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Amide functionalized aminobisphenolato MoO_2 and WO_2 complexes: Synthesis, characterization, and alkene epoxidation catalysis

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ABSTRACT

The use of dioxidomolybdenum(VI) and -tungsten(VI) complexes supported by a variety of structurally different tri- and tetradentate aminobisphenolato ligands as pre-catalysts in the epoxidation of alkenes is well established. However, under the widely used standard 1 mol-% catalyst loadings these types of complexes generally show modest activity only. Recently, amide functionalities in the ligand design of various aminomonophenolato MoO_2 complexes have been shown to lead to heightened catalytic activity in alkene epoxidation. In this paper we show that similar ligand amide functionalization can lead to significant enhancement in the alkene epoxidation activity of aminobisphenolato MoO_2 complexes. Although the W variants showed much lower performance in comparison, the epoxidation activity of the Mo congeners is generally *ca.* two orders of magnitude higher than previously reported for structurally related aminobisphenolato complexes. An interesting phenomenon dubbed as "dilution effect" was discovered, wherein pre-catalyst loadings as low as 0.01 mol-% may be realized without significantly reduced impact in activity. Moreover, the [pre-catalyst]:[oxidant] molar ratio – an often overlooked reaction parameter in the literature – was found to be critical for optimal catalytic performance.

1. Introduction

High-valent oxidomolybdenum(VI) and -tungsten(VI) centers are found in a variety of metalloenzymes that take part in oxygen atom transfer (OAT) reactions, in which oxygen is transferred from or to a suitable donor/acceptor molecule [1,2]. In light of the oxygen activating nature of the M(VI)=O (M = Mo, W) moieties, many metal-organic model compounds have been studied in oxidation catalysis relevant to fine and bulk chemical industries, and the research is on-going. Epoxidation is a particularly attractive oxidative transformation due to availability of starting materials and high degree of functionalizability of the products. Oxidation of alkenes is one of the primary approaches to obtaining epoxides and, on one hand, allows capitalization of the wide variety of readily available olefinic feedstock chemicals. On the other hand, the synthetic versatility and thus importance of the epoxide functional group is highlighted by the fact that they readily undergo stereospecific ring-opening reactions in the presence of various nucleophiles, providing 1,2-difunctional compounds useful as intermediates in the synthesis of fine chemicals [3,4].

Epoxides are obtained from alkenes in a number of ways. In a laboratory setting, organic peracids such as *m*-chloroperbenzoic acid are still frequently used as stoichiometric epoxidation reagents [4]. Transition metal-catalyzed epoxidation in the presence of organic hydroperoxides is in turn often utilized industrially. For example, molybdenum complexes such as $[Mo(CO)_6]$ have been exploited as catalysts in the industrial Halcon/ARCO hydroperoxide process, which provides chemically valuable propylene oxide [5]. To attain high reactivity in various oxidation reactions such as epoxidation, the electronic and steric features of ligands are generally used to modulate the reactivity of metal centers. In this regard, aminebisphenols are a large family of versatile multidentate proligands, because they generally form air and moisture stable complexes with virtually all transition metals and are

Abbreviations: ARCO, Atlantic Richfield Company; Dipp, 2,6-di-isopropylphenyl; GC–MS, gas chromatography mass spectrometry; HB, hydrogen bond or hydrogen bonding-; IR, infrared (spectroscopy); NMR, nuclear magnetic resonance (spectroscopy); TBHP, *tert*-butyl hydroperoxide; TBHP(aq), 80 w-% (*ca.* 8.0 M) aqueous *tert*-butyl hydroperoxide; TBHP(dec), *ca.* 5.5 M *tert*-butyl hydroperoxide in decane; TOF, turnover frequency TON = turnover number.

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relatively easy to synthesize and functionalize [6]. Specifically, aminobisphenolato ligands featuring an O_3N/O_2N_2 donor sets are interesting in a bioinorganic sense, as they structurally resemble some biological ligands found *e.g.,* in vanadium-dependent haloperoxidases [7,8].

Recently, dioxidomolybdenum(VI) complexes **1**–**7** (Scheme 1) supported by hydrogen-bond (H-bond, HB) donating capable amide functionalized aminomonophenolato ligands have been reported to be exceedingly active epoxidation pre-catalysts, reaching TONs up to 110,000 at 0.5 ppm catalyst loading relative to some substrates [9]. It has been suggested that HB donors such as amides in the ligand backbone may help to stabilize reaction intermediates during epoxidation, manifesting as enhanced activity of the catalysts [9]. Inspired by these results, we were interested to learn whether or not amide functionalization of aminobisphenolato ligands leads to similar enhancement in epoxidation activity in respective dioxidomolybdenum(VI) complexes, due to obvious structural similarities between these ligand platforms (Scheme 1). To this end, five new aminobisphenolato ligands featuring amide pendant arms and their corresponding dioxidomolybdenum(VI) and -tungsten(VI) complexes **Mo1**–**Mo5** and **W1**–**W4** were designed, synthesized, characterized, and evaluated as pre-catalysts in alkene epoxidation.

