Dioxidomolybdenum(VI) and –tungsten(VI) complexes with tetradentate amino bisphenolates as catalysts for epoxidation

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Abstract: Sixteen molybdenum and tungsten complexes with tripodal or linear tetradentate amino bisphenol ligands were studied as catalysts for the epoxidation of *cis*-cyclooctene, 1-octene, styrene, limonene and α-terpineol. These complexes can be divided into different categories upon key features, *i.e.* central metal (Mo vs. W), side-arm donor (O *vs*. N), hybridization of the N-donor (pyridine *vs*. amine), ligand geometry (tripodal *vs*. linear diamine) and sterical hindrance (Me *vs*. *tert*-Bu substituents in the phenol part). All complexes can catalyse selectively the epoxidation of *cis*-cyclooctene by *tert*-butylhydroperoxide whereas the activities and selectivities towards other olefins (1-octene, styrene, limonene and α-terpineol) show large differences. When H_2O_2 was used as an oxidant in the epoxidation of *cis*-cyclooctene, only two of eight Mo complexes and four of eight W complexes showed any activity. This study revealed no clear correlations between the Mo and W catalyst structures and their activities.

Introduction

Molybdenum and tungsten are relatively similar group 6 d-block metals considering their physical and metallurgical properties as well as their occurrence in Nature.[1] Also, they have several identical chemical properties and can form structurally analogous compounds. On the other hand, there are significant differences in the chemistry of these two metals, therefore compounds of the same structure may contrast in their formation, stability, reactivity and biochemical role. These differences can be clearly seen when comparing the properties of some Mo-enzymes with those of their W analogues. For example, the native Mo centre in sulphite oxidase and nitrate reductase can be replaced by W at the same coordination site. However, these enzymes have significant differences in their properties whereas the substitution of Mo by W makes them less active or completely inactive.[2,3] However, sometimes the artificial model compounds show reverse oxygen-atom transfer (OAT) reactivity. For example, the complex [WO$_2$Cl(L^{ONN})] is a significantly more efficient catalyst for the OAT reaction from DMSO to PMe$_3$ than its counterpart [MoO$_2$Cl(L^{ONN})] (HL^{ONN} = 1-methyl-4-(2-hydroxy-3,5-di-*tert*-butylbenzyl)-1,4-diazepane).[4] The best molybdenum-based catalysts reported for the epoxidation of *cis*-cyclooctene so far are some low-valent complexes, such as a dinuclear Mo(III) complex [Mo$_2$(OtBu)$_6$][5] and a Mo(II) *ansa*-complex [Mo(η^5-C$_5$H$_4$(CH(CH$_2$)$_3$)-η^1-CH)(CO)$_3$][6]. In addition, many dioxidomolybdenum(VI) [7-13] and a handful of dioxidotungsten(VI) complexes [14-17] with a number of different ligands are studied due to their relevance to the catalytic epoxidation of alkenes. Although the Mo and W catalysed epoxidation reactions are well known, the reaction mechanisms are still under discussion. The most likely mechanism includes the addition of peroxide into a terminal M=O group while the resulting peroxido ligand is capable of transferring an oxygen atom to the alkene. [18] As the reactions are supposed to be metal-mediated, the rates and selectivities may depend on several factors,

e.g. the sterical bulkiness of the ligands, rigidity of the coordination sphere and lability of the donors. To compare the activities of Mo and W complexes with different ligand geometries, we used a series of *cis*-MoO$_2^{2+}$ and *cis*-WO$_2^{2+}$ complexes with tripodal or linear tetradentate amino bisphenol ligands as epoxidation catalysts (Chart 1). In general, amino bisphenolates are versatile ligands that allow the modification of the coordination sphere around the metal centre. Substituents at the phenolate rings as well as the position and nature of the side chain donors are tuneable features, thus different electronic and steric properties are available.[19] We have previously prepared these Mo and W compounds using MoO$_2$(acac)$_2$ and W(eg)$_3$ as starting materials, respectively [20,21], whereas other authors have reported different high-yield syntheses for some of these compounds. These procedures are based on MoO$_2$Cl$_2$(dme) (for **Mo2b**), MoO$_2$Cl$_2$ (for **Mo3b**) or WO$_2$Cl$_2$(dme) (for **W2b** and **W3b**).[22,23] In present study, inexpensive molybdate and tungstate salts were used in acidic media in which the *cis*-MO$_2^{2+}$ species are generated.

