic experiments with W complexes **3a** and



Scheme 2. Substrates **S1**–**S5** used in epoxidation experiments with complexes **2a**, **2b** and **3a**, **3b**.

Table 2. Summary of epoxidation results u **2a**, **2b** and **3a**, **3b** with TBHP.

	2a		**2b**		**3a**		**3b**	
	Yield (Sel.)[a] [%]	t[b] [h]	Yield (Sel.)[a] [%]	t[b] [h]	Yield (Sel.)[a] [%]	t[b] [h]	Yield (Sel.)[a] [%]	t[b] [h]
S1	>99 (100)	2	>99 (100)	1	85 (100)	24	70 (100)	24
S2	40 (100)	24	25 (100)	24	<5 (n.d.)	24	<5 (n.d.)	24
S3	17 (43)	24	14 (30)	24	<5 (n.d.)	24	<5 (n.d.)	24
S4[c]	61 (63)	4	64 (70)	6	10 (14)	24	20 (34)	5
S5[c]	48 (50)	24	46 (58)	24	<5 (n.d.)	24	<5 (n.d.)	24

[a] Maximum yield of epoxide, selectivity (Sel.) to epoxide given in brackets; n.d.: not determined. [b] Time to reach maximum yield of epoxide, maximum experiment time was 24 h. [c] Sum of both possible diastereoisomers.

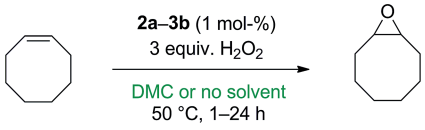
Table 3. Epoxidation of cyclooctene using H_2O_2.[a]

	2a		2b		3a		3b	
	Yield (Sel.)[b] [%]	*T* [h]	Yield (Sel.)[b] [%]	*t* [h]	Yield (Sel.)[b] [%]	*t* [h]	Yield (Sel.)[b] [%]	*t* [h]
$CHCl_3$	39	4	59	4	40	4	36	4
$CHCl_3$	>99	20	>99	20	>99	20	>99	20
DMC	16	4	13	4	80	4	71	4
DMC	34	20	45	20	>99	20	>99	20
Neat	58	4	2	4	15	4	0	4
Neat	>99	20	95	20	40	20	0	20

[a] Cyclooctene (0.45 mmol), 3 equiv. H_2O_2 (50% in water), cat. (1 mol-%), solv. [0.45 M] or neat, 50 °C. Monitored by GC with mesitylene as internal standard. [b] Selectivity for cyclooctene oxide was 100%.

3b we detected oxidation products of decane (solvent of oxidant TBHP, e.g. 4-decanone, 5–10%), which could point to a possible catalytic activity in alkane oxidation for **3a** and **3b**.

By designing tripodal bisphenolate complexes bearing a hydroxy group in one arm, we sought to achieve efficient catalytic epoxidation using eco-friendly conditions. To do so, we tested **2a**, **2b** and **3a**, **3b** as catalysts for epoxidation of cyclooctene using aqueous hydrogen peroxide as oxidant instead of TBHP solutions in decane. The advantage of using H_2O_2 is that only water is present as a byproduct at the end of the reaction, instead of *tert*-butanol and decane. More importantly, dimethyl carbonate, a non-toxic and non-hazardous solvent,[25] was tested as a solvent substitute for chloroform. Catalytic experiments using H_2O_2 in neat conditions were also performed (Scheme 3). Results are summarized in Table 3.



Scheme 3. Epoxidation of cyclooctene with complexes **2a**, **2b** and **3a**, **3b** under eco-friendly conditions.