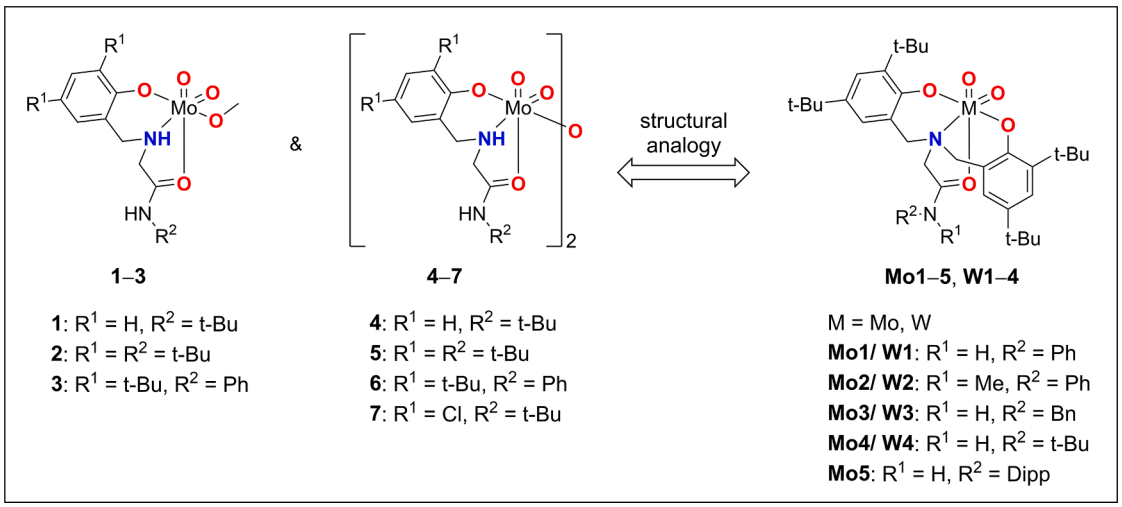
The results from these investigations reveal that HB donating amide pendant arms endow **Mo1**–**Mo5** and **W1**–**W4** with multiple attractive properties. Similarly to **1**–**7**, the catalyst loading of **Mo1**–**Mo4** (**Mo5** could not be evaluated in catalysis due to poor solubility) may be lowered to 0.01 mol-% relative to substrate, with no significant detrimental impact to their activity in the epoxidation of *cis*-cyclooctene. However, reduced performance was observed with more challenging alkene substrates, and the W-variants **W1**–**W4** generally performed markedly worse compared to their Mo counterparts across all tested alkene substates. The molar ratio between Mo pre-catalysts and oxidant ([Mo]:[TBHP], where TBHP = *tert*-butylhydroperoxide) – a frequently overlooked reaction parameter in the literature – was systematically investigated and found to be crucial for optimal catalytic performance. Additionally, all complexes readily crystallize, with single-crystals suitable for XRD obtained as fast as in 15 min after the introduction of ligand and metal precursors in methanol. This synthetic utility is attributed to the bulky, amphiphilic nature of the ligands, as well as to the propensity of the complexes to participate in intermolecular H-bonding *via* the amide pendant arms, as observed in the crystal structures (Supporting information). It is anticipated that these properties may be readily exploited when synthesizing complexes of other (transition) metals as well using the ligands described herein.

2. Experimental

2.1. Catalytic experiments

The preliminary alkene epoxidation reactions of all complexes were performed using **S1** as the benchmark substrate in standard conditions i.e., reactions were performed in chloroform with a 24 h reaction time, 50 °C reaction temperature and using two equivalents of aqueous TBHP (80% TBHP(aq), *ca.* 8.0 M solution in 3:2 di-*tert*-butylperoxide:water) relative to substrate. The conversion of the reactions was evaluated by ^{1}H NMR spectroscopy after the 24-hour period. For 1 and 5 mol-% experiments 1–6 mg of catalyst was dissolved in 1 mL $CDCl_3$ and treated with appropriate amount of substrate and TBHP(aq). For lower loadings **S1** solution containing 20 μL mL^{-1}, corresponding to a molar concentration of *ca.* 0.153 M was prepared in $CDCl_3$. Similarly, catalyst concentrations of 1.53×10^{-4} to 1.53×10^{-6} M *i.e.*, 0.1–0.001 mol-% relative to substrate were used. The catalyst solutions were prepared in $CHCl_3$. In a typical run, 500 μL substrate solution and 500 μL catalyst solutions were combined in a screw-capped scintillation vial. The solutions were then treated with *ca.* 19.2 μL TBHP(aq) solutions and then maintained at 50 °C for 24 h.

For reaction progress monitoring, **S1** oxidation was followed by in-situ ^{1}H NMR spectroscopy at 50 °C. The procedure for these experiments was similar than described above for the 24-hour reactions, with the exception that the reactant solutions were combined directly in 5 mm o.d. NMR tubes, and that the 0.153 M substrate $CDCl_3$ solutions additionally contained 0.078 M 1,2-dichloroethane (1,2-DCE) as the internal standard. Due to the very low solubility of the W complexes, their catalytic activity could not be reliably assessed using similar stock solution approach. For **S1** oxidation catalyzed by **W1**–**W4**, as well as **S2**–**S5** oxidation catalyzed by **Mo1**–**Mo4**, a Heidolph Parallel Synthesizer 1 was used. In a typical experiment, the respective amount of catalyst (usually 2–3 mg of complex for 1 mol-% catalyst loading) was suspended in 0.5 mL of the respective solvent ($CHCl_3$ or 1,2-DCE) in a 5 mL reactor equipped with a magnetic stir-bar and mixed with the substrate, 50 μL of mesitylene (internal standard) and heated to the respective reaction temperature (50 or 80 °C). Then the oxidant (usually 2 or 3 equiv. TBHP(dec), *ca.* 5.5 M *n*-decane solution, or H_2O_2 with respect to substrate) was added. Aliquots for GC–MS (20 μL) were withdrawn at given time intervals, quenched with MnO_2 and diluted with ethyl acetate. The reaction products were analyzed 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%).



Scheme 1. Structures of the previously reported amide functionalized aminomonophenolato dioxidomolybdenum(VI) complexes **1**–**7**[9], as well as structurally related **Mo1**–**Mo5** and **W1**–**W4** prepared in this work. Bn = benzyl. Dipp = 2,6-diisopropylphenyl. Coordinating atoms and ligands shown in bold and color.

3. Results and discussion

3.1. Alkene epoxidation catalysis

For complexes **1**–**7**, excellent catalytic results were obtained with complexes featuring *tert*-butyl substituents in the phenolato moiety and either *N*-*tert*-butyl- or *N*-phenylacetamide pendant arms [9]. As such, *N*-phenyl- and *N*-*tert*-butylacetamide pendant arms were opted for all studied complexes (**Mo1, W1** and **Mo4, W4**, respectively). Additionally, *N*-benzylacetamide and *N*-methyl-*N*-phenylacetamide substituted complexes (**Mo3, W3** and **Mo2, W2**, respectively) were also designed. In **Mo2**/ **W2**, which act as control pre-catalysts, any HB donating effects are blocked by the methylated amide group, whereas the benzyl group in **Mo3**/**W3** acts as a "dangling" group, possibly interfering with any HB donating effects. **Mo5** featuring a severely hindered 2,6-di-isopropyl-phenylacetamide pendant arm was also synthesized but could not be evaluated in catalysis due to poor solubility (Supporting Information).

