Oxygen atom transfer catalysis by dioxidomolybdenum(VI) complexes of pyridyl aminophenolate ligands

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A series of new cationic dioxidomolybdenum(VI) complexes \([\text{MoO}_2(L^5)]\text{PF}_6\) (2–5) with the tripodal tetradeutate pyridyl aminophenolate ligands HL2–HL5 have been synthesized and characterized. Ligands HL2–HL5 carry substituents in the 4-position of the phenolate ring, viz. Cl, Br and NO2, respectively, whereas the ligand HL6, \(\text{N}(\text{2-hydroxy-3,5-di-tert-butylbenzyl})\text{-N,N-bis(2-pyridylmethyl)}\)amine, is a derivative of 3,5-di-tert-butylsalicylaldehyde. X-ray crystal structures of complexes 2, 3 and 5 reveal that they have a distorted octahedral geometry with the bonding parameters around the metal centres being practically similar. Stoichiometric oxygen atom transfer (OAT) properties of S with PPh3 were investigated using UV–Vis, \(^{31}\text{P}\) NMR and mass spectrometry. In CH3Cl2 solution, a dimeric Mo(V) complex \([\text{MoO}2\text{(L5)}]_2\text{PF}_6\) 6 was formed while in methanol solution an air-sensitive Mo(V) complex \([\text{MoO}2\text{(OCH}_3\text{)}\text{(L5)}]_2\) 7 was obtained. The solid-state structure of the \(\mu\)-oxo bridged dimer 6 was determined by X-ray diffraction. Complex 7 is unstable under ambient conditions and capable of reducing DMSO, thus showing reactivity analogous to that of DMSO reductases. Similarly, the OAT reactions of complexes 2–4 also resulted in the formation of dimeric Mo(V) and unsaturated monomeric Mo(V) complexes that are analogous to complexes 6 and 7. Catalytic OAT at 25 °C could also be observed, using complexes 1–5 as catalysts for oxidation of PPh3 in deuterated dimethylsulfoxide (DMSO-\(d_6\)), which functioned both as a solvent and oxidant. All complexes were also tested as catalysts for sulfoxidation of methyl-\(\text{p}\)-tolylsulfide and epoxidation of various alkene substrates with tert-butyl hydroperoxide (TBHP) as an oxidant. Complex 1 did not exhibit any sulfoxidation activity under the conditions used, while 2–5 catalyzed the sulfoxidation of methyl-\(\text{p}\)-tolylsulfide. Only complexes 2 and 3, with ligands containing halide substituents, exhibited good to moderate activity for epoxidation of all alkene substrates studied, and, in general, good activity for all molybdenum(VI) catalysts was only exhibited when cis-cyclooctene was used as a substrate. No complex catalysed epoxidation of cis-cyclooctene when an aqueous solution of H2O2 was used as potential oxidant.

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1. Introduction

Mononuclear molybdenum enzymes are widely distributed in nature, and they are generally involved in oxygen atom transfer reactions to or from biological oxygen acceptors/donors [1–3]. These enzymes also contribute to the carbon, nitrogen, and sulfur cycles and their active sites contain an organic cofactor which consists of a molybdenum atom and one or two organic pterin derivatives [4,5]. The mononuclear molybdenum enzymes can be divided into two subcategories - hydroxylases and oxotransferases - under the Hille classification [3]. The latter class can be subdivided into two families based on their structures, i.e. the sulfite oxidase (SO) and DMSO reductase (DMSOR) families [3].

A number of complexes have been studied as structural and/or functional models for molybdenum-containing oxotransferase enzymes that catalyse oxygen atom transfer (OAT) reactions.
The OAT reactions between phosphines and oxygen donors have been studied as models for biological reactions. The generally accepted mechanism for oxygen atom transfer to a phosphine proceeds via bonding between the phosphine and one of the oxo ligands which leads to a transient intermediate, and concomitantly bridged electron transfer to the molybdenum center [14,15]. This general type of mechanism – for both oxidative and reductive OAT – has been studied and is strongly supported by numerous computational studies [16–19]. Oxidomolybdenum species containing N-, O- and S-donor ligands have been studied extensively as catalysts for OAT reactions [20–24].

Sulfoxides are important synthons for the synthesis of natural and artificial compounds and are used in medicinal chemistry [25–27]. Similarly, epoxides are valuable intermediates and targets in laboratory synthesis, and are important feedstocks in pharmaceutical, agrochemical, and chemical industry [28–31]. Molybdenum-based catalysts are effective for the epoxidation of functionalized olefins. Oxidomolybdenum complexes also have potential applications in the field of asymmetric epoxidation of chiral alkenes [32,33]. We are interested in the development of new, relatively inexpensive molybdenum(VI) based catalysts for catalytic oxidation reactions that are also significant in the chemical industry, such as sulfoxidation and epoxidation reactions [34–39]. We have also investigated the reactivities of molybdenum oxo complexes as bioinspired models for molybdenum-containing OAT enzymes [1,40].

