cis-Dioxomolybdenum(VI) Complexes Containing Chiral Ligands: Synthesis and Catalytic Application in Olefin Epoxidation

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Abstract: Novel *cis*-dioxomolybdenum(VI) complexes containing chiral ligands have been prepared and fully characterized, including structural determinations by X-ray diffraction. The first monometallic dioxomolybdenum(VI) complex containing a chiral *N,N',O*-tridentated ligand is reported. The new complexes were evaluated as catalysts for epoxidation of olefins using *tert*-butyl hydroperoxide and H_2O_2 as oxidants. They were found to be efficient catalysts affording good chemoselectivity but low enantioselectivity.

Keywords: Dioxomolybdenum (VI), oxazoline, X-ray structures, modelling, olefin epoxidation.

1. INTRODUCTION

Catalytic epoxidation of olefins is both a major industrial technology and an essential synthetic method. In general, epoxides can be prepared by the reaction of olefins with hydrogen peroxide or alkylhydroperoxides, catalyzed by transition metal complexes [1-3]. The use of oxo-molybdenum complexes for the industrial-scale epoxidation of alkenes has been extensively explored over the last 40 years, beginning with homogeneous Mo(VI) catalysts in the Halcon and Arco processses.[4] Since then, considerable effort has been directed towards the development of enantioselective epoxidation protocols using chiral molybdenum catalysts [5-16]. However, little success has been achieved up to now [17-19]. The weak coordination of ligands to molybdenum center is probably the main reason why all attempts to develop enantioselective epoxidations have failed, leading in most cases to low enantiomeric excess; only high asymmetric induction could be achieved at low conversions [12]. So far, the only example of high enantioselectivity obtained using a chiral molybdenum complex was reported by Yamamoto and co-workers in 2006 [20]. They successfully developed a simple method for asymmetric oxidation of olefins using a chiral bis-hydroxamic acid-molybdenum complex to obtain excellent yields and selectivities. However, the nature of the molybdenum catalyst is unkown, since it was prepared in situ by reaction of $[MoO_2(acac)_2]$ with the hydroxamic acid, and no attempts to isolate the well-defined molybdenum complex was described. More recently, Zhou and co-workers achieved moderate to high enantioselectivity in the epoxidation of styrene derivatives based on molybdenum catalysts formed in situ by reaction of $[MoO_2(acac)_2]$ with amino alcohols [21].

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During the last years, we have been studying the coordination of oxazoline ligands to molybdenum and their application in olefin epoxidation [22-25]. Some of us reported the preparation of the first chiral molybdenum(VI) complexes of the type *cis*-$[MoO_2(\kappa^2\text{-}N,O\text{-L})_2]$ where L represents anionic chiral bidentate oxazolinylphenolate ligands [23]. The activity trends observed for different catalytic systems studied by us proved that the coordination of a non-labile chiral ligand, such as oxazolinyl-pyridine ligands, appeared crucial to induce selectivity in the epoxidation process, in particular for the limonene epoxidation. As a result of these findings, we considered to expand our studies to the coordination of monoanionic tridentate and bidentate oxazoline-based ligands to molybdenum.

Here we describe the application of new dioxo-molybdenum complexes (**1** and **4**) containing chiral tridentate and bidentate anionic oxazoline-based ligands (**I** and **III**) in alkenes epoxidation. We have also explored the catalytic behavior of complex **3** containing the chiral amido-pyridine ligand **II.**

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of *cis*-Dioxomolybdenum(VI) Complexes

The optically pure (hydroxyalkyl)pyridinooxazoline ligand **I** was prepared following the synthetic pathway depicted in Scheme 1. The starting compound 2-(hydroxyethyl) pyridine was transformed into 6-cyano-2-(hydroxyethyl) pyridine in a sequence involving oxidation by *m*-chloroperbenzoic acid to the corresponding N-oxide, followed by treatment with N,N-dimethylcarbamoyl chloride and trimethylsilyl cyanide. The resulting nitrile was then mixed with the appropriate aminoalcohol and a catalytic amount of copper chloride(II) to yield the desired oxazoline **I** in moderate yield (36% overall yield). Compound **I** was isolated as a yellow solid and characterized by NMR spectrocopy and

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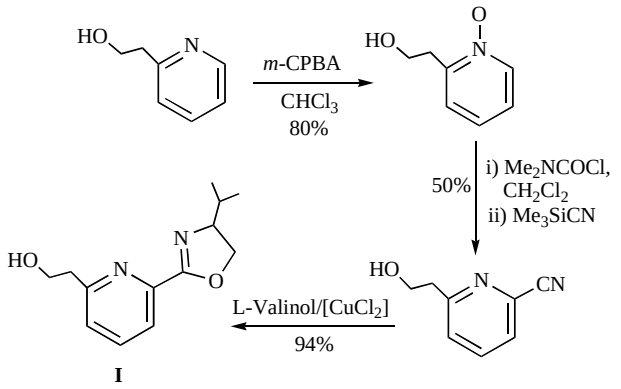
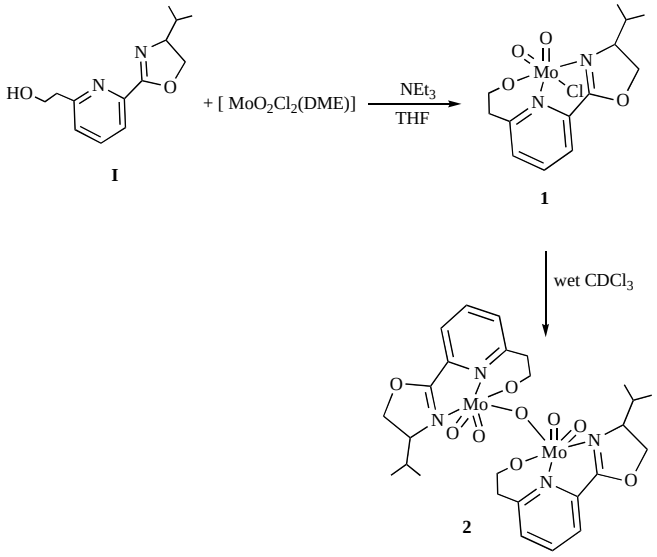
mass spectrometry. Details on the NMR characterization are given in the Supporting Information (Figs. **S1** and **S2**).



