Studies on olefin epoxidation with *t*-BuOOH catalysed by dioxomolybdenum(VI) complexes of a novel chiral pyridyl alcoholate ligand

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The chiral dioxomolybdenum(VI) complexes [MoCl{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$(O)_2$(THF)] and [Mo{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$_2(O)_2$] have been prepared in good yields by reaction of the solvent substituted complex [$MoCl_2O_2(THF)_2$] with one or two equivalents of chiral 2′-pyridyl alcohol. The optically active aminoalcohol was obtained by reaction of 2-pyridyllithium with (−)-(2*S*,5*S*)-8-trimethylsilyloxymenthone. The complexes are active catalysts in the homogeneous epoxidation of cyclic and linear olefins, dienes and terpenes by *t*-BuOOH. They present remarkable activity and excellent product selectivity in cyclooctene epoxidation (cyclooctene oxide was obtained in quantitative yield). In the case of limonene, regioselectivity is high in favour of the epoxidation of the internal cyclic double bond. Ring opening activity was also observed for α-pinene oxide, producing campholenic aldehyde and epoxy campholenic aldehyde.

Epoxides are important organic intermediates since they undergo ring-opening reactions with a variety of reagents to give mono- or bi-functional organic products.[1] In general, epoxides can be prepared by oxidation using hydrogen peroxide or alkylhydroperoxides in the presence of high-valent early transition-metal catalysts.[2] Dioxomolybdenum(VI) complexes have proven to be particularly effective catalysts or catalyst precursors for the epoxidation of olefins. Representative general formulae include [$MoX_2O_2(L^1)_n$], [$MoX(L^2)_m(O)_2(L^1)_n$] and [$Mo(L^2)_m(O)_2(L^1)_n$]. The ligand surrounding of the molybdenum(VI) centre can be fine-tuned by either variation of X (Cl, Br, CH_3) or L [mono- or bidentate neutral (L^1) or anionic (L^2) *N*,*O*,*S*-ligand].[3] Oxo complexes with nitrogen, oxygen and/or sulfur donor ligands are of special interest due to their relevance to the active sites of certain molybdoenzymes. Asymmetric catalysis is made possible by the presence of chiral chelating ligands.[4] One of the difficulties in this area is the development of ligands that are stable to oxidation and straightforward to synthesise, with the possibility of changing electronic and steric characteristics by simple variation of the starting material.

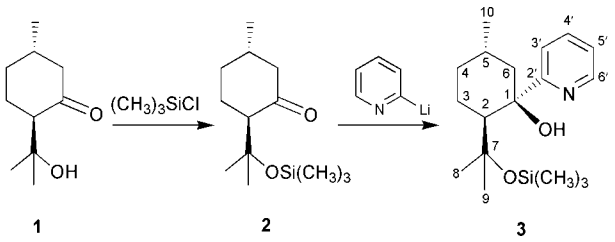
Dioxomolybdenum(VI) complexes containing achiral 2′-pyridyl alcoholate ligands have been shown to have great potential in the oxidation of terminal olefins with molecular oxygen.[5] The anionic ligand complexes the metal centre with a coordinative bond to the nitrogen of the pyridine ring and a covalent single bond to the alcoholate oxygen. A broad variety of the parent alcohol ligands are generally accessible by the reaction of 2-lithiopyridine with either symmetrical or unsymmetrical ketones, yielding achiral or chiral molecules, respectively. Dioxomolybdenum(VI) complexes of the type [MoCl(L*)$(O)_2$(S)] and [Mo(L*)$_2(O)_2$] (L* = bidentate chiral 2′-pyridyl alcoholate, S = monodentate neutral solvent molecule) have recently been described.[6] These homogeneous catalysts showed good activity in the epoxidation of *trans*-methylstyrene using *t*-butyl hydroperoxide (*t*-BuOOH), but the enantiomeric excesses were no higher than 25%.[6a,d] The present work concerns the synthesis and characterisation of new chiral dioxomolybdenum(VI) pyridyl alcoholate complexes of the type [MoCl(L*)$(O)_2$(THF)] and [Mo(L*)$_2(O)_2$], and an evaluation of their catalytic activity in the epoxidation of olefins other than *trans*-methylstyrene, namely 1-octene, 2-octene, cyclooctene, limonene, α-pinene and styrene.