The catalytic properties of all complexes were evaluated in the epoxidation of **S1**–**S5** (Scheme 2). First, the activity of the complexes was assessed in the epoxidation of the benchmark substrate *cis*-cyclooctene (**S1**) [10]. Under standard conditions all complexes are active at 1 mol-% catalyst loadings (Fig. 1). While **Mo1**–**Mo4** reach practically full conversion and selectivity, complexes **W1**–**W4** are markedly inferior, reaching only modest conversions with rather poor selectivity for the epoxide, a phenomenon frequently observed in other WO_2 systems including organometallic cylopentadienyl complexes [11–15] as well as octahedral dioxido complexes [16–19]. It should be noted that some W complexes, such as $[WCl_2(O)_2(OPMePh_2)_2]$, reported by Luck and Jimtaisong, have been reported to be more active in epoxidation compared to the Mo analog when H_2O_2 is used as the terminal oxidant [17]. In fact, some W complexes show superior activity relative to their Mo congeners in reactions utilizing H_2O_2 as the terminal oxidant, whereas Mo complexes are often superior when TBHP is used as the oxidant [14]. In a study by Herrmann and co-workers, dioxido Mo/W complexes based on chiral 2′-pyridinyl alcoholate ligands show identical enantiocontrol in asymmetric epoxidation, although the W variants are slightly slower than their Mo analogs [18]. This study highlights a notion that W complexes are inferior epoxidation catalysts relative to Mo due to kinetic factors primarily, but operate via a similar catalytic mechanism [18].

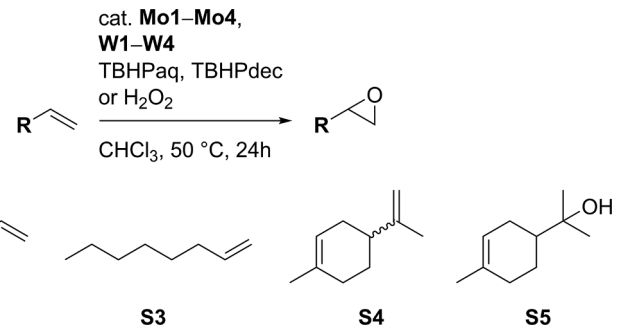
Mo1–**Mo4** have a very high initial reaction rate after a variable induction period lasting from about 15 min to two hours, reaching full conversion at the 16 h mark (Fig. 1). The W-variants show similarly rapid initial activity, attaining conversions of 20–35% during the initial three hours of reaction (Fig. 1). However, unlike with **Mo1**–**Mo4**, the epoxide yield is lowered afterwards, most likely due to over oxidation and hydrolysis to diol [20], or associated ring-opening reactions [11, 21]. From the Fig. 1 it may be concluded that **Mo1**–**Mo4** as well as **W1**–**W4** collectively show rather similar activity to one another, and that no significant SAR (structure-activity relationship) effects can be obviously drawn at 1 mol-% catalyst loadings.

Amide functionalized dioxidomolybdenum(VI) complexes **1**–**7** retained their epoxidation activity at extremely low pre-catalyst loadings approaching 5 ppm (0.0005 mol-%) relative to **S1** [9]. Other, more challenging substrates **S3**–**S5** were also efficiently converted to the corresponding epoxide at low 0.001 mol-% pre-catalyst loadings. Moreover, the complexes remained active in protic solvents such as alcohols and when using H_2O_2 as the terminal oxidant. As such, due to obvious structural similarities between **1, 7** and **Mo1**–**Mo4**/**W1**–**W4**, low catalyst loadings were tested for **Mo1**–**Mo4** and **W1**–**W4** as well (Fig. 2). Remarkably, for **Mo1**–**Mo4** catalyst loadings as low as 0.01 mol-% can be realized in **S1** oxidation, with moderate activity still present. In terms of TONs and TOFs, best results are obtained at 0.01 mol-% catalyst loadings: TONs of 5300, 1500, 3500 and 3700, and maximal TOFs 920, 210, 600 and 240 h^{-1} are obtained, in order, for **Mo1**–**Mo4**, respectively. These figures are one to two orders of magnitude higher than generally reported for aminobisphenolato MoO_2 complexes [22–28].

At 0.1 mol-% loading **Mo1** and **Mo4** reach nearly quantitative conversion in 16 h, whereas **Mo2** and **Mo3** reach 54% and 68% conversions, respectively. Even down to 0.01 mol-%, **Mo1, Mo3** and **Mo4** still reach moderate conversions up to 52%. At 0.1 mol-% the kinetic curves of the reactions follow typical 1st order-like behavior, whereas at 0.01 mol-%, except for **Mo1**, the kinetics start to become linear, conceivably due to saturation of the catalysts. It is noteworthy that with **Mo1** and **Mo4**, the conversion *vs.* time profiles are affected only barely by lowering the catalyst loadings from 1 to 0.1 mol-%. Interestingly, **Mo2**, having a blocked HB donating capability, shows least activity from all tested Mo complexes, although not significantly so. This may be interpreted as the HB donating effect having a beneficial effect on catalysis. In contrast, **W1**–**W4** are completely inactive below 1 mol-% loadings (data not shown). For this reason, follow-up catalytic investigations were performed for **Mo1**–**Mo4** only.

To evaluate the wider epoxidation potential of **Mo1**–**Mo4** beyond **S1**, more challenging substrates styrene (**S2**), 1-octene (**S3**), racemic limonene (**S4**) and α-terpineol (**S5**) were tested (Table 1 entries 1–4). **S2**, although typically relatively easily oxidized, may give a number of products aside from styrene oxide such as over oxidation products phenylacetaldehyde, styrene glycol, benzaldehyde as well as benzoic acid [29]. Thus, **S2** is a good indicator of selectivity of a catalyst, although reaction conditions may also play a role in this regard. Linear terminal alkenes such as **S3** are good indicators of overall epoxidation power, as they are much more difficult to epoxidize in comparison to internal alkenes, and especially cyclic internal alkenes such as **S1**, for which ring strain is also a factor [30,31]. Terpene substrates such as **S4** and **S5** are also difficult to epoxidize [10]. While both offer similar difficulty in terms of oxidizability, **S4**, having two olefinic sites, gives indications of the regioselectivity of a catalyst, while **S5** gives a measure of chemoselectivity, as well as functional group tolerance of catalysts.

Catalytic data for **Mo1**–**Mo4** are given in Table 1 entries **1**–**4**. For substrate **S2** as well as **S5**, complexes **Mo1**–**Mo4** are unselective towards the corresponding epoxide. In the case of **S2**, a nearly full conversion is obtained, with benzaldehyde being formed solely in all cases, indicating



Scheme 2. General reaction scheme of epoxidations catalyzed by **Mo1**–**Mo4** and **W1**–**W4** tested with the substrates **S1**–**S5** as shown.