There are previous reports on metal complexes with phosphines carrying di-2-picolylamine substituents at the ortho positions. For example, the tripodal ligands HL1-HL5 [Fig. 1] are known to readily form coordination compounds with Mg(II), Zn(II) [41], Fe(III) [42], V(V) [43], Eu(III) and Yb(III) [44]. The catalytic activities of complexes based on these ligands have been studied, e.g. the catechol dioxigenase and proton reduction properties of iron complexes [42,48], ring-opening polymerization of ε-caprolactone with zinc complexes [41], and catalytic activities for ethylene polymerization of vanadium complexes [43].

We have previously reported the dioxidomolybdenum(VI) complex 1 of the pyridylaminophenolate ligand HL1 but its catalytic oxidation chemistry was not studied [1]. In this contribution, we present the syntheses and characterizations of four MoO2(VI) complexes (2–5) containing related pyridyl aminophenolate ligands with different electron-donating and -withdrawing groups on the ligand backbone (Fig. 1 and Scheme 1), and explore the catalytic applications of 1–5 in oxygen atom transfer, sulfoxidation and epoxidation reactions with various substrates. A dinuclear oxido-bridged molybdenum(VI) complex 6 and a mononuclear MoO2(V) complex 7 were isolated as products in the OAT reactions of 5 with PPh3.

2. Results and discussion

2.1. Synthesis and characterization of complexes

The tripodal tetradentate pyridylaminophenolate ligands HL1-HL5 were prepared in a straightforward manner by reductive amination, a known procedure starting from di-(2-picolyl)amine and the corresponding salicylaldehyde [42,45,46]. Complex 1 was prepared following a published procedure [1], and the other complexes were synthesised analogously. The reaction of [MoO2Cl2] with the tripodal ligands HL2-HL5 in the presence of NaOMe and KPF6 in methanol results in the formation of cationic complexes of the type [MoO2(Ln)2]+ (Scheme 1). In each case, the reaction mixture was diluted with diethyl ether and hexane, filtered through a pad of Celite and evaporated to dryness. Crystallisation from methanol gave pure products in 61–75% yields. Complexes 2–5 can also be prepared in similar yields (ca. 60–75%) by the reaction of HL2–HL5 with other molybdenum precursors, such as [MoO2(acac)3] or [MoO2Cl2(dmso)3], following the synthetic protocol described above.

The tripodal ligands HL1–HL5 can coordinate to the cis-dioxidomolybdenum moiety to form two possible configurational isomers, i.e. the methylpyridyl groups may be coordinated cis or trans to each other. One isomer (isomer A in Fig. 2; X = H) has these two pyridyl side-arms donor located in trans positions to the phenolate and oxido ligands whereas in another isomer (B), the phenolate moiety is trans to one oxido ligand. Previous studies on Mo and Fe complexes, for example [MoO2(L1)2]+ [1], [FeCl2(L1)] [46,47], and [FeCl2(L1)]2[48] have shown that such ligands tend to coordinate with the pyridyl arms cis to each other (Fig. 2, isomer A), a feature that was confirmed by DFT calculations. The structures of the two isomers based on complex 1 [1] were optimized and these optimized structures are shown in Fig. 2. Isomer A was computed to be 9.3 kcal/mol more stable than isomer B. As already mentioned, complex 1 is a known compound, but was prepared during this work to evaluate its catalytic efficiency.

The solubility in common solvents varies with the electron-withdrawing and electron-releasing substituents on the phenyl rings. Complexes 2–4 are readily soluble in methanol and acetonitrile but they are less soluble in chlorinated solvents (CHCl3, CH2Cl2). Complex 5 is soluble in both polar and non-polar organic solvents due to the presence of the tert-butyl substituents. All complexes were characterized by 1H, 13C, 31P and 19F NMR, IR spectroscopy and mass spectrometry (Spectroscopic data are given in the Supplementary Information, Figs. S1–S11). The structures of complexes 2, 3 and 5 were also verified by single-crystal X-ray crystallography (vide infra). As anticipated, complexes 2–5 have relatively similar NMR and IR spectra. The infrared spectra of all studied complexes showed two strong bands around 880–905 and 910–950 cm−1 which are assigned to asymmetric and symmetric M=O stretches, respectively [49–52]. The 1H NMR spectra were recorded in CD3OD solutions while the chemical shifts for the phenolate ring protons as well as for the two inequivalent pyridine rings were seen around 6.5–9.3 ppm as 11 sharp signals for 2–4 and 10 resonances for 5 (cf. ref 1). This indicates that the two pyridyl side-arm donors are located in cis to each other, so isomer A (Fig. 2) is the prevalent species in solution. The chemical shifts for the two tert-butyl groups of 5 are within the expected region. The singlets of the six N–CH3 methylene protons exhibit separated resonances

![Fig. 1. Structures of the tripodal ligands employed in the study.](image-url)
within the range 4–6 ppm which is consistent for all three pendant arms of the ligand being inequivalent. The NMR spectra match well with the solid-state structures (vide infra).

