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Chiral bis(oxazoline) and pyridyl alcoholate dioxo-molybdenum(VI) complexes: synthesis, characterization and catalytic examinations

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Dedicated to Professor Dr Henri Brunner on the occasion of his 65th birthday

Abstract

A group of chiral molybdenum(VI) complexes comprising $MoO_2Cl_2L^{**}$, $MoO_2Cl(THF)L^*$ and $MoO_2L^*_2$ [L** = chiral bis(oxazoline) and L* = chiral 2′-pyridyl alcoholate] have been prepared in good yields by reaction of the solvent substituted complex $MoO_2Cl_2(THF)_2$ with one or two equivalents of chiral ligand. Optically active aminoalcohols (L*) were obtained by reaction of the appropriate organolithium compound with (−)-menthone, (+)-8-phenylisomenthone, (−)-8-phenylmenthone, (+)-camphor and (−)-thujone. The molybdenum complexes were characterized by multinuclear NMR (^1H, ^{13}C, ^{17}O, ^{95}Mo) spectroscopy, IR spectroscopy and elemental analysis. ^{95}Mo-NMR data reflected the donor capability of the organic ligands, whereas ^1H-NMR and IR data were comparatively indifferent to the changes in the Lewis base ligand. The complexes were evaluated as catalysts for the asymmetric epoxidation of *trans*-β-methylstyrene by *tert*-butylhydroperoxide. The bis(oxazoline) complexes showed good catalytic activity but had low optical yields. Complexes of the type $MoO_2Cl(THF)L^*$ (L* = chiral 2′-pyridyl alcoholate) also exhibited high catalytic activity and enantiomeric excesses of up to 23%. The corresponding $MoO_2L^*_2$ alcoholate complexes were considerably less active with comparable optical yields.

Keywords: Chiral ligands; Epoxidation; Molybdenum; Oxazoline; Oxide complexes; 2′-Pyridyl alcoholate

1. Introduction

Currently, there is considerable interest in the synthesis of chiral oxometallate complexes and their use as catalysts for asymmetric olefin epoxidation [1]. In the field of oxomolybdenum chemistry, several approaches have been reported [2]. The catalytically active species is normally prepared in situ from $MoO_2(acac)_2$, *tert*-butylhydroperoxide (TBHP) and an excess of chiral *N*/*O* or *O*/*O*-ligands, e.g. *N*-alkyl ephedrines [2a], *N*-methylprolinols [2b] or diisopropyl tartrates [2d]. One of the difficulties in this area is the development of suitable chiral ligands that are stable to oxidation and straightforward to synthesize, with the possibility of changing electronic and steric characteristics by simple variation of the starting material. One class of ligands that meets these pre-requisites are 2′-pyridyl alcohols, which are readily accessible by the reaction of 2-lithiopyridine with either symmetrical or unsymmetrical ketones [3], yielding chiral or achiral molecules, respectively. Herrmann and coworkers prepared complexes of the type MO_2L_2 (M = Mo, W, L = achiral 2′-pyridyl alcoholate) and tested them as catalysts for the selective oxidation of olefins with molecular oxygen or TBHP

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[4]. In a recent development of this work, chiral 2′-pyridyl alcohols were prepared and the resulting chiral dioxomolybdenum complexes exhibited good catalytic activity and substantial optical induction [5].

Another class of chiral chelating ligands that seems to meet the requirements outlined above are the C_2-symmetric bis(oxazolines). They are easily prepared from readily available amino alcohols [6]. The most extensively studied ligand of this series is that where the two oxazolines are separated by a methylene bridge and thereby form a six-membered chelate with the metal. Bis(oxazoline) metal complexes have emerged as efficient enantioselective catalysts for a variety of organic transformations, including carbon–carbon bond forming reactions, aziridinations, cyclopropanations, hydrosilylation, Diels–Alder and hetero Diels–Alder reactions [7]. To our knowledge, the synthesis and catalytic potential of dioxomolybdenum–bis(oxazoline) complexes has not been reported. We recently reported the synthesis of *cis*-MoO_2^{2+} complexes of the type $MoO_2X_2L_n$ (X = Cl, Br, CH_3) with mono- and bi-dentate nitrogen and oxygen ligands [8a–d]. The activity of the dissolved complexes as catalysts in olefin epoxidation with TBHP was also tested. We have extended this synthetic methodology to include chiral ligands L and now wish to report on the preparation and characterization of a series of complexes with chiral 2′-pyridyl alcoholates and methylenebis(oxazolines). Their catalytic potential has been evaluated in the asymmetric epoxidation of *trans*-β-methylstyrene using TBHP as oxidant.

2. Results and discussion

2.1. Chiral ligand synthesis

The chiral bis 1,3-oxazolinyl-propanes **1**–**3** were prepared according to a literature procedure (see Section 4). The 2′-pyridyl alcohol ligands **4**–**9** are accessible by reaction of 2-pyridyl-lithium with appropriate prochiral ketone precursors (Scheme 1). As expected, ligands **4**–**7** were obtained as single diastereoisomers (diastereospecific) [1b,3a]. In the case of (−)-menthone, (+)-8-phenylisomenthone, (−)-8-phenylmenthone, and (+)-camphor, the carbonyl group is only accessible from one stereo side. However, lithiopyridine can attack the carbonyl group of (−)-thujone on either the α or β face, resulting in the synthesis of two diastereoisomers, **8** and **9**, in a ratio of 73:27 (by NMR), which were separated by chromatography. The two forms of the (−)-thujone-derivatives (**8** and **9**), as well as the other desired ligands **4**–**7**, were fully characterized, and the absolute stereochemistry of the ligands was confirmed (see Section 4.2).

2.2. Synthesis of chiral dioxomolybdenum(VI) compounds *1a*–*13a*

As a consequence of our interest in asymmetric chiral molybdenum complexes, we have been evaluating the potential utility of chiral 4,4′-disubstituted bis(oxazolines) such as **1**–**3** as bidentate ligands. These organic ligands with donor functionalities, such as nitrogen, react readily with complexes of the type $MoO_2Cl_2(THF)_2$ [9] to form the octahedrally coordinated complexes $MoO_2Cl_2L^{**}$ [L** = bis(oxazoline)] **1a**–**3a** at room temperature in good isolated yields (Scheme 2). The product complexes are soluble in dichloromethane and precipitate from the reaction mixture upon addition of diethyl ether. They are stable at room temperature but decompose rapidly in the presence of air.

By reacting one equivalent of the chiral 2′-pyridyl alcohol ligands **4**–**9** with $MoO_2Cl_2(THF)_2$ in a similar fashion, a variety of other chiral complexes of the type $MoO_2Cl(THF)L^*$ (L* = chiral 2′-pyridyl alcoholate) are accessible in nearly quantitative yields according to Scheme 3.

The complexes belonging to this family (**4a**–**9a**) are more soluble in organic solvents than compounds **1a**–**3a**, or other similar complexes of the type MoO_2Cl_2L [8], and do not precipitate from the reaction mixtures (they are significantly soluble in diethyl ether). They can be purified by washing with *n*-hexane. Dissolution and recrystallizaton of the product complexes **4a**–**9a** of the composition $MoO_2Cl(THF)L^*$ from $NCCH_3$ gave the $NCCH_3$ adducts of the type $MoO_2Cl(NCCH_3)L^*$. Likewise, if the complexes were dissolved in dichloromethane and pyridine added, the pyridine-substituted compounds, $MoO_2Cl(pyridine)L^*$, were obtained. The composition has been confirmed by elemental analysis and ^{1}H-NMR spectroscopy.