Results and discussion

Synthesis of dioxomolybdenum(VI) complexes

The starting material used for the synthesis of the chiral ligand was *cis*-*p*-menthane-3,8-diol, a commercially available natural product. Oxidation of this diol with CrO_3 gives the ketone derivative (+)-(2*R*,5*S*)-2-(1-hydroxy-1-methylethyl)-5-methylcyclohexanone (**1**).[7] Treatment of **1** with $(CH_3)_3SiCl$ in CH_2Cl_2 gives (−)-(2*S*,5*S*)-8-trimethylsilyloxymenthone (**2**). The 2′-pyridyl alcohol ligand **3** can then obtained as the sole diastereomer (100% diastereoselectivity) by a method involving condensation of 2-pyridyllithium with the chiral ketone **2** (Scheme 1).[5,6a,d,8]

Reaction of the chiral 2′-pyridyl alcohol ligand **3** with [$MoCl_2O_2(THF)_2$] in CH_2Cl_2, in a 1 : 1 molar ratio, gives the chiral complex [MoCl{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$(O)_2$(THF)] (**4**) in nearly quantitative yield

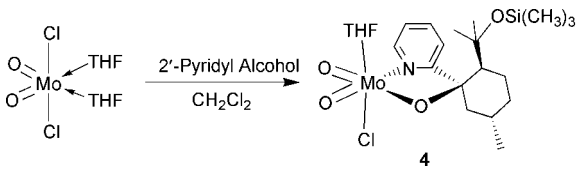


1 2 3

Scheme 1

after evaporation of the reaction mixture and washing with hexane. The driving force for this reaction is most likely the formation of a stable five-membered ring chelate (Scheme 2).

Complex **4** is more soluble in organic solvents than other related complexes of the type $[MoCl_2O_2L]$,[3] and does not precipitate from the reaction mixture (it is significantly soluble in diethyl ether). It can only be purified by washing with hexane or pentane. When the reaction is performed in dichloromethane or THF, complexes of the type $[MoCl(L^*)(O)_2(THF)]$ are produced but, for example, dissolution and recrystallisation of **4** from acetonitrile gives the acetonitrile adduct $[MoCl\{(1R,2S,5S)$-8-trimethylsilyloxy-1-(2-pyridyl)mentholato$\}(O)_2(NCMe)]$, as evidenced by ^{1}H NMR and elemental analysis.



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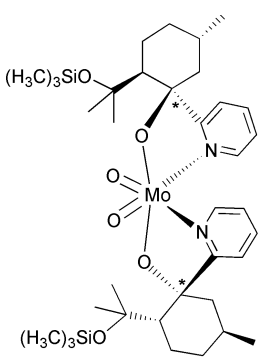
Scheme 2

The dioxomolybdenum(VI) bis-2′-pyridyl alcoholate complex **5** was prepared by three different processes: (a) treatment of $[MoCl_2O_2(THF)_2]$ with 2 equiv. of the ligand under reflux; (b) treatment of $[MoCl_2O_2(THF)_2]$ with 2 equiv. of the ligand and 2 equiv. of TlOEt at room temperature; (c) treatment of $[Mo(acac)_2O_2]$ (a common starting material for ligand exchange reactions[5,6a,b]) with 2 equiv. of the ligand under reflux. In all three cases the corresponding molybdenum complex was obtained in high yield. Complexes **4** and **5** are air and moisture sensitive and must be handled and stored under a moisture-free inert gas atmosphere.