I

Scheme 1. Synthesis of the oxazoline ligand **I**.

Treatment of the previously described ligand **I** with $[MoO_2Cl_2(DME)]$ (DME = dimethoxyethane) in the presence of triethylamine gave the corresponding enantiomerically pure dioxo complex $[MoO_2Cl(\kappa^3\text{-}N,N,O\text{-}\mathbf{I})]$ (**1**) isolated as yellow solid after purification by column chromatography (Scheme **2**) [26]. Complex **1** was easily hydrolyzed in wet deuterated solvents giving the μ-oxo dimolybdenum compound $[MoO_2(\kappa^3\text{-}N,N,O\text{-}\mathbf{I})]_2(\mu\text{-}O)$ (**2**), indicating that compound **1** is rather sensitive to moisture and decompose readily in the presence of traces of water.



I **1** **2**

Scheme 2. Synthesis of molybdenum complexes **1** and **2**.

The IR spectrum of complex **1** showed two strong bands at 911 and 938 cm^{-1} attributed to the asymmetric and symmetric Mo=O stretches for a *cis*-$[MoO_2]^{2+}$ moiety [13-14, 22-25]. Complex **2** exhibited characteristic bands for both terminal (911 and 938 cm^{-1}) and μ-oxo (805 cm^{-1}) stretches in accord with related dioxo-μ-oxo molybdenum compunds described in the literature [23, 26-29]. Results of elemental analyses were consistent with their composition. Mass spectrum was also performed to characterize complex **1**. Positive ion ESI-MS experiments in methanol showed the molecular ion peak at *m/z* 365 $[M\text{-}Cl]^+$. Its ^1H NMR spectrum at 298K showed, as expected, the signals corresponding to the (hydroxyalkyl)pyridinooxazoline ligand shifted to lower fields upon coordination. The ^{13}C NMR spectrum also demonstrated that the ligand is bound to the dioxomolybdenum core, displaying the signal of the pyridine carbon close to the nitrogen atom shifted downfield compared to that of the free ligand. ^{95}Mo NMR spectrum showed one symmetrical peak at δ + 67.5 (width at middle height: 358 Hz) (see Fig. (**7**) in Supporting information). A variable temperature ^1H NMR study (298 K- 193 K) evidenced up to three isomers at 273 K (see Fig. (**5**) in Supporting information). The origin of these isomers can be probably due to the two arrangements of the tridentated ligand in a pseudo-octahedral environment, giving meridional and facial isomers. Due to the polyhedron chirality, the *mer* isomer leads to two diastereoisomers because of the optically pure oxazoline moiety. The *fac* arrangement can form three stereoisomers. In order to rationalize the experimental observations, a modelling study was carried out, optimizing the different geometries by means of density functional theory (see Supporting information Fig. (**7**)). However, assignments of the NMR signals to each of the isomers could not be done due to the complexity of the NMR spectrum displaying many resonances.

The structure of $[MoO_2Cl(\kappa^3\text{-}N,N,O\text{-}\mathbf{I})]$ (**1**) was established by single-crystal X-ray analysis. The structure and selected bond lengths and angles are shown in Fig. (**1**). The structure reveals a six-coordinate Mo atom in a distorted octahedral surronding, with a *mer* coordination of the ligand, rendering the ligand skeleton almost planar. The molybdenum oxo groups show the expected mutual *cis* configuration with a *trans* pyridine and a *trans* chloro atom. The *trans* disposition of the oxo group with the chloro atom is unexpected for this type of complexes, since related tridentate N_2O phenolate complexes of tungsten adopt a distorted octahedral structure with the two nitrogen donor atoms being located *trans* to the oxo groups, and with the phenolate oxygen opposite the chloro ligand [30]. Although a number of X-ray diffraction studies have been reported concerning the bidentated coordination of pyridine and quinoline derivatives [31], only three bimetallic dioxomolybdenum(VI) complexes have been described containing anionic tridentated ligands [32-34]. Therefore, complex **1** represents the first X-ray characterization for a monometallic molybdenum complex bearing a *N,N',O*-tridentated ligand [35, 33]. The Mo-Cl bond are relatively long (2.52 Å) because of the strong *trans* influence of the oxo ligand; the expected range of Mo-Cl bond distances in *cis*-dioxo Mo(VI) complexes are 2.36-2.41 Å [36, 37]. The Mo=O bond lengths [Mo-O2, 1.6968(19) and Mo-O3, 1.6994(19)] are in the expected range of *cis*-dioxo Mo(VI) complexes [38]. The Mo-O single bond distance is in the range typical of Mo(VI) alkoxides [39, 40].