Mo: Me (**Mo1a**), ^{t}Bu (**Mo1b**)   Me (**Mo2a**), ^{t}Bu (**Mo2b**)
W: Me (**W1a**), ^{t}Bu (**W1b**)   Me (**W2a**), ^{t}Bu (**W2b**)

Me (**Mo3a**), ^{t}Bu (**Mo3b**)   Me (**Mo4a**), ^{t}Bu (**Mo4b**)
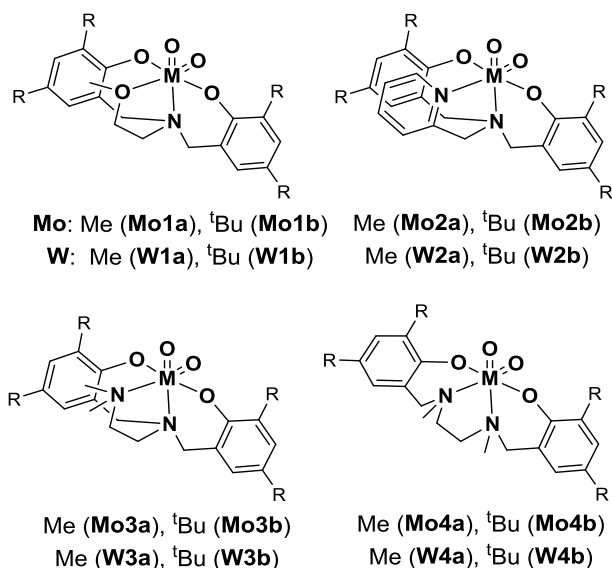Me (**W3a**), ^{t}Bu (**W3b**)   Me (**W4a**), ^{t}Bu (**W4b**)

Chart 1. Molybdenum and tungsten catalysts used in this study.

Our final aim is to find correlation between the structures and epoxidation activities of dioxidomolybdenum(VI) and –tungsten(VI) amino bisphenolates. To have some quantitative comparison, we used complexes with different structural parameters and tested their activity in catalytic oxidations. The altered parameters were (*i*) central metal: Mo vs. W, (*ii*) side-arm donor: O vs. N, (*iii*) hybridisation of the N-donor: pyridyl (sp^2) vs. amine (sp^3), (*iv*) ligand geometry: tripodal diamine vs. linear diamine, (*v*) sterical hindrance: Me substituents vs. *tert*-Bu substituents in the phenol part. Consequently, a total of eight Mo complexes (labelled **Mo1a/b** to **Mo4a/b**) and eight W complexes

(labelled **W1a/b** to **W4a/b**) (Chart 1) were tested in epoxidation experiments with five different substrates (Chart 2) using *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) as oxidants.
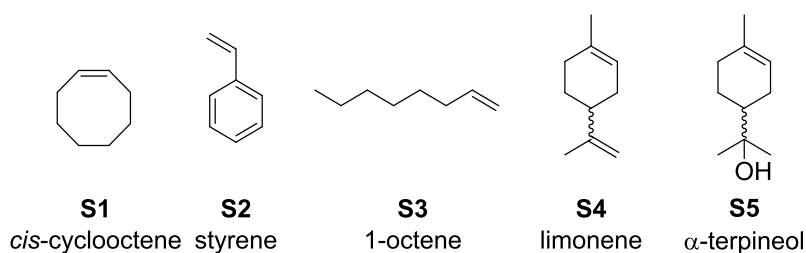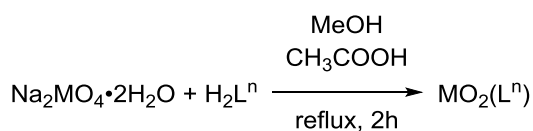

S1	S2	S3	S4	S5
cis-cyclooctene	styrene	1-octene	limonene	α-terpineol

Chart 2. Five substrates tested for epoxidation.

Results and Discussion

Catalyst syntheses.