Complexes **4** and **5** display symmetric and asymmetric IR stretching vibrations for the *cis*-dioxo unit in the expected range (940–910 cm^{-1}).[3,9] The other bands in the IR spectra are assigned to the vibrational signals of the bound ligands. The ^{1}H NMR spectrum of complex **4** shows the peaks corresponding to the coordinated THF and the chiral ligand. The ^{13}C NMR spectra demonstrate that the ligand is bound to the dioxomolybdenum core. Thus, the signal for the 2′-carbon atom of the pyridine ring is found at δ 168.32 for **4** and δ 166.63 for **5**, both shifted downfield compared to that for the free ligand (δ 160.11). This indicates a shift of electron density from the aromatic ring to the molybdenum centre. Unfortunately, in $CDCl_3$ it is not possible to observe the signals for the quaternary alcoholate carbon atoms (C^1) because they are hidden under the solvent peak.



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Catalysis of oxidation reactions

The catalytic performance of $[MoCl\{(1R,2S,5S)$-8-trimethylsilyloxy-1-(2-pyridyl)mentholato$\}(O)_2(THF)]$ (**4**) was studied for the epoxidation of a variety of olefins using *t*-BuOOH as oxidant at 55 °C under air atmosphere (1 atm), without solvent. The catalyst is active in the oxidation of all these substrates. The conversion *vs.* time profiles are shown in Fig. 1 and reveal the different reactivity of **4** towards the various cyclic olefins. We were unable to detect any induction period in all cases. Initial activities varied between 7.2 mol mol_{Mo}^{-1} h^{-1} for styrene and 229.6 mol mol_{Mo}^{-1} h^{-1} for cyclooctene (Table 1). With the exception of α-pinene, the main reaction product was the corresponding epoxide. In the absence of catalyst (under identical reaction conditions) no reaction was observed.

The selectivity to epoxide *vs.* conversion profiles are shown in Fig. 2. The complex $[MoCl(L^*)(O)_2(THF)]$ (**4**) is very effective for the epoxidation of cyclooctene. Within 24 h the reaction was complete and selectivity towards the epoxide was 98.8% (Table 1). The corresponding diol was formed as a minor byproduct. Catalytic activity was very high during the first 15 min but then decreased significantly (Fig. 1). Similar autoretardation effects were reported for other dioxomolybdenum(VI) complexes used as catalysts under identical reaction conditions.[10] These effects were attributed to the reaction of the active Mo complex with *t*-butyl alcohol, which is inevitably formed during the epoxidation reaction by decomposition of *t*-BuOOH (used in excess).

Styrene oxidation in the presence of complex **4** produced styrene epoxide as the only product up to 29% conversion (at 7 h, Fig. 1 and 2). At 24 h styrene conversion was 49.8% and the selectivity to the epoxide dropped to 54.0% due to the formation of the corresponding diol (28.1% selectivity) and smaller amounts of other unidentified products (Table 1). Styrene oxide yields (*ca.* 25% at 24 h) are comparable to those reported for other octahedrally coordinated dioxomolybdenum(VI) complexes, under identical reaction conditions.[3c] The lower reactivity of styrene to epoxide formation compared to aliphatic cyclic olefins such as cyclooctene may be due in part to the presence of the electron attracting aro-

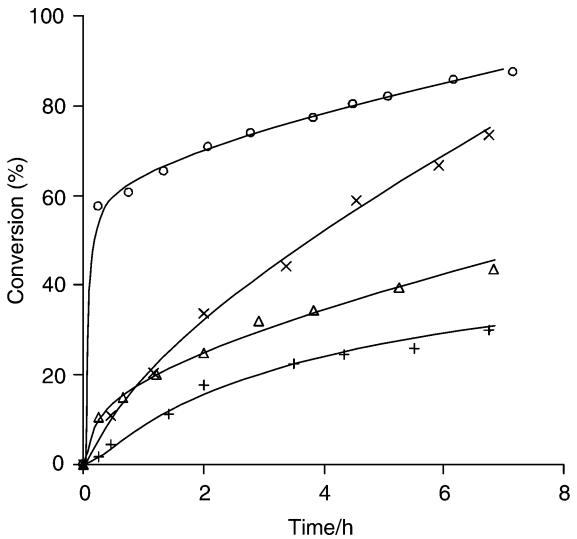
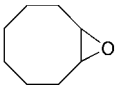
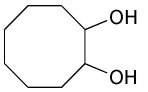
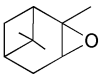
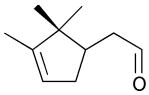
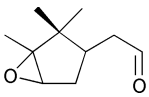
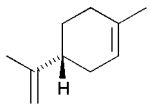
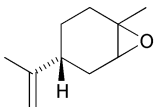
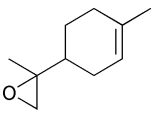
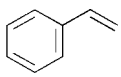
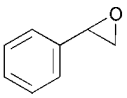
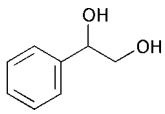


