First Dioxomolybdenum(VI) Complexes Containing Chiral Oxazoline Ligands: Synthesis, Characterization and Catalytic Activity

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The *cis*-$[MoO_2(N,O)_2]$ complexes containing chiral oxazoline ligands (*N,O*) [**1**: *N,O* = **A**, (4′*R*)-2-(4′-ethyl-3′,4′-dihydroxazol-2′-yl)phenolato; **2**: *N,O* = **B**, (4′*S*)-2-(4′-isopropyl-3′,4′-dihydroxazol-2′-yl)phenolato] were synthesised and characterised, both in solution and in the solid state. These pseudo-octahedral neutral complexes were obtained as mixtures of diastereomers due to the chirality of the ligand and at the metal centre (Δ or Λ). Theoretical DFT calculations corroborate the isomer distribution. For complex **1**, the two major diastereomers, **Δ-*N-cis*-1** and **Λ-*N-trans*-1**, crystallised independently and the molecular structures were determined by single-crystal X-ray diffraction. NMR experiments at 800 MHz for **2** allowed the determination of the isomeric composition in solution. The product distribution depends on the coordinating nature of the solvent. Complexes **1** and **2** catalyse the oxidation of triphenylphosphane and styrene.

Introduction

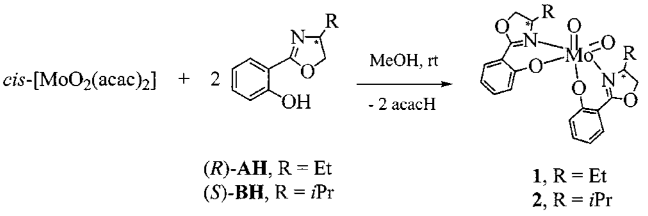
Transition metal oxo compounds are involved in oxygen transfer chemistry in both biological[1] and industrial processes.[2] Molybdenum complexes have been extensively studied, especially as models for heterogeneous oxidation catalysts and as the active site of oxo-transfer, molybdenum-containing enzymes.[3] Until recently, most oxo compounds used as oxidation catalysts contained sterically demanding sulfur ligands, since they were believed to be suitable models.[4] Indeed, the nature of the ligands around the molybdenum centre is critical for the success of the catalytic reaction.[5]

To understand oxo-transfer properties, numerous dioxomolybdenum complexes involving a wide range of ligands have been prepared and characterized.[6] Bidentate *S,S*-, *N,N*-, *O,O*- or *N,O*-donor ligands are common in monometallic complexes with the $[MoO_2]^{2+}$ core.[7] Among them, *N*-donor ligands[8] are of interest because they are robust in oxygen transfer reactions. In particular, chiral oxazoline ligands are especially useful in many organic transformations.[9] However, to the best of our knowledge, this kind of ligand has not been studied with molybdenum systems.

Therefore, we decided to synthesise neutral, monometallic complexes containing anionic ligands with oxazoline moieties. Here we describe the synthesis and characterization, both in solution and in the solid state, of new chiral oxomolybdenum complexes containing phenolatooxazoline ligands of the general formula *cis*-$[MoO_2(N,O)_2]$ (where *N,O* = **A** or **B**). Moreover, we report on the ability of these complexes to act as oxo transfer reagents in oxidation processes.

Results and Discussion

A one-pot reaction of $[MoO_2(acac)_2]$ and the optically pure oxazoline ligands [(*R*)-**AH**, (*S*)-**BH**) in methanol afforded the neutral dioxomolybdenum (VI) complexes **1** and **2**, respectively (Scheme 1), in a similar manner to that reported for Mo[10] and other metals (Ni, Pd, Mn).[11] All the compounds were obtained in high yields and are stable both in the solid state and in solution, although after several days in chloroform some oxazoline decoordination was detected by ^1H NMR spectroscopy.