In an attempt to prepare the anionic 2-pyridine-(hydroxyethyl)oxazoline ligand **A** shown in Scheme 3, we carried out the reaction of 2-cyanopyridine with the (2*S*)-2-amino-1,4-butanediol following similar procedures described for the synthesis of related functionalized-oxazolines [41]. However, instead of the desired functionalized oxazoline **A**,

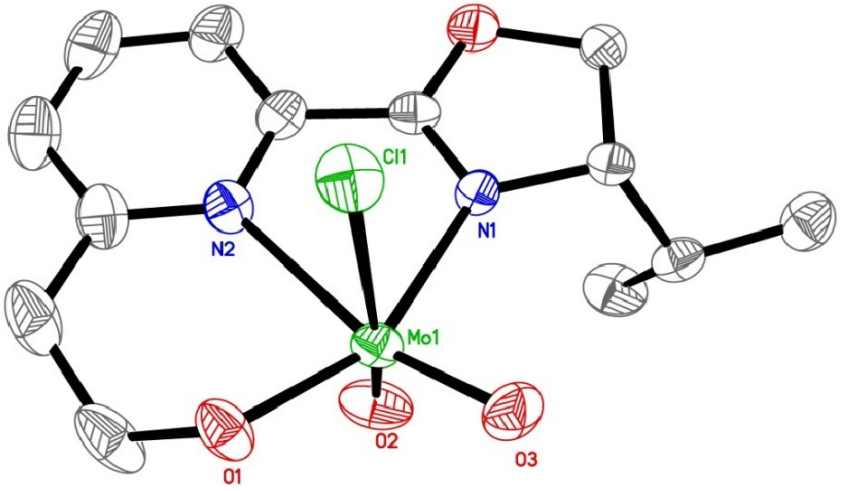
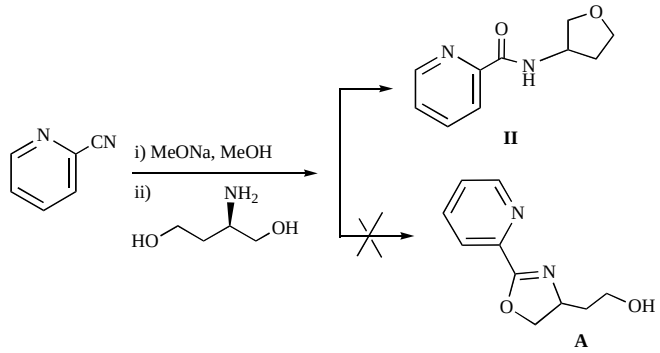


Fig. (1). Molecular view of compound **1** with ellipsoids representing 50% probability. H atoms are omitted for clarity. Selected bond distances distances (Å) and angles (º): Mo(1)-O(2) 1.6968 (19), Mo(1)-O(3) 1.6994 (19), Mo(1)-O(1) 1.8802 (19), Mo(1)-N(1) 2.188 (2), Mo(1)-N(2) 2.373 (2), Mo(1)-Cl(1) 2.5266 (9), O(2)-Mo(1)-O(3) 105.16 (11), O(2)-Mo(1)-O(1) 97.87 (9), O(3)-Mo(1)-N(1) 95.58 (9), O(2)-Mo(1)-Cl(1) 161.15 (8).

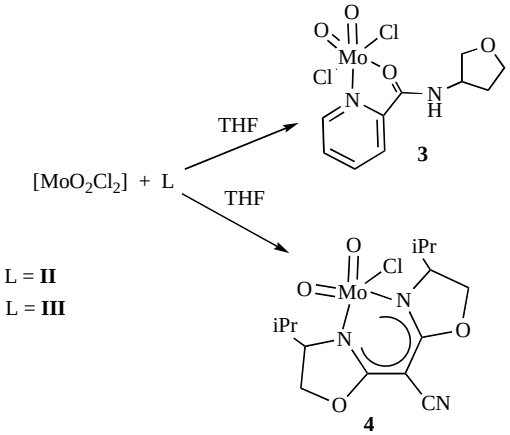


Scheme 3. Synthesis of the pyridine amide ligand **II**.

the pyridinamide ligand **II** was isolated in 23% yield, Scheme **3**.

$[MoO_2Cl_2]$ reacts with one equivalent of ligand **II** to form complex **3** in nearly quantitative yield (Scheme **4**). The dioxomolybdenum(VI) complex **3** was obtained as an air stable microcrystalline orange solid and was fully charaterized by multi-nuclear (^{1}H, ^{13}C, ^{95}Mo) NMR and IR spectroscopy, mass spectrometry, elemental analysis and X-ray diffraction analyses.

The infrared spectrum of **3** exhibited two very strong ν((Mo=O) bands at 950 and 914 cm^{-1}, characteristic of the symmetric and asymmetric stretching vibrations of the *cis*-$[MoO_2]^{2+}$ fragment [22-25]. The ^{1}H NMR spectrum of complex **3** displayed five multiplets at δ 4.68, 4.05-3.94, 3.84, 2.45, and 2.15 assigned to the inequivalent protons of the furanyl ring, three resonances at δ 9.32, 8.36 and 7.99 for the pyridyl protons, and a broad singlet at δ 8.93 assigned to the N-H proton. Its ^{13}C NMR spectrum demonstrated that the ligand is bound to the dioxomolybdenum core. Thus, the signal for the carbon atom of the carbonyl group was found at δ 168.0, shifted downfield compared to that of the free



Scheme 4. Synthesis of molybdenum complexes **3** and **4**.

ligand which appears at δ 164.3. Its ^{95}Mo NMR spectrum displayed a sharp signal at +189.7 ppm (width at middle height: 217 Hz).