Fig. 1 Conversion profiles for the different olefins in the presence of **4**: cyclooctene (○); styrene (+); α-pinene (△); (*R*)-(+)-limonene (×).

Table 1 Olefin oxidations using *t*-BuOOH in the presence of **4**

Substrate	Initial activity[a]/mol mol_{Mo}^{-1} h^{-1}	Conversion[b] (%)	Product	Selectivity[c] (%)
 Cyclooctene	229.6	100.0		98.8
				1.2
 α-Pinene	42.0	63.0		11.7
				6.5
				63.2
 (*R*)-(+)-Limonene	24.1 (20.6)[d]	90.4 (89.5)		71.2 (82.6)
				9.4 (6.2)
 Styrene	7.2	49.8		54.0
				28.1

[a] Calculated as mmol converted substrate/(mmol catalyst × 0.25 h). [b] Converted substrate after 24 h of reaction. [c] With the exception of cyclooctene oxidation, other unidentified products were formed during the reaction. [d] Results in parentheses are for the corresponding reaction with (*S*)-(−)-limonene.

matic ring, which decreases the electron density at the olefinic double bond, making it less susceptible to electrophilic attack. A comparison of turnover frequencies of olefin epoxidation with complex **4** shows that it is less reactive towards the terminal carbon–carbon double bond of 1-octene (which has a lower electronic density) than a more substituted olefin such as 2-octene: turnover frequencies (during 4 h of reaction) were 1.4 mol_{oct} mol_{Mo}^{-1} h^{-1} and 10.6 mol_{oct} mol_{Mo}^{-1} h^{-1} for 1-octene and 2-octene, respectively. In both systems, the corresponding epoxide was the only observed product.

The oxidation of α-pinene in the presence of complex **4** gave a broad product spectrum, including α-pinene oxide, campholenic aldehyde and epoxy campholenic aldehyde, and small amounts of other unidentified products (Table 1). Selectivity to α-pinene oxide reached a maximum of *ca.* 53% at 25% conversion (Fig. 2), and after 24 h it decreased to 11.7% at 63.0% conversion (Table 1). Campholenic aldehyde, an important intermediate used in the synthesis of sandalwood fragrances, may be formed by the rearrangement of α-pinene oxide on a Lewis or Brönsted acidic centre, involving ring opening of the epoxide.[11] A similar mechanism may be involved for complex **4**, since molybdenum is in its highest oxidation state (6+) and has Lewis acid character. Furthermore, a preliminary experiment using α-pinene oxide as the substrate, under identical reaction conditions, produced campholenic aldehyde and epoxy campholenic aldehyde (20 and 39% selectivity, respectively, at 65% α-pinene oxide conversion).

The reactivity of complex **4** (which has a stereogenic center) towards the oxidation of (1*R*)-(+)-α-pinene or (1*S*)-(−)-α-pinene was similar. These stereoisomeric olefins were used as starting materials in separate reactions and the results are roughly the same as those obtained for racemic α-pinene: 57.7 and 54.6% conversion for (1*R*)-(+)-α-pinene and (1*S*)-(−)-α-pinene, respectively, at 24 h. These results suggest that both stereoisomers of α-pinene react at the same rate with complex **4**. The product distribution (not including stereochemistry) remained practically unchanged. Thus, after 24 h, selectivities

