Dioxomolybdenum(VI) complexes containing chiral oxazolines applied in alkenes epoxidation in ionic liquids: A highly diastereoselective catalyst

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ABSTRACT

New monometallic dioxomolybdenum complexes, **2** and **3**, containing the bis(oxazoline) **B** and the oxazolinyl-pyridine **C** respectively, have been prepared and fully characterized both in solution and solid state, including the single-crystal X-ray diffraction analysis for **2**, which represents the first structure of a Mo(VI) complex coordinated to a bis(oxazoline). These complexes, together with the bimetallic system **1**, were used as catalytic precursors for alkenes epoxidation (cyclooctene, (R)-limonene, trans-β-methylstyrene) in imidazolium- and pyrrolidinium-based ionic liquids, exhibiting a high chemoselectivity towards the epoxide formation, mainly for cyclooctene and (R)-limonene epoxidation, without formation of the corresponding diols. In [BMP][NTf$_2$] (BMP = butyl methyl pyrrolidinium; NTf$_2$ = bis(trifluoromethanesulfonyl)amide), complex **1** exclusively gave trans(R)-limonene 1,2-epoxide, while monometallic catalytic systems led to a low diastereoselectivity. ^{95}Mo NMR studies helped to understand the catalytic behaviour of **1** and **2** in ionic liquid medium.

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1. Introduction

Epoxides represent useful intermediates for the synthesis of fine chemicals including drugs and fragrances [1]. High-valent oxo-metal complexes have found applications as efficient catalysts for oxidation processes under homogeneous as well as heterogeneous conditions [2]. In particular, molybdenum systems are commercially applied to the production of propylene oxide using alkyl hydroperoxides as oxidants [3]. With the aim to overcome the metal leaching using homogeneous catalysts, several methodologies have been developed in order to immobilize the catalyst and reuse the catalyst without loss of catalytic efficiency. One of these approaches consists in the use of biphasic systems to preserve the homogeneous advantages of the catalysts [4]. Ionic liquids (ILs), solvents exhibiting negligible vapour pressure, thermal stability and high polarity, being their physico-chemical properties easily tuneable depending on the nature of the ions involved, turn into a convenient substitute to volatile organic solvents and a suitable medium to immobilize the catalyst [5]. These features confer them a wide number of applications in organic synthesis, mainly in catalysis [6]. IL phase containing the active catalyst could be readily reused without significant loss of catalytic activity [7], fact particularly interesting for asymmetric catalysis, due to the high added

value of the chiral catalysts [8]. The pioneering work in this field was published by Chauvin and co-workers in 1995, concerning the use of N,N′-dialkylimidazolium salts in biphasic catalysis for Rh-catalysed olefin hydroformylation, isomerisation and asymmetric hydrogenation, demonstrating the feasibility to recover the catalyst [9]. However, the first works using neat ILs appeared later, in 2000, when Song's team reported that N,N′-dialkylimidazolium derivatives could be appropriated solvents to perform enantioselective alkene epoxidations [10] and ring opening of epoxides [11]. Although many applications in metal-catalysed organic transformations have been reported in the last two decades as stated by the literature mentioned above, few reports have been published concerning the olefin epoxidation catalysed by oxomolybdenum complexes in ionic liquid medium, being imidazolium-based ionic liquids (Im-ILs) the solvents of choice for the most studies. The first article was published in 2004 by Valente and co-workers where cyclooctene epoxide was obtained in several imidazolium-based ionic liquids using dioxomolybdenum(VI) complexes as catalytic precursors, getting a better catalyst recycling for that containing a tridentated amine [12]. Kühn et al. evaluated the catalytic behaviour of cyclopentadienyl-molybdenum complexes for cyclooctene epoxidation in Im-ILs, demonstrating the importance of the anion nature in the subsequent ring opening giving the corresponding diol [13]. The catalytic activity could be improved and the selectivity tuned using cyclopentadienyl ansa-bridged molybdenum complexes in the appropriate Im-IL [14]. Under microwave-assisted heating in [BMI][BF$_4$], cyclopentadienyl molybdenum