In contrast to the observations with TBHP, tungsten complexes **3a** and **3b** showed higher catalytic epoxidation activities in reactions using H_2O_2; conversion of cyclooctene to cyclooctene oxide was found to be quantitative in chloroform. Interestingly, the tungsten complexes showed excellent activity when epoxidations were performed in dimethyl carbonate instead of $CHCl_3$. Reactions were found to be two times faster, reaching 80% yield of epoxide using **3a** and 71% using **3b** after 4 h. Because of their low solubilities in H_2O_2 solution and cyclooctene, **3a** and **3b** showed limited activity when reactions were performed in the absence of solvent. Reduced activity could be expected using molybdenum complexes **2a** and **2b** with H_2O_2 as oxidant when compared to tungsten complexes, as already observed in the literature.[23,33,34] For this reason, examples of Mo/H_2O_2 catalytic systems are scarce.[33,35] However, quantitative conversion of cyclooctene could be achieved with Mo complexes **2a** and **2b**, using $CHCl_3$ as solvent or, more importantly, under neat conditions. In the latter case, data shows an induction period for complex **2b**, but complex **2a** bearing a short arm with a hydroxy group exhibits good activity (59% yield after 4 h). To investigate the role of the hydroxy group during the catalytic reaction, a molybdenum complex similar to **2a** but bearing a methoxy group instead of a hydroxy group was synthesized following a previously reported procedure.[16] This complex was tested as a catalyst for cyclooctene epoxidation under the conditions described in Table 3. When using DMC as solvent, the yield of epoxide reached 20% after 4 h and 55% after 24 h; the complex with the methoxy group showing better activity than **2a**. Under neat reaction conditions, the yield reached 44% after 4 h and 97% after 24 h, the methoxy catalyst exhibited similar activity to that of **2a**. These results indicate that the presence of the hydroxy group in the arm of the catalysts does not significantly affect the catalytic reaction nor does it increase the activity of the complexes. Despite this observation, the complexes **2a**, **2b** and **3a**, **3b** are interesting catalysts relative to previously reported systems using eco-friendly conditions. Morlot et al.,[21m] reported the synthesis of molybdenum complexes that could catalyze cyclooctene epoxidation under neat reaction conditions with very good activity (88% yield and 89% selectivity after 5.5 h for epoxide using 1 mol-% [Mo] catalyst), but using TBHP as oxidant. Vrdoljak et al.[21p] used similar conditions (TBHP/water, no added solvent) for cyclooctene epoxidation catalyzed by molybdenum and tungsten complexes and faced selectivity issues (53% selectivity for the epoxide in the best case). Jimtaisong et al.,[23] used molybdenum complexes with H_2O_2 in acetonitrile or ethanol but only observed moderate yields (35% after 24 h in the best case). The best catalytic systems using H_2O_2 as oxidant are the cyclopentadienyloxido-molybdenum and -tungsten complexes reported by Dinoi et al.,[34] exhibiting high activity at low catalyst loading but requiring MeCN as added solvent. In the present study, complexes **2a** and **2b** are active Mo catalysts using H_2O_2 without added solvents, and **3a** and **3b** are very active catalysts using H_2O_2 and a more eco-friendly solvent than MeCN.

Conclusions

Four new molybdenum and tungsten complexes, **2a**, **2b** and **3a**, **3b**, with tetradentate tripodal aminobisphenolate ligands bearing a hydroxy group in one arm were synthe-

sized and fully characterized. The complexes were tested as catalysts for epoxidation of cyclooctene in eco-friendly conditions, using aqueous solutions of H_2O_2 as oxidant and dimethyl carbonate (DMC) as solvent or neat conditions as substitutes for chlorinated solvents. Molybdenum complexes **2a** and **2b** converted cyclooctene to its epoxide in more than 95% yield using H_2O_2 without added solvent, and tungsten complexes **3a** and **3b** showed very high activity in cyclooctene epoxidation using H_2O_2 and DMC as solvents (80% and 71% yield, respectively, after 24 h). These results highlight the potential of aminobisphenolate molybdenum and tungsten-based complexes as epoxidation catalysts amenable to eco-friendly conditions. Since complexes **2a** and **2b** were also able to convert different substrates (styrene, 1-octene, terpenes) using TBHP in $CHCl_3$, future applications of eco-friendly conditions to these more challenging epoxidation reactions may be readily envisioned.