There are several ways to prepare dioxidomolybdenum(VI) and –tungsten(VI) complexes with amine bisphenol ligands. The molybdenum(VI) complexes are typically made from relative stable, commercially available precursors $MoO_2(acac)_2$ or MoO_2Cl_2 in high yields reactions [24-30], whereas a few examples are based on the use of an acidic solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [30-32]. However, the synthesis of corresponding W compounds is more tedious, and they are typically made under dry conditions using air- and moisture-sensitive $[WO_2Cl_2(dme)]$ (dme = 1,2-dimehoxyethane) and ligands as free bases or sodium salts [30]. We have earlier prepared such compound applying the reaction of free ligands and $[W(eg)_3]$ (eg = ethylene glycolate dianion) in alcohol solutions in the presence of ambient moisture [20,24,33]. As these two tungsten precursors are not commercially available, they must be freshly prepared prior to the syntheses. In this study, all catalyst complexes were prepared following a straightforward procedure using stable and inexpensive molybdate and tungstate salts as metal precursors. Stoichiometric amounts of a metal precursor $Na_2MO_4 \cdot 2H_2O$ (M = Mo, W) and a tetradentate amino bisphenol H_2L^n were refluxed in acidified MeOH solution. The reaction mixtures were then cooled to room temperature to obtain products in 65-85 % yields as yellow (Mo) or white (W) crystalline solids (Scheme 1). Tungsten complexes **W2b** and **W4b** were formed in rather low yields under such conditions, therefore overnight heating and excess of tungstate was used to complete the reactions in approx. 65 % yields based on the ligands. The applied synthetic procedure is superior to the earlier ones as it employs inexpensive and stable starting materials and the products are easily isolated in a pure form from the reaction mixtures. Moreover, there is no need for the use of tedious inert atmosphere techniques.

$$\text{Na}_2\text{MO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{L}^n \xrightarrow[\text{reflux, 2h}]{\substack{\text{MeOH}\\ \text{CH}_3\text{COOH}}} \text{MO}_2(\text{L}^n)$$

Scheme 1. Formation of the catalysts

All compounds were characterised by IR and ^{1}H NMR spectroscopy and found to be identical to those prepared earlier by different synthetic procedures.[20-23] The *cis*-MO$_2$ functionalities are seen as two distinctive absorption maxima in the expected IR region. Precisely, the symmetric and asymmetric stretches are observed at 915–935 and 890–905 cm^{-1} for Mo complexes and at 935–950 and 900–910 cm^{-1} for W complexes, respectively.[22,30,31,34-37] The NMR spectra show the anticipated resonances for the coordinated ligands, particularly the benzylic methylene protons of the ligand backbones show typical doublets for *trans*-coordinated amino bisphenolates. The solid state structure of **W4a** was also verified by single crystal X-ray diffraction analysis (Figure 1). As expected, the two oxido O atoms are *cis* with respect to one another and to the two phenolate O atoms of the ligand whereas the N donors of the ligand backbone are trans to the oxo groups. In general, the nearly C_2 symmetric distorted octahedral structure of **W4a** is isostructural with **Mo4a**.[21]
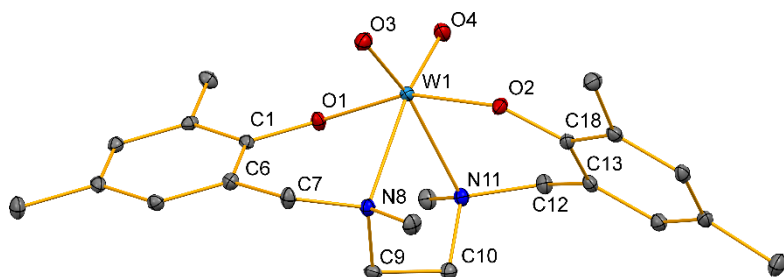

Figure 1. The molecular structure of **W4a**. The hydrogen atoms are omitted for clarity. Selected bonding distances (Å) and angles (°): W1-O1: 1.9194(19); W1-O2: 1.954(2); W1-O3: 1.731(2); W1-O4: 1.732(2); W1-N8: 2.401(2); W1-N11: 2.392(2); O1-W1-O2: 159.05(9); O3-W1-O4: 108.44(11); O3-W1-N11: 161.98(9); O4-W1-N8: 162.02(10).

Epoxidations. All catalysts were tested for the epoxidation of five different olefin substrates using three equiv. of *tert*-butylhydroperoxide (TBHP) as oxidant and with 1 mol% of catalyst in CHCl$_3$ solution at 50 °C (Scheme 2). Conversions were determined by GC mass spectrometry. The five investigated olefin substrates *cis*-cyclooctene **S1**, 1-octene **S2**, styrene **S3**, racemic limonene **S4** and racemic α-terpineol **S5** are depicted in Chart 2 and results are summarized in Table 1. All eight Mo complexes convert **S1** completely to its epoxide in high to excellent selectivities within 24 h, whereas yields were generally lower for more challenging alkenes. With **S2**, all eight complexes show very low conversion (<20%) and