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complexes led to the exclusive formation of olefin epoxide [15]. Montilla et al. have recently studied olefins epoxidation catalysed by oxodiperoxo- and dioxoperoxo-molybdenum(VI) complexes in Im-ILs using urea-epoxide and hydrogen peroxide as oxidants [16]. Oxodiperoxomolybdenum(VI) complexes have also become active in the epoxidation of oleate derivatives using hydrogen peroxide as oxidant in Im-ILs, being reused up to five consecutive runs with slight loss of activity [17]. With the aim to improve the immobilization of the catalyst in the ionic liquid phase, Poli and co-workers have used Mo(VI) complexes containing Schiff base ligands tagged with sulfonated groups, but after the third recycling the activity considerably decreases [18]. Different molybdenum precursors have been recently applied in olefins epoxidation using Im-ILs and 1-butyl-4-methylpyridinium tetrafluoroborate, without observing remarkable differences between both kind of ILs [19]. To the best of our knowledge, only heterogenized oxomolybdenum complexes onto supports such as mesoporous silicates [20] have led to reasonable recycling although somewhat activity loss is observed comparing with the corresponding homogenous systems [21]. Concerning enantioselective epoxidation in ILs, only two contributions have been reported up to now (involving Im-ILs and pyridinium derivatives), using a dioxomolybdenum(VI) complex containing a chiral tetradentate bisoxazoline ligand [22] and an amino acid-pendant arm-cyclopentadienylmolybdenum(II) complex [23]; asymmetric induction could not be achieved in any case.

Based on our previous experience with oxomolybdenum complexes containing oxazoline ligands in epoxidation of olefins in organic solvents [24,25], we planned to study this kind of complexes in olefin epoxidation reactions in ionic liquid medium. Bimetallic complex **1** (Fig. 1) was previously described by us as an efficient catalyst for cyclooctene epoxidation and what is more interesting, leading to an important diastereomeric induction for the epoxidation of (R)-limonene [25]. Besides this system containing a bidentated oxazolinyl-pyridine ligand (**A**) (Fig. 1), we have synthesized and fully characterized two new dioxomolybdenum complexes containing a bis(oxazoline) (**B**) and a tridentate oxazolinyl-pyridine (**C**) ligands, complexes **2** and **3**, respectively (Fig. 1). In addition to Im-ILs, we have used for the first time in these processes pyrrolidinium-based ILs as solvents in order to study the influence of the nature of the ionic liquid in the catalytic process.

2. Experimental

2.1. General

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. The ionic liquids [BMI][PF$_6$] 99.5%, [BMI][NTf$_2$] 99% and [BMP][NTf$_2$] 99% were purchased from Solvionic and heated at 70 °C under vacuum overnight before use. Tert-butylhydroperoxide (TBHP) was purchased from Aldrich as ca. 5.5 M solution in n-decane over molecular sieves. [MoO$_2$Cl$_2$], cyclooctene and trans-stylbene were purchased from Aldrich; (R)-limonene from Sigma–Aldrich and trans-β-methylstyrene from Acros Organic. H$_2$O$_2$ (aq) (30%) was purchased from VWR Prolabo. Ligands **A** [26], **B** [27] and complex **1** [25a] were obtained following the procedure previously described. ^{1}H, ^{13}C{^{1}H} and ^{95}Mo NMR spectra were recorded on Bruker Avance 300 and Bruker Avance 400 at 293 K. Chemical shifts were reported downfield from standards. IR spectra were carried out on pellets of dispersed samples of the corresponding compounds in KBr and were obtained on an IR Varian 640-IR FTIR spectrometer. GC routine analyses were carried out using a Perkin Elmer Clarus 500 gas chromatograph (25 m × 0.32 mm methyl siloxane with 5% de phe-

nyl siloxane (BPX5) column) with a FID detector and Perkin Elmer Clarus 5605 mass spectrometer.