Scheme 1

A relevant feature of these hexacoordinate complexes is the relative position of the bidentate anionic *N,O* oxazoline ligands, which leads to the formation of several geometrical isomers. According to the relative position of the iminic nitrogen atoms and the oxo groups, three arrangements are expected: a) the two oxazoline nitrogen atoms *cis* to both oxo groups (*N-cis*); b) each nitrogen atom *trans* to one oxo group (*N-trans*) and c) one nitrogen atom *cis* to the oxo groups and one *trans* to one oxo group (*N-cis,trans*) (Scheme 2). Owing to the asymmetrical environment

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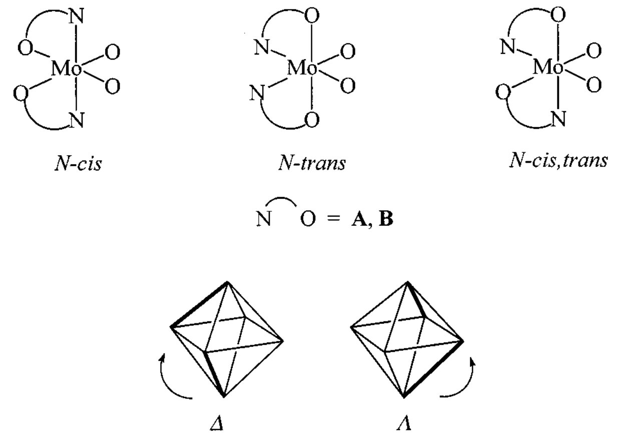
around the metal atom, each of these possibilities has a pair of isomers, Δ and Λ. Therefore, for each complex, six diastereomers are possible.



Scheme 2

Solid State Structures

The IR spectra for these Mo complexes exhibit two very strong absorption bands at ca. 920 and 890 cm^{-1}, which were assigned to the *cis*-[MoO_2] fragment. In addition, a strong signal at ca. 1620 cm^{-1} corresponds to the stretching of the C=N imine bond.

For complex **1**, monocrystals corresponding to two isomers were isolated from a dichloromethane/diethyl ether solution upon recrystallization. The crystal structures of complexes **Δ-*N-cis*-1** and **Λ-*N-trans*-1** determined by single-crystal X-ray diffraction analysis are shown in Figure 1 and 2, respectively.

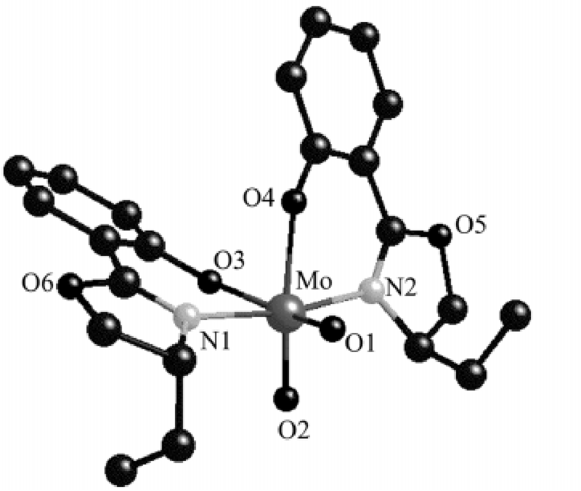


Figure 1. View of the molecular structure of complex **Δ-*N-cis*-1**; hydrogen atoms have been omitted for clarity

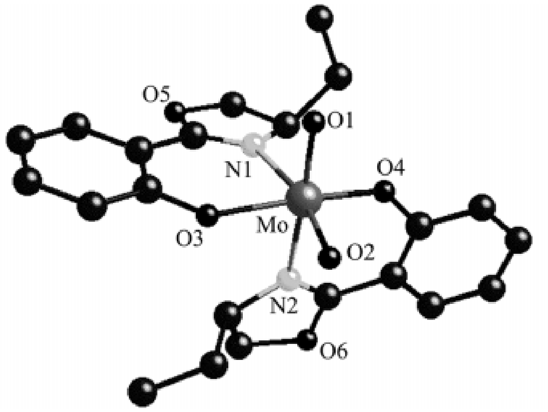


Figure 2. View of the molecular structure of complex **Λ-*N-trans*-1**; hydrogen atoms have been omitted for clarity