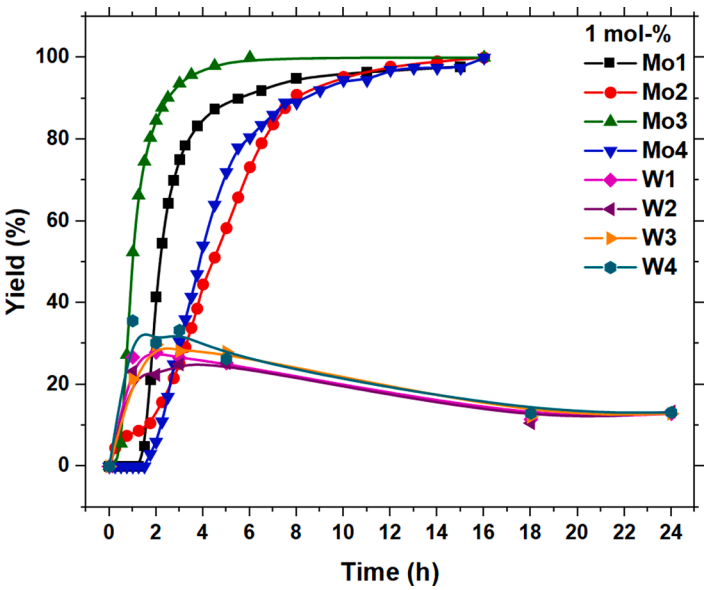


Fig. 1. The yield of cyclooctene oxide *vs.* time profiles of **Mo1**–**Mo4** and **W1**–**W4** catalyzed epoxidation of **S1** performed at 1 mol-% catalyst loading. Reaction conditions for experiments with Mo: [**S1**] = 0.0765 M, [TBHP(aq)] = 0.153 M, [Mo] = 7.65×10^{-4} M in 1 mL $CDCl_3$:$CHCl_3$ (1:1, *V:V*), $T = 50$ °C. The conversion of **S1** was monitored by ^{1}H NMR spectroscopy using 0.038 M 1,2-dichloroethane as an internal standard. For W experiments typically, 2–3 mg of a W complex was suspended in 0.5 mL $CHCl_3$ with 1 eq. **S1** and 2 eq. TBHP (dec) at $T = 50$ °C with 50 μL mesitylene as internal standard.

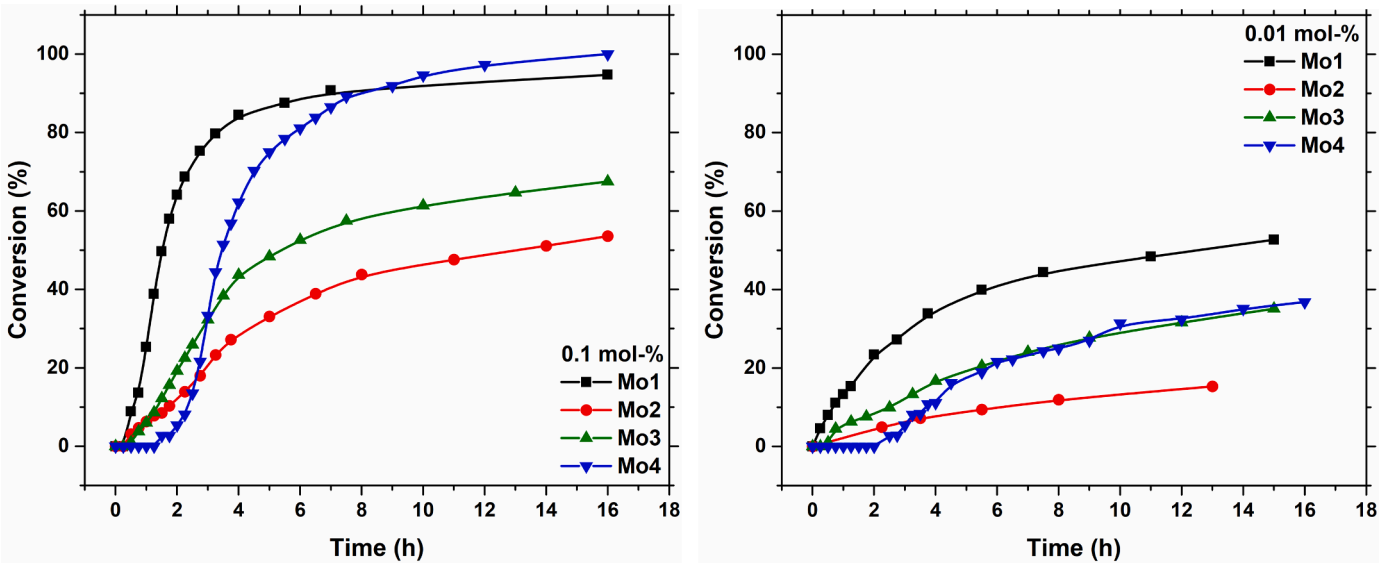


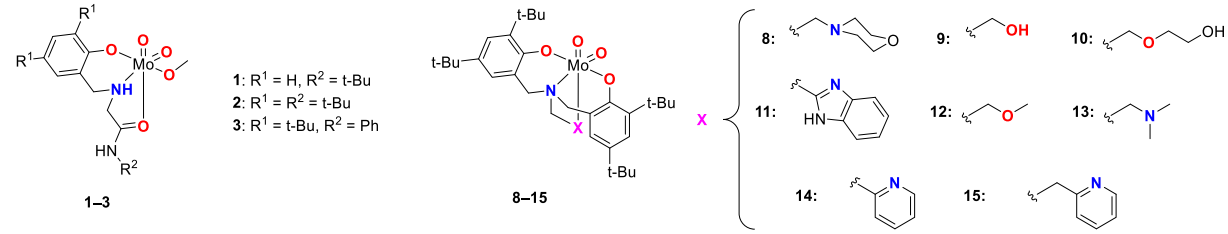
Fig. 2. The conversion of cyclooctene oxide *vs.* time profiles of **Mo1**–**Mo4** in the epoxidation of **S1** showing high catalytic activity at sub 1 mol-% catalyst loadings (*cf.* Fig. 1). Data obtained with in-situ ^{1}H NMR spectroscopy. Reaction conditions: [**S1**] = 0.0765 M, [TBHP(aq)] = 0.153 M, [Mo] = 7.65×10^{-4} to 7.65×10^{-6} M in 1 mL $CDCl_3$:$CHCl_3$ (1:1, V:V), $T = 50$ °C. The conversion of **S1** was monitored using 0.038 M 1,2-dichloroethane as an internal standard.

over-oxidation of the epoxide [29]. In contrast, with **S5**, there is no conversion at all with any of the studied complexes, highlighting the challenging nature of this substrate. It is also possible that the pre-catalysts are poisoned by the alcohol functional group in **S5**, since other, simpler alcohols, were observed to readily inhibit epoxidation of **S1** (see Table S4). Oxidation of **S4**, on the other hand, affords the corresponding limonene oxide in high yield (66–89%) and decent to moderate selectivity (36–78%), although **Mo4** seems to be inactive. All complexes show comparable activity in the epoxidation of **S3**, reaching 27–70% conversion and 83–95% selectivity. Higher conversion of **S3** is obtained by lengthening the reaction time to 48 h. Interestingly, and as observed solely in the case of **S1** so far, the catalytic potential of **Mo1**–**Mo4** is seemingly increased with successive dilution: At 0.1 mol-% **S3** is still epoxidized by **Mo1, Mo3** and, notably, with **Mo4**, which showed no activity at 1 mol-%. No conversion could be observed at 0.01 mol-% catalyst loadings with any of the pre-catalysts, however.