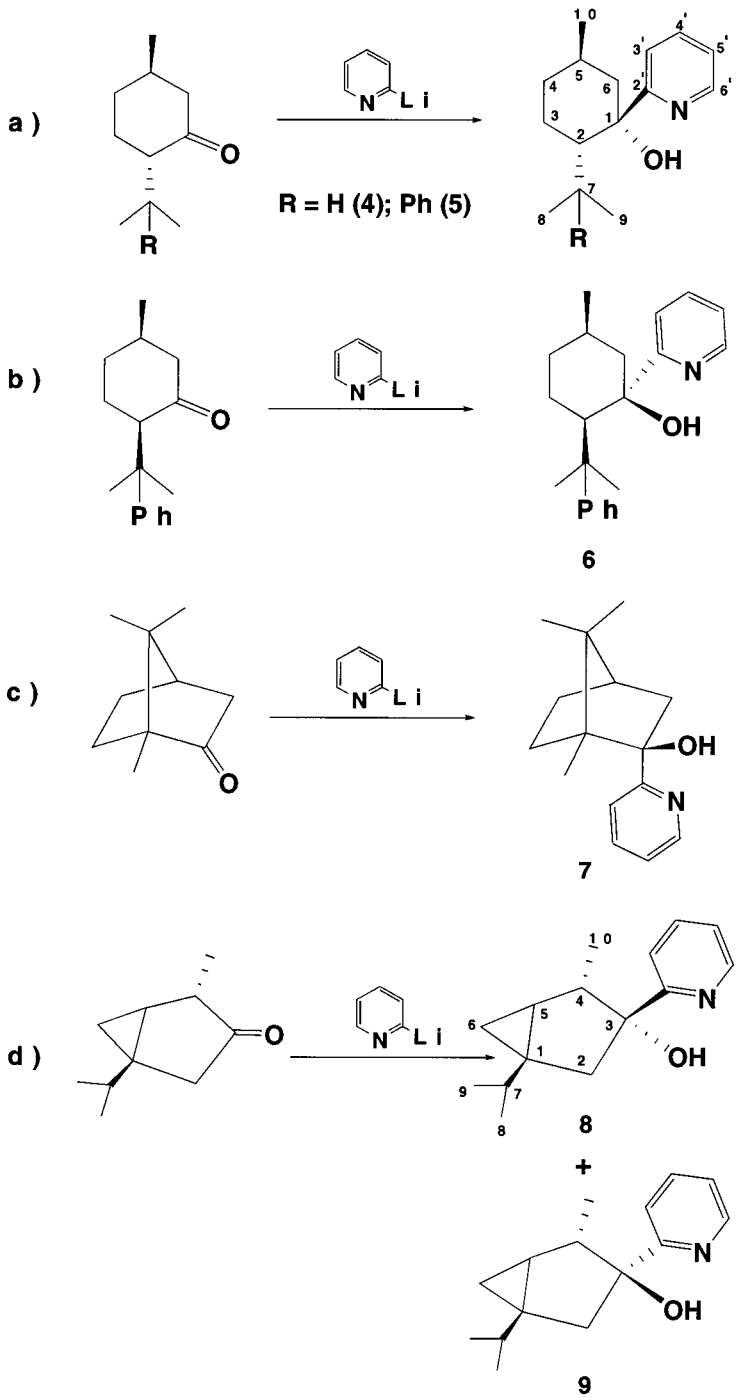
Dioxomolybdenum(VI) 2′-pyridyl alcoholate complexes, $MoO_2L_2^*$ **10a**–**13a**, were prepared by two different methods, both starting from $MoO_2Cl_2(THF)_2$. The first, method (a) Section 4.5, involved the addition of two equivalents of ligand and subsequent reflux to force the reaction to completion. The driving force for this reaction is the formation and liberation of HCl (Scheme 4). The second, method (b) Section 4.5, involved the addition of two equivalents of ligand and two equivalents of TlOEt. The corresponding molybdenum complexes were obtained in high yields.

The complexes **10a**–**13a** do not decompose readily in laboratory atmosphere, and all of them can be handled in air for brief periods of time. This is a remarkable difference to **1a**–**9a**, all of which are air and moisture sensitive and can only be handled and stored under moisture-free inert gas atmosphere. Another noteworthy aspect is the difference in solubility. Complexes **10a**–**13a** are significantly less soluble than either

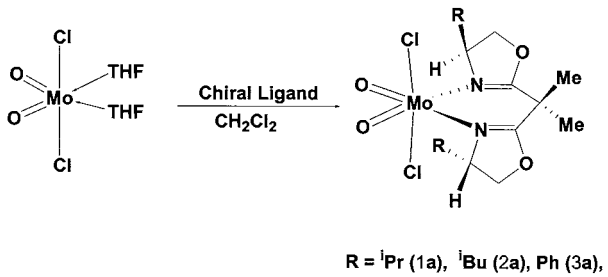
$MoO_2Cl_2L^{**}$, [L** = bis(oxazoline)] **1a**–**3a**, or $MoO_2Cl(Solv)L^*$ (L* = chiral 2′-pyridyl alcoholate). However, all of the complexes are sufficiently soluble in polar organic solvents to obtain solution ($^1H/^{13}C/^{95}Mo$) NMR spectra of good quality (see below). The complexes **1a**–**13a** display their Mo=O stretching vibrations in the expected IR range [8a–d]. The symmetric and asymmetric vibrations are observed at ca. $940 \pm 20\ cm^{-1}$ and ca. $910 \pm 10\ cm^{-1}$, respectively.

2.3. NMR spectroscopy

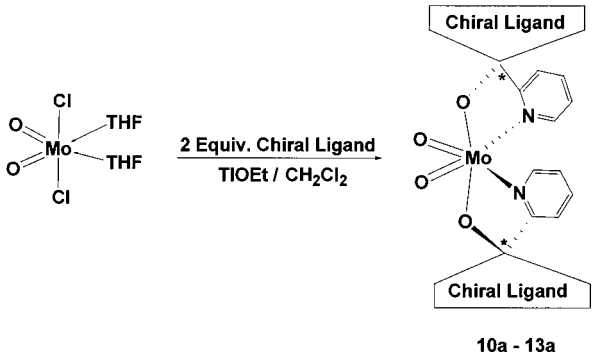
The ^1H-NMR spectra of the molybdenum(VI) bis(oxazoline) complexes **1a**–**3a** do not differ substantially from those of the respective free bis(oxazoline) ligands. In contrast, the molybdenum(VI) 2′-pyridyl alcoholate complexes **4a**–**9a** show broader signals compared with the free ligands, and the sets change their appearance significantly upon heating or cooling the solution. This



Scheme 1.



Scheme 2.



Scheme 4.

is comparable to the Lewis-base adducts of RRe(VII)O_3 complexes, which have also been applied successfully as oxidation catalysts [8c,10]. These complexes usually undergo rapid temperature-dependent ligand-exchange processes [10a,b]. This is of special importance in the case of chiral ligands, since these Re(VII) systems do not show significant enantioselectivity if applied in asymmetric epoxidation processes [10]. The ^{1}H-NMR spectra of complexes **10a**–**13a** with two 2′-pyridyl alcoholate ligands do not show noteworthy thermal changes and are not significantly different from the spectra of the free ligands.

In complexes **4a**–**13a** the ^{13}C-NMR signals for the quaternary alcoholate carbon atom ($C^{2'}$) and also C^1 (Scheme 1) are shifted downfield, which indicates coordination of the ligand to the metal center. However, for the complexes $MoO_2L_2^*$, **10a**–**13a**, the downfield shifts for C^1 are considerably more pronounced than the complexes of the type $MoO_2Cl(THF)L^*$, **4a**–**9a**, e.g. $\delta(^{13}C) = 77.17$ ppm for **4**, 79.38 ppm for **4a** and 92.82 ppm for **10a**. This indicates a more significant shift of electron density towards the molybdenum center in the $MoO_2L_2^*$ family than in the $MoO_2Cl(THF)L^*$ family.