When the reaction of 5 with PPh3 in dichloromethane was studied under N2 atmosphere, the solution turned red and then the colour changed to dark purple. After half an hour, the solution was filtered and the dark purple solid was collected. The 1H NMR spectrum of the complex showed rather complicated and broad signals indicating the formation of a paramagnetic Mo(V) complex. The UV–vis spectrum is consistent with the dimeric complex prepared previously by the reaction of 1 under similar conditions [1]. The formation of the dark purple Mo(V) dimer [(μ-O)(MoO(L))2] (PF6)2 6 was verified by the observation of a peak in its electrospray high resolution mass spectrum that matches the expected empirical formula (see Fig. S12 and Scheme 2). Single crystal X-ray crystallographic analysis revealed that 6 is a dinuclear oxo-bridged Mo(V) complex (see Fig. S13 and crystallographic data summarized in Table S1).

When the reaction of 5 with 1.5 equivalents of PPh3 was studied in a methanol solution, the yellow colour of the solution turned red within fifteen minutes. The reaction led to the formation of OPPh3 (as identified by 31P NMR) and a reduced oxidomolybdenum(IV) complex. The red complex was identified as the mononuclear complex [Mo(IV)O(OCH3)(L)] (L = pyridine aminophenolate ligand) through a high resolution mass spectrum, which shows a molecular ion peak [M]+ with a characteristic molybdenum pattern (see Fig. S14). The red complex reduces biological oxygen donors such as dimethyl sulfoxide (DMSO) albeit in a slow reaction, as evidenced by the reformation of 5 seen by UV–Vis spectroscopy. This phenomenon is also closely related with our previous studies [1]. Unfortunately, while the reduced oxidomolybdenum(IV) complex 7 was found to be comparatively stable in DMSO solution under anaerobic conditions at room temperature, all attempts to isolate the desired complex 7 were unsuccessful, leading only to the formation of small amounts of the dark purple Mo(V) oxo dimer 6 (vide supra), as previously observed also for the analogous reduced oxidomolybdenum(IV) complex formed from 1 [1].

The analogous oxygen atom transfer reactions to PPh3 were studied under equivalent conditions for complexes 2–4 in both dichloromethane and methanol. The results were analogous to the above-mentioned reactions; in the potentially coordinating solvent methanol, red unstable Mo(IV) complexes of the general formula [MoO(OCH3)(L)] (L = pyridine aminophenolate ligand) could be identified, while in the usually non-coordinating solvent dichloromethane, purple [(μ-O)(MoO(L))2]2+ complexes were formed. The Mo(V) dimers and unstable Mo(IV)O(OCH3) complexes were characterized by 1H NMR and UV–vis spectroscopy, respectively, and the spectra correspond to those for 6 and 7.

Fig. 2. Two possible configurational isomers for the studied complexes with the DFT-optimized structures of each isomer of complex 1 [1].

Scheme 2. Synthesis of Mo(V) dimer [(μ-O)(MoO(L))2](PF6)2 6.
Electrospray ionization (ESI) mass spectrometry was used for the characterization of complexes 2–7. The mass spectrum of 2 shows a molecular ion [M]+ peak at \( m/z = 468 \) and a ligand molecular ion at \([HL^2 + H]^+\) at \( m/z = 340 \). Similarly, complexes 3 and 4 exhibit peaks at \( m/z = 512 \) and \( m/z = 479 \), respectively, which can be assigned to the molecular ion [M]+ peak. The ligand molecular ions were observed at \([HL^2 + H]^+\) at \( m/z = 384 \) and \([HL^4 + H]^+\) at \( m/z = 351 \), accordingly. Complex 5 is identified as a molecular ion [M]+ peak at \( m/z = 546 \) and the corresponding ligand peak \([HL^5 + H]^+\) at \( m/z = 418 \). In addition, in solution 5 shows a Mo(V) dimeric complex as molecular ion ([μ-O][MoO(L)])₂ + NaOMe at \( m/z = 1126 \) due to the samples injected as dichloromethane solutions, preceded and followed by methanol. The characteristic molecular ion peaks for complexes 6 and 7 are at \( m/z = 1073 \) and \( m/z = 561 \), respectively.