To summarize: **Mo1**–**Mo4** show very high catalytic activity for epoxidation of benchmark **S1** within 24 h in chloroform, especially below the widely used literature standard 1 mol-% catalyst loading. However, catalytic activity is quenched in alcohols and MeCN, whereas less polar and non-coordinating DCM and 1,2-DCE afford lower, but still comparable results to the optimal solvent, chloroform. Non-polar solvents *n*-hexane and toluene generally afford poor results. The tungsten variants **W1**–**W4** had a significantly inferior performance in all epoxidations. In general, the epoxidations followed the trends reported in the literature [9,25,26,28,32–35] namely that **S1** gives the oxide in high yield and selectively, whereas the oxidation of **S2** gives a good conversion with poor selectivity to epoxide, and oxidation of terminal alkene **S3** is selective but slow (poor conversion). However, the oxidation of **S4** was achieved with moderate conversion and selectivity using **Mo1**–**Mo3**, but not **Mo4. S5** did not react with any of the pre-catalysts, indicating that the OH group of the substrate may deactivate the complexes.

All reactions worked equally well with TBHP(aq) and TBHP(dec),

Table 1
Comparison of substrate **S1**–**S5** conversion (selectivity for epoxide in parentheses) catalyzed by **Mo1**–**Mo4** and various other aminophenolato supported MoO_2 complexes reported in the literature. The coordinating atoms and ligands are colored.



#	Cat.	Load (mol-%)	S1	S2	S3	S4	S5	Refs.
1	**Mo1**	5[a]; 1[b]; 0.1[c]; 0.01[d]	90[a]; 98[b]; 95[c]; 53[d]	100 (0)[b]	43 (95)[b]; 18 (95)[c]; 0 (0)[d]	89 (70)[b]	0 (0)[b]	tw.
2	**Mo2**	5[a]; 1[b]; 0.1[c]; 0.01[d]	14[a]; 100[b]; 54[c]; 15[d]	100 (0)[b]	34 (95)[b]; 0 (0)[c]; 0 (0)[d]	73 (70)[b]	0 (0)[b]	tw.
3	**Mo3**	5[a]; 1[b]; 0.1[c]; 0.01[d]	21[a]; 100[b]; 67[c]; 35[d]	100 (0)[b]	42 (95)[b]; 27 (95)[c]; 0 (0)[d]	66 (70)[b]	0 (0)[b]	tw.
4	**Mo4**	5[a]; 1[b]; 0.1[c]; 0.01[d]	75[a];100[b];100[c]; 37[d]	100 (0)[b]	0 (0)[b]; 20 (95)[c]; 0 (0)[d]	0 (0)[b]	0 (0)[b]	tw.
5	**1**	0.001	41 (89)	61 (8)	0 (0)	60 (11)	0 (0)	[9]
6	**2**	0.001	68 (95)	0 (0)	0 (0)	51 (42)	81 (31)	[9]
7	**3**	0.001	79 (95)	83 (34)	0 (0)	95 (49)	0 (0)	[9]
8	**8**	1	>95	65 (27)	28 (>95)	>95 (32)	81 (30)	[26]
9	**9**	1	>99	17 (43)	40 (100)	61 (63)	48 (50)	[28]
10	**10**	1	>99	14 (30)	25 (100)	64 (70)	46 (58)	[28]
11	**11**	2.5	–	42	–	–	–	[24]
12	**12**	1	90	12 (19)	39 (88)	49 (54)	0 (0)	[25]
13	**13**	1	60	18 (32)	32 (83)	35 (36)	0 (0)	[25]
14	**14**	1	79	16 (28)	27 (79)	39 (55)	0 (0)	[25]
15	**15**	2.5	–	52	–	–	–	[22]
16	**15**	5.0	–	54	–	–	–	[22]

Reaction conditions: $CHCl_3/CDCl_3$, $T = 50\,°C$, $t = 16$ h for **S1**, 24 h for S2–S5. Standard reactant molar ratios [Mo]:[**S1**–**S5**]:[TBHP] = 1:100:200 (for 1 mol-% experiments), with [Mo] loading altered accordingly for 5, 0.1 and 0.01 mol-% experiments while [TBHP]:[substrate] molar ratio held constant at 200:100. Reactions involving **11** and **15** performed in toluene at $T = 65\,°C$ and with $t = 26$ h. tw. = This work. Catalyst loading and substrate conversion accordingly given at [a] 5 mol-%, [b] 1 mol-%, [c] 0.1 mol-% and [d] 0.01 mol-% relative to **S1**–**S5** for **Mo1**–**Mo4** (for entries 1–4).

indicating that the small water content in TBHP(aq), which however becomes significant relative to active catalysts at very low pre-catalyst loadings, did not seem to have a detrimental effect on the catalysis overall. A possible explanation for this behavior is the highly lipophilic coordination environment near the metal centers, imparted by the di-*tert*-butyl phenolato moieties, which may hinder or prevent the approach and subsequent coordination of water to the metal centers. Similarly, the coordination of H_2O_2 is equally hindered, which manifests as inactivity of the pre-catalysts when H_2O_2 is used as the oxidant. However, alcohols and TBHP have comparatively more amphiphilic character than H_2O/H_2O_2. Thus, TBHP acts as a competent oxidant in non-coordinating solvents, whereas alcohols such as MeOH and EtOH effectively poison the pre-catalysts, regardless of used oxidant. Moreover, in reactions that are performed in chloroform and in the presence of TBHP(aq), a biphasic system will form to a certain extent, because water is not miscible with chloroform. In other words, the poisoning effects of water towards catalysis in chloroform are mitigated because it remains trapped within the aqueous phase, whereas all complexes, substrates and TBHP are effectively confined in the lipophilic phase. This also explains why TBHP(dec) shows similar performance relative to TBHP(aq) as an oxidant: As far as the pre-catalysts, oxidant and substrate are concerned, the lipophilic reaction environment is likely similar using both oxidants. By extension, poor performance of aqueous H_2O_2 may be explained by considering that the opposite is also true: H_2O_2 is more soluble in water than in chloroform, and thus unable to act as competent oxidant. In other tested reaction solvents that show amphiphilic character, such as alcohols, MeCN, etc.; H_2O_2 and TBHP are both effectively outcompeted by the relatively large excess of coordinating solvents. The sensitivity of the catalytic activity to solvent medium delivering the oxidant molecule to the metal center has been noted earlier *e.g.*, for dinuclear Mo/W complexes of the type $[(Cp^*)_2M_2O_5]$ (Cp^* = pentamethylcyclopentadienyl, M = Mo, W) as well [14]. In this report by Poli and co-workers, the W variants showed superior activity over the Mo congeners when aqueous H_2O_2 was used as the oxidant. In contrast, the Mo version showed best performance using TBHP(dec), whereas the water content in TBHP(aq) hindered their catalytic performance [14].