In both structures, the molecules show a distorted octahedral geometry around the molybdenum atom (Table 1). An expansion of the dioxo fragment O(1)−Mo−O(2) from 90° to 100.7° and 105.4° was observed for **Δ-*N-cis*-1** and **Λ-*N-trans*-1**, respectively, as reported for similar complexes.[10b,12] Furthermore, the N(1)−Mo−N(2) angle showed a contraction from 180° to 168.8° for **Δ-*N-cis*-1**, and from 90° to 75.4° for **Λ-*N-trans*-1**. A similar trend was observed for the O(3)−Mo−O(4) angle, from 90° to 80.5° and from 180° to 158.8° for **Δ-*N-cis*-1** and **Λ-*N-trans*-1**, respectively. The bite angles O(3)−Mo−N(1) and O(4)−Mo−N(2) were ca. 79° in both cases, an observation which is consistent with other dioxomolybdenum six-membered *N,O*-coordinated complexes.[10a,13]

Table 1. Selected bond lengths (Å) and bond angles (°) for **Δ-*N-cis*-1** and **Λ-*N-trans*-1** (with esd's in parentheses)

	Δ-*N-cis*-1	**Λ-*N-trans*-1**
Mo−O(1)	1.700(2)	1.6991(14)
Mo−O(2)	1.708(2)	1.704(2)
Mo−O(3)	2.056(2)	1.964(2)
Mo−O(4)	2.045(2)	1.9541(14)
Mo−N(1)	2.149(3)	2.334(2)
Mo−N(2)	2.151(3)	2.312(2)
O(1)−Mo−O(2)	100.73(13)	105.37(8)
O(3)−Mo−N(1)	79.18(9)	78.91(6)
O(4)−Mo−N(2)	79.39(9)	78.15(6)
O(3)−Mo−O(4)	80.49(9)	158.81(7)
N(1)−Mo−N(2)	168.80(10)	75.37(6)

The Mo−O bond lengths for the dioxo group were ca. 1.7 Å in both structures, as reported previously.[14] The distances Mo−N for **Λ-*N-trans*-1** [Mo−N(1) = 2.31 Å and Mo−N(2) = 2.33 Å] were longer than for **Δ-*N-cis*-1** (Mo−N ≈ 2.15 Å) due to the oxo *trans* influence. However, the molybdenum phenolic oxygen lengths either in **Δ-*N-cis*-1** or **Λ-*N-trans*-1** showed a negligible influence of the geometrical arrangement.

To date, no *N-cis* dioxo bis(bidentate-*N,O*) molybdenum complexes have been described in the solid state in the literature. As this arrangement is only observed for complexes containing polydentate ligands, and is constrained by coordination requirements,[15] we carried out theoretical studies. DFT calculations for complex **1** showed that **Δ-*N-cis*-1** was the most stable conformer and that **Λ-*N-trans*-1** and **Λ-*N*-**

***cis,trans*-1** were higher in energy by 2.6 and 10.9 kcal·mol^{-1}, respectively. Removal of the substituent at the stereocentre showed the same energy trend, but values were similar for Λ-*N-trans* and Λ-*N-cis,trans* (1.85 and 2.32 kcal·mol^{-1}, respectively). Therefore, the relative stability of Δ-*N-cis* and Λ-*N-trans* was independent of the substituent, while Λ-*N-cis,trans* was not.

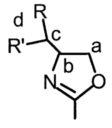
NMR Spectroscopic Studies

NMR spectroscopy allowed us to detect the presence of several species for these molybdenum complexes in solution. To assign accurately the signals, the monocrystals obtained for complex **1**, ***N-cis*-1** and ***N-trans*-1**, were independently dissolved in deuterated chloroform at 233 K. Under these conditions, the spectra showed mainly the presence of the isomer found in the crystal. Remarkable differences in the chemical shifts for H_b were observed. Compared to the free oxazoline [$\delta(H_b) = 4.10$], for ***N-cis*-1**, the signal shifted downfield ($\delta = 4.68$), but upfield for ***N-trans*-1** ($\delta = 3.72$; Table 2). This behaviour can be attributed to interactions with the oxo groups, as shown by the average interatomic distances H···O=Mo from the crystallographic data (for ***N-cis*-1**, ca. 3.2 Å and for ***N-trans*-1**, ca. 4.6 Å).