^{95}Mo-NMR spectra for all the complexes were available in good quality. The bis(oxazoline) complexes **1a**–**3a** provide very well defined signals around $\delta(^{95}Mo) \approx 138$ ppm, the 2′-pyridyl alcoholate complexes **4a**–**9a** display their ^{95}Mo signal between ca. 310 and 230 ppm, and the 2′-pyridyl alcoholate complexes **10a**–**13a** give their ^{95}Mo signals around 50 ppm (Table 1). These observed chemical shift values are in good agreement with both the literature values of related

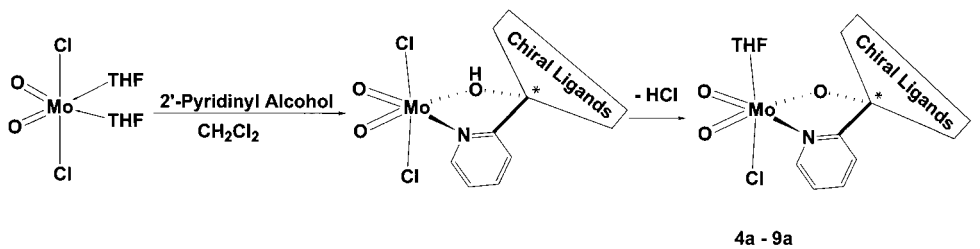
Table 1
^{95}Mo-NMR data of the complexes (CD_2Cl_2, room temperature)

Compound	$\delta(^{95}Mo)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)
1a	139.9	60
2a	138.8	60
3a	137.4	40
4a[a]	308.5	190
4a	289.0	300
5a[a]	287.2	200
5a	277.0	300
6a[a]	283.7	200
6a	278.0	290
7a	230.7	670
8a	239.5	600
9a	233.3	620
10a[a]	51.0	110
10a	41.1	250
11a	53.4	120
12a	48.3	120
13a	49.8	120
$MoO_2Cl_2(DMF)_2$ (**14**)	171.5	120

[a] Recorded in $NCCH_3$.

complexes [8] and that expected based on the donor capabilities of the L and X ligands involved.

Solvent effects were not observed for the $MoO_2Cl_2L^{**}$ complexes **1a**–**3a** [L** = bis(oxazoline)] and the $MoO_2L_2^*$ complexes **10a**–**13a** (L* = 2′-pyridyl alcoholate). However, NMR analysis of the $MoO_2Cl(THF)L^*$ complexes **4a**–**9a** (L* = 2′-pyridyl alcoholate) in two different solvents (CD_2Cl_2 and $NCCD_3$) gave, not unexpectedly, slightly different re-



Scheme 3.

sults (Table 1). This observation indicates that the ligand surrounding of the metal center is influenced by the solvent. In the coordinating solvent $NCCD_3$, the THF in $MoO_2Cl(THF)L^*$ is substituted by $NCCD_3$, giving $MoO_2Cl(NCCD_3)L^*$. The ^{95}Mo-NMR shift of the complexes **4a**–**9a** is similar to that of the acetonitrile-substituted complex [$\delta(^{95}Mo) = 278$ ppm] [8].

^{17}O enrichment of the oxo group in the complex $MoO_2Cl_2(DMF)_2$ (**14**) was carried out by treatment of a solution of the unlabeled complex in CH_2Cl_2 with excess $H_2^{17}O$, in a manner analogous to that previously reported for ^{18}O enrichment of **14** using $H_2^{18}O$ [11]. The labeled complexes $Mo^{17}O_2Cl_2(NCCH_3)_2$ (**15**) and $Mo^{17}O_2Cl_2(THF)_2$ (**16**) were then obtained by recrystallization of $Mo^{17}O_2Cl_2(DMF)_2$ from $NCCH_3$ and THF, respectively. All three complexes displayed their ^{17}O chemical shifts for the Mo=O group at about 1016 ppm, which is at the high-field end of the expected range for transition-metal oxo-complexes in high oxidation states, indicating a comparatively electron-deficient molybdenum(VI) center (Table 2). Reaction of labeled $Mo^{17}O_2Cl_2(THF)_2$ with two equivalents of the chiral 2′-pyridyl alcohols **4**–**6** and **8** (method (a), Section 4.5) gave the ^{17}O-enriched complexes **10a**–**13a**. The ^{17}O-NMR signal for the oxo groups of these complexes appeared as a single sharp line at about 900 ppm, shifted by about 120 ppm upfield compared with the solvent-substituted complexes $MoO_2Cl_2(S)_2$ (Table 2). This shift reflects the higher electron density in the complexes due to the donor capability of the *N*/*O* ligands. The complexes of the type $MoO_2X_2L_2$ [8a] (X = Cl, Br, L = 4-methyl-amino-pent-3-ene-2-one, 4-anilino-pent-3-ene-2-one) show their ^{17}O chemical shifts at slightly lower field (930–970 ppm).

Table 2
^{17}O-NMR chemical shifts for the Mo=O group of ^{17}O-enriched complexes (CD_2Cl_2, room temperature)

Compound	$\delta(^{17}O)$ (ppm)
10a	898
11a	899
12a	890
13a	902
$Mo^{17}O_2Cl_2(DMF)_2$ (**14**)	1017
$Mo^{17}O_2Cl_2(NCCH_3)_2$ (**15**)	1016
$Mo^{17}O_2Cl_2(THF)_2$ (**16**)	1014

Table 3
Results after 4 h reacting in the catalytic epoxidation of *trans*-β-methylstyrene by TBHP at 55°C in the presence of methylenebis(oxazoline) complexes **1a**–**3a** and 2′-pyridyl alcoholate complexes **4a**–**13a**. See text and Section 4 for reaction details

Compound	Conversion (%)	ee (%)
1a	59	–
2a	72	–
3a	86	–
4a	76	2 (*S*,*S*)
10a	47	5 (*S*,*S*)
5a	66	2 (*S*,*S*)
11a	46	1 (*S*,*S*)
6a	75	16 (*R*,*R*)
7a	59	12 (*S*,*S*)
12a	23	3 (*S*,*S*)
8a	69	18 (*S*,*S*)
13a	51	23 (*S*,*S*)
9a	81	11 (*R*,*R*)

2.4. Chiral dioxomolybdenum(VI) complexes in asymmetric epoxidation catalysis

The design of new metal catalysts for enantioselective epoxidation of unfunctionalized *trans*-disubstituted alkenes remains a challenge in the field of asymmetric oxidation [12]. Two of the best reported enantiomeric excesses (ee) for the catalytic oxidation of *trans*-β-methylstyrene are 77 and 59% using chiral Cr-salen [13] and chiral *trans*-dioxoruthenium(VI) porphyrin [12b] catalysts, respectively. These catalysts have a limitation, which is their modest catalytic activity, usually below 120 turnovers/h [14]. Several molybdenum(VI) complexes have proven to be very active catalysts for the epoxidation of olefins with hydroperoxides [8,15]. As far as asymmetric epoxidation is concerned, enantiomeric excesses of up to 53% are known with functionalized olefins as substrate, e.g. allylic alcohols or amides [2b], whereas for unfunctionalized olefins only one catalyst was known until recently, yielding 14% ee [16].