2.2. Synthesis of 2-(6-(4,5-dihydro-4-isopropyloxazol-2-yl)pyridin-2-yl)ethanol, **C**

m-CPBA (13.55 g, 70%, 55.0 mmol) was added to 2-(hydroxyethyl)pyridine (5.64 g, 45.8 mmol) in chloroform (150 mL) at 0 °C and stirred for 30 min. The suspension was then warmed at room temperature and stirred for 24 h. Residual m-CPBA was destroyed by the addition of paraformaldehyde (2.0 g, 66.6 mmol CH$_2$O). After stirring for 2 h, ammonia was bubbled through the reaction mixture for 10 min. The suspension was then dried with Na$_2$SO$_4$, filtered and the cake washed with dichloromethane (250 mL). Evaporation of the solvent gave 5.42 g (38.95 mmol, 85% yield) of 2-(hydroxyethyl)pyridine-N-oxide. To a solution of this N-oxide (0.47 g, 3.36 mmol) in CH$_2$Cl$_2$ (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$_2$CO$_3$ (25 mL). Both phases were separated, the aqueous layer was extracted with CH$_2$Cl$_2$ (2× 15 mL) and the combined organic extracts were dried over Na$_2$SO$_4$. Evaporation under reduced pressure gave a brown-red oil which was purified by flash chromatography on silica gel (15 cm × 4 cm column, ethyl acetate:hexane = 1:1, followed by ethyl acetate) to give the expected nitrile product like a white product (0.25 g, 1.60 mmol, 50%).

This nitrile (2.50 mg, 1.69 mmol) was mixed with (R)-2-amino-3-methylbutan-1-ol (2.62 mg, 2.54 mmol) and a pinch of CuCl$_2$ under dried conditions. The neat reaction mixture was stirred at 100 °C under reduced pressure overnight, and then dichloromethane (20 mL) was added and the organic phase was washed with water (3× 15 mL), dried (Na$_2$SO$_4$) and solvent eliminated under reduced pressure, to give the expected oxazoline **C** (3.76 mg, 1.60 mmol, 94%). [α]$_D^{24}$ = −50 (c 0.3, CHCl$_3$). HRMS (CI, CH$_4$) found m/z: 235.1445; C$_{13}$H$_{18}$N$_2$O$_2$ + H requires: 235.1447. IR(KBr): 1660 cm^{-1} (st, C=N); 3374 cm^{-1} (st, C–OH). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ: 0.93 (3H, d, 6.7 Hz), 1.04 (3H, d, J = 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$_2$Cl$_2$) 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).

2.3. Synthesis of [MoO$_2$Cl$_2$(κ^2-N,N-**B**)], **2**

The bis-oxazoline **B** (0.147 g, 1.15 mmol) dissolved in THF (5 mL) was added to a THF solution (15 mL) of [MoO$_2$Cl$_2$(DME)] [28] (0.100 g, 1.14 mmol) at −78 °C. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The solid obtained was successively washed with ether (3× 10 mL) and pentane (3× 10 mL). Recrystallization from CH$_3$CN afforded a light yellow solid. Yield: 0.130 g (60%). HRMS (ES) found m/z: 581.0885 [M−Cl]$^+$; C$_{25}$H$_{30}$ClMoN$_2$O$_6$ requires 581.0860. IR(KBr): 1655 cm^{-1} (st, C=N); 939 and 910 cm^{-1} (Mo=O) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ: 1.70 (s, 6H), 3.42 (s, 6H), 3.93 (dd, 2H, 10.24 and 3.05 Hz), 4.04 (dd, 2H, 10.29 and 4.61 Hz), 5.00 (m, 2H), 5.70 (d, 2H, 4.88 Hz), 7.41 (m, 10H) ppm. ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ: 24.2 (C–CH$_3$), 40.0 (C), 58.7 (O–CH$_3$), 72.2 (CH$_2$), 75.0 (N–CH), 83.9 (O–CH), 126.4
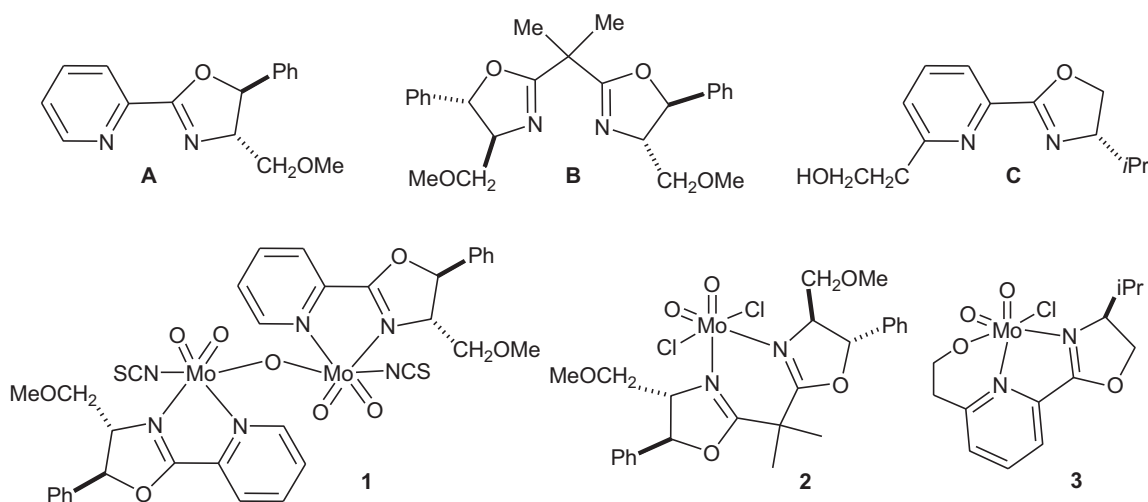
Fig. 1. Oxazoline-based ligands (A–C) and their corresponding dioxomolybdenum(VI) complexes (**1**–**3**).