Fig. (**2**) shows the molecular structure of **3** determined by X-ray diffraction analysis, along with selected bond distances and angles. The molecular structure of complex **3** revealed an octahedral coordination with the molybdenum atom coordinating to the pyridine nitrogen atom and the carbonyl oxygen atom of the chelating ligand, and with two chloride atoms *trans* to each other, and two oxygen atoms in *cis* position. This geometric arrangement is comparable to that found in related *cis*-dioxomolydenum complexes containing bidentate ligands [42]. Mo-Cl, Mo=O, and Mo-O bond lengths are within the expected values [38, 43].

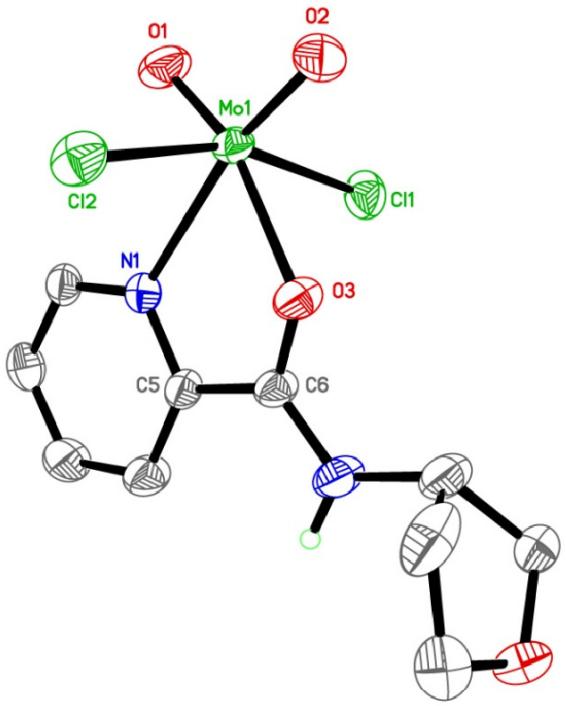


Fig. (2). Molecular view of compound **3** with ellipsoids representing 50% probability. H atoms are omitted for clarity. Selected bond distances distances (Å) and angles (º): Mo(1)-O(1) 1.690 (2), Mo(1)-O(2) 1.693 (2), Mo(1)-O(3) 2.1871 (19), Mo(1)-N(1) 2.350 (2), Mo(1)-Cl(2) 2.3629 (8), Mo(1)-Cl(1) 2.3991 (8), O(3)-C(6) 1.248 (3), O(1)-Mo(1)-O(2) 106.04 (12), O(3)-Mo(1)-N(1) 69.37 (7), Cl(2)-Mo(1)-Cl(1) 160.51 (3).

Molybdenum complexes bearing monoanionic bisoxazolinate ligands (Box) have not been reported so far in the literature, despite the interesting catalytic results displayed by complexes incorporating these monoanionic ligands [44]. The reaction of the cyanobisoxazoline **III**, prepared as previously described in the literature [45], with $[MoO_2Cl_2]$ affords complex **4** in quantitative yield (Scheme 4). The proposed structure of **4** is in accord with the analytical data derived from NMR, IR spectroscopy, elemental analysis and mass spectrometry. ^1H and ^{13}C NMR spectra of **4** showed a singlet set of resonances for the Box ligand. Its IR spectrum displayed two characteristic *cis*-dioxo (MO_2) vibrational bands at 918 and 957 cm^{-1} assigned to the asymmetric and symmetric stretchings, respectively. Electrospray ionization mass spectrum of an acetonitrile solution of **4** showed a peak at *m/z* 462 in the negative ion mode corresponding to $[M+Cl]^-$.

Catalytic Studies in Olefin Epoxidation

Complexes **1**-**4** were tested as catalysts for olefin epoxidation using *cis*-cyclooctene, (*R*)-limonene and β-methylstyrene as substrates, and *tert*-butyl hydroperoxide (TBHP in decane) as oxidant in chloroform at 55 °C. The formation of the corresponding epoxides was analysed by GC. Control experiments showed that no epoxide was formed in a measurable extent in the absence of catalyst. As shown in Table **1**, complexes **1**-**4** were efficient catalysts toward oxidation of cyclooctene affording quantitative conversion to the corresponding epoxide. Comparing the activity of complexes **1** and **4**, both containing oxazoline-based ligands, higher activity was achieved by **1**, giving quantitative conversion of the epoxide in 30 min with a turnover frequency (TOF) of 469 mol mol^{-1} h^{-1} (calculated at 10 min). Catalysts **1** and **2** exhibited identical activity, indicating that the μ-oxo dimer **2** and the chloride **1** are readily converted to a common active species. Similar results were described by Finney and co-workers [33]. Complex **3** bearing the pyridino amido ligand **II** led to the best TOF (6125 mol mol^{-1} h^{-1} calculated at 10 min) without observing any induction period.