Complexes **1a**–**13a** were evaluated as potential catalysts for the asymmetric epoxidation of *trans*-β-methylstyrene using TBHP as oxidant in toluene as solvent at 55°C. The ratio of substrate:oxidant:catalyst used was 100:200:1. Conversions and enantiomeric excesses are given in Table 3. The methylenebis(oxazoline) complexes **1a**–**3a** catalyzed the oxidation of *trans*-β-methylstyrene with moderate to good activity, complete stereoretention, but low asymmetric induction. A general observation is that catalyst activity increases in the order **1a** (R = isopropyl) < **2a** (R = isobutyl) < **3a** (R = Ph) and, therefore, clearly depends on the nature of the substituent at the C(4) position on the oxazoline ring. For complex **3a** the reaction proceeded smoothly, and conversion of the substrate reached 80% after 4 h. Complete conversion was achieved within 24 h. For all three complexes, (1*R*, 2*R*)-*trans*-β-methylstyrene oxide was formed in very slight excess (4–6% ee) at the beginning of the reaction, but as the reaction proceeded the ee values decreased to almost zero. This may be due in part to deleterious effects from *tert*-butanol, which is inevitably formed in excess during the reaction from TBHP [5]. This results in an increase of the polarity of the solvent (toluene). Since for unfunctionalized olefins only non-covalent interactions between the catalytically

active species and the substrate can contribute to optical induction, it is clear that polar solvent molecules impair these interactions leading to a lower ee Alternatively, *tert*-butanol may act as a competitive achiral monodentate ligand. These effects have already been discussed in the literature.

Better enantioselectivities were obtained for the 2′-pyridyl alcoholate complexes **4a**–**13a**. In all cases, the epoxidation of *trans*-β-methylstyrene proceeded with complete retention of configuration. A survey of the catalytic activity after 4 h reaction reveals good conversions of around 70% for complexes of the type $MoO_2Cl(THF)$ L*, i.e. with one equivalent of chiral ligand (Table 3). Complexes with two equivalents of ligand, $MoO_2L_2^*$, gave considerably lower conversions of substrate (ca. 50%). The ee depends on the type of chiral ligand employed and much less on the number of equivalents. The highest optical inductions were achieved with complexes containing the ligand **8** (Scheme 3). Thus, the (*S*,*S*)-epoxide was obtained in 18% ee for complex **8a** (one equivalent of ligand) and 23% for complex **13a** (two equivalents of ligand). However, when complex **9a** was used there was an inversion of the optical induction compared with **8a** and the (*R*,*R*)-epoxide was obtained in 11% ee. The same effect is evident when comparing complexes **5a** and **6a**. This clearly indicates that the stereochemical outcome of these reactions is primarily determined by the type of ligand enantiomer employed. Comparison of the complexes with ligands derived from menthone (**4a** and **5a**, **10a** and **11a**) reveals that changing the substituent at the C(2) position on the cyclohexan-1-ol ring from isopropyl to 1-methyl-1-phenylethyl did not have a noticeable effect on either the resulting conversions or ee values. Complexes **10a** and **12a** have already been reported by Herrmann et al., who carried out similar catalytic experiments to ours with *trans*-β-methylstyrene as substrate and TBHP as oxidant (chloroform as solvent) [5].

^{17}O-NMR was used to study the reaction of the ^{17}O-labeled complexes **10a** and **13a** with TBHP and cyclohexene (25°C, CD_2Cl_2). Upon addition of TBHP to a solution of **13a** (catalyst:oxidant, 1:200) the ^{17}O-NMR signal for the oxo group shifted from 904 ppm to 894 ppm. In the case of complex **10a** the resonance shifted from 898 to 884 ppm. In both cases, two additional weak broad peaks appeared at 254 ppm and 205 ppm, attributed to the $(CH_3)_3CO$ and OH groups, respectively, of TBHP [17a]. Subsequent addition of cyclohexene (catalyst:oxidant:substrate = 1:200:100) resulted in the appearance of a new sharp line at −7.3 ppm that grew in intensity with time relative to the other peaks in the spectrum. This was attributed to cyclohexene oxide, which increased in concentration with time [17b]. Addition of the olefin did not result in significant changes to the signals in the spectrum arising from the catalysts or the oxidant. The shift to higher fields of the resonances of the Mo=O group point toward coordination of $(CH_3)_3COO$ to the d^0 Lewis acid molybdenum(VI) center. This would be in line with the current assumptions concerning the mechanism of catalytic epoxidations with oxomolybdenum(VI) complexes and TBHP as oxidant. Studies with peroxomolybdenum complexes established that the oxygen transferred to the olefin derives from TBHP and not from the peroxo ligand [15b]. Herrmann et al. suggested that an 'oxenoid' oxygen is generated and that this is subsequently transferred to the olefin. They proposed that since complexes of the type MoO_2L_2 (L = bidentate *N*/*O* ligand, e.g. 2′-pyridyl alcoholate) are coordinatively saturated by an octahedral coordination sphere and the oxo ligands are 'chemically inert', the reaction mechanism must involve a dissociative step with respect to the chelating ligand [5]. The stereodifferentiation should then be produced by the chiral centers through weak π–π interactions between the ligand and the aromatic olefin. However, the experimental evidence for these assumptions is not yet completely convincing.

Considering the spectroscopic results obtained for the catalyst precursors **1a**–**13a**, and the catalytic activity of the three types of catalyst precursor ($MoO_2X_2L_2$ (**1a**–**3a**), $MoO_2X(THF)L$ (**4a**–**9a**), and MoO_2L_2 (**10a**–**13a**)) under examination, we can at least give some explanations for their differences in activity and chiral induction. Complexes of the type $MoO_2X_2L_2$ are of moderate catalytic activity (TOFs ca. 150 h^{-1}), moderate Lewis acidity ($\delta(^{17}O) \approx 950$ ppm, $\delta(^{95}Mo) \approx 140$ ppm) and do not show any chiral induction, probably due to the coordinative lability of the oxazoline ligands. This coordinative lability can be seen by comparing the (temperature-dependent) ^1H-NMR-spectra of the complexes **1a**–**3a** to the spectra of the free ligands **1**–**3**. Compounds of the type $MoO_2X(THF)L$ are more Lewis acidic ($\delta(^{95}Mo) \approx 250$ ppm), less sterically crowded (the ligand sphere contains a weakly coordinated, easy to replace solvent molecule) and display turnover frequencies usually significantly higher than 150 h^{-1}. The ligands are coordinated more strongly to the metal center (one bond is covalent). Therefore, enantiomeric induction can be achieved. However, since alcohols and water can react with the coordinatively unsaturated complexes, their original activity is not maintained for very long and the ee diminishes after some time. The complexes of the type MoO_2L_2 are the least Lewis acidic of the complexes described in this work ($\delta(^{17}O) \approx 900$ ppm, $\delta(^{95}Mo) \approx 50$ ppm) and contain two strongly bound ligands (two covalent interactions). Accordingly, they are not very active (TOFs < 100 h^{-1}). The ee is low because of the significant steric crowding of the chiral ligands. In general, it has to be noted that ligands containing a bulky group in α-posi-

tion to the connecting oxygen atom (**4**–**6**) are significantly less active than molecules with only hydrogen atoms or methyl ligands in this position (**8**).

3. Conclusions

Chiral oxomolybdenum(VI) derivatives of the general formulae $MoO_2Cl_2L^{**}$, $MoO_2Cl(THF)L^*$ and MoO_2L_2 [L** = chiral bis(oxazoline) and L* = chiral 2′-pyridyl alcoholate] have been prepared and characterized. Considerable activity differences have been found in the asymmetric catalytic epoxidation of *trans*-β-methylstyrene with TBHP. Although optical yields, in general, were low, the results with 2′-pyridyl alcoholate ligands are promising in the context of asymmetric epoxidation of unfunctionalized olefins by molybdenum complexes. A clear ligand dependence on enantioselectivity was observed, which suggests that further optimization of the appropriate chiral ligands and/or use of alternative oxidants could lead to more effective epoxidation systems. This, together with the study of the nature of the catalytically active species, is currently under investigation in our laboratories.