3.1.1. Dilution effect

It has been demonstrated that all epoxidation experiments conducted using **Mo1**–**Mo4** at a first glance show a rather unusual phenomenon we have dubbed as the "dilution effect" wherein the performance (both relatively and absolutely speaking) of the pre-catalysts is seemingly enhanced, in terms of better TOF values, with the lowering of the catalyst loading (Fig. 3). This behavior is not anticipated for completely stable and soluble pre-catalysts, for which the epoxidation rate is expected to be 1st order in catalyst concentration [36]. The phenomenon would also suggest that only a minor proportion of the complexes are active at any given time during catalysis, as also suggested by the groups of Kühn and Poli in their studies involving complexes based on cyclopentadienyl and Schiff base ligands [11–13,34,37,38].

The effect of the [Mo]:[TBHP] relationship was tested by conducting the **S1** oxidations with **Mo1**–**Mo4** using a variable molar ratio between [Mo]:[TBHP], additionally by using an increased 5 mol-% catalyst loadings relative to **S1**. It was expected that an increase in catalyst loading to 5 mol-% would lead to reduced catalytic performance if TBHP loadings were not changed accordingly. Indeed, raising the catalyst loading to 5 mol-% relative to **S1** without appropriately modifying [TBHP] loading, *i.e.*, having a [**Mo1**]:[**S1**]:[TBHP] molar ratio of 5:100:200 (and thus a [**Mo1**]:[TBHP] molar ratio of 1:40) leads to significantly lesser performance relative to standard 1 mol-% experiments, which have a [**Mo1**]:[**S1**]:[TBHP] molar ratio of 1:100:200 by default (Fig. 3). For example, with **Mo1**, by changing the [**Mo1**]:[**S1**]:[TBHP] molar ratio to 5:100:1000, thus affording a [Mo]:[TBHP] molar ratio of 1:200, *i.e.* the same as in the standard 1 mol-% experiments, almost identical behavior between the 1 and 5 mol-% experiments is observed (Fig. 3). Although the [substrate]:[oxidant] molar ratio in these experiments is changed to 1:10, this was found to have a negligible

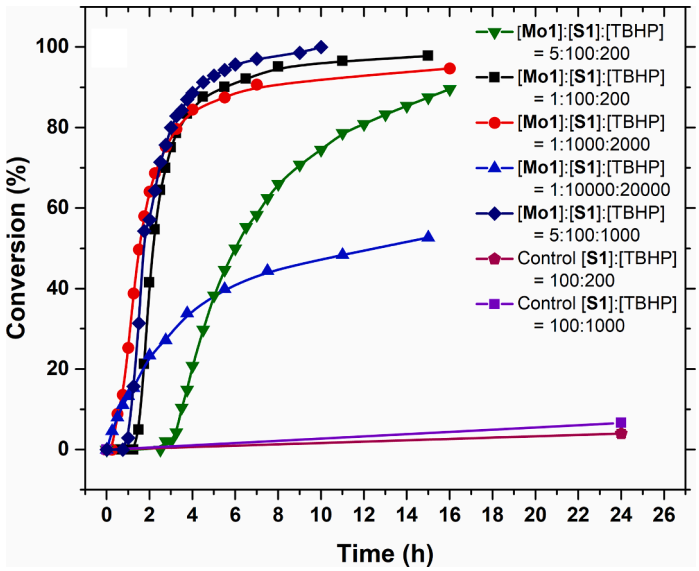


Fig. 3. The **S1** epoxidation conversion *vs.* time profiles as monitored by in-situ ^{1}H NMR spectroscopy in $CDCl_3$. The impact of [**Mo1**]:[TBHP] molar ratio ("dilution effect") in the epoxidation of **S1**. Reaction conditions: [**S1**] = 0.0765 M, [TBHP(aq)] = 0.153 M or 0.765 M, [Mo] = 7.65×10^{-4} to 7.65×10^{-6} M in 1 mL $CDCl_3$:$CHCl_3$ (1:1, V:V), T = 50 °C. The conversion of **S1** was monitored using 0.038 M 1,2-dichloroethane as an internal standard.

effect to the non-catalytic autoxidation of **S1** compared to the standard 1:2 used in the other experiments (Fig. 3). Similar results were observed for the other pre-catalysts **Mo2**–**Mo4** (Supporting Information Figs. S84–S87).

These experiments reveal that the molar ratio between the pre-catalysts and TBHP is extremely important. Using a 5 mol-% pre-catalyst loading relative to substrate, while not intrinsically detrimental to catalysis, must be accompanied by an appropriate increase in oxidant loading so that a [Mo]:[TBHP] molar ratio of at least 1:200 is reached. Similarly, the seemingly elevated activity of all pre-catalysts at 0.1 and 0.01 mol-% catalyst loadings simply originates from the very large excess of TBHP relative to Mo pre-catalysts ([Mo]:[TBHP] molar ratio as low as 1:20,000) in these experiments, which strongly drives the formation of the active catalysts. In this way, thanks to the large difference in [Mo]:[TBHP] molar ratios, the *absolute* amount of activated catalyst is higher in the 0.1 mol-% experiments than in the 1 or 5 mol-% experiments.