Experimental Section

General: Unless otherwise specified, all experiments were performed under atmospheric conditions with standard laboratory equipment. Commercially available chemicals and solvents were used as received and no further purification or drying operations were performed. Syntheses of ligands **1a** and **1b**[11,26,27] and the precursor complexes $[W(eg)_3]$[28] and $[WO_2(acac)_2]$[36] have been published previously. Flash purifications were carried out on a Biotage Isolera ISO-4SV automatic flash purification system with UV detection at 254 and 280 nm. A gradient program was used with EtOAc and cyclohexane mixtures (4–18% of the ester) as eluent. The ^1H and ^{13}C NMR spectra were recorded with a Bruker Optics Instrument 300 MHz or a Varian Inova 500 MHz spectrometer. Peaks are denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t) and multiplet (m), Ar denotes aromatic protons. Chemical shifts are reported in ppm and are referenced using the residual solvent peak. Electron impact Mass spectra were recorded with an Agilent Technologies 5975C inert XL MSD instrument using the direct insertion technique. Results are denoted as cationic mass peaks, unit is the mass/charge ratio. Gas chromatography mass spectroscopy measurements (GC–MS) have been performed with a gas chromatograph type Agilent 7890 A (column type Agilent 19091J–433), coupled to an Agilent 5975 C mass spectrometer. Samples for infrared spectroscopy were measured using a Bruker Optics ALPHA FT-IR Spectrometer. IR bands are reported with wave number [cm^{-1}] and intensities (br = broad, vs. = very strong, s = strong, m = medium, w = weak). A Heidolph Parallel Synthesizer 1 was used for all epoxidation experiments. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Vienna using a EuroVector EA3000 instrument.

X-ray Structure Determination: X-ray data collection was performed with a Bruker AXS SMART APEX 2 CCD diffractometer by using graphite-monochromated Mo-K_α radiation (0.71073 Å) from a fine-focus sealed tube at 100 K. SHELXS-97[37] was used as structure solution and structure refinement program (Table 4). Full-matrix least-squares on F^2 was employed as refinement method. Further details on the solution of the structures can be found in the supporting information. Crystallographic data (excluding structure factors) for the compounds reported in this article were deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers.

CCDC-1043407 (for **2a**), 1043408 (for **2b**), 1043409 (for **3a**), 1043410 (for **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Epoxidation of Olefins: In a typical experiment, catalyst (2–3 mg, 1 mol-%) were dissolved in 1 mL of the respective solvent, mixed with substrate (1 equiv., [0.45 M]), mesitylene (10 μL as an internal standard) and heated to the respective reaction temperature. Oxidants (3 equiv.) were then added. Aliquots for GC–MS (20 μL) were withdrawn at given time intervals, quenched with MnO_2 and

Table 4. Selected crystallographic data and structure refinement data for **2a**, **2b**, **3a** and **3b**.

	2a	**2b**	**3a**	**3b**
Empirical formula	$2(C_{32}H_{49}MoNO_5)\cdot C_2H_3N$	$C_{34}H_{53}MoNO_6$	$C_{32}H_{49}NO_5W\cdot CH_4O$	$C_{34}H_{53}NO_6W$
Crystal description	needle, yellow	needle, yellow	needle, yellow	plate, yellow
Crystal size	0.27 × 0.12 × 0.06 mm	0.28 × 0.10 × 0.09 mm	0.28 × 0.12 × 0.05 mm	0.20 × 0.20 × 0.04 mm
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
Unit cell dimensions	a = 10.8267(3) Å	a = 10.5571(3) Å	a = 10.6420(3) Å	a = 10.5340(4) Å
	b = 15.4947(4) Å	b = 11.6945(3) Å	b = 11.3195(3) Å	b = 11.6582(4) Å
	c = 20.8325(6) Å	c = 27.1485(8) Å	c = 27.6060(8) Å	c = 27.2429(11) Å
	α = 109.4953(13)°			
	β = 91.5192(12)°	β = 96.8380(10)°	β = 93.6295(10)°	β = 97.029(2)°
	γ = 100.5836(12)°			
Z	2	4	2	4
Reflections collected/unique	38263/18764	24944/9687	22397/9617	28896/9682
Significant unique reflections	14385 with $I > 2\sigma(I)$	8690 with $I > 2\sigma(I)$	8731 with $I > 2\sigma(I)$	8258 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0326, 0.0518	0.0212, 0.0243	0.0209, 0.0277	0.0318, 0.0353
Completeness to θ = 30.0°	99.7%	99.7%	99.5%	99.9%
Refinement method	full-matrix least squares on F^2			
Data/parameters/restraints	18764/817/5	9687/421/2	9617/410/2	9682/412/0
Goodness-of-fit on F^2	1.009	1.039	1.095	1.035
Final R indices	R_1 = 0.0350,	R_1 = 0.0246,	R_1 = 0.0213,	R_1 = 0.0234,
[$I > 2\sigma(I)$]	wR_2 = 0.0805	wR_2 = 0.0620	wR_2 = 0.0429	wR_2 = 0.0528
R indices (all data)	R_1 = 0.0559,	R_1 = 0.0291,	R_1 = 0.0252,	R_1 = 0.0320,
	wR_2 = 0.0889	wR_2 = 0.0647	wR_2 = 0.0438	wR_2 = 0.0558

diluted with HPLC grade EtOAc. The reaction products were analysed by GC–MS (Agilent Technologies 7890 GC System), and the epoxide produced from each reaction mixture was quantified vs. mesitylene as the internal standard.