Complexes **1**, **3** and **4** were also active using H_2O_2 as oxidant. The epoxidation of cyclooctene with H_2O_2 (30% in water) carried out in EtOH afforded moderate yield of the corresponding epoxide in a selective manner with the three catalytic systems (Table **1**, entries 2, 5 and 7, respectively). However, no further conversion of cyclooctene was observed after 24 h of reaction indicating the instability of the catalysts under the reaction conditions.

This study was further extended to the catalytic epoxidation of (*R*)-limonene with TBHP under similar conditions. All complexes displayed good activity achieving quantitative conversions of 1,2-epoxy-limonene in few hours (Table **1**, entries 8-10). However, no diastereoisomeric induction of (*R*)-limonene took place even lowering the temperature to 25 °C.

Next, we investigated the epoxidation of *trans*-(β)-methylstyrene, a model substrate for *trans*-olefins, in order to explore the capability of these catalytic precursors to promote asymmetric induction. Quantitative formation of the corresponding epoxide was formed in nearly racemic mixture (≤6% ee) when complex **1** was used as catalyst. No improvement in the enantioselectvity was observed by either lowering the reaction temperature or using toluene as solvent instead of chloroform. For complexes **3** and **4**, no asymmetric induction was obtained even at low conversions. However, in all cases the catalytic reaction was selective to the corresponding epoxide.

3. EXPERIMENTAL SECTION

General General Procedures

$[MoO_2Cl_2(DME)]$ was prepared following the method described in the literature [46]. All other reagents were used as received from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 MHz. Infrared (IR) spectra were recorded on samples as KBr pellets using a Mattson 7000

Table 1. Olefin Epoxidation Catalyzed by Complexes 1-4 [a]

Entry	Catal.	Olefin	Oxidant/solvent	t (h)	Yield (%)[b]	Trans/cis (%)
1	**1**	cyclooctene	TBHP/$CHCl_3$	1	100	
2	**1**	cyclooctene	H_2O_2/EtOH	22	42	
3	**2**	cyclooctene	TBHP/$CHCl_3$	1	100	
4	**3**	cyclooctene	TBHP/$CHCl_3$	0.33	99	
5	**3**	cyclooctene	H_2O_2/EtOH	16	50	
6	**4**	cyclooctene	TBHP/$CHCl_3$	3	96	
7	**4**	cyclooctene	H_2O_2/EtOH	22	32	
8	**1**	(*R*)-limonene	TBHP/$CHCl_3$	1	94	52/48
9	**3**	(*R*)-limonene	TBHP/$CHCl_3$	0.33	99	50/50
10	**4**	(*R*)-limonene	TBHP/$CHCl_3$	3	91	51/49
11	**1**	*trans*-b-methylstyrene	TBHP/$CHCl_3$	4	83	
12	**3**	*trans*-b-methylstyrene	TBHP/$CHCl_3$	1	60	
13	**4**	*trans*-b-methylstyrene	TBHP/$CHCl_3$	4	28	

[a] All reactions were carried out using a catalyst: substrate: oxidant ratio 1:100:200 in $CHCl_3$ when TBHP is used as oxidant and in EtOH for H_2O_2 at 55 ºC unless otherwise stated.
[b] Yield determined by GC.

FT-IR spectrometer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, nitrogen was employed as drying and nebulizing gas. Optical rotations were determined on a Perkin Elmer 241 polarimeter. Elemental analyses were performed in our laboratories at ITQB.

X-Ray Diffraction Studies

X-Ray data for complexes **1** and **3** were collected at low temperature (180 for **1** and 193 for **3** K) using an oil-coated shock-cooled crystal on Bruker-AXS APEX II diffractometer with MoKα radiation (λ = 0.71073 Å). Semiempirical absorption corrections were employed [47]. The structures were solved by direct phase determination (SHELXS-97) [48] and refined for all non-hydrogen atoms by full matrix least-square methods on F2 and subject to anisotropic refinement [49]. Crystal data and structure refinement are summarized in Table **2**. Modelling studies have been carried out using the following software: SPARTAN'06 for Windows and Linux. Wave function, Inc. 18401 Von Karman Avenue, suite 370. Irvine, CA 92612, USA.

CCDC 817351 and CCDC 815128 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* charge *via* www.ccdc.cam.ac.uk/conts/retrieving.htcm-3 (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of 6-(2-Hydroxyethyl) Pyridine-2-Carbonitrile

m-CPBA (9.98 g; 44.53 mmol) was added to a chloroform (60 mL) solution of 2-(hydroxyethyl)pyridine (4.2 mL; 37.28 mmol) at 0 ºC during 30 min. The suspension was warmed to room temperature and stirred for 24 h. Residual m-CPBA was destroyed by the addition of paraformaldehyde (0.78 g; 26 mmol). After being stirred for 2 h, ammonia was bubbled through the reaction mixture for 10 min. The thick suspension which formed was dried with Na_2SO_4 and filtered. The filtrate was concentrated to dryness to yield a residue which was washed with CH_2Cl_2 (250 mL). Evaporation of the solvent gave 4.60 g (31.70 mmol, 85 % yield) of 2-(hydroxyethyl)pyridine-N-oxide.