(CH), 128.9 (CH), 129.3 (CH), 138.2 (C), 171.1 (C=N) ppm. ^{95}Mo NMR (26.08 MHz, CD$_2$Cl$_2$) δ: +136.6 ppm.

2.4. Synthesis of [MoO$_2$Cl(κ^3-N,N′,O-**C**)], **3**

To a pale brown solution of **C** (3.26 mg, 1.39 mmol) in THF (10 mL), triethylamine (0.19 mL, 1.39 mmol) was added and the mixture was stirred for 30 min. The resulting solution was then transferred to a colorless solution of [MoO$_2$Cl$_2$(DME)] [28] (3.84 mg, 1.33 mmol) in THF (20 mL) at −78 °C. After few minutes of the addition, the solution turned to violet with the formation of a precipitate. The mixture was kept stirring overnight at room temperature. The solution was then filtered, and then purified by a silica gel column with ethyl acetate as eluent. The solvent was then eliminated under reduced pressure to give a pale yellow solid. The solid obtained was successively washed with ether (3× 10 mL) and pentane (3× 10 mL). Recrystallization from CH$_3$CN afforded light yellow solid. Yield: 193 mg (35%). MS (ES) m/z 365 [M−Cl]$^+$. Anal. Calcd for C$_{13}$H$_{17}$ClMoN$_2$O$_4$: C, 39.36; H, 4.32; N, 7.06%. Found: C, 39.24; H, 4.65; N, 6.50%. IR(KBr): 1661 (C=N); 939 and 910 (Mo=O) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ: 0.94 (3H, d, 6.8 Hz), 0.98 (3H, d, 7.1 Hz), 2.67 (1H, m), 3.50 (2H, m), 4.65 (1H, m), 4.75 (2H, st, 8.5 Hz), 4.90 (1H, m), 5.14 (1H, m), 7.67 (1H, d, 7.91 Hz), 7.90 (1H, d, 7.50 Hz), 8.07 (1H, pt). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ: 14.3 (CH$_3$), 18.3 (CH$_3$), 28.8 (CH), 38.0 (CH$_2$), 70.2 (N−CH), 73.1 (O−CH$_2$), 75.0 (O−CH$_2$), 123.7 (CH), 130.1 (CH), 139.8 (CH), 140.1 (C), 159.2 (C=N), 166.7 (C). ^{95}Mo NMR (26.08 MHz, CD$_2$Cl$_2$) δ: +67.5 ppm.

2.5. Mo-catalysed olefin epoxidation in dichloromethane

The molybdenum catalytic precursor (0.025 mmol of Mo: 11.6 mg for **1**; 6.2 mg for **2**; 4.0 mg for **3**) was dissolved in 1 mL of dichloromethane. 1 mmol of olefin (110 mg for cyclooctene and 136 mg for (R)-limonene) was then added, followed by a ca. 5.5 M tert-butyl hydroperoxide aqueous solution (for **1**, 0.27 mL, 1.50 mmol; for **2** and **3**, 0.36 mL, 2.00 mmol). The mixture was then stirred for 22 h at 55 °C for cyclooctene epoxidation and at 30 °C for (R)-limonene. The catalytic mixture was then quenched by addition of MnO$_2$ and Na$_2$SO$_4$ in order to destroy peroxides and remove water, and filtered through celite. Analyses of organic products were performed by gas chromatography.