For complex **2**, we distinguished four compounds in deuterated chloroform solution, with a ratio of 42:11:5:1. For complex **1**, the signals of the different species were less split, but in addition to the signals corresponding to the two major isomers (in a relative ratio of 17:8), other less-intense signals were also observed. No isomeric composition change was observed in either compound in the temperature range studied (from 233 K to 323 K).

The ^{1}H NMR spectra (monodimensional and 2D NOESY experiments) revealed that the two anionic *N,O* ligands (**A** and **B** fragments) are equivalent for the two major isomers, *N-cis* and *N-trans* (Table 2), for both complexes **1** and **2**. This observation suggests that, in solution, the pseudo-octahedral environment around the metal atom is more symmetric than in the solid state, where the two oxazoline ligands are inequivalent. However, the anionic ligands in the *N-cis,trans* isomer are not equivalent, as observed in the 800 MHz ^{1}H NMR spectrum for complex **2**

Table 2. Selected ^{1}H NMR spectroscopic data[a] (δ) for **1** ($CDCl_3$, 500 MHz, 298 K), **2** ($CDCl_3$, 800 MHz, 298 K) and **I** (CD_3COCD_3, 250 MHz, 200 K)



1, R = H, R' = CH_3
2, R = R' = CH_3

Complex	H_a[b]	H_b	H_c	H_d	$H_{aromatic}$
***N-cis*-1**	4.74 (dd, 2 H, 10.0, 8.0) 4.39 (dd, 2 H, 8.0, 6.0)	4.68 (m, 2 H)	2.24 (m, 2 H) 1.97 (m, 2 H)	0.93 (t, 6 H, 7.5)	7.62 (dd, 2 H, 7.75, 1.5) 7.03 (td, 2 H, 7.75, 1.5) 6.61 (td, 2 H, 7.5, 0.75) 6.04 (d, 2 H, 8.0)
***N-trans*-1**	4.23 (pd, 4 H, 7.0)	3.72 (m, 2 H)	2.17 (m, 2 H) 1.83 (m, 2 H)	0.80 (t, 6 H, 7.5)	7.71 (dd, 2 H, 8.0, 2.0) 7.44 (td, 2 H, 7.75, 1.5) 7.00 (dd, 2 H, 8.2, 1.5) 6.91 (td, 2 H, 7.5, 1.0)
***N-cis*-2**	4.66 (pt, 2 H, 8.4) 4.54 (pdd, 2 H, 8.4, 6.0)	4.73 (m, 2 H)	2.94 (m, 2 H)	1.04 (d, 6 H, 7.2) 0.83 (d, 6 H, 7.2)	7.67 (dd, 2 H, 8.0, 1.6) 7.07 (td, 2 H, 8.0, 1.6) 6.66 (pt, 2 H, 7.2) 6.09 (d, 2 H, 8.8)
***N-trans*-2**	4.38 (dd, 2 H, 8.8, 4.8) 4.12 (t, 2 H, 9.6)	3.80 (m, 2 H)	2.82 (m)[c]	0.91 (d, 6 H, 6.4) 0.75 (d, 6 H, 7.2)	7.76 (pdd, 2 H, 7.6, 2.0) 7.50 (td, 2 H, 8.0, 1.6) 7.04 (m, 2 H) 6.95 (m, 2 H)
***N-cis,trans*-2**	4.86 (pdd, 1 H, 10.4, 8.8) 4.78 (pdd, 1 H, 10.0, 8.4) 4.67 (pdd, 1 H, 8.4, 6.0)[d]	5.75 (m, 1 H) 5.13 (m, 1 H)	3.25 (m, 1 H)[c]	1.18 (d, 3 H, 6.4) 1.09 (d, 3 H, 7.2) 1.07 (d, 3 H, 7.2) 0.94 (d, 3 H, 7.2)	7.73 (dd, 1 H, 8.0, 1.6) 7.58 (pdd, 1 H, 7.6, 2.0) 7.46 (m, 1 H) 7.43 (m, 1 H) 6.62 (m, 1 H) 6.61 (m, 1 H) 6.11 (d, 1 H, 8.8) 5.83 (d, 1 H, 8.8)
I	4.55 (m, 2 H) 4.28 (bt, 2 H, 9.3)	3.81 (m, 2 H)	2.67 (m, 2 H)	0.79 (d, 3 H, 6.7) 0.68 (d, 3 H, 6.7)	7.77 (bd, 2 H,7.9) 7.59 (bt, 2 H,7.9) 7.03 (m, 4 H)