[MoO_2(1a)] (2a): Ligand **1a** (0.305 g, 0.61 mmol) was dissolved in hot acetonitrile (5 mL) and added to a solution of [$MoO_2(acac)_2$] (0.2 g, 0.61 mmol) in acetonitrile (5 mL). The orange mixture was stirred and heated at 70 °C to dissolve all solid material. After 20 min. stirring, the yellow precipitate was filtered and washed with cold acetonitrile to afford **2a** in 66% yield (0.25 g). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.29 (d, J = 2.4 Hz, 2 H), 6.98 (d, J = 2.4 Hz, 2 H), 4.47 (d, J = 13.7 Hz, 2 H), 3.91 (d, J = 13.7 Hz, 2 H), 3.76 (t, J = 5.3 Hz, 2 H), 2.96 (t, J = 5.6 Hz, 2 H), 1.40 (s, 18 H), 1.29 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 158.73, 142.99, 137.23, 124.10, 123.58, 122.25 (Ar-C), 62.68 (CH_2), 58.49 (CH_2), 55.47 (CH_2), 35.17 [$C(CH_3)_3$], 34.48 [$C(CH_3)_3$], 31.81 (CH_3), 30.28 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2958, 1471, 1439, 1262, 1171, 928 (w, Mo=O), 917 (w, Mo=O), 874, 855, 757, 561, 473 cm^{-1}. $C_{32}H_{49}MoNO_5 \cdot 0.5CH_3CN \cdot 0.45H_2O$ (652.3): calcd. C 60.76, H 7.94, N 3.22; found C 60.51, H 7.66, N 2.97.

[MoO_2(1b)] (2b): Ligand **1b** (0.332 g, 0.61 mmol) was dissolved in hot acetonitrile (5 mL) and added to a solution of [$MoO_2(acac)_2$] (0.2 g, 0.61 mmol) in acetonitrile (5 mL). The orange mixture was stirred and heated at 70 °C to dissolve all solid material. After 20 min. stirring, the yellow precipitate was filtered and washed with cold acetonitrile to afford **2b** in 74% yield (0.30 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, J = 2.4 Hz, 2 H), 6.99 (d, J = 2.4 Hz, 2 H), 4.46 (dd, J_1 = 4.6, J_2 = 2.8 Hz, 2 H), 4.24 (d, J = 13.8 Hz, 2 H), 4.10 (m, 2 H), 4.05 (t, J = 5.8 Hz, 2 H), 3.99 (d, J = 13.9 Hz, 2 H), 3.33 (t, J = 6.2 Hz, 1 H), 2.99 (t, J = 5.8 Hz, 2 H), 1.44 (s, 18 H), 1.29 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.21, 143.32, 137.11, 124.29, 123.65, 122.26 (Ar-C), 77.37 (CH_2), 67.20 (CH_2), 61.04 (CH_2), 60.71 (CH_2), 53.78 (CH_2), 35.22 [$C(CH_3)_3$], 34.48 [$C(CH_3)_3$], 31.77 (CH_3), 30.34 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2950, 1470, 1438, 1358, 1242, 1227, 1203, 1168, 1044, 931 (Mo=O), 896 (s, Mo=O), 880, 844, 831, 755, 744, 601, 580, 557, 494 cm^{-1}. $C_{34}H_{53}MoNO_6$ (667.8): calcd. C 61.16, H 8.00, N 2.10; found C 61.44, H 7.89, N 2.28.

[WO_2(1a)] (3a): Ligand **1a** (0.137 g, 0.275 mmol) was dissolved in $CHCl_3$ (5 mL) and added to a suspension of [$W(eg)_3$] (0.1 g, 0.275 mmol) in methanol (5 mL). The orange mixture was stirred and heated at 60 °C. After few minutes stirring, a white solid precipitated. The solid was filtered and washed with cold methanol and **3a** was isolated in 34% yield (0.07 g).