selectivity (10-32%) to styrene oxide, with phenylacetaldehyde and benzaldehyde being the two main side products. Oxidative cleavage of the C=C double bond in styrene is commonly observed under epoxidation conditions, and only a few selective catalysts have been reported in literature. [9,38-40] In case of **S3**, the eight catalysts show large differences with respect to the activity. The highest activity was displayed by **Mo1a** with a conversion to 1-octene oxide of 71% after 24 h. Complex **Mo2b** displayed an induction period with no activity in the first 7 h, after which it became active and showed a conversion of 27% after 24 h. With the other six complexes, the reactions started without any induction periods and followed a very similar time-conversion profile reaching conversions between 32 and 47% after 24 h.
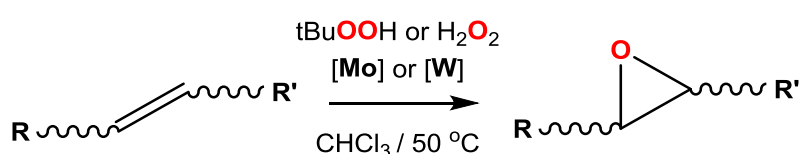
Scheme 2. Epoxidation of the olefinic substrates.
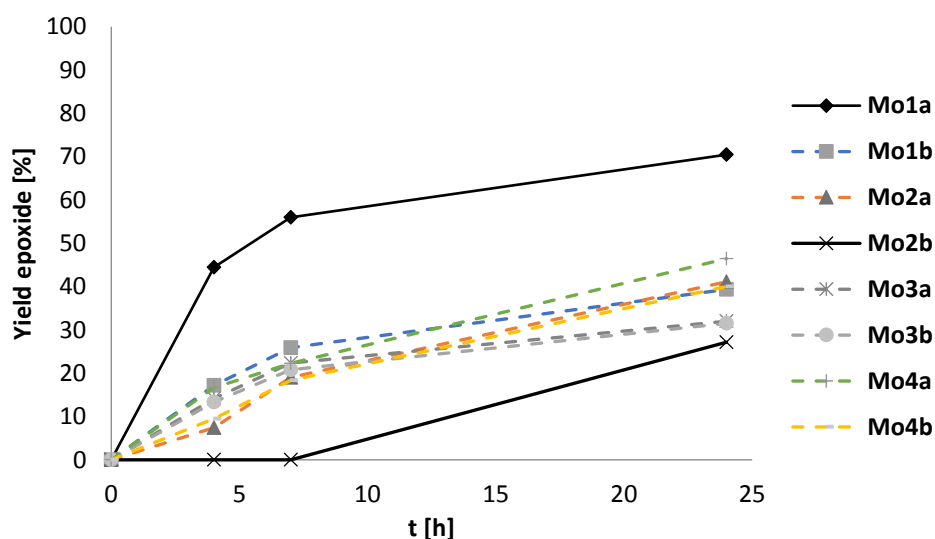

Figure 2. Time-conversion plot of epoxidation of 1-octene.

For limonene **S4**, all eight complexes are unselective, generating a variety of side products over the course of the reaction. Two of those could be identified as limonene dioxide and the ketone carvone. Except for **Mo2b**, all complexes showed a maximum conversion after 3 h, after which the product limonene oxide was consumed again, due to over-oxidation. Only **Mo2b** displayed a constant increase of epoxide yield over the 24 h measuring time reaching a maximum yield of limonene oxide of 39%. The epoxidation of limonene was repeated at 25 °C to potentially decrease side reactions and over-oxidation

of the initially formed epoxides. Under such conditions, complexes **Mo2a** and **Mo2b**, which carry the pyridine side-arm, did not show any conversion. Complexes **Mo3a** and **Mo3b**, with the coordinating dimethylamine side-arm, and complexes **Mo4a** and **Mo4b**, with the linear tetradentate ligands, show an induction period at 25 °C in the first four hours. In contrast to this, **Mo1a** and **Mo1b** with the methoxy side-arm group do not show this induction period. This behaviour may reflect the donor qualities of the side-arm functional group, supposing that de-coordination from the Mo initiates the catalytic cycle. At 25 °C, the pyridine side-arm in **Mo2a** and **Mo2b** seems to coordinate too strongly rendering the complex inactive. Finally for substrate **S5** all eight complexes showed a similar performance than for **S4**, but with even lower conversion (<20%) and selectivity numbers. Since alcohols are known to compete for the vacant coordination site with the substrate, the low conversion for **S5** is most likely caused by the same effect. The tungsten catalysts showed generally lower epoxidation activities compared to their Mo counterparts, a fact which has been observed previously.[15,35,41-43] For **S1** a wide range of activities was observed, with complex **W4a** showing the best (78%) and complex **W2b** the lowest (16%) conversion after 24 h. With **S2** and **S4** the tungsten catalyst showed much lower activities (< 20%) and selectivities (< 20%) due to over-oxidation of formed epoxide, while with **S3** and **S5** no conversion was observed. We have earlier studied structurally related Mo and W complexes bearing tetradentate tripodal amino bisphenolate ligands with either a hydroxyl ethylene substituent or a hydroxyl glycolene substituent.[33] In present study, **Mo1 – Mo4** were generally less active than those complexes, which carry a dangling OH group in the side-arm. However, all Mo complexes catalyzed the epoxidation of styrene more completely than their OH-substituted counterparts. Similarly, the activities of **W1 – W4** towards epoxidation of *cis*-cyclooctene were slightly lower than found for corresponding complexes carrying an OH side-arm donor.