[a] Multiplicity (d, doublet; dd, doublet of doublets; m, multiplet; p, pseudo; t, triplet; td, triplet of doublets), relative integration, and coupling constants (in Hz) in parentheses. − [b] For atom labelling, see figure above table. − [c] Two overlapped multiplets for the ***N-trans*-2** and ***N-cis,trans*-2** isomers. − [d] One proton under δ = 4.66 signal of ***N-cis*-2** isomer.

(Table 2). For this compound, the 2D NOESY spectra did not show exchange signals (at various mixing times: 250, 500 and 600 ms at 800 MHz) among the three isomers (***N-cis*-2**, ***N-trans*-2** and ***N-cis,trans*-2**). In addition, a fourth species (**I**) was observed, which showed broader signals and exchange signals with ***N-cis*-2** and ***N-trans*-2**.

Nevertheless, in deuterated acetone at 200 K, a mixture of two compounds (6:1) was observed, where **I** can be assigned to the more abundant species and the minor species seems to be ***N-cis*-2**. At higher temperatures, other signals associated with ***N-cis,trans*-2** appear and those belonging to **I** became less intense. A similar behaviour was observed for a solution of complex **2** in $CDCl_3/CD_3CN$ (1:1). These data indicate that acetone or acetonitrile compete with the oxazoline nitrogen for coordination to the metal. Therefore, the observed exchange process described above could be associated to the rupture of one Mo−N bond of one of the two major isomers (*N-cis* or *N-trans*) and subsequent nitrogen coordination to the metal, giving the other isomer (*N-trans* or *N-cis*).

Oxo-Transfer Reactions

The stoichiometric oxidation of PPh_3 by **1** or **2** was carried out in $CDCl_3$ at room temperature, and the solution was analysed by ^{31}P NMR spectroscopy. Total conversion of PPh_3 to $OPPh_3$ occurred in less than an hour and in 80 minutes with complex **2** and **1**, respectively, as shown in Figure 3.

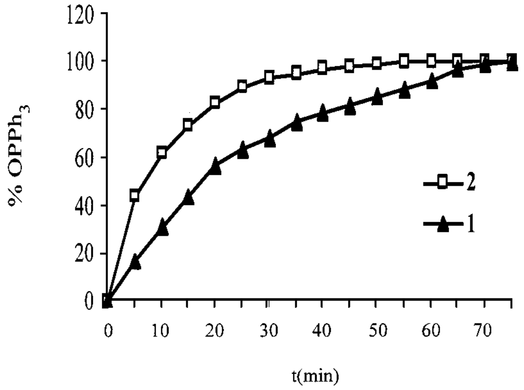


Figure 3. Plot of percent of triphenylphosphane formed against time for **1** or **2**

When complexes **1** and **2** reacted with an excess of PR_3 and DMSO, a fast reaction was observed, transforming the substrate into the corresponding oxide in a catalytic manner [Equation (1)].

$$PPh_3 + (CH_3)_2SO \xrightarrow{[Mo]} OPPh_3 + (CH_3)_2S \qquad [Mo] = \mathbf{1, 2} \tag{1}$$