2.2. Description of the X-ray crystal structures

Single crystals of 2, 3 and 5 suitable for crystallographic analysis were obtained from concentrated methanol solutions at \(-4 \) °C and their solid-state structures were determined by X-ray diffraction. The crystallographic data together with the collection and refinement parameters for complexes are summarized in the Supplementary Material, Table S2. Selected bond distances and angles are listed in the Supplementary Material, Table S3. In all structures, there is one catenionic complex and one PF₆ anion in the asymmetric unit. The molecular structure of 2 is illustrated in Fig. 3, and the analogous structures of 3 and 5 are shown in the Supplementary Material as Figs. S15 and S16, respectively. All complexes have a distorted octahedral geometry in which the two cis-positioned oxido ligands bind strongly to the Mo(VI) ion, while the geometrical parameters are very similar. The two pyridyl rings are almost perpendicularly aligned relative to each other in complexes 2, 3 and 5, the N(1)-Mo(2)-N(3) angle is 84.35(10)° for 2, 84.15(9)° for 3 and 83.38(7)° for 5, respectively. In the three complexes, the three oxygen donor atoms are in the fac arrangement of a distorted octahedron where all three donor groups are about 105°–108° apart. The structures confirm that two nitrogen atoms in the pyridine rings of the chelating amine bis-pyridine phenolate ligand are located in cis positions with the N(1)-Mo(1)-N(2) and N(3)-Mo(1)-N(2) bond angles are 70.87(10)° and 71.98(9)° for 2, 70.86(9)° and 71.70(9)° for 3 and 71.32(7)° and 71.91(6)° for 5, respectively. One pyridyl group is coordinated trans to the arylxy ligand and the other one is trans to the oxido ligand O3 while the central amine nitrogen N2 of the ligand backbone is coordinated trans to the terminal oxido ligand O2. The bond distances of the oxido ligands O2 and O3 and the O (2)–Mo(1)–O(3) angle of complexes 2, 3 and 5 are within the expected range and comparable with previously reported six-coordinate dioxidomolybdenum complexes [1,2,1]. The Mo(1)–N(3) bond distance, 2.298(3) Å for 2, 2.302(2) Å for 3 and 2.3120(18) Å for 5, respectively, that is slightly longer than the Mo(1)–N1 bond distance, 2.183(3) Å for 2, 2.181(2) Å for 3 and 2.192(2) Å for 5, respectively due to the strong trans influence of the oxido ligand compared to the phenolate moiety. The bond distances Mo(1)–N1 and Mo(1)–N(3) are seemingly shorter than the Mo(1)–N(2) bond distance (2.322(3) Å for 2, 2.332(2) Å for 3 and 2.3116(18) Å for 5, respectively) indicating that the central nitrogen atom of the ligand backbone is coordinated more weakly to the Mo centre than the pyridine N-donors. All these Mo–N distances are shorter than in previously reported [MoO₂(L₂)] complexes with Mo–N bond lengths > 2.30 Å, where L–O₂⁻ is the corresponding tripodal ligand with one pyridyl and two phenolate rings [53].

Single crystals of 6 were grown from acetonitrile solution with excess of NaBP₄ in order to ascertain the dimeric framework. Unfortunately, the very thin needle-shaped crystals gave weak diffraction patterns with Mo-Kα radiation leading to the high R-values because of the lack of the good quality data set. However, the dimeric nature of 6 could be proven (see Fig. S2).

3. Catalysis studies

3.1. Catalytic oxygen atom transfer

Catalytic oxygen atom transfer (OAT) properties of complexes 1–5 to the non-biological substrate triphenylphosphine were investigated (Scheme 3) in deuterated dimethyl sulfoxide (DMSO d₆) while the reaction course was followed by 31P NMR. Preliminary experiments showed that reactions are very fast with catalyst loadings of 1–10 mol % at 65 °C. Under such conditions, PPh₃ was fully oxidized into OPPh₃ (as seen by 31P NMR at around 27 ppm) within 1–2 min with all studied complexes. To further probe the catalytic profiles of the catalysts, the reactivity screening was carried out with low catalyst loadings (1 mol %) at 25 °C. Complex 2 exhibited the fastest reaction rate with a half-life of approximately 5 min compared to complexes 1 and 3, which showed the half-lives of approximately 15 min. The sterically more hindered complex 5 showed a lower rate of reaction (half-life approx. 1 h) under similar conditions. Under these experimental conditions, PPh₃ was formed in a 98% yield with catalyst 2 after 1 h while with catalysts 1, 3 and 5, 3 hrs were required to reach a 95% yield. The calculated turn-over frequencies (TOFs) for complexes 1, 2, 3 and 5 were of the same order of magnitude, ranging from 104 h⁻¹ to 296 h⁻¹, after an induction period of around 15 min whereas 4 showed the lowest activity (TOF = 40 h⁻¹). The data obtained in the OAT experiments is summarized in Table 1.