The most promising way of achieving significant enantioselectivity in catalytic oxidations with molecules of the type MoO_2X_2L currently appears to be the replacement of the ligand Cl by a chiral organic substituent R*. This substituent R* would be stable to ligand exchange reactions, which always and unavoidably influence the ligands L*, so that the ee in chiral olefin epoxidations should be significantly higher than in the cases examined to date.

4. Experimental

4.1. Materials and methods

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_2O over Na–benzophenone ketyl; CH_2Cl_2 and $NCCH_3$ over CaH_2), distilled under argon and kept over 4 Å molecular sieves (3 Å for $NCCH_3$).

Microanalyses were performed at the ITQB and the Mikroanalytische Labor of the Technical University of Munich (M. Barth). ^{1}H-NMR spectra were recorded at 300 MHz and 400 MHz on Bruker CXP 300 and Bruker Avance DPX-400 spectrometers, respectively. ^{13}C-NMR spectra were measured at 100.28 MHz on a JEOL JNM GX-400 and a Bruker Avance DPX-400, ^{17}O-NMR spectra were measured at 54.14 MHz on a JEOL JNM GX-400, and ^{95}Mo-NMR spectra were measured at 26.07 MHz on a Bruker Avance DPX-400. IR spectra were measured on a Unican Mattson Mod 7000 FTIR spectrometer and a Perkin–Elmer FT-IR spectrometer using KBr pellets. Catalytic runs were monitored by chiral GC methods on a Hewlett-Packard (HP5970 B) instrument equipped with a Chiraldex γ-TA column (Alltech) and integration unit (HP 3394).

The precursor materials MoO_2Cl_2 [18], $MoO_2Cl_2(THF)_2$ and $MoO_2Cl_2(NCCH_3)_2$ [9] were prepared as described previously. (−)-Menthone, (−)-8-phenylmenthol, (+)-camphor and (−)-thujone were purchased from Aldrich and used as received. (+)-8-Phenylisomenthone [19] and (−)-8-phenylmenthone [20] were prepared as published or with minor changes. 2,2-Bis[(4*S*)-4-isopropyl-1,3-oxazolin-2-yl]propane (**1**), 2,2-bis[(4*S*)-4-isobutyl-1,3-oxazolin-2-yl)]propane (**2**) and 2,2-bis[4(*S*)-4-phenyl-1,3-oxazolin-2-yl)]propane (**3**) were prepared according to literature procedures [7a,21].

4.2. Synthesis of the chiral 2′-pyridyl alcohols **4**–**9**

4.2.1. General procedure

A solution of 2-bromopyridine (70.0 mmol) in diethyl ether (6.0 ml) was added to a solution of ^{n}BuLi (44.0 ml, 1.6 M/*n*-hexane, 70.4 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 the appropriate ketone (65.0 mmol) in diethyl ether (20 ml). After stirring for 3 h at room temperature (r.t.), the mixture was filtered (Celite) and the residue washed several times with diethyl ether (150 ml). The combined filtrate and washings were concentrated and washed with 10% NaOH (2 × 60 ml) and brine (100 ml). The combined organic layers were then dried over Na_2SO_4 and the solvent removed to give an oil or a brown residue, which was purified by flash chromatography.

4.2.2. (1*S*,2*S*,5*R*)-5-Methyl-2-isopropyl-1-(2′-pyridyl)-cyclohexan-1-ol (**4**)

Eluent, *n*-hexane:EtOAc; 9:1. Yield: 92%. M.p. 58–60°C. $[\alpha]_D^{20}$ −22.3° (*c* 1, $CHCl_3$). EA, IR (KBr), ^{1}H- and ^{13}C-NMR data were in agreement with Refs. [1b,5].

4.2.3. (1*S*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)-1-(2′-pyridyl)cyclohexan-1-ol (**5**)

Eluent, *n*-hexane:EtOAc; 9:1. Yield: 94% (white solid). Anal. Found: C, 81.52; H, 8.81; N, 4.55. Calc. for $C_{21}H_{27}NO$ (309.45): C, 81.51; H, 8.79; N, 4.53%. M.p. 63–64°C. $[\alpha]_D^{20}$ +49.6° (*c* 1, $CHCl_3$). IR (KBr, *v* cm^{-1}): 3338 vs (OH), 3061 s, 2945 vs, 2930 vs, 1591 vs, 1398 vs, 769 vs, 702 vs, 575 s. ^{1}H-NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 8.40 (d, 1H, H$^{6'}$); 7.38 (br, 1H, H$^{4'}$); 7.08–7.01 (m, 7H, Ph and H$^{3'/5'}$); 5.84 (br, 1H, OH); 2.21–2.17 (m, 1H); 1.94–1.80 (m, 2H); 1.57–1.53

(m, 2H); 1.38–1.34 (m, 1H); 1.28 (s, 3H, CH_3); 0.97–0.82 (m, 2H); 0.77 (d, 3H, CH_3); 0.73 (s, 3H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 165.22 ($C^{2'}$); 152.68 (Ph); 146.53 ($C^{6'}$); 136.27 ($C^{4'}$); 127.98 (Ph); 126.41 (Ph); 125.09 ($C^{3'}$); 121.70 ($C^{5'}$); 76.26 (C^1); 53.52; 53.25; 42.17; 36.01; 28.51; 27.24; 25.30; 22.28 (see Scheme 1 for numbering).

4.2.4. (1R,2R,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)-1-(2′-pyridyl)cyclohexan-1-ol (6)

Eluent, *n*-hexane:EtOAc; 9:1. Yield: 92% (white solid). Anal. Found: C, 81.52; H, 8.81; N, 4.55. Calc. for $C_{21}H_{27}NO$ (309.45): C, 81.51; H, 8.79; N, 4.53%. M.p. 91–92°C. $[\alpha]_D^{20}$ −78.1° (*c* 1, $CHCl_3$). IR (KBr, *v* cm^{-1}): 3333 vs (OH), 3060 s, 2943 vs, 2930 vs, 1593 vs, 1398 vs, 769 vs, 771 vs, 704 vs. ^{1}H-NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 8.42 (d, 1H, $H^{6'}$); 7.47 (br, 1H, $H^{4'}$); 7.26–7.03 (m, 7H, Ph and $H^{3'/5'}$); 5.40 (s, 1H, OH); 2.31–2.27 (m, 1H); 2.07–1.85 (m, 3H); 1.59–1.37 (m, 4H); 1.20 (s, 3H, CH_3); 0.90 (d, 3H, CH_3); 0.73 (s, 3H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 166.85 ($C^{2'}$); 152.61 (Ph); 146.64 ($C^{6'}$); 136.36 ($C^{4'}$); 127.97 (Ph); 126.41 (Ph); 125.19 ($C^{3'}$); 121.60 ($C^{5'}$); 77.97 (C^1); 53.52; 50.09; 42.58; 32.99; 29.13; 28.41; 26.29; 20.30 (see Scheme 1 for numbering).

4.2.5. (1R,2R,4R)-1,7,7-Trimethyl-2-(2′-pyridyl)-bicyclo[2.2.1]heptan-2-ol (7)

Eluent, *n*-hexane:EtOAc; 9:1. Yield: 83%. M.p. 56–57°C. $[\alpha]_D^{20}$ −32.1° (*c* 1, $CHCl_3$). EA, IR (KBr), ^{1}H- and ^{13}C-NMR data were in agreement with Refs. [1b,3,5].