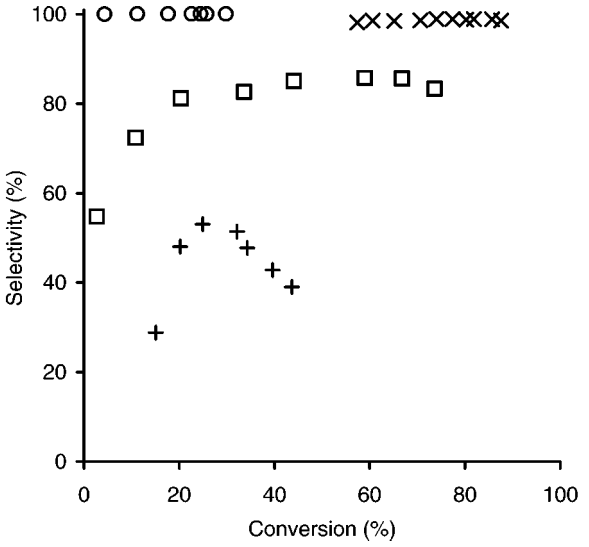


Fig. 2 Selectivity to epoxide *vs.* conversion for the different olefins in the presence of **4**: cyclooctene oxide (×); styrene oxide (○); α-pinene oxide (+); limonene oxide (□).

to α-pinene oxide, campholenic aldehyde and epoxy campholenic aldehyde were 15.3, 8.6 and 50.2%, respectively, for (1*R*)-(+)-α-pinene oxidation, and 11.5, 9.8 and 58.1%, respectively, for (1*S*)-(−)-α-pinene oxidation. It was not possible to identify the stereochemical nature of the different products to check if these reactions are stereospecific.

The catalytic activity of complex **4** in the oxidation of (*R*)-(+)-limonene or (*S*)-(−)-limonene was similar (*ca.* 90% conversion at 24 h, Table 1). Limonene oxide was always the main product and 8,9-epoxy-*p*-menth-1-ene was formed as a side product. For both substrates, maximum selectivity to limonene oxide was *ca.* 86% at 59% conversion (Fig. 2), which decreased to 71.2 and 82.6% for (*R*)-(+)-limonene and (*S*)-(−)-limonene oxidation, respectively (at *ca.* 90% conversion after 24 h, Table 1).

The catalytic performance of [Mo{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$_2$(O)$_2$] (**5**) was compared to that of [MoCl{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}(O)$_2$(THF)] (**4**) for the oxidation of cyclooctene and (*R*)-(+)-limonene. The initial activity of **5** (54.2 and 6.7 mol mol$_{Mo}^{-1}$ h^{-1} for cyclooctene and limonene, respectively) was significantly lower than that observed for **4** (Table 1). This may be accounted for by the fact that compound **5** has a more rigid coordination sphere with two bulky bidentate *N*,*O*-ligands. In the case of **4**, the presence of a labile coordinated THF molecule may facilitate the formation of the catalytically active species either by activation of the *t*-BuOOH or the olefin. Despite the slower initial reaction rate, within 24 h the olefin conversion in the presence of **5** was similar to that obtained in the presence of **4**: 100% for cyclooctene and 88.4% for (*R*)-(+)-limonene. Product selectivity was roughly the same for both catalysts. Cyclooctene oxidation in the presence of **5** gave a quantitative yield of cyclooctene oxide while (*R*)-(+)-limonene oxidation produced limonene oxide and 8,9-epoxy-*p*-menth-1-ene with 79.7 and 7.1% selectivity, respectively, at 88.4% conversion.

Conclusions

The chiral oxomolybdenum(VI) derivatives [MoCl{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}(O)$_2$(THF)] (**4**) and [Mo{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$_2$(O)$_2$] (**5**), prepared from [MoCl$_2$O$_2$(THF)$_2$] and the chiral ligand, are active catalysts in the homogeneous epoxidation of cyclic and linear olefins by *t*-BuOOH. The monosubstituted complex **4** is more active than **5**. Activity and selectivity are highest in cyclooctene epoxidation (cyclooctene oxide was obtained in quantitative yield). Regioselective epoxidation of the more substituted internal, or cyclic, double bonds is observed. In spite of being chiral, complexes **4** and **5** do not discriminate significantly between both enantiomerically pure forms of the substrates α-pinene and limonene. Ring opening activity was also observed for α-pinene oxide, producing campholenic aldehyde and epoxy campholenic aldehyde.