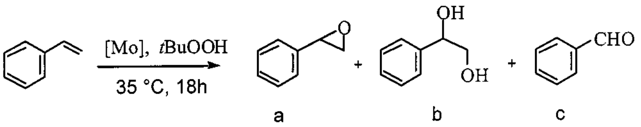
After three days, no phosphane was detected in either case. The colour of the reaction mixtures changed from yellow to yellow-green for complex **2**, and from yellow to yellow-orange for **1**. These reactions contrast with other disubstituted dioxomolybdenum compounds such as $[MoO_2(S_2CNR_2)_2]$,[16] which immediately turns purple (Mo^V), thus our results indicate that the oxo transfer process with complex **1** or **2** does not involve a Mo^V-oxo intermediate.

Styrene Epoxidation

Complexes **1** and **2** were also tested as catalytic precursors in styrene epoxidation, using several oxidants: DMSO, hydrogen peroxide and *t*BuOOH. Conversion of the substrate was only observed with the organic peroxide. No epoxide was obtained in the absence of the molybdenum complex.

The activity obtained with complexes **1** and **2** (25−29% conversion of the olefin) was relatively low when compared, under identical experimental conditions, with other dioxomolybdenum systems such as $[MoO_2(S_2CNEt_2)_2]$ and $[MoO_2(NCS)_2(bipy)]$, but was similar to $[MoO_2(acac)_2]$ (Table 3). However, **1** and **2** showed a better selectivity towards styrene oxide and its diol than the other complexes tested, while benzaldehyde, the cleavage product, was produced in a small amount (10.4−11.5%). The asymmetric induction for **1** and **2** was practically negligible (ca. 2% *ee*).

Table 3. Mo-catalyzed styrene epoxidation[a] with *t*BuOOH as oxidant



[Mo]	Conv. (%)[b]	**a** (%)[c]	**b** (%)[c]	**c** (%)[c]
1	29.0	12.8	5.8	10.4
2	25.0	8.8	4.7	11.5
$[MoO_2(acac)_2]$	26.0	2.8	6.4	17.0
$[MoO_2(S_2CNEt)_2]$	42.0	6.1	10.6	25.4
$[MoO_2(NCS)_2(bipy)]$	66.5	13.0	4.6	48.8

[a] Reaction conditions: 0.05 mmol of catalyst, 2 mmol of olefin, 3 mmol of *t*BuOOH and 2 cm^3 of toluene at 35 °C for 18 h. − [b] Yield based on amount of oxygenated products as determined by GC chromatography. − [c] Yield based on reacted styrene determined by GC chromatography.

Conclusions

We conclude that the oxazoline ligands [(*R*)-**AH** and (*S*)-**BH**] allow the stabilisation of molybdenum(VI) complexes of general formula *cis*-$[MoO_2(N,O)_2]$ (**1** and **2**), which are obtained as mixtures of three diastereomers due to the ligand and metal chirality. The structural elucidation of these mixtures was performed by means of NMR spectroscopy and X ray diffraction. Theoretical studies (DFT) have allowed us to corroborate that the Δ-*N-cis* coordination is the most stable arrangement. Moreover, a fourth species, **I**, is present in solution. In chloroform, the major compound is Δ-*N-cis*, an arrangement which until now has only been observed for polydentate ligands. In contrast, in coordinating solvents (acetone and acetonitrile), **I** becomes the major species. Although the catalytic activity of complexes **1** and **2** in styrene oxidation is relatively low, the selectivity towards styrene oxide and its diol is important under the mild experimental conditions tested.

Experimental Section

General: All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum line techniques. The solvents were purified by standard procedures and distilled under nitrogen.[17] *cis*-[MoO$_2$(acac)$_2$][18] and the ligands (*R*)-**AH** and (*S*)-**BH**[19] were prepared as described previously. NMR spectra were recorded on Bruker Avance 600, Bruker Avance 800, Varian XL-500, Varian Gemini or Bruker DRX 250 spectrometers. Chemical shifts are reported downfield from standards (TMS for ^{1}H NMR spectra and H$_3$PO$_4$ for ^{3}P NMR spectra). IR spectra were recorded on a Nicolet 520 FT-IR and Bruker IFS 55 FTIR spectrometer. FAB mass spectra were obtained on a Fisons V6-Quattro instrument. The GC-MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column) interfaced to a Hewlett-Packard 5971 mass selective detector. Enantiomeric excesses were determined by GC on a FS-cyclodex-β-I/P column. Elemental analyses were carried out by the Serveis Cientifico-Tècnics de la Universitat de Barcelona in an Eager 1108 microanalyzer.