All Mo and W complexes were also investigated as catalysts in the epoxidation of **S1** using H_2O_2 as the oxidant under otherwise similar conditions. Among the Mo complexes only **Mo1b** and **Mo3b** convert **S1** to the epoxide (82 and 89% respectively), while among the W complexes **W1b** and **W3b** were found to be active (25 and 89 % respectively). These results hint towards the need of a free coordination site for the catalyst to be active with H_2O_2. This might explain why the pyridine coordinated **M2a/b** and the ethylene bridged **M4a/b** (M = Mo or W) complexes are unreactive. Comparing the other complexes seemingly does not elucidate a correlation between structure and activity. This is possibly explained with the fact that the H_2O_2 reactions lead to biphasic reaction mixtures (H_2O/CHCl$_3$). Thus, the catalysts need to be hydrolytically stable, exhibiting a free coordination site for the reaction with the peroxide and should also furthermore demonstrate phase transfer properties. The fact that only *tBu*-substituted complexes **Mo1b, Mo3b, W1b,** and **W3b** are active catalysts with H_2O_2 potentially points to such a phase

transfer capability. Thus, subtle differences in the structure favour one or the other reactivity leading to the found seemingly random correlation.

Conclusions

Dioxidomolybdenum(VI) and –tungsten(VI) complexes with tripodal or tetradentate amino bisphenol ligands can be easily prepared using inexpensive salts $Na_2MO_4 \cdot 2H_2O$ (M = Mo, W) as metal precursors. In total, eight Mo and eight W complexes were tested for the catalytic epoxidation of olefins. The structural features of different metal complexes were varied by the design of amino bisphenol ligands, *i.e.* the side-arm donors of the tripodal ligands (O vs. N), hybridisation of the N-donor (pyridine vs. amine), ligand geometry (tripodal vs. linear diamine) and sterical hindrance (Me vs. *tert*-Bu substituents in the phenol part). Dioxidomolybdenum(VI) complexes with tetradentate amino phenolates catalyse selectively epoxidation of *cis*-cyclooctene by TBHP whereas for other alkenes (1-octene, styrene, limonene and α-terpineol) the activities and selectivities were generally lower. Altogether, W complexes show lower activities than their Mo congeners when using TBHP as an oxidant. On the other hand, when H_2O_2 was used as an oxidant in the epoxidation of *cis*-cyclooctene, only complexes with *tBu*-substituents presented noticeable activity. Under applied turn-over conditions, no clear correlations between the catalyst structure and the activity were found. The coordination sphere around the metals centre is rather rigid and only moderately dependent on the structural parameters of the ligand. The different catalytic activity of diverse complexes may therefore be caused by different hydrolytic stabilities and solubilities instead of different coordination geometries.

Experimental Section

Chemicals and solvents were of commercial origins and were used without further purification if not otherwise stated. Syntheses and manipulations of the catalysts were carried out under ambient atmosphere.

Syntheses. Complexes (except **W2b** and **W4b**) were prepared mixing stoichiometric amounts (1.0 mmol) of a metal precursor $Na_2MO_4 \cdot 2H_2O$ (M = Mo, W) and amino bisphenol H_2L^n in 10 ml of MeOH. Acetic acid (0.2 ml) was added and the reaction mixtures were heated to the reflux temperature for two hours, cooled to the room temperature and filtered to obtain crystalline solid products. Complexes **W2b** and **W4b** were made by heating 2.0 mmol of sodium tungstate and 1.0 mmol of ligand for 16 hours. Molybdenum complexes were bright yellow whereas tungsten complexes were white or pale yellow. Compounds were characterised by IR and ^1H NMR to be identical with those prepared earlier by different synthetic procedures. (see Table 2).