To a solution of this N-oxide (0.47 g, 3.36 mmol) in CH_2Cl_2 (50 mL), N,N-dimethylcarbamoyl chloride (0.36 mL, 3.36 mmol) was drop wise added; after 2.5 h, trimethylsilyl cyanide (0.54 mL, 4.03 mmol) was also added. The mixture was stirred overnight at room temperature followed by 8 h at reflux and then cooled at room temperature; 1 equiv each of N,N-dimethylcarbamoyl chloride and trimethylsilyl cyanide were again added. After an additional night of stirring at reflux, the reaction was quenched by addition of a saturated aqueous solution of Na_2CO_3 (25 mL). Both phases were separated, the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic extracts were dried over Na_2SO_4. Evaporation under reduced pressure gave a brown-red oil which was purified by flash chromatography on silica gel (15x4 cm column, ethyl acetate:hexane = 1:1, followed by ethyl acetate) to give 6-(2-hydroxyethyl) pyridine-2-carbonitrile as a white product (0.25 g, 1.60 mmol, 50 %).

Synthesis of 2-(6-(4,5-Dihydro-4-Isopropyloxazol-2-Yl)Pyridin-2-Yl)Ethanol (I)

6-(2-Hydroxyethyl)pyridine-2-carbonitrile (250 mg, 1.69 mmol) was mixed with (*R*)-2-amino-3-methyl-1-butanol (262 mg; 2.54 mmol) and a pinch of $CuCl_2$ under dry condi-

Table 2. Crystal Data and Structure Refinement for Complexes 1 **and** 3

	Complex 1	**Complex 3**
Empirical formula	$C_{13}H_{17}ClMoN_2O_4$	$C_{10}H_{12}Cl_2MoN_2O_4$
Formula weight	396.68	391.06
T (K)	180(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Orthorombic, P 21 21 21	Monoclinic, P 21
a (Å)	8.3931(18)	8.4049(2)
b (Å)	9.447(2)	18.4313(4)
c (Å)	20.148(5)	9.3117(2)
a (°)	90	90
b (°)	90	101.8820(10)
g (°)	90	90
Volume ($Å^3$)	1597.6(6)	1411.6(5)
Z, Calculated density (Mg/m^3)	4, 1.649	4, 1.840
Absorption coefficient (mm^{-1})	1.003	1.317
F(000)	800	776
Crystal size (mm)	0.34 x 0.10 x 0.06	0.60 x 0.40 x 0.08
θ range for data collection (°)	5.19 to 26.35	2.21 to 30.30
Limiting indices	-10<=h<=10, -11<=k<=11, -25<=l<=25	-11<=h<=11, --26<=k<=26, --13<=l<=13
Reflections collected / unique	8108 / 3181 [R(int) = 0.0262]	26678 / 8259 [R(int) = 0.0268]
Completeness to theta	26.35 (98.8%)	30.30 (99.7%)
Max. and min. transmission	0.9423 and 0.7266	0.9020 and 0.5054
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/Restraints/Parameters	3181/0/192	8259/172/397
Goodness-of-fit on F^2	1.068	1.012
Final R indices [I>2s(I)]	R1 = 0.0231, wR2 = 0.0483	R1 = 0.0275, wR2 = 0.0669
R indices (all data)	R1 = 0.0250, wR2 = 0.0488	R1 = 0.0299, wR2 = 0.0685
Largest diff. peak and hole (e $Å^3$)	0.644 and – 0.422	0.603 and – 0.573

tions. The neat reaction mixture was stirred at 100 ºC at reduced pressure for 20 h. Sublimed amino alcohol occasionally had to be scraped down into the reaction mixture from vessel walls. After 20 h, CH_2Cl_2 (40 mL) was added to the reaction mixture and the solution was filtered. The filtrate was washed with water (15 mL x 3 times), the organic layer was dried with Na_2SO_4, and all volatiles were evaporated under vacuum to yield **1** as a brown oil (376 mg, 1.60 mg, 94 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 0.93 (3H, d, 6.7 Hz), 1.04 (3H, d, 6.7 Hz), 1.88 (1H, m), 3.08 (H_2, t, 5.6 Hz) 4.08 (2H, t, 5.6 Hz), 4.14 (1H m), 4.19 (2H, pq), 4.47, 4.50 (2H, dd, 9.01 Hz; 9.01 Hz), 7.28 (1H, d, 7.91 Hz), 7.70 (1H, pt), 7.94 (1H, d, 7.7 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 18.5 (CH_3), 19.4 (CH_3), 33.1 (CH), 39.6 (CH_2), 62.1.9 (O-CH_2), 71.9 (O-CH_2), 73.2 (N-CH), 125.6 (CH), 137.4 (CH), 122.1 (CH), 146.9 (C), 160.8 (C=N), 162.9 (C); $[\alpha]_D^{24}$ = - 50.0 (C = 0.3; $CHCl_3$). MS (ESI): m/z = 193 (M^+). HRMS (CI, CH_4) found m/z: 235.1445; $C_{13}H_{18}N_2O_2$+H requires: 235.1447.