Dioxo-bis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydroxazol-2′-yl)phenolato-*N,O*]molybdenum(VI) (1): A solution of (+)-(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenol (0.258 g, 1.350 mmol) in CH$_3$OH (5 cm^3) at room temperature was added to a solution of [MoO$_2$(acac)$_2$] (0.200 g, 0.617 mmol) in CH$_3$OH (20 cm^3). The reaction mixture was stirred for 4 h and the light orange precipitate was filtered and recrystallised from CH$_2$Cl$_2$/diethyl ether (2:1). Yield: 0.251 g (80%). − C$_{22}$H$_{24}$MoN$_2$O$_6$ (508.38): calcd. C 51.98, H 4.76, N 5.51; found C 50.90, H 4.86, N 5.40. − MS (FAB positive): *m/z* = 508 [M$^+$]. − IR(KBr): $\tilde{\nu}$ = 1648 (st, C=N), 910, 882 (Mo=O) cm^{-1}.

Dioxo-bis[(4′*S*)-2-(4′-isopropyl-3′,4′-dihydroxazol-2′-yl)phenolato-*N,O*]molybdenum(VI) (2): A solution of (−)-(4′*S*)-2-(4′-isopropyl-3′,4′-dihydrooxazol-2′-yl)phenol (0.277 g, 1.350 mmol) in CH$_3$OH (5 cm^3) at room temperature was added to a solution of [MoO$_2$(acac)$_2$] (0.200 g, 0.617 mmol) in CH$_3$OH (20 cm^3). The reaction mixture was stirred for 4 h and the yellow precipitate was filtered and recrystallised from CH$_2$Cl$_2$/diethyl ether (2:1). Yield: 0.288 g (87%). − C$_{24}$H$_{28}$MoN$_2$O$_6$ (536.43): calcd. C 53.74, H 5.26, N 5.22; found C 53.50, H 5.29, N 5.25. − MS (FAB positive): *m/z* = 537 [M$^+$]. − IR (KBr): $\tilde{\nu}$ = 1650 (st, C=N), 919, 885 (Mo=O) cm^{-1}.

Oxidation of PPh$_3$ by Complex 1 or 2: A solution of PPh$_3$ (30 mg, 0.115 mmol) in CDCl$_3$ (0.6 cm^3) was added to **1** (20 mg, 0.039 mmol) or **2** (20 mg, 0.037 mmol) in an NMR tube and the solution was monitored immediately by ^{31}P{^{1}H} NMR spectroscopy at 25 °C. The first kinetic point was taken at t = 5 min. The reaction was followed by integrating the signals corresponding to triphenylphosphane and triphenylphosphane oxide.

Oxidation of PPh$_3$ by DMSO in the Presence of Complex 1 or 2: DMSO (0.5 cm^3) was added to a mixture of **1** (20 mg, 0.039 mmol) or **2** (20 mg, 0.037 mmol) and an excess of PPh$_3$ (30 mg, 0.115 mmol) in CDCl$_3$ (0.6 cm^3). An aliquot of this solution was transferred to an NMR tube and the solution was monitored immediately by ^{31}P{^{1}H} NMR at 25 °C. The first kinetic point was taken at t = 5 min. The reaction was followed by integrating the signals corresponding to triphenylphosphane and triphenylphosphane oxide.