Alternative Synthesis of 3a: To a solution of [$WO_2(acac)_2$] (0.2 g, 0.48 mmol) in acetonitrile (5 mL) was added a solution of **1a** (0.24 g, 0.48 mmol) in acetonitrile (5 mL). The yellow-orange mixture was stirred and heated at 70 °C. After 20 min, the yellow precipitate was filtered and washed with cold acetonitrile to ultimately afford **3a** as an off-white solid in 69% yield (0.24 g). ^{1}H NMR (300 MHz, [D_4]MeOH): δ = 7.28 (d, J = 2.5 Hz, 2 H), 7.04 (d, J = 2.5 Hz, 2 H), 4.45 (d, J = 13.1 Hz, 2 H), 3.81 (d, J = 13.2 Hz, 2 H), 3.75 (t, J = 6.0 Hz, 2 H), 2.84 (t, J = 6.1 Hz, 2 H), 1.44 (s, 18 H), 1.28 (s, 18 H) ppm. ^{13}C NMR (75 MHz, [D_4]MeOH, 298 K): δ = 159.33, 142.61, 139.10, 125.41, 125.07, 124.15 (Ar-C), 61.67 (CH_2), 63.09 (CH_2), 57.24 (CH_2), 35.95 [$C(CH_3)_3$], 35.03 [$C(CH_3)_3$], 32.19 (CH_3), 30.73 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2959, 1477, 1440, 1264, 1241, 1203, 1172, 948 (s, W=O), 918 (w, W=O), 876, 857, 757, 560, 473 cm^{-1}. $C_{32}H_{49}NO_5W$ (711.59): calcd. C 54.01, H 6.94, N 1.97; found C 53.33, H 7.02, N 1.97.

[WO_2(1b)] (3b): Ligand **1b** (0.149 g, 0.275 mmol) was dissolved in $CHCl_3$ (5 mL) and added to a suspension of [$W(eg)_3$] (0.1 g, 0.275 mmol) in methanol (5 mL). The orange mixture was stirred and heated at 70 °C. After 2 h stirring, the white precipitate was filtered off and washed with cold methanol affording **3a** in 53% yield (0.11 g). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.37 (d, J = 2.4 Hz, 2 H), 6.97 (d, J = 2.4 Hz, 2 H), 4.48 (d, J = 13.8 Hz, 2 H), 4.40 (dd, J_1 = 4.5, J_2 = 2.6 Hz, 2 H), 4.06 (m, 2 H), 4.00 (d, J = 13.8 Hz, 2 H), 3.96 (t, J = 5.8 Hz, 2 H), 3.07 (t, J = 5.8 Hz, 2 H), 2.86 (t, J = 5.8 Hz, 1 H), 1.46 (s, 18 H), 1.29 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 157.00, 143.55, 138.35, 124.68, 123.44, 122.01 (Ar-C), 68.99 (CH_2), 62.51 (CH_2), 61.43 (CH_2), 54.36 (CH_2), 35.20 [$C(CH_3)$], 34.46 [$C(CH_3)$], 31.79 (CH_3), 30.33 (CH_3) ppm. IR (ATM): $\tilde{\nu}$ = 2949, 1473, 1439, 1359, 1242, 1226, 1203, 1167, 1040, 954, 944 (w, W=O), 899 (s, W=O), 880, 848, 832, 757, 746, 602, 559, 496 cm^{-1}. $C_{34}H_{53}NO_6W$ (755.65): calcd. C 54.04, H 7.07, N 1.85; found C 53.91, H 6.93, N 1.96.

Supporting Information (see Footnote on the first page of this article) Further X-ray crystallographic details for each structure, the crystal structure data and structure refinement data, as well as stereoscopic ORTEP plots of compounds **2a**, **2b**, **3a** and **3b**.

Acknowledgments

Financial support by the Austrian Science Fund (FWF) (grant number P26264-N19) is gratefully acknowledged. This work was carried out within the framework of EU COST Action CM1003, Biological oxidation reactions – mechanisms and design of new catalysts. M. K. H. thanks the European Commission for an Erasmus Mundus predoctoral fellowship.

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Received: January 20, 2015
Published Online: April 27, 2015