3.1.2. Induction period

In addition to the dilution effect, a variable induction period prior to reaction onset was observed in many of the epoxidation experiments conducted using **Mo1**–**Mo4** (*cf.* Figs. 1 and 2). The behavior of **Mo1** and **Mo4** *i.e.*, the pre-catalysts showing the longest induction periods, was further examined in the presence of excess TBHP(aq) (Figs. 4 and S92). As highlighted by **Mo1** (Fig. 4) these experiments demonstrate that the length of the induction period may be removed entirely if the pre-catalysts are incubated in the presence of excess TBHP(aq) prior to addition **S1**. If, on the other hand, the pre-catalysts are incubated in the presence of **S1** for 3–6 h prior to addition of TBHP(aq), the induction period persists. The experiments above also demonstrate that the incubation of the pre-catalysts with TBHP has a tangible effect on catalysis, even when the ^{1}H NMR spectra of the complexes during catalysis remain

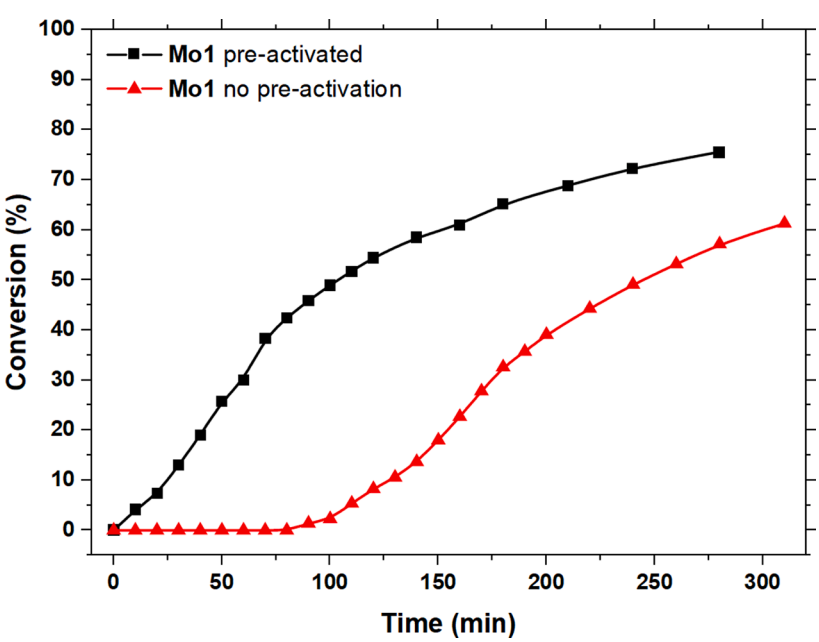


Fig. 4. The **S1** epoxidation conversion *vs.* time profiles as monitored by in-situ ^{1}H NMR spectroscopy in $CDCl_3$ showing the impact of **Mo1** pre-activation by TBHP on the conversion. Reaction conditions: [**S1**] = 0.0765 M, [TBHP(aq)] = 0.153 M, [Mo] = 7.65×10^{-4} to 7.65×10^{-6} M in 1 mL $CDCl_3$:$CHCl_3$ (1:1,V:V), T = 50 °C. The conversion of **S1** was monitored using 0.038 M 1,2-dichloroethane as an internal standard. Incubation time 3–6 h in the presence of **S1** (no pre-activation) or TBHP (pre-activated).

unchanged. This behavior may be indicative of a reversible equilibrium between the catalytic resting state (the species observed by NMR, corresponding to the pre-catalyst themselves) and the active forms, as suggested by Kühn [39] and Poli [34,37].

3.1.3. Comparison of catalysis

In the present study it has been established that **Mo1**–**Mo4** invariably show high catalytic activity in the epoxidation of **S1** at sub 1 mol-% catalyst loadings, akin to **1**–**7** that inspired us to prepare **Mo1**–**Mo4** in the first place. The slightly inferior performance of the HB donor blocked **Mo2** relative to the other tested complexes could hint that **Mo1, Mo3** and **Mo4** may benefit from the presence of the amide NH moiety. However, these SAR effects are only clearly visible in the epoxidation of **S1**, and in fact, **Mo1**–**Mo4** collectively behave rather similarly across **S2**–**S5** (Table 1 entries 1–4).

Indeed, the catalytic prowess of **Mo1**–**Mo4** across **S1**–**S5** is similar not only when compared to one another, but with regards to many other MoO_2 aminobisphenolato supported complexes as well, notwithstanding the very high activity of **Mo1**–**Mo4** in the epoxidation of **S1** (Table 1). MoO_2 complexes **8**–**10** featuring *N*-morpholine, ethylalcohol and 2-ethoxyethanol pendant arms reported by us earlier show rather similar activity in comparison **Mo1**–**Mo4** across substrates **S1**–**S5** (Table 1 entries 8–10): With **S2**, the reactions afford moderate conversions with modest selectivity (conv. 14–65%, sel. 27–43%). Since **Mo1**–**Mo4** yielded no epoxide from **S2**, even though full conversion was reached, 8–10 may be considered superior. Substrate **S3** is modestly converted with a good selectivity (conv. 25–40%, sel. 95%), and so results are comparable with **Mo1**–**Mo4**, for which activity was, however, present at 0.1 mol-% as well. Likewise, **S4** is epoxidized similarly in the presence of 8–10 than with **Mo1**–**Mo4**. Rather interestingly, however, **S5**, which is completely unreactive in the presence of **Mo1**–**Mo4**, seems to afford the corresponding epoxide in a reasonable conversion and selectivity with **8**–**10** (conv. 46–81%, sel. 30–58%) [26,28].

The catalytic prowess of **Mo1**–**Mo4** also quite closely match that of **12**–**14**, MoO_2 aminobisphenolato complexes featuring 2-methoxyethyl, *N,N*-dimethylethyl and methylpyridyl pendant arms, respectively, reported by us earlier [25]. These pre-catalysts show rather similar activity with **S3**–**S5** than **Mo1**–**Mo4** (Table 1 entries 12–14). For instance, **S3** and **S4** are epoxidized with comparable conversions and selectivities, and **12**–**14** are deactivated with **S5**, similarly to **Mo1**–**Mo4**. However, **Mo1**–**Mo4** are much more active in the epoxidation of **S1**, whereas **S2** is more efficiently epoxidized with **12**–**14**. It should be emphasized that **12**–**14** have not been evaluated in alkene epoxidation at a catalyst loading below 1 mol-%, and so comparisons at these loadings cannot adequately be done.