![Scheme 3](image)

3.2. Catalytic sulfidation

The oxidation of methyl-p-tolyl sulfide with two equivalents of tert-butyl hydroperoxide as the oxygen atom source was studied using dioxidomolybdenum complexes 1–5 as catalysts (Scheme 4). The reactions were run under atmospheric conditions in deuterated methanol solution and the reaction course was monitored by ¹H NMR. In control experiments that were run in the absence of catalysts no sulfide was obtained. Complex 1 was found to be inactive as a sulfidation catalyst under the conditions employed. The reason for this lack of activity is not clear; it may be that the Mo(VI) peroxo complex that is expected to be formed during the reaction is too unstable. In other experiments, the catalytic reactions started immediately without any noticeable
induction times. After a one-hour reaction, the highest yield (97%) of a sulfoxide product was observed with catalyst 4 and the lowest yield (60%) was obtained for 3. Moreover, the sulfoxidations were found to be selective, without any sign of the formation of sulfone. All values obtained in the sulfoxidation experiments are listed in Table 2.

Table 2
Catalytic sulfoxidation of methyl-p-tolylsulfide by tert-BuOOH at 25 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%) a</th>
<th>TON b</th>
<th>TOF (h⁻¹) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>30</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>23</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>97</td>
<td>77</td>
<td>308</td>
</tr>
<tr>
<td>4</td>
<td>97</td>
<td>59</td>
<td>236</td>
</tr>
</tbody>
</table>

Reaction conditions: 1 mol % of catalysts (1-5), 2.0 equivalents of tert-BuOOH at 25 °C. a Yield of the product measured by 1H NMR after 1 h. b TON calculated after 15 min of reaction as (mol product) (mol catalyst)⁻¹. c TOF calculated after 15 min of reaction as (mol product) (mol catalyst)⁻¹ (t/h⁻¹).

From the observed catalytic activities in olefin epoxidation, it can be concluded that complexes 1-5 are very sensitive to the substituents present in the ligand backbone. The presence of halide substituents like Cl in complex 2 and Br in complex 3 results in epoxidation catalysts with reasonable activity. The absence of substituents, as in 1, or the presence of Bu-groups (5) or a NO₂-group (4) do not result in active epoxidation catalysts.

Using Hammett σₚ constants as qualitative indicators of the relative electron-withdrawing/electron-donating properties of the different substituents, it may be noted that the most strongly electron-withdrawing substituent (NO₂, complex 4) leads to the best performance in sulfoxidation of methyl-p-tolylsulfide (Table 2) but the worst performance (with the exception of non-substituted HL1, complex 1) in catalytic epoxidations (Table 3). It may also be noted that the chloro-substituted complex 2 and the bromo-substituted complex 3 show the same catalytic activities, within experimental error of detection, with chlorine and bromine possessing identical σₚ constants. These two complexes with weakly 3.3. Catalytic epoxidation

Complexes 1-5 were tested as catalysts for the epoxidation of five olefinic substrates, viz. cis-cyclooctene S1, 1-octene S2, styrene S3, limonene S4 and α-terpineol S5 (Fig. 4). In the case of S4 and S5, the racemic mixtures of the D- and L-enantiomers were used. The reactions were carried out with three equivalents of tert-butylhydroperoxide (TBHP) as an oxidant and 1 mol % catalyst loadings. The reactions were run at 50 °C in CHCl₃ solutions and conversions to epoxides were followed by GC–MS.

As expected, all five molybdenum complexes did show catalytic activity with S1, albeit with highly different activities (Table 3). Whereas the two halogenated complexes 2 and 3 showed complete conversion of cyclooctene to epoxide within seven and four hours respectively, complexes 1, 4 and 5 only showed low to moderate activity with cyclooctene S1 (Table 3). For the more challenging substrates S2-S5, again only complexes 2 and 3 showed some catalytic activity (Table 3). For 1-octene S2, complexes 1, 4 and 5 showed no conversion of substrate, for substrates S3-S5, complexes 1, 4 and 5 displayed conversion of substrate, but low selectivity to epoxide due to over-oxidation despite the relatively low excess of oxidant. For example, in styrene epoxidation phenyl acetaldehyde and benzaldehyde were formed; for limonene and α-terpineol formation of the respective ketones was observed in GC–MS spectrometry (Table 3).

Fig. 4. Olefinic substrates used for epoxidation experiments. In the cases of S4 and S5, racemic mixtures of the R- and S-isomers were used.