2.6. Mo-catalysed olefin epoxidation in ionic liquid

The molybdenum catalytic precursor (0.025 mmol of Mo: 11.6 mg for **1**; 0.01 mmol of Mo: 6.2 mg for **2**; 4.0 mg for **3**) was dissolved in 1 mL of ionic liquid ([BMI][PF$_6$], [BMI][NTf$_2$] or [BMP][NTf$_2$]) and CH$_2$Cl$_2$ (2.5 mL for [BMI][PF$_6$] and 1.5 mL for [BMI][NTf$_2$] and [BMP][NTf$_2$]). 1 mmol of olefin (110 mg for cyclooctene and 136 mg for (R)-limonene) was then added, followed by a ca. 5.5 M tert-butyl hydroperoxide aqueous solution (for **1**, 0.27 mL, 1.50 mmol; for **2** and **3**, 0.36 mL, 2.00 mmol). After reaction, several solvent extractions were performed with diethyl ether (14× 1 mL). 0.5 mL of the extracted sample was then quenched by addition of MnO$_2$ and Na$_2$SO$_4$ in order to destroy peroxides and remove water, and then diluted with diethyl ether (up to 1.5 mL). The resulting slurry was then filtered on celite and eluted with diethyl ether. Analyses of organic products were performed by gas chromatography.

2.7. Crystal structure determination

Yellow crystals of **2** obtained from an acetonitrile dissolution of the complex were selected and mounted at 180 K on a Bruker Kappa APEX II Quazar using a microfocus source with molybdenum radiation ($\lambda_{Mo\,K\alpha}$ = 0.71073 Å). Crystal data are summarized in Table 1. The structure was solved by direct methods [29] and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2 [30]. ORTEP view was generated from the corresponding software [31]. CCDC 800942 contains the supplementary crystallographic data for this paper. These data can be obtained free of 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).

3. Results and discussion

3.1. Ligands and their corresponding dioxomolybdenum(VI) complexes

Pyridino-oxazoline **A** [26] and bis(oxazoline) **B** [27] were prepared as previously described. 2,6-Difunctionalized pyridino-oxazoline **C** was obtained in a three-step sequence from commercially available 2-pyridine ethanol, which was first activated by oxidation of the pyridine moiety by treatment with m-CPBA (m-chloroperbenzoic acid). This intermediate was further modi-

Table 1
Crystal data and structure refinement for complex **2**.

	Complex **2**
Empirical formula	$C_{25}H_{30}Cl_2MoN_2O_6$
Formula weight	621.35
T (K)	180(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1$
a (Å)	11.8113(5)
b (Å)	14.5654(4)
c (Å)	16.3202(6)
α (°)	90
β (°)	105.570(2)
γ (°)	90
Volume (Å³)	2704.63(17)
Z, calculated density (Mg/m³)	4, 1.526
Absorption coefficient (mm⁻¹)	0.724
$F(000)$	1272
Crystal size (mm)	$0.16 \times 0.04 \times 0.04$
θ range for data collection (°)	5.19 to 26.37
Limiting indices	$-10 \le h \le 14, -18 \le k \le 17, -20 \le l \le 17$
Reflections collected/unique	17498/10545 [R(int) = 0.0241]
Completeness to theta	26.37 (98.8%)
Max. and min. transmission	0.9716 and 0.9600
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10545/1/657
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0294, wR2 = 0.0590
R indices (all data)	R1 = 0.0340, wR2 = 0.0612
Largest diff. peak and hole (eÅ³)	0.332 and −0.313

fied by cyanation reaction using trimethylsilyl cyanide to give 6-(2-hydroxyethyl)pyridine-2-carbonitrile in 50% yield. The nitrile derivative led to the formation of the oxazoline heterocycle in 90% yield, by condensation with L-valinol catalysed by copper dichloride (Scheme 1). Ligand **C** was obtained with a moderate overall yield (36%).