4.2.6. (1S,3R,4S,5R)-1-Isopropyl-4-methyl-3-(2-pyridyl)bicyclo[3.1.0]hexane-3-ol (8)

Eluent, *n*-hexane:EtOAc; 9:1. Yield: 70.0%. Anal. Found: C, 77.68; H, 9.02; N, 5.98. Calc. for $C_{15}H_{21}NO$ (231.34): C, 77.88; H, 9.15; N, 6.05%. $[\alpha]_D^{20}$ +49.5° (*c* 1, $CHCl_3$). IR (KBr, *v* cm^{-1}): 3403 vs (OH), 3049 s, 2959 vs, 2930 vs, 1593 vs, 1470 vs, 1433 vs, 1384 vs, 779 vs, 750 vs. ^{1}H-NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 8.48 (d, 1H, $H^{6'}$); 7.64 (br, 1H, $H^{4'}$); 7.36 (d, 1H, $H^{3'}$); 7.14 (t, 1H, $H^{5'}$); 4.53 (s, 1H, OH); 2.18–2.01 (comp, 3H); 1.55–1.43 (m, 2H); 1.04 (d, 3H, CH_3); 0.91 (d, 3H, CH_3); 0.84 (d, 3H, CH_3); 0.51 (br, 2H). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 162.86 ($C^{2'}$); 144.58 ($C^{6'}$); 136.75 ($C^{4'}$); 121.88 ($C^{3'}$); 119.62 ($C^{5'}$); 85.84 ($C^{1'}$); 52.11; 48.57; 36.69; 33.59; 30.83; 26.73; 20.56; 19.87; 13.00.

4.2.7. (1S,3S,4S,5R)-1-Isopropyl-4-methyl-3-(2-pyridyl)bicyclo[3.1.0]hexane-3-ol (9)

Eluent, *n*-hexane:EtOAc; 9:1. Yield: 25.0%. Anal. Found: C, 77.68; H, 9.02; N, 5.98. Calc. for $C_{15}H_{21}NO$ (231.34): C, 77.88; H, 9.15; N, 6.05%. $[\alpha]_D^{20}$ +6.3° (*c* 1, $CHCl_3$). IR (KBr, *v* cm^{-1}): 3398 vs (OH), 3005 s, 2957 vs, 2928 vs, 1593 vs, 1464 vs, 1433 vs, 1402 vs, 1066 vs, 781 vs, 752 vs. ^{1}H-NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 8.44 (d, 1H, $H^{6'}$); 7.73 (br, 1H, $H^{4'}$); 7.39 (d, 1H, $H^{3'}$); 7.15 (t, 1H, $H^{5'}$); 5.44 (s, 1H, OH); 2.55–2.51 (br, 1H); 2.36 (d, 1H); 2.00 (d, 1H); 1.50–1.43 (m, 1H); 1.22 (br, 1H); 1.03 (d, 3H, CH_3); 0.90 (d, 3H, CH_3); 0.79 (d, 3H, CH_3); 0.43 (s, 1H); 0.30 (br, 1H). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 165.08 ($C^{2'}$); 146.53 ($C^{6'}$); 137.22 ($C^{4'}$); 121.81 ($C^{3'}$); 129.98 ($C^{5'}$); 81.16 ($C^{1'}$); 49.65; 46.56; 33.26; 32.67; 29.32; 19.91; 12.86; 11.20.

4.3. Preparation of complexes of the type $MoO_2Cl_2L^{**}$ [L** = 2,2-bis[2-(4(S)-isopropyl-1,3-oxazolinyl)]propane (1), 2,2-bis[2-(4(S)-isobutyl-1,3-oxazolinyl)]propane (2) and 2,2-bis[2-(4(S)-phenyl-1,3-oxazolinyl)]propane (3)]

4.3.1. General procedure

A solution of $MoO_2Cl_2(THF)_2$ (0.77 g, 2.24 mmol) in CH_2Cl_2 (15 ml) was treated with bis(oxazoline) L** [L** = **1**, **2**, and **3**, 2.24 mmol]. The color of the solution changed to yellow. After 60 min, the solution was filtered, evaporated to dryness and washed with diethyl ether–*n*-hexane.

4.3.2. MoO_2Cl_2(2,2-bis[2-(4(S)-isopropyl-1,3-oxazolinyl)]propane) (1a)

Yield: 93%. Anal. Found: C, 38.87; H, 5.50; N, 5.97. Calc. for $C_{15}H_{26}Cl_2MoN_2O_4$ (465.22): C, 38.73; H, 5.63; N, 6.02%. Selected IR data (KBr, *v* cm^{-1}): 2958 s, 2871 m, 952 m, 912 vs (Mo=O), 910 vs (Mo=O). ^{1}H-NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 5.19 (d, 2H); 4.73 (d, 2H); 4.64 (br, 1H); 4.13 (s, 2H); 2.95 (br, 1H); 1.95 (s, 6H, CH_3); 1.19 (d, 6H, CH_3); 1.08 (d, 6H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 171.6; 73.40; 69.64; 31.96; 29.43; 24.89; 19.54; 14.00.

4.3.3. MoO_2Cl_2(2,2-bis[2-(4(S)-isobutyl-1,3-oxazolinyl)]propane) (2a)

Yield: 91%. Anal. Found: C, 41.20; H, 5.97; N, 5.57. Calc. for $C_{17}H_{30}Cl_2MoN_2O_4$ (492.27): C, 41.39; H, 6.13; N, 5.68%. Selected IR data (KBr, *v* cm^{-1}): 2958 s, 2871 m, 952 m, 912 vs (Mo=O), 910 vs (Mo=O). ^{1}H-NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 5.57 (dd, 2H); 4.75 (dd, 2H); 4.58 (t, 2H); 2.57 (m, 2H); 1.93–1.39 (m, 10H, CH_3); 1.19 (d, 6H, CH_3); 1.08 (s, 6H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 171.1; 73.90; 69.23; 25.92; 25.93; 19.24; 14.26.

4.3.4. MoO_2Cl_2(2,2-bis[2-(4(S)-phenyl-1,3-oxazolinyl)]propane) (3a)

Yield: 97%. Anal. Found: C, 47.52; H, 4.28; N, 4.99. Calc. for $C_{21}H_{22}Cl_2MoN_2O_4$ (533.25): C, 47.30; H, 4.16; N, 5.25%. Selected IR data (KBr, *v* cm^{-1}): 3032 m, 2987 m, 2910 m, 1474 s, 1456 s, 1383 s, 1230 vs, 1123 vs, 943 m (Mo=O), 917 vs (Mo=O), 766 s, 698 s, 541 m.

^{1}H-NMR (CD_2Cl_2, 400 MHz, r.t., δ ppm): 7.37–7.27 (m, 10H, Ph); 5.94 (dd, 2H); 4.84 (t, 2H); 4.12 (dd, 2H); 1.87 (s, 6H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 172.7; 139.9; 128.90; 127.81; 76.61; 71.99; 40.86; 25.96.

4.4. Preparation of complexes of the type $MoO_2Cl(S)L^*$ (L^* = chiral 2′-pyridyl alcoholate)

4.4.1. General procedure

A solution of $MoO_2Cl_2(THF)_2$ (0.68 g, 2.00 mmol) in CH_2Cl_2 (10 ml) was treated with one equivalent of ligand. The resulting turbid solution was stirred for a further 30 min. The solvent was evaporated, and the product washed with *n*-hexane and dried under vacuum.