Table 3
Conversion of substrate (selectivity to epoxide) for complexes 1–5.

<table>
<thead>
<tr>
<th>[%]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclooctene, S1</td>
<td>48 (81)</td>
<td>&gt;95 (99)</td>
<td>&gt;95 (99)</td>
<td>59 (97)</td>
<td>86 (93)</td>
</tr>
<tr>
<td>1-octene, S2</td>
<td>no conv.</td>
<td>33 (92)</td>
<td>29 (97)</td>
<td>no conv.</td>
<td>no conv.</td>
</tr>
<tr>
<td>styrene, S3</td>
<td>unsel.</td>
<td>64 (22)</td>
<td>59 (63)</td>
<td>unsel.</td>
<td>unsel.</td>
</tr>
<tr>
<td>limonene, S4</td>
<td>unsel.</td>
<td>&gt;95 (35)</td>
<td>&gt;95 (47)</td>
<td>unsel.</td>
<td>unsel.</td>
</tr>
<tr>
<td>α-terpineol, S5</td>
<td>unsel.</td>
<td>70 (22)</td>
<td>88 (53)</td>
<td>unsel.</td>
<td>unsel.</td>
</tr>
</tbody>
</table>

General conditions: 1 mol % catalyst, 0.5 mL CHCl₃, 50 °C, 3 equiv. TBHP, conversion of substrate (selectivity to epoxide) after 24 h; no conv. = no substrate conversion, unsel. = selectivity to epoxide × 10%; [a] max. yield of epoxide reached after 7 h; [b] max. yield of epoxide reached after 4 h.
electron-withdrawing substituents exhibit the best catalytic performances in epoxidation but are the two worst (bar complex 1) catalysts for sulfoxidation. The mediocre performance of complex 4 in phosphine oxidation runs counter to earlier observations where the presence of a strongly electron-withdrawing substituent (e.g. –NO2) in para-position on a molybdenum-coordinating phenolate leads to increased rate of phosphine oxidation [54,55]. This suggests that it is not simply the electronic influence of the substituent that is responsible for catalyst activity in the present study. Other factors, like catalyst stability in the presence of a large amount of oxidant, may also play a vital role. The poor catalytic performance by complex 1 is puzzling and difficult to rationalize.

4. Conclusion

Five triopodal tetratetradenate pyridyl aminophenolate ligands, with varying electronic and steric properties depending on the nature of the substituents on the phenolate ring were used to prepare a series of mononeric molybdenum(VI) complexes of the general formula [MoO2(L4)3]PF6 (1–5).

5. Experimental section

5.1. General procedures and materials

Unless otherwise noted, all experiments involving metal complexes were carried out under atmospheric conditions with standard laboratory equipment. Commercial grade reagents and solvents were purchased from commercial suppliers (Fisher Scientific and Sigma-Aldrich) and used without further purification. The ligands HL1-HL2 were synthesized according to published procedures [42,45,46]. The 1H, 13C, 31P and 19F NMR spectra were recorded on a Varian Inova 500 MHz instrument spectrometer. NMR chemical shifts are reported in ppm using deuterated methanol or chloroform as solvents, and referenced to the residual solvent peak as internal standard; 31P NMR chemical shifts are referenced to external H3PO4. Peaks are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qq), sextet (qqq), septet (qqqqq), octet (qqqqqqq) and unresolved multiplets (br, m or unresolved). Coupling constants are given in Hz. The IR spectra were measured with a Bruker Optics, Vertex 70 spectrophotometer with a diamond ATR setup; resonances are listed with wave numbers (cm−1) and intensities (br = broad, v = very strong, s = strong, m = medium, w = weak). Mass spectrometry was performed on Waters ZQ 4000 or Waters QToF Xevo-G2 spectrometers. The samples were injected as MeCN and MeOH solutions for 6 and 7 and measured on a Waters QToF Xevo-G2 spectrometer. Results are denoted as cationic mass peaks; unit is the mass/charge ratio. Gas chromatography mass spectrometry (GC–MS) measurements were performed with an Agilent 7890 A gas chromatograph (column type, Agilent 19091 J–433), coupled to an Agilent 5975C mass spectrometer.

5.2. Preparation of complexes 2–5

General procedure: The complexes were prepared by the reaction of [MoO2Cl2] (1.0 mmol) with the respective ligand HL1 (1.0 mmol), KPF6 (1.20 mmol) and NaOMe (1.25 mmol) in 20 mL of methanol. The reaction mixture was stirred for 4 h and placed in a freezer overnight to yield a precipitate which was removed by filtration. Diethyl ether (10 mL) and hexane (10 mL) were added to the filtered solution to precipitate more white solid, which was also removed by filtration through a Celite pad. The yellow solution was kept at −4 °C overnight. Removal of the solvent at reduced pressure afforded the relevant product which was dried under vacuum. The pure products were recrystallized from concentrated methanol solutions at −4 °C and isolated after a week.