Synthesis of 2-pyridinecarboxamido-tetrahydrofurane (II)

In a 250 cm^3 three-necked flask are introduced successively (2S)-2-Amino-1,4-butanediol (1.6 g; 15.4 mol), 2-cyanopyridine (2.03 g; 19.5 mmol), and 0.318 g of potassium carbonate, followed by a solution of 10 cm^3 glycerol in

18 cm^3 of dry ethylene glycol. The resulting mixture was brought to 105 °C under nitrogen for 24 h. The reaction solution was extracted with CH_2Cl_2 (3 x 15 mL), washed with water (3 x 10 cm^3) and dried with Na_2SO_4. The solid was then purified by flash chromatography (AcOEt/MeOH/NEt_3, 100:2:0.5). Yield: 0.70 g (23.0%) of a yellow oild. $[\alpha]_D^{24}$ = + 150. ^{1}H NMR (400MHz, CD_2Cl_2): δ=1.99 (m, 1H, C*H*$_2$), 2.31 (m, 1H, C*H*$_2$), 3.80 (m, 1H, C*H*$_2$), 3.87 (m, 1H, C*H*$_2$), 3.98 (m, 2H, C*H*$_2$), 4.73 (m, 1H, NC*H*), 7.43 (m, 1H, C*H*), 7.84 (m, 1H, C*H*), 8.19 (m, 1H, C*H*), 8.54 (m, 1H, C*H*). ^{13}C NMR (100MHz, CD_2Cl_2): δ = 33.3 (*C*H$_2$), 50.2 (*C*H), 67.2 (*C*H$_2$), 73.5 (*C*H$_2$), 122.3 (*C*H), 126.4 (*C*H), 137.4 (*C*H), 149.7 (*C*H), 149.6 (*C*),164.1 (*C*=O), MS (ESI): m/z = 193 $[M]^+$.

Synthesis of [$MoO_2Cl(\kappa^3$-*N,N,O*-I)] (1)

A solution of **I** (381 mg, 1.63 mmol) in THF (30 mL) was transferred, via canula, to a colorless solution of MoO_2Cl_2(DME) (486 mg, 1.68 mmol) in THF previously cooled to -78 ºC. The mixture was stirred for 15 min followed by warming to room temperature, and addition of triethylamine (0.23 mL, 1.63 mmol). After being stirred for 16 h at room temperature, the mixture was filtered and the filtrate was concentrated to dryness. The remaining solid was purified by flash chromatography (CH_2Cl_2/ethyl acetate) to yield compound **1** (226 mg, 35%) as a yellow crystalline solid. $C_{13}H_{17}ClN_2O_4Mo$ (398): calcd. C 39.36, H 4.32, N 7.06; found C 39.24, H 4.65, N 6.50. [α]20D (c, solvent). ^{1}H NMR (400MHz, CD_2Cl_2): δ=0.94 (d, 6.8 Hz, 3H, C*H*$_{3isop}$), 0.98 (d, 7.1 Hz, 3H, C*H*$_{3isop}$), 2.67 (m, 1H, C*H*$_{isop}$), 3.50 (m, 2H, C*H*$_2$-py), 4.65 (m, 1H, OC*H*$_{2oxazoline}$), 4.75 (st, 8.5 Hz, 2H, OC*H*$_{2oxazoline}$), 4.90 (m, 1H, NC*H*$_{oxazoline}$), 5.14 (m, 2H, OC*H*$_2$CH$_2$-py), 7.67 (d, 7.91 Hz, 1H, *py*), 7.90 (d, 7.50 Hz, 1H, *py*), 8.07 (pt, 1H, *py*); ^{13}C NMR (100MHz, CD_2Cl_2): δ = 166.7 (*C*$_{py}$-CH_2CH_2O), 159.2 (N*C*HO$_{oxazoline}$), 140.1 (*C*py), 139.8 (*C*H$_{py}$), 130.1 (*C*H$_{py}$), 123.7 (*C*H$_{py}$ H), 75.0 (NCH*C*H$_2$O$_{oxazoline}$), 73.1 (O*C*H$_2$CH$_2$), 70.2 (N*C*H) 38.0 (OCH$_2$*C*H$_2$), 28.8 (*C*H(CH$_3$)$_{2isop}$), 18.3 (CH(*C*H$_3$)$_{2isop}$), 14.3 (CH(*C*H$_3$)$_{2isop}$). ^{95}Mo NMR (26.08 MHz, CD_2Cl_2): δ= +67.5. MS (EI) m/z (%) = 365 $[M-Cl]^+$. IR (KBr): ν= 938 (vs), 911 (vs) [ν(Mo=O)] cm^{-1}.

Synthesis of [$MoO_2(\kappa^3$-*N,N,O*-I)]$_2$(μ-O) (2)

Treatment of complex **1** with wet $CDCl_3$ for 15 min afforded complex **2**, which was isolated as a crystalline yellow solid in quantitative yield after removing the solvent under vaccum. $C_{27}H_{37}ClN_4O_9Mo_2$ (753.48): calcd. C 42.29, H 4.64, N 7.59; found C 42.28, H 5.08, N 7.63. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.01 (6H, pd, 4.2 Hz, C*H*$_{3isop}$), 2.94 (1H, m, C*H*$_{isop}$), 3.59 (2H, m, C*H*$_2$-py), 4.79 (2H, st, 8.5 Hz,OC*H*$_2$ CH$_2$-py), 4.93 (1H, m NC*H*$_{oxazoline}$), 4.98 (1H, m OC*H*$_{2oxazoline}$), 5.20 (1H, m, OC*H*$_{2oxazoline}$), 7.66 (1H, d, 7.91 Hz, *py*), 7.88 (1H, d, 7.68 Hz, *py*), 8.07 (1H, pt, *py*).IR (KBr): 1592 [C=N], 938 (vs), 911 (vs) [ν(Mo=O)], 805 (vs) [ν(Mo-O-Mo)] cm^{-1}.