Molybdenum-Catalysed Styrene Epoxidation: The precursor (0.05 mmol of complex: 25.7 mg for **1**; 27.1 mg for **2**) was dissolved in

Table 4. Crystal data for complexes **Δ-*N*-*cis*-1** and **Λ-*N*-*trans*-1**

	Δ-*N*-*cis*-1	**Λ-*N*-*trans*-1**
Empirical formula	C$_{22}$H$_{24}$MoN$_2$O$_6$	C$_{22}$H$_{24}$MoN$_2$O$_6$
Molecular weight	508.37	508.37
Crystal size, mm	0.2 × 0.15 × 0.08	0.3 × 0.25 × 0.2
Temperature, K	293(2)	150(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a, Å	10.007 (2)	9.239 (2)
b, Å	10.857 (2)	9.408 (2)
c, Å	10.075 (2)	24.300 (5)
α, deg	90	90
β, deg	90.70 (3)	90
γ, deg	90	90
V, Å^3	1094.5 (4)	2112.2 (8)
Z	2	4
Density (calcd.), g·cm^{-3}	1.543	1.599
Absorption coefficient, mm^{-1}	0.640	0.663
F(000)	520	1040
θ range for data collection	2.04 to 27.53°	1.68 to 27.49°
Reflections collected	28888	23583
Data/restraints/parameters	5027/1/282	4775/0/282
Independent reflections	5027 [R(int) = 0.0435]	4779 [R(int) = 0.0374]
Final R indices [$I > 2\sigma(I)$]	$R1$[a] = 0.0305 $wR2$[b] = 0.0760	$R1$[a] = 0.0252 $wR2$[b] = 0.0753
R indices (all data)	$R1$ = 0.0369 $wR2$ = 0.0808	$R1$ = 0.0271 $wR2$ = 0.0831
GOF on F^2	0.899	0.693
Absolute structure parameter	0.02 (3)	−0.03 (2)
Largest diff. peak and hole, e·Å^{-3}	0.340 and −0.581	0.499 and −0.584

[a] $R1 = \Sigma|F_o| - \Sigma|F_c|/|F_o|$. − [b] $wR2 = \{\Sigma[w(F^2{}_o - F^2{}_c)]/\Sigma[w(F^2{}_o)^2]\}^{1/2}$.

2 cm^3 of toluene. Styrene (208 mg, 2 mmol) was added, followed by an aqueous solution of *tert*-butyl hydroperoxide (*t*BuOOH/H_2O: 3:2; 0.19 cm^3, 3 mmol). The mixture was stirred for 18 h at 35 °C, until no conversion of styrene was observed (monitored by gas chromatography). After removing the solvent under reduced pressure, the oil was purified by column chromatography (SiO_2; ethyl acetate). The conversion of styrene was determined by gas chromatography. The enantiomeric excesses were determined by gas chromatography.

Crystallography: The crystallographic data for **Δ-*N-cis*-1** and **Λ-*N-trans*-1** are summarized in Table 4. Single crystals were grown by diffusing diethyl ether into a dichloromethane solution of the isomer mixture, thereby obtaining orange (**Δ-*N-cis*-1**) and yellow (**Λ-*N-trans*-1**) crystals.

The crystal data for both isomers were collected using a Delf Instrument FAST TV area-detector diffractometer positioned at the window of a rotating-anode. Intensities were collected with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), using the $\omega/2\theta$ scan technique. Structures were solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares on F_o^2 using SHELXL-97.[20] Data were corrected using the SORTAV program.[21] All hydrogen atoms were included in idealised positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153158 (**Λ-*N-trans*-1**) and -153159 (**Δ-*N-cis*-1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical Calculations: The geometry of the isomers ***N-cis***, ***N-trans*** and ***N-cis,trans*** was optimized[22] in vacuo by means of the GAUSSIAN98 package of programs.[23] Ab initio molecular orbital calculations were carried out at the Hartree−Fock (HF) level with methods based on Density Functional Theory (DFT), and using the standard 3−21G basis set. We used Becke′s three-parameter functional (B3)[24] which includes the Slater exchange along with corrections involving the gradient of electron density, and the correlation functional of Lee, Yang and Parr, which includes both local and nonlocal terms (LYP).[25,26] The parameters are those determined by Becke by fitting to the G1 molecule set.[24b,27]

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