In another study, **S2** was catalytically epoxidized in the presence of MoO_2 aminobisphenolato complexes featuring benzimidazole (**11**) and ethylpyridyl (**15**) based pendant arms, respectively [22,24]. There are two interesting features regarding these reported catalytic experiments. Firstly, the catalytic reactions do not benefit at all by raising the catalyst loading from 2.5 mol-% to 5.0 mol-% in terms of conversion (Table 1 entries 11, 15 and 16) [22,24]. This phenomenon was observed across all studied pre-catalysts, and it has been attributed to poor solubility of the catalysts [22]. However, it seems more likely that **15** is instead subject to the same "dilution effect" we encountered with **Mo1**–**Mo4** in this study. Namely, the catalytic experiments performed using **15** and other pre-catalysts in the study have a [Mo]:[TBHP] molar ratio difference of 1:50 at the lowest, and not exceeding 1:125. Given our findings in this report, increasing the molar ratio difference to a factor of no less than 1:200, and perhaps optimally 1:2000, might induce a significant enhancement in activity of the complexes, without affecting the autoxidation of **S2**. Unfortunately, this was not tested with **15** [22]. Similar behavior was observed for MoO_2 complexes supported by aminobisphenolato ligands featuring methylpyridyl pendant arms in the same paper [22].

In any event, **Mo1**–**Mo4** perform significantly weaker when compared to **1**–**7** (Table 1 entries 5–7). For the monomeric **1**–**3**, the catalyst loading may be lowered to 0.001 mol-% with respect to **S1, S2, S4** and **S5**, with highest TONs in the range of *ca.* 75,000 (for **S1** and **2**), 28,000 (for **S2** and **3**), 47,000 (for **S4** and **3**) and 25,000 (for **S5** and **2**) [9]. Thus, **1**–**7** may be subject to the same dilution effect as **Mo1**–**Mo4**, but remain active even with challenging substrates at a very low catalyst loading, unlike **Mo1**–**Mo4**. Hydrogen bonding capable motifs in the ligand design have been implicated earlier to be able to enhance the epoxidation activities of various dioxidomolybdenum(VI) complexes bearing ligands featuring alcoholate pendant arms [28,40] as well as amide pendant arms [9]. It is suggested that such moieties are able to stabilize incoming oxidant molecules, such as TBHP or H_2O_2, *via* hydrogen bonding, and/or aid in hydrogen atom shuttling, activating the oxidant and effecting oxygen transfer to the substrate [9,26]. These reports essentially invoke a mechanism wherein oxidant activation is at least partly ligand-assisted, unlike the generally accepted mechanism(s), where oxidant activation and eventual substrate oxidation are effected by H-bonding and shuttling interactions between oxidant molecules and terminal metal oxido ligands [34,37,39,41–43]. However, the extremely high catalytic activity of **1**–**7** may not entirely be governed by the presence of an NH containing amide functionality. In fact, John and co-workers have recently evaluated several MoO_2 complexes featuring tri- and tetradentate aminobisphenolato ligands in deoxydehydration of styrene glycol [44]. Their studies reveal that heightened catalytic activity is observed with coordinatively unsaturated complexes featuring tridentate ligands, as opposed to coordinatively saturated complexes containing tetradentate ones [44]. Similarly, enhanced activity may be observed by removing a phenolato arm from the ligand backbone, effectively leading to dinuclear complexes essentially similar to **4**–**7** [44]. Thus, **Mo1**–**Mo4** may show reduced performance relative to **1**–**7** due to steric factors imparted by the bulky tetradentate aminobisphenolato ligands.

4. Summary and conclusions

Nine benchtop stable dioxidomolybdenum(VI) and –tungsten(VI) complexes **Mo1**–**Mo5** and **W1**–**W4** supported by new dianionic tetradentate amide functionalized aminobisphenolato ligands were designed, synthesized, and characterized. All complexes were found to crystallize very easily in methanol, possibly thanks to intermolecular HB effects from the neutral amide moieties. These properties may be readily exploited when synthesizing complexes based on other transition metals as well.

All complexes except **Mo5** were evaluated in the epoxidation of selected alkene substrates. The catalytic activity of **Mo1**–**Mo4** in the epoxidation of **S1** was found to be very high, and catalyst loadings as low as 0.01 mol-% could be realized without significant loss of activity, similar to **1**–**7**, reported in the literature. Dubbed the "dilution effect", the high activity of **Mo1**–**Mo4** below 1 mol-% loadings was experimentally shown to be result of very high [Mo]:[TBHP] molar ratio differences (as large as 1:20,000), facilitating formation of active catalysts by the action of TBHP. Interaction of the pre-catalysts with TBHP was also shown to account for induction periods seen for some of the tested complexes. **Mo1**–**Mo4** are one to two orders of magnitude more active in the epoxidation of **S1** than other MoO_2 aminobisphenolato supported complexes reported in the literature. However, the activity of **Mo1**–**Mo4** with more challenging alkene substrates **S2**–**S5** is similar based on comparison. Likewise, the tungsten derivatives **W1**–**W4** showed typically poor behavior in all epoxidations, in accordance with the literature. Aside from any possible benefits of having an amide NH moiety in the ligand design, this study also reveals that ligand sterics might be more important in determining the catalytic activity of MoO_2 aminobisphenolato complexes in epoxidation. This proposition is also in line with the work of Poli et al. who suspect that five-coordinate systems show elevated catalytic activity relative to six-coordinate systems [34].

Work has already begun in our laboratories to further probe the

effects of the "dilution effect", and to see whether other aminobisphenolato supported MoO_2 complexes reported by us earlier also display heightened catalytic activity at very low [Mo]:[TBHP] ratios. Specifically, the impact of any HB effects and/or ligand sterics in tri- and tetradentate aminobisphenolato ligands will be focused upon and studied experimentally and computationally in the future.

Associated content

Supporting Information. The Supporting Information includes all experimental procedures, compound characterization data, all spectra of new compounds, catalysis data, as well as crystallographic data. CCDC reference numbers 2,157,984 (**Mo1**), 2,157,985 (**Mo2**), 2,157,986 (**Mo3**) 2,129,453 (**Mo4**), 2,158,304 (**Mo5**), 2,157,987 (**W1**), 2,157,988 (**W2**), 2,157,989 (**W3**) and 2,129,454 (**W4**) and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interests.

CRediT authorship contribution statement

Pasi Salonen: Conceptualization, Formal analysis, Investigation, Validation, Methodology, Visualization, Writing – original draft. **Jörg A. Schachner:** Formal analysis, Investigation, Validation, Methodology, Writing – original draft. **Anssi Peuronen:** Formal analysis, Methodology, Writing – original draft. **Manu Lahtinen:** Formal analysis, Methodology. **Ferdinand Belaj:** Formal analysis, Methodology. **Nadia C. Mösch-Zanetti:** Supervision, Resources, Project administration, Writing – review & editing. **Ari Lehtonen:** Supervision, Resources, Project administration, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Anssi Peuronen reports financial support was provided by Academy of Finland.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.113034.

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