4.4.2. $MoO_2Cl(THF)$\{(1S,2S,5R)-5-methyl-2-isopropyl-1-(2′-pyridyl)cyclohexan-1-olato\} (**4a**)

Yield: 92%. Anal. Found: C, 48.47; H, 6.48; N, 3.07. Calc. for $C_{19}H_{30}ClMoNO_4$ (467.85): C, 48.78; H, 6.46; N, 2.99%. IR (KBr, ν cm^{-1}): 3099 m, 2953 s, 2872 m, 1605 s, 1516 m, 1454 s, 1386 m, 1298 m, 1058 m, 941 vs (Mo=O), 918 vs (Mo=O), 870 m, 775 s, 756 m, 687 m, 648 m. ^{1}H-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 8.49 (br, 1H, H$^{6'}$); 8.05 (t, 1H, H$^{4'}$); 7.52–7.45 (m, 2H, H$^{5'/3'}$); 3.90 (s, THF); 2.12–1.81 (m, 4H + THF); 1.74–1.69 (m, 2H); 1.49 (d, 1H); 1.35–1.26 (m, 1H); 1.12–1.04 (m, 1H); 1.00 (d, 3H, CH_3); 0.93 (d, 3H, CH_3); 0.77 (d, 3H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 163.13 (C$^{2'}$); 148.92 (C$^{6'}$); 142.20 (C$^{4'}$); 125.21 (C$^{3'}$); 122.24 (C$^{5'}$); 79.38 (C^1); 69.64 (THF); 51.32 (C^6); 50.65 (C^2); 34.99 (C^4); 28.85 (C^5); 28.37 (C^{10}); 25.91 (THF); 23.90 (C^5); 22.49 (C^8); 21.90 (C^3); 18.63 (C^9).

4.4.3. $MoO_2Cl(THF)$\{(1S,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)-1-(2′-pyridyl)cyclohexan-1-olato\} (**5a**)

Yield: 88%. Anal. Found: C, 54.86; H, 5.98; N, 2.50. Calc. for $C_{25}H_{34}ClMoNO_4$ (543.95): C, 55.20; H, 6.30; N, 2.58%. IR (KBr, ν cm^{-1}): 3048 m, 2983 s, 1605 s, 1518 m, 1454 s, 1382 m, 1298 m, 1049 m, 941 vs (Mo=O), 918 vs (Mo=O), 889 m, 796 s, 702 s, 572 m, 553 m. ^{1}H-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 8.18 (d, 1H, H$^{6'}$); 7.71 (t, 1H, H$^{4'}$); 7.37 (t, 1H, H$^{5'}$); 7.13–6.91 (m, 5H, Ph); 6.72 (d, 1H, H$^{3'}$); 3.90 (s, THF); 2.46–2.15 (m, 2H); 1.99–1.93 (m, 2H); 1.90 (s, THF); 1.76–1.69 (m, 2H); 1.45–1.39 (m, 2H); 1.35 (d, 3H, CH_3); 1.25 (s, 3H, CH_3); 0.91 (d, 3H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 168.40; 151.49; 147.70; 139.81; 128.49; 126.25; 125.45; 124.06; 78.34 (C^1); 69.92 (THF); 56.26; 51.29; 41.53; 35.55; 31.14; 29.29; 25.92 (THF); 23.83; 21.90.

4.4.4. $MoO_2Cl(THF)$\{(1R,2R,5R)-5-methyl-2-(1-methyl-1-phenylethyl)-1-(2′-pyridyl)cyclohexan-1-olato\} (**6a**)

Yield: 91%. Anal. Found: C, 54.93; H, 6.00; N, 2.40. Calc. for $C_{25}H_{34}ClMoNO_4$ (543.95): C, 55.20; H, 6.30; N, 2.58%. IR (KBr, ν cm^{-1}): 3057 m, 2970 s, 2933, 2878, 1604 s, 1475 m, 1454 s, 1388 m, 1298 m, 1031 m, 941 vs, 920 vs (Mo=O), 875 m, 785 s, 702 s. ^{1}H-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 8.22 (d, 1H, H$^{6'}$); 7.45 (t, 1H, H$^{4'}$); 7.15–6.84 (m, 7H, H$^{5'/3'}$ + Ph); 4.09 (s, THF); 2.46–2.44 (m, 2H); 2.12–1.99 (m, 2H); 1.95 (s, THF); 1.77–1.68 (m, 2H); 1.45–1.39 (m, 2H); 1.42 (s, 3H, CH_3); 1.29 (s, 3H, CH_3); 1.18 (d, 3H, CH_3). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 168.67; 150.98; 147.56; 139.90; 128.29; 126.21; 125.49; 123.90; 79.10 (C^1); 70.90 (THF); 50.34; 41.68; 32.29; 31.61; 30.32; 27.96; 25.55 (THF); 19.23.

4.4.5. $MoO_2Cl(THF)$\{(1R,2R,4R)-1,7,7-trimethyl-2-(2′-pyridyl)bicyclo[2.2.1]heptan-2-olato\} (**7a**)

Yield: 93%. Anal. Found: C, 48.65; H, 5.76; N, 2.80. Calc. for $C_{19}H_{28}ClMoNO_4$ (465.83): C, 48.99; H, 6.06; N, 3.01%. IR (KBr, ν cm^{-1}): 2961 s, 2876, 1603 s, 1523 s 1456 s, 1392 m, 1298 m, 1072 m, 959 vs, 918 vs (Mo=O), 866 m, 771 s, 682 m, 570 m. ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 164.56; 147.69; 139.63; 124.78; 123.54; 81.78 (C^1); 69.61 (THF); 55.93; 50.00; 47.27; 44.39; 29.08; 26.15 (THF); 24.34; 20.00; 10.17.

4.4.6. $MoO_2Cl(THF)$\{(1S,3R,4S,5R)-1-isopropyl-4-methyl-3-(2-pyridyl)bicyclo[3.1.0]hexane-3-olato\} (**8a**)

Yield: 96.0%. Anal. Found: C, 48.58; H, 5.83; N, 2.90. Calc. for $C_{19}H_{28}ClMoNO_4$ (465.83): C, 48.99; H, 6.06; N, 3.01%. IR (KBr, ν cm^{-1}): 2959 s, 2930 m, 2874, 1608 s, 1521 m 1456 s, 1385 m, 1298 m, 1087 m, 941 vs (Mo=O), 916 vs (Mo=O), 771 s, 579 m. ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 157.63 (C$^{2'}$); 145.57 (C$^{6'}$); 140.32 (C$^{4'}$); 123.72 (C$^{3'}$); 120.55 (C$^{5'}$); 87.65(C^1); 68.22 (THF); 52.88; 48.06; 36.45; 31.99; 29.14; 24.35 (THF); 19.17; 18.35; 11.80.

4.4.7. $MoO_2Cl(THF)$\{(1S,3S,4S,5R)-1-isopropyl-4-methyl-3-(2-pyridyl)bicyclo[3.1.0]hexane-3-olato\} (**9a**)

Yield: 91.0%. Anal. Found: C, 48.58; H, 5.83; N, 2.90. Calc. for $C_{19}H_{28}ClMoNO_4$ (465.83): C, 48.99; H, 6.06; N, 3.01%. IR (KBr, ν cm^{-1}): 2957 s, 2926 m, 2872, 1606 s, 1456 s, 1398 m, 1298 m, 1067 m, 937 vs (Mo=O), 920 vs (Mo=O), 839 m, 773 s, 651m. ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 158.03 (C2′); 147.07 (C$^{6'}$); 140.93 (C$^{4'}$); 124.74 (C$^{3'}$); 121.33 (C$^{5'}$); 86.85 (C^1); 68.62 (THF); 51.98; 49.44; 40.62; 31.40; 30.08; 27.40 (THF); 23.14; 18.61; 11.33.