Synthesis of [$MoO_2Cl_2(\kappa^2$-*N,O*-II)] (3)

To a THF solution (10 mL) of MoO_2Cl_2 (181 mg,0.911 mmol) at -78 ºC was added the oxazolinyl-pyridine ligand **II** (203 mg, 1.06 mmol) in THF (5 mL). After 2 h under stirring at room temperature, the solvent was removed under reduced pressure. The remaining solid was washed with ether (3 x 10 mL). Recrystallization from CH_3CN/ether (1/4) afforded light orange solid of the title compound. Yield: 291 mg (90 %). $C_{10}H_{12}Cl_2N_2O_4Mo$ (391.06). MS (ESI) m/z 390 $[M-Cl+CH_3OH+H]^+$. IR (KBr): υ = 1626 (st) [C=O], 950 and 914 (vs) [ν(Mo=O)] cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 2.15 (m, 1H, C*H*$_2$), 2.43 (m, 1H, C*H*$_2$), 3.81 (dd, J = 14.0, 8.5 Hz, 1H, C*H*$_2$), 4.07 – 3.80 (m, 3H, C*H*$_2$), 4.86 (m, 1H, C*H*), 7.98 (pt, J = 6.1, 1H, C*H*), 8.41 – 8.35 (m, 2H, C*H*), 8.91 (s, 1H N*H*), 9.42 (pd, J = 5.2 Hz, 1H, *py*), ^{13}C NMR (100 MHz; CH_3CN): δ = 33.3 (*C*H$_2$) 55.3 (*C*H), 68.2 (CH_2), 73.3 (*C*H$_2$), 126.2 (*C*H), 131.7 (*C*H), 143.2 (*C*H), 145.4 (*C*H$_2$CO), 152.5 (*C*), 168.0 (C=O) ppm. ^{95}Mo NMR (26.08 MHz, CD_3CN): δ= +189.7.

Synthesis of [$MoO_2Cl_2(\kappa^2$-*N,N*-III)] (4)

A solution of **III** (304 mg, 1.15 mmol) in THF (mL) was added to a solution of MoO_2Cl_2 (228 mg, 1.14mmol) in THF (15 mL) at -78 °C. The reaction mixture was allowed to warm up to room temperature and was stirred for 2 h. All volatiles were removed under vacuum to yield **4** (340 mg, 70 %) as an orange solid which was washed with diethy ether. $C_{14}H_{20}ClN_3O_4Mo$ (425.72): calcd. C 39.50, H 4.74, N 9.87; found C 39.70, H 4.56, N 9.73. ^{1}H NMR (400MHz, CD_3CN) δ=0.92 (st, 8.1 12H, C*H*$_3$), 1.96 (m, 2H, C*H*), 4.18 (sq, 8.7, 14.9, Hz, 2H, C*H*), 4.66 (pt, 6.6 Hz, 2H, C*H*$_2$) ,4.86 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, CH_2Cl_2): δ = 18.1 (CH_3), 30.0 (CH), 32.5 (CH), 47.7 (C=C), 62.2 (CH_2), 72.6 (CH_2), 118.0 (C≡N), 161.0 (C=C), 171.5 (C=N). IR (KBr) = 1601 [C=N], 957 and 918 [ν(Mo=O)] cm^{-1}. MS (EI) m/z (%) = 462 $[M+Cl]^-$.

General Procedure for Epoxidation Experiments

The catalytic reactions were performed in a reaction vessel equipped with a magnetic stirrer and immersed in an oil bath at the appropriate temperature. A catalyst:olefin: oxidant 1:100:200 was used, with 2 mL of solvent ($CHCl_3$ when the reaction was performed using TBHP and EtOH for H_2O_2. Olefin, appropriate solvent, mesitylene (as internal standard), and the catalyst were placed into the reaction vessel, and the oxidant (TBHP or H_2O_2) was added to the mixture. The course of the reaction was monitored by quantitative GC analysis. Samples taken were diluted with CH_2Cl_2 and treated with Na_2SO_4 and MnO_2 to remove water and destroy the excess of peroxide. The resulting slurry was filtered, and the filtrate was injected into a GC column. The conversion of the olefin and the formation of the corresponding epoxide were calculated from calibration curves (r2 = 0.999) recorded prior to the reaction.

CONCLUSION

In conclusion, we have synthesized and fully characterized novel dioxomolybdenum(VI) complexes bearing chiral ligands. The first X-ray characterization of a monometallic molybdenum complex bearing a *N,N',O*-tridentated ligand is described. The catalytic application of these new complexes in olefin epoxidation showed their efficiency in the epoxidation of cyclooctene, limonene and methylstyrene achieving

high conversions and selectivity, although no enantioselectivity was obtained.

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from Fundação para a Ciência e a Tecnologia (FCT) of Portugal through project PTDC/QUI-QUI/098682/2008, CNRS, Université Paul Sabatier and Ministerio de Ciencia e Innovación (CTQ2010-15292). J. A. Brito thanks FCT for grant SFRH/BD/30917/2006. The National NMR Network (REDE/1517/RMN/2005) was supported by POCI 2010 and Fundação para a Ciência e a Tecnologia. We thank REDE71504/REM/2005, M. C. Almeida and Dr. A. Coelho for providing data from the Elemental Analyses and Mass Spectrometry Services at ITQB. We are grateful to Marc Vedrenne for his valuable support in relation to ^{95}Mo NMR spectra.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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Received: March 28, 2011 Revised: May 9, 2011 Accepted: May 15, 2011