Experimental

General

All preparations and manipulations were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and Et$_2$O over Na/benzophenone ketyl; CH$_2$Cl$_2$ and NCCH$_3$ over CaH$_2$), distilled under nitrogen and kept over 4 Å molecular sieves (3 Å for NCCH$_3$). Microanalyses were performed at the ITQB by Mrs Zara Tavares. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, on a Bruker CXP 300 spectrometer. IR spectra were measured on a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets or Nujol mulls.

The precursor materials MoCl$_2$O$_2$[12] and [MoCl$_2$O$_2$(THF)$_2$][13] were prepared as described previously. Oxidation of (+)-*cis*-*p*-menthane-3,8-diol (Aldrich) with CrO$_3$ gave (+)-(2*R*,5*S*)-2-(1-hydroxy-1-methylethyl)-5-methylcyclohexanone (**1**).[7] 1-Octene (98%), 2-octene (97%), cyclooctene (95%), styrene (99%), α-pinene (98%), (1*R*)-(+)-α-pinene (98%), (1*S*)-(−)-α-pinene (98%), (*R*)-(+)-limonene (97%, 98% ee) and (*S*)-(−)-limonene (96%) were obtained from Aldrich.

Synthesis of ligands

(−)-(2*S*,5*S*)-8-Trimethylsilyloxymenthone (2). (CH$_3$)$_3$SiCl (2.24 g, 20.5 mmol) was added dropwise *via* syringe to a solution of (+)-(2*R*,5*S*)-2-(1-hydroxy-1-methylethyl)-5-methylcyclohexanone (**1**) (2.34 g, 13.7 mmol), DMAP (1.68 g, 13.7 mmol) and Et$_3$N (1.39 g, 13.7 mmol) in CH$_2$Cl$_2$ (15 mL) at 0 °C. The reaction mixture was stirred for 2 h at room temperature. The mixture was diluted with water (50 mL) and extracted with diethyl ether (3 × 80 mL). The combined organic layers were washed with H$_2$O (100 mL) and brine (100 mL). The organic solution was dried over Na$_2$SO$_4$ and the solvent removed to give a colourless oil (3.6 g), this was purified by flash chromatography (SiO$_2$; hexane–AcOEt 8 : 2) to afford the pure oil compound **2** (3.31 g, 99%). Anal. calc. for C$_{13}$H$_{26}$O$_2$Si (242.43): C, 64.40; H, 10.81; found: C, 64.38; H, 10.76%. $[\alpha]_D^{20}$ − 25.1° (*c* 1, CHCl$_3$). IR (Nujol, ν/cm^{-1}): 2958 vs, 2928 vs, 2873 s, 2850 m, 1711 vs, 1456 s, 1378 s, 1362 s, 1260 vs, 1249 vs, 1206 m, 1182 s, 1151 vs, 1122 s, 1091 s, 1038 vs, 839 vs, 755 vs, 712 m, 685 m, 542 s, 491 m. ^{1}H NMR (CDCl$_3$, 300 MHz, r.t., δ): 2.36–2.28 (m, 3H); 2.04–1.90 (m, 3H); 1.60–1.44 (m, 2H); 1.37 (s, 3H, CH$_3$); 1.27 (s, 3H, CH$_3$); 1.02 (d, 3H, CH$_3$); 0.11 (s, 9H, CH$_3$).