[MoO2(L3)3]PF6, 2, orange-red crystals, 0.40 g (65%). 1H NMR (500 MHz, CD3OD) δ 9.24 (d, J = 5.2 Hz, 1H), 8.79 (d, J = 5.2 Hz, 1H), 8.29 (t, J = 7.7 Hz, 1H), 7.91 (d, J = 5.2 Hz, 1H), 7.86 (d, J = 5.2 Hz, 1H), 7.72 (d, J = 5.2 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.46 (s, 1H), 7.12 (t, J = 7.7 Hz, 2H), 6.52 (d, J = 5.2 Hz, 1H), 5.32 – 5.24 (m, 2H), 4.93 (d, J = 10.9 Hz, 1H), 4.51 (dd, J = 14.3, 9.0 Hz, 2H), 4.22 (d, J = 17.9 Hz, 1H). 13C NMR (126 MHz, CD3OD) δ 157.87, 156.47, 154.66, 153.52, 151.82, 150.40, 144.04, 144.42, 141.65, 130.39, 127.72, 126.90, 125.02, 123.98, 122.80, 118.89 (Ar), 65.64, 60.44 (CH2). 31P NMR (202 MHz, CDCl3) δ −144.22 (hept, J = 713.4 Hz).

[MoO2(L2)3]PF6, 3, red crystals, 0.46 g (71%). 1H NMR (500 MHz, CD3OD) δ 9.27 (d, J = 5.2 Hz, 1H), 8.82 (d, J = 5.2 Hz, 1H), 8.32 (t, J = 7.7 Hz, 1H), 7.94 (d, J = 5.2 Hz, 1H), 7.90 (t, J = 7.7 Hz, 1H), 7.76 (t, J = 7.7 Hz, 1H), 7.63 (s, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 5.2 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 6.50 (d, J = 8.6 Hz, 1H), 5.31 (dd, J = 14.3, 9.0 Hz, 2H), 4.94 (d, J = 15.4 Hz, 1H), 4.54 (dd, J = 14.3, 9.0 Hz, 2H), 4.25 (d, J = 17.9 Hz, 1H). 13C NMR (126 MHz, CD3OD) δ 158.47, 156.67, 152.63, 154.68, 153.45, 150.04, 144.05, 141.70, 133.39, 133.24, 126.96, 125.02, 124.41, 122.16, 119.27, 115.01 (Ar–C), 66.56, 60.45 (CH2). 31P NMR (202 MHz, CDCl3) δ −144.22 (hept, J = 713.4 Hz).

[MoO2(L1)3]PF6, 4, red crystals, 0.38 g (61%). 1H NMR (500 MHz, CD3OD) δ 9.26 (d, J = 5.2 Hz, 1H), 9.13 (d, J = 5.2 Hz, 1H), 8.88 (d, J = 5.2 Hz, 1H), 8.78 (d, J = 5.2 Hz, 1H), 8.61 (t, J = 7.7 Hz, 1H), 8.42 (s, 1H), 8.31 (t, J = 7.7 Hz, 1H), 7.96 (t, J = 7.7 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 5.34 (t, J = 16.6 Hz, 2H), 5.07 (d, J = 15.4 Hz, 1H), 4.98 (d, J = 15.4 Hz, 1H), 4.62 (d, J = 15.4 Hz, 1H), 4.39 (d, J = 15.4 Hz, 1H). 31P NMR (202 MHz, CDCl3) δ −144.22 (hept, J = 713.4 Hz).

[MoO2(L4)3]PF6, 5, deep red crystals, 0.52 g (75%). 1H NMR (500 MHz, CD3OD) δ 9.18 (d, J = 5.2 Hz, 1H), 8.70 (d, J = 5.2 Hz, 1H), 8.16 (td, J = 7.3, 1.5 Hz, 1H), 7.91 (d, J = 5.2 Hz, 1H), 7.78 (td, J = 7.8, 1.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 5.2 Hz, 1H), 7.23 (d, J = 5.2 Hz, 1H), 7.13 (d, J = 5.2 Hz, 1H), 5.37 (d, J = 15.4 Hz, 1H), 5.12 (dd, J = 14.3, 9.0 Hz, 2H), 4.65
(d, J = 15.4 Hz, 1H), 4.50 (d, J = 15.4 Hz, 1H), 4.36 (d, J = 15.4 Hz, 1H), 1.31 (s, 9H), 1.20 (s, 9H). 13C NMR (126 MHz, CDCl3) δ 155.56, 155.52, 155.11, 152.54, 150.31, 147.01, 143.79, 141.62, 138.02, 126.90, 125.63, 124.64, 122.53, 121.27 (Ar-C), 67.43, 62.71, 60.30 (CH2), 34.97, 34.63, 31.37, 29.97 (CH3).