4.5. Preparation of complexes of the type $MoO_2L^*_2$ (L^* = chiral 2′-pyridyl alcoholate)

Method (a). A solution of $MoO_2Cl_2(THF)_2$ (0.38 g, 1.11 mmol) in CH_2Cl_2 (10 ml) was treated with two equivalents of ligand. The solution became milky and a precipitate formed. After 6 h in reflux, the suspension was evaporated to dryness to yield a powder, which was washed with diethyl ether–*n*-hexane.

Method (b). A solution of $MoO_2Cl_2(THF)_2$ (0.38 g, 1.00 mmol) in CH_2Cl_2 (10 ml) was treated with two equivalents of ligand and two equivalents of TlEOt. The turbid reaction mixture was left stirring for 2 h and then the suspension was evaporated to dryness. After washing with *n*-hexane, the residue was extracted with dichloromethane and the solution taken to dryness to yield a powder, which was washed with diethyl ether–*n*-hexane several times.

4.5.1. $MoO_2\{(1S,2S,5R)$-5-methyl-2-isopropyl-1-(2′-pyridyl)cyclohexan-1-olato$\}_2$ (**10a**)

EA, IR (KBr), ^{1}H- and ^{13}C-NMR data were in agreement with Refs. [1b,5].

4.5.2. $MoO_2\{(1S,2S,5R)$-5-methyl-2-(1-methyl-1-phenylethyl)-1-(2′-pyridyl)cyclohexan-1-ol$\}_2$ (**11a**)

Yield: 86.0%. Anal. Found: C, 67.82; H, 6.94; N, 3.78. Calc. for $C_{42}H_{52}MoN_2O_4$ (744.83): C, 67.73; H, 7.04; N, 3.76%. IR (KBr, ν cm^{-1}): 3055 m, 2945 s, 2920, 2868, 1599, 1474 s, 1435 s, 1390 m, 1368, 1068 m, 916 s (Mo=O), 895 vs (Mo=O), 769 vs, 701 vs, 643 m, 580 m, 559m, 482s. ^{1}H NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 8.76 (br, 1H, H$^{6'}$); 7.70 (br, 1H, H$^{4'}$); 7.41–6.99 (m, 7H, Ph and H$^{3'/5'}$); 2.38–2.29 (m, 1H); 1.89–1.78 (m, 2H); 1.52–1.33 (m, 2H); 1.31–1.29 (m, 1H); 1.25 (s, 3H, CH_3); 1.12–0.99 (m, 1H); 0.85 (d, 6H, CH_3); 0.70 (s, 6H, CH_3).

4.5.3. $MoO_2\{(1R,2R,4R)$-1,7,7-trimethyl-2-(2′-pyridyl)-bicyclo[2.2.1]heptan-2-olato$\}_2$ (**12a**)

EA, IR (KBr), ^{1}H- and ^{13}C-NMR data were in agreement with Refs. [1b,5].

4.5.4. $MoO_2\{(1S,3R,4S,5R)$-1-isopropyl-4-methyl-3-(2-pyridyl)bicyclo[3.1.0]hexane-3-olato$\}_2$ (**13a**)

Yield: 81.0%. Anal. Found: C, 61.56; H, 6.95; N, 4.68. Calc. for $C_{40}H_{30}MoN_2O_4$ (588.50): C, 61.22; H, 6.85; N, 4.76%. IR (KBr, ν cm^{-1}): 3046 m, 2948 s, 2871, 1602, 1473 s, 1437 s, 1365 m, 1292, 1159 m, 1088 m, 1053 m, 1020 m, 923 vs (Mo=O), 906 vs (Mo=O), 781 s, 764 s, 696 m, 642 m, 570m, 534 m. ^{1}H-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 8.60 (d, 2H, H$^{6'}$); 7.73 (t, 2H, H$^{4'}$); 7.36 (d, 2H, H$^{3'}$); 7.15 (t, 2H, H$^{5'}$); 3.04–3.00 (m, 4H); 2.43 (br, 4H); 2.28–1.98 (m, 4H); 1.46–1.18 (m, 6H); 1.12 (d, 6H, CH_3); 0.85 (d, 6H, CH_3); 0.84 (d, 6H, CH_3); 0.57 (s, 2H). ^{13}C-NMR (CD_2Cl_2, 300 MHz, r.t., δ ppm): 165.36; 147.45 (d, C$^{6'}$); 139.29; 122.29; 119.72; 103.5 (C^1); 50.91; 44.48; 37.54; 33.93; 30.92; 28.67; 21.12; 20.16; 15.38.

4.6. O-labeling studies

The labeled complex $Mo^{17}O_2Cl_2(DMF)_2$ (**14**) was prepared according to the published procedure using $H_2^{17}O$ [12]. IR (KBr, ν cm^{-1}): 941 s, 928 vs, 904 vs, 891 s, 870 vs, 860 s (Mo=O). Labeled complexes $Mo^{17}O_2Cl_2(NCCH_3)_2$ (**15**) and $Mo^{17}O_2Cl_2(THF)_2$ (**16**) were prepared by recrystallization of **14** from $NCCH_3$ and THF, respectively.

Labeled complexes $Mo^{17}O_2L^*_2$ were prepared using method (a) (Section 4.5) with starting material $Mo^{17}O_2Cl_2(THF)_2$ (**16**).

$Mo^{17}O_2\{(1S,2S,5R)$-5-methyl-2-isopropyl-1-(2′-pyridyl)cyclohexan-1-olato$\}_2$ (**10a**). IR (KBr, ν cm^{-1}): 957 s, 948 vs, 916 vs, 895 vs, 864 s (Mo=O).

$Mo^{17}O_2\{(1S,2S,5R)$-5-methyl-2-(1-methyl-1-phenylethyl)-1-(2′-pyridyl)cyclohexan-1-olato$\}_2$ (**11a**). IR (KBr, ν cm^{-1}): 957 s, 946 m, 917 vs, 895 vs, 862 s (Mo=O).

$Mo^{17}O_2\{(1R,2R,4R)$-1,7,7-trimethyl-2-(2′-pyridyl)-bicyclo[2.2.1]heptan-2-olato$\}_2$ (**12a**). IR (KBr, ν cm^{-1}): 970 s, 946 m, 912 vs, 896 m (Mo=O).

$Mo^{17}O_2\{(1S,3R,4S,5R)$-1-isopropyl-4-methyl-3-(3′-pyridyl)bicyclo[3.1.0]hexane-3-olato$\}_2$ (**13a**). IR (KBr, ν cm^{-1}): 976 s, 952 m, 923 vs, 906 vs, 854 m (Mo=O).

4.7. Catalytic epoxidation reactions with compounds **1a**–**13a**

200 mg of *trans*-β-methylstyrene (1.7 mmol), 100 mg of mesitylene (internal standard) and 1.0 mol% of **1a**–**13a** as catalyst (17 μmol) were dissolved in 2 ml of dry toluene. After addition of 615 μl of TBHP solution (5.5 M) the reaction mixture was stirred for up to 16 h at 55°C.

The course of the reaction was monitored by quantitative GC-analysis. Samples were taken every 30 min, diluted with dichloromethane, and chilled in an ice bath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and magnesium sulfate was added. The ee and conversion was determined on a chiral GC column. The conversion was calculated from a calibration curve ($r^2 = 0.999$) recorded prior to use. The products were identified by GC–MS and co-injection of reference substances.

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