(+)-(1*R*,2*S*,5*S*)-8-Trimethylsilyloxy-1-(2-pyridyl)menthol (3). A solution of 2-bromopyridine (1.83 g, 11.6 mmol) in diethyl ether (4 mL) was added to a solution of *n*BuLi (6.7 mL, 1.6 M in hexane, 10.7 mmol) in diethyl ether (100 mL) at −70 °C. The red solution was stirred for 30 min at −70 °C and then treated with a solution of **2** (2.16 g, 8.9 mmol) in diethyl ether (6 mL). The reaction mixture was stirred for 30 min at −70 °C. The mixture was diluted with water (50 mL) and extracted with diethyl ether (3 × 80 mL). The combined organic layers were washed with H$_2$O (100 mL) and brine (100 mL). The organic solution was dried over Na$_2$SO$_4$ and the solvent removed to give an oil (3.28 g), this was purified by

flash chromatography (SiO_2; hexane–AcOEt 9 : 1) to afford the pure colourless oil compound **3** (2.43 g, 85%). Anal. calc. for $C_{18}H_{31}NO_2Si$ (321.53): C, 67.24; H, 9.72; N, 4.35; found: C, 67.19; H, 9.68; N, 4.25%. $[\alpha]_D^{20} + 0.9°$ (*c* 1, $CHCl_3$). IR (Nujol, ν/cm^{-1}): 3441 vs, 3052 s, 3001 s, 2951 vs, 2868 s, 2843 m, 1587 vs, 1568 s, 1455 s, 1431 s, 1398 s, 1384 s, 1366 m, 1287 m, 1251 s, 1213 m, 1173 s, 1163 s, 1141 m, 1121 m, 1092 m, 1001 vs, 956 m, 922 m, 891 vs, 841 vs, 781 s, 752 vs, 734 m, 559 m. ^{1}H NMR ($CDCl_3$, 300 MHz, r.t., δ, see Scheme 1 for atom numbering): 8.48 (d, 1H, $H^{6'}$); 7.81 (d, 1H, $H^{4'}$); 7.67–7.62 (m, 1H, $H^{5'}$); 7.10–7.06 (m, 1H, $H^{3'}$); 5.51 (s, 1H, OH); 2.31–2.25 (m, 1H); 1.91–1.77 (m, 4H); 1.52–1.37 (m, 2H); 1.21 (s, 3H, CH_3); 1.19–1.09 (m, 1H); 0.85 (d, 3H, CH_3); 0.63 (s, 3H, CH_3), 0.07 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz, r.t., δ): 160.11 ($C^{2'}$); 148.00; 136.97; 121.28; 119.93; 80.09 (C^1); 78.95, 52.23; 50.03; 34.98; 32.19; 27.99; 24.07; 22.29; 2.75.

Synthesis of dioxomolybdenum(VI) complexes

[MoCl{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$(O)_2$(THF)] (4). A solution of $[MoCl_2O_2(THF)_2]$ (0.53 g, 1.54 mmol) in CH_2Cl_2 (10 mL) was treated with the aminoalcohol ligand **3** (0.50 g, 1.54 mmol). The resulting turbid solution was stirred for a further 30 min. The solvent was evaporated and the product washed with hexane, then dried under vacuum (0.80 g, 93%). Anal. calc. for $C_{22}H_{38}ClMoNO_5Si$ (556.03): C, 47.52; H, 6.89; N, 2.52; found: C, 47.48; H, 6.75; N, 2.45%. IR (KBr, ν/cm^{-1}): 3105 m, 2956 s, 2924 m, 2868 m, 1620 s, 1476 m, 1455 s, 1440 s, 1370 m, 1296 m, 1253 s, 1167 m, 1055 s, 940 vs, 916 vs (Mo=O), 881 m, 844 s, 753 s, 687 s, 647 m, 583 m. ^{1}H NMR ($CDCl_3$, 300 MHz, r.t., δ): 8.91 (br, 1H, $H^{6'}$); 7.94 (t, 1H, $H^{4'}$); 7.47–7.45 (m, 2H, $H^{5'/3'}$); 3.83 (s, THF); 2.03–2.01 (br, 3H); 1.90–1.81 (m, 2H); 1.86 (s, THF); 1.63–1.57 (m, 1H); 1.33 (s, 3H, CH_3); 1.26–1.24 (m, 1H); 1.02–0.99 (m, 1H); 0.88 (d, 3H, CH_3); 0.53 (s, 3H, CH_3); 0.10 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz, r.t., δ): 168.32 ($C^{2'}$); 151.30; 137.97; 123.22; 123.11; 120.51; 67.60 (THF); 51.23; 50.96; 47.79; 33.53; 31.02; 29.56; 25.83; 24.66 (THF); 24.53; 20.69; 0.86.