Bimetallic complex **1** was prepared as previously described by our group [25]. New mono-metallic dioxomolybdenum(VI) complexes containing chiral oxazoline-based ligands were prepared by treatment of [MoO₂Cl₂(DME)] (DME = dimethoxyethane) with the corresponding ligand in THF at room temperature (Scheme 2).

In the solid state, IR spectra of **2** and **3** exhibit a very strong band around 1650 cm⁻¹ due to the oxazoline imine bond (for **2**, 1655 cm⁻¹; for **3**, 1653 cm⁻¹) and two strong bands in 890–940 cm⁻¹ range corresponding to Mo=O stretching vibrations (for **2**, 910 and 939; for **3**, 895 and 933 cm⁻¹). Single crystals of **2** were obtained from acetonitrile solution (Fig. 2). This structure represents the first example reported in the literature for
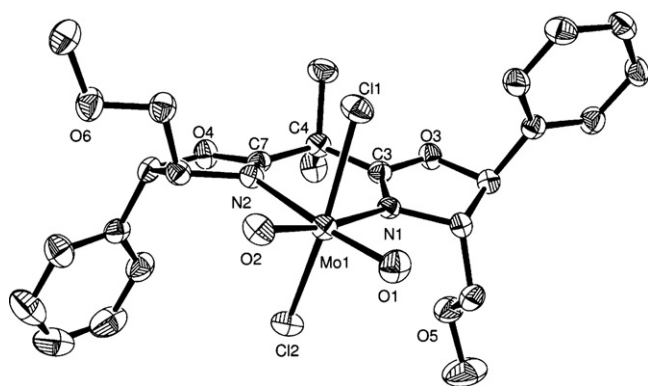
dioxomolybdenum(VI) complexes containing bis(oxazolines) [32]. A distorted octahedral arrangement around the metal atom is observed, with both chlorine atoms in a trans position. Nitrogen atoms are thus trans placed in relation to the oxo groups, leading to relatively long Mo–N bond distances (Mo–N1 = 2.326 Å and Mo–N2 = 2.309 Å), due to the oxo trans influence as previously observed for other oxomolybdenum(VI) complexes containing oxazoline ligands [24]. The six-membered metallacycle adopts a very flat conformation; the deviation of each atom from the equatorial plan constituted by the six atoms of the ring is really small (Mo1: 0.057 Å; N1: −0.13 Å; C3: 0.065 Å; C4: 0.10 Å; C7: −0.15 Å; N2: 0.056 Å). The angle between both heterocycle oxazoline rings is ca. 22°.
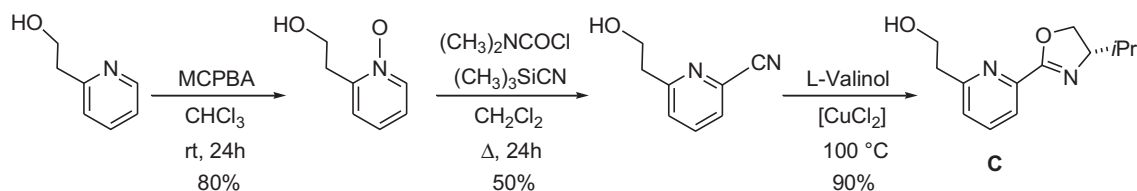
Concerning the structural characterisation in solution, ¹H NMR spectrum of **2** only exhibited one set of signals indicating a C₂ symmetry for the bidentated ligand upon coordination. The non-aromatic protons of the heterocycle are down-fielded in relation to the free ligand (see Fig. S2 in Supplementary Information), in particular the C–H close to the nitrogen atom ($\Delta\delta$ = +0.78 ppm); this deshielding can be attributed to the interaction of the proton with the oxo groups as shown by the average interatomic distance H⋯O=Mo from the crystallographic data (2.61 Å), in agreement with our previous observations for oxo- and peroxomolydenum(VI) complexes [24,25a]. ⁹⁵Mo NMR spectrum of **2** in solution showed one symmetric signal (width at middle height: 700 Hz) at +136.6 ppm (see Fig. S1 in Supplementary Information), pointing to the presence of only one isomer in solution in agreement with other related oxomolybdenum(VI) complexes containing bis(oxazoline) ligands [33]. Comparing with analogous structures containing bipyridine ligands, e.g. [MoO₂Br₂(4,4′-tBu-bipyridine)] [34] which shows a chemical shift at +243.3 ppm [35], the up-fielded shift observed for complex **2** indicates a lower electron-donor ability of the bis(oxazoline) than that exhibited by related bipyridine oxo-molybdenum(VI) complexes, which induces a lower electronic density around the metallic centre [35]. ⁹⁵Mo NMR spectrum of **3** containing the N,N′,O-tridentated anionic ligand **C** showed one sharp symmetrical peak (width at middle height: 358 Hz) at lower chemical shift (+67.5 ppm) (see Fig. S1 in Supplementary Information). Comparing the three dioxomolybdenum complexes containing oxazoline-based ligands (**1**, **2**, **3**), the most electron rich metal centre corresponds to complex **2** (+136.6 ppm), followed by **3** (+67.5 ppm), while complex **1** (−76.0 ppm) [25b] contains the molybdenum atom exhibiting the lowest electronic density.
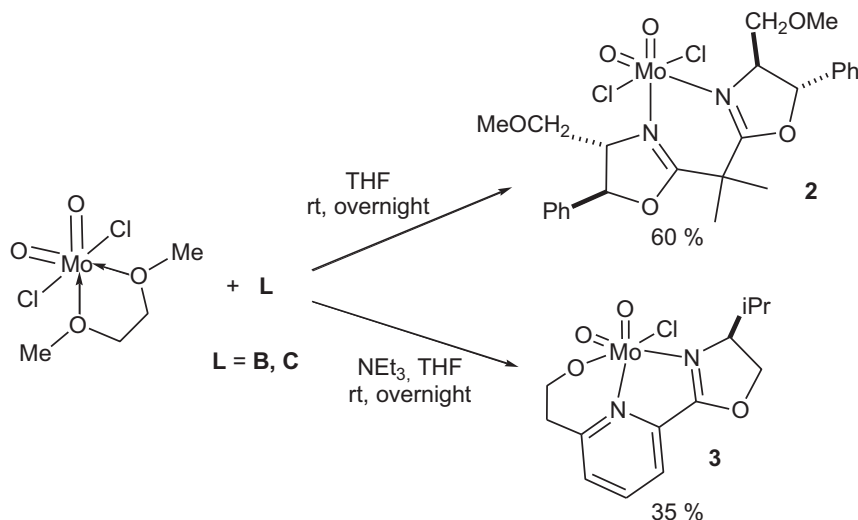
3.2. Catalytic epoxidation