Preparation of complex [μ-O][MoO(OCH3)(L5)]2(PF6)2. A solution of PPh3 (0.03 mmol) was added under nitrogen atmosphere. A red colour appeared immediately upon addition of the PPh3 to the complex solution. After stirring for 15 min, the UV–Vis and mass data were recorded for [μ-O][MoO(OCH3)(L5)]2(PF6)2. 6 was isolated by filtration as a dark purple solid (0.025 mmol, 35% yield). UV–vis in MeCN: λmax, nm (ε, M⁻¹cm⁻¹): 209 (49166), 275 (11023), 402 (3163). ESI-MS: m/z = 546 [4]+, 418 [HL3 + H]+, [μ-O][MoO-(L3-O)]2 + NaOMe]⁺ at m/z 1126.

Preparation of complex [MoO(OCH3)(L5)]2. 7. Complex 5 (0.02 mmol) was dissolved in 5 mL of methanol and PPh3 (0.03 mmol) was added under nitrogen atmosphere. A red colour appeared immediately upon addition of the PPh3 to the complex solution. After stirring for 15 min, the UV–Vis and mass data were recorded for 5. UV–vis in MeOH: λmax, nm (ε, M⁻¹cm⁻¹): 227 (98723), 265 (29615), 404 (6568), 570 (9111). HRMS: m/z = 1073.3405 [6]+, 1114.3145 [6 + MeCN]⁺.

5.3. Catalytic oxygen atom transfer reactions

The OAT reactions of PPh3 (0.2 mmol) catalysed by complexes 1–5 (0.002 mmol) were run in DMSO at 25 °C. The reaction progress was monitored by 31P NMR using a fifteen-minute interval, measuring the disappearance of a resonance at −6 ppm for PPh3 and the appearance of a signal for OPPh3 at approx. 27 ppm. The 31P spectrum was externally referenced to 85% H3PO4.

5.4. Sulfoxidation reactions

In these experiments, complexes 1–5 were tested as catalysts for the oxidation of methyl-p-tolyl sulfide at room temperature in CD2OD solutions using 1:2 M ratios of substrate/tert- BuOOH (0.19 M: 0.38 M) and 10 μL of 1,2-dichloroethane was added as an internal standard in a 5 mm NMR tube. The complete selectivity towards the sulfoxide was monitored by 1H NMR spectroscopy at fifteen-minute intervals. The reaction rates were estimated on the basis of the integrated intensities of substrate and product spectra. In the sulfoxidation test, the sulfide methyl singlet at 2.27 was turned to the sulfide methyl singlet at 2.75 ppm.

5.5. Epoxidation of olefins

A Heidolph Parallel Synthesizer 1 was used. In a typical epoxidation experiment 2–3 mg of the respective catalyst was dissolved in 0.5 mL of CHCl3 and the substrate was added. Mesitylene was used as internal standard. After the experiment temperature was reached tert-butylhydroperoxide was added to start the reaction and aliquots for GC–MS measurements were withdrawn at given time intervals. The GC samples were quenched with MnO2, diluted with ethyl acetate and measured. All yields obtained by GC have an esd of ± 5%.

5.6. DFT modelling details

The reported calculations were performed with the hybrid meta exchange–correlation functional M06 [56], as implemented by the Gaussian 09 program package [57]. The Mo atom was described by Stuttgart-Dresden effective core potentials (ECP) and an SDD basis set [58], while a 6-31G(d)’ basis set was employed for the remaining atoms [59]. All computations were performed using an ultrafine grid and Grimme’s dispersion correction [60].

The reported geometries for the isomers of complex 1 (species A and B) represent fully optimized ground states (positive eigenvalues). The computed frequencies were used to make zero-point and thermal corrections to the electronic energies; the reported free energies are quoted in kcal/mol relative to the specified standard. The geometry-optimized structures presented here have been drawn with the Jmol molecular visualization and manipulation program [61].

CRediT authorship contribution statement

Md Kamal Hossain: Investigation, Writing - original draft, Writing - review & editing. Jörg A. Schachner: Investigation, Writing - original draft. Matti Haukka: Investigation. Michael G. Richmond: Investigation, Writing - original draft. Nadia C. Mösch-Zanetti: Supervision, Writing - original draft. Ari Lehtonen: Supervision, Writing - original draft. Ebbe Nordlander: Conceptualization, Supervision, Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115234.