Epoxidation experiments. A Heidolph Parallel Synthesizer 1 was used for all epoxidation experiments. In a typical experiment, 2-3 mg of catalyst (1 mol %) were dissolved in 0.5 mL of $CHCl_3$ and mixed with substrate (1 equiv.) and 50 μL of mesitylene (internal standard) and heated to the respective reaction temperature (50 °C). Then the oxidant (3 equiv 5.5 M *tert*-butylhydroperoxide in decane or 30% H_2O_2 in water) was added. Aliquots for GC–MS (20 μL) were withdrawn at given time intervals, quenched with MnO_2 and diluted with HPLC grade ethyl acetate. 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 (uncertainty is ±5%).

Crystallography. Single crystals of **W4a** were obtained from a reaction mixture and the X-ray data was collected and analysed according to the procedure reported earlier by our group.[44] Crystallographic data for **W4a**: formula $C_{22}H_{30}N_2O_4W$, M_r = 570.33, monoclinic, space group $P2_1/c$, a = 18.4271(2), b = 7.16235(10), c = 16.0267(2) Å, β = 97.4991(13)°, Z = 4, V = 2097.15(5) Å^3, T = 123 K, ρ_{calc} = 1.806 g cm^{-3}, F(000) = 1128.0, μ(Mo-K$_\alpha$) = 10.464 mm^{-1}, 6761 data, 3942 unique (R_{int} = 0.0185), 268 parameters, final R_1 (I>2σ(I)) = 0.0214, wR_2 = 0.0521, GOF = 1.091. CCDC 1484210 contains the supplementary crystallographic data. 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.

Acknowledgements

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Table 1. Summary of epoxidation results (Yield (selectivity) [%][a]) of Mo and W complexes with 1 mol% catalyst loading

Entry		Mo1a	Mo1b	Mo2a	Mo2b	Mo3a	Mo3b	Mo4a	Mo4b
1	S1	93 (94)	>99 (>99)	98 (>99)	>99 (>99)	98 (>99)	>99 (>99)	98 (>99)	98 (99)
2	S1[b]	no conv.	82 (83)	no conv.	no conv.	no conv.	89 (91)	no conv.	no conv.
3	S2	6 (10)	12 (19)	14 (20)	16 (28)	unsel.	18 (32)	9 (12)	unsel.
4	S3	71 (98)	39 (88)	41 (81)	27 (79)	32 (84)	32 (83)	47 (92)	40 (92)
5	S4[c]	unsel.	21 (22)	33 (34)	39 (55)	39 (40)	35 (36)	13 (14)	40 (41)
6	S4[d]	38 (39)	49 (54)	no conv.	no conv.	37 (61)	48 (57)	25 (64)	4 (12)
		W1a	W1b	W2a	W2b	W3a	W3b	W4a	W4b
7	S1	32 (72)	51 (78)	23 (60)	16 (53)	50 (77)	54 (78)	78 (82)	46 (65)
8	S1[b]	no conv.	25 (67)	no conv.	no conv.	unsel.	89 (91)	no conv.	no conv.

Unsel. = unselective towards epoxide, over-oxidation of epoxide; no conv. = no conversion of substrate. **Mo1a-4b**: for **S5** yields of epoxide were below 20%, results are not shown. **W1a-4b**: for **S2** and **S4** yields of epoxide were below 20% due to over-oxidation, for **S3** and **S5** no conversion of substrate was observed, results are not shown; [a] yield of (selectivity to) epoxide after 24 h. [b]H_2O_2 as an oxidant; [c] sum of *cis* and *trans* epoxide is given; [d] at 25 °C, sum of *cis* and *trans* epoxide is given.

Table 2. The yields of the catalyst precursors.

	Yield	Reference for spectral characterisation		Yield	Reference for spectral characterisation
Mo1a	77 %	[24]	W1a	64 %	[24]
Mo1b	89 %	[24]	W1b	82 %	[24]
Mo2a	87 %	[24]	W2a	82 %	[24]
Mo2b	87 %	[22,24]	W2b	67 %	[22,24]
Mo3a	73 %	[24,45,46]	W3a	80 %	[24]
Mo3b	95 %	[23,24]	W3b	92 %	[23,24]
Mo4a	77 %	[21]	W4a	77 %	[20]
Mo4b	78 %	[21]	W4b	78 %	[20]