In the present work, olefin epoxidations (cyclooctene, (R)-limonene and trans-β-methylstyrene) using tert-butylhydroperoxide in decane as oxidant, were carried out in the presence of room temperature ionic liquids, catalysed by preformed dioxomolybdenum complexes containing oxazoline-based ligands, **1**–**3** (Fig. 1); for comparative purposes, reactions in dichloromethane were also evaluated. Complexes and tBuOOH were soluble in all the solvents tested; olefins were immiscible in the three ionic liquids tested, [BMI][PF₆], [BMI][NTf₂] and [BMP][NTf₂] (BMI = 1-butyl-3-methyl-imidazolium; BMP = butyl methyl pyrrolidinium; NTf₂ = bis(trifluoromethanesulfonyl)amide).

Cyclooctene epoxidation was chosen as benchmark reaction in order to compare the activity of complex **1** in different media (Scheme 3). In all cases, the olefin was exclusively converted into cyclooctene epoxide without observing the formation of by-products (Table 2).

Under the same catalytic conditions, higher activity was observed in dichloromethane than in neat ionic liquids, [BMI][PF₆], [BMP][NTf₂] and [BMI][NTf₂] (entries 1–4, Table 2), probably due to

Fig. 2. ORTEP view of compound **2** with ellipsoids representing 50% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)–O(1) 1.686(2), Mo(1)–O(2) 1.695(2), Mo(1)–Cl(1) 2.383(1), Mo(1)–Cl(2) 2.368(1), Mo(1)–N(1) 2.326(2), Mo(1)–N(2) 2.309(2), N(1)–Mo(1)–N(2) 76.41(8), O(1)–Mo(1)–O(2) 105.35(11), Cl(1)–Mo(1)–Cl(2) 160.57(3).