[Mo{(1*R*,2*S*,5*S*)-8-trimethylsilyloxy-1-(2-pyridyl)mentholato}$_2$$(O)_2$] (5). *Method* (*a*). A solution of $[MoCl_2O_2(THF)_2]$ (0.32 g, 0.93 mmol) in CH_2Cl_2 (10 mL) was treated with 2 equiv. of the aminoalcohol ligand **3**. The solution became milky and after 2 h at reflux, the mixture was evaporated to dryness to yield a powder, which was washed with hexane (0.67 g, 94%).

Method (*b*). A solution of $[MoCl_2O_2(THF)_2]$ (0.32 g, 0.93 mmol) in CH_2Cl_2 (10 mL) was treated with 2 equiv. of the alcohol ligand **3** and 2 equiv. of TlOEt. The reaction mixture was left stirring for 4 h and then the suspension was evaporated to dryness. After washing with hexane, the residue was extracted with dichloromethane and the solution taken to dryness to yield a powder, which was washed with hexane several times (0.63 g, 88%).

Method (*c*). A solution of $[Mo(acac)_2O_2]$ (0.25 g, 0.77 mmol) in THF (10 mL) was treated with 2 equiv. of the aminoalcohol ligand **3** (0.49 g, 1.53 mmol). The reaction mixture was refluxed for 2 h and then the solution was evaporated to dryness. The oily solid was washed several times with hexane and dried to yield a white powder (0.54 g, 92%). Anal. calc. for $C_{36}H_{60}MoN_2O_6Si_2$ (769.00): C, 56.23; H, 7.86; N, 3.64; found: C, 56.12; H, 7.75; N, 3.58%. IR (KBr, ν/cm^{-1}): 3071 m, 2949 s, 2868 m, 2846 m, 1569 s, 1519 s, 1476 m, 1455 s, 1434 s, 1385 s, 1367 m, 1290 m, 1249 vs, 1202 m, 1160 s, 1021 s, 959 vs, 922 vs, 907 vs (Mo2O), 856 m, 838 s, 776 s, 684 s, 644 m, 551 m. ^{1}H NMR ($CDCl_3$, 300 MHz, r.t., δ): 8.56 (br, 2H, $H^{6'}$); 7.72 (t, 2H, $H^{4'}$); 7.26–7.24 (m, 4H, $H^{5'/3'}$); 2.18–2.02 (m, 2H); 1.95–1.77 (m, 4H); 1.67–1.58 (m, 2H); 1.46–1.40 (m, 4H); 1.16 (s, 6H, CH_3); 1.04–0.97 (m, 4H); 0.84 (d, 6H, CH_3); 0.61 (s, 6H, CH_3); 0.06 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz, r.t., δ): 166.63 ($C^{2'}$); 146.58; 137.26; 121.18; 54.62; 52.44; 34.21; 30.53; 27.30; 26.51; 26.29; 20.91; 1.49

Catalytic reactions with the molybdenum compounds

The catalytic reactions were performed under an air atmosphere, in a reaction vessel equipped with a magnetic stirrer, immersed into a thermostated oil bath (55 °C). A 1% molar ratio of catalyst/substrate was used (7.3 mmol olefin and 73 μmol complex **4** or **5**) and 5.5 M *t*-butyl hydroperoxide in decane (2 mL, 11 mmol) was used as oxidant. Samples were withdrawn periodically and analysed using a gas chromatograph (Varian 3350) equipped with a capillary column (SPB-5, 20 m × 0.25 mm × 0.25 μm) and a flame ionisation detector. The products were quantified using calibration curves and n-nonane or undecane as internal standard (added after the reaction), and identified by GC-MS (HP 5890 Series II GC; HP 5970 Series Mass Selective Detector) using He as carrier gas.

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