Scheme 1. Synthesis of ligand **C** following a three-step synthetic strategy.

Scheme 2. Synthesis of mono-metallic complexes **2** and **3** containing bidentated oxazoline-based ligands, **B** and **C**, respectively.

phase transfer limitations because cyclooctene is immiscible with these ionic liquids. When the reaction was carried out in the presence of dichloromethane as co-solvent (addition of the necessary amount in order to get one single phase), the activity in IL/CH$_2$Cl$_2$ was slightly higher than that observed in dichloromethane (entries 1 vs 5, 7 and 9, Table 2). Comparing imidazolium-based IL containing two different anions, PF$_6$ and NTf$_2$, no remarkable differences were observed (entries 5 and 9, Table 2), in contrast to the benefit effect previously reported using [BMI][NTf$_2$] [13,36].

The reaction monitoring carried out during 6 h evidenced that the reaction did not progress after 2 h of reaction using imidazolium-based ILs (up to ca. 85% conversion), however, in the pyrrolidinium IL, the reaction smoothly advanced during the reaction time, pointing to a higher catalyst stability in [BMP][NTf$_2$] than in imidazolium-based ILs (Fig. 3). At lower temperatures and longer times, the catalytic system in [BMP][NTf$_2$]/CH$_2$Cl$_2$ was also active, giving 67% substrate conversion at 30 °C, achieving 80% conversion at 40 °C after 22 h (entries 11 and 12, Table 2). Hydrogen peroxide was used instead of tBuOOH, but unfortunately the system

was almost inactive (entry 13, Table 2). For the following studies, [BMP][NTf$_2$] was chosen as ionic liquid due to the higher catalyst stability and the lower amount of co-solvent required in comparison with imidazolium-based ILs.

The catalytic system **1** in [BMP][NTf$_2$] was recycled up to 3 times at 40 °C preserving its catalytic behaviour (Fig. 4). The same trend was observed when re-additions of olefin and oxidant were done; this fact clearly points to a catalyst deactivation with the recycling. In [BMI][PF$_6$], the catalyst could be reused up to 5 times without loss of activity working at 40 °C; but at higher temperature (55 °C), the recycling was not effective (activity loss after the first run), probably

Table 2
Cyclooctene epoxidation catalysed by bimetallic dioxomolybdenum complex **1** in different solvents[a].

| Entry	Solvent	Co-solvent	T (°C)	Oxidant	Conv. (%)[b]
1	CH$_2$Cl$_2$	–	40	tBuOOH	78
2	[BMI][PF$_6$]	–	55	tBuOOH	42
3	[BMP][NTf$_2$]	–	55	tBuOOH	63
4	[BMI][NTf$_2$]	–	55	tBuOOH	72
5	[BMI][PF$_6$]	CH$_2$Cl$_2$[c]	55	tBuOOH	85
6	[BMI][PF$_6$]	CH$_2$Cl$_2$[c]	40	tBuOOH	68
7	[BMP][NTf$_2$]	CH$_2$Cl$_2$[d]	55	tBuOOH	90
8	[BMP][NTf$_2$]	CH$_2$Cl$_2$[d]	40	tBuOOH	68
9	[BMI][NTf$_2$]	CH$_2$Cl$_2$[d]	55	tBuOOH	87
10[e]	[BMI][NTf$_2$]	CH$_2$Cl$_2$[d]	30	tBuOOH	74
11[e]	[BMP][NTf$_2$]	CH$_2$Cl$_2$[d]	30	tBuOOH	67
12[e]	[BMP][NTf$_2$]	CH$_2$Cl$_2$[d]	40	tBuOOH	80
13[e]	[BMP][NTf$_2$]	CH$_2$Cl$_2$[d]	30	H$_2$O$_2$	4

[a] Results obtained from duplicated tests. Reaction conditions: 1 mmol cyclooctene, 1.5 mmol tBuOOH in decane (ca. 5.5 M) and 0.025 mmol Mo for 4 h in 1 mL of solvent.
[b] Determined by GC; only cyclooctene epoxide was formed.
[c] 2.5 mL of dichloromethane.
[d] 1.5 mL of dichloromethane.
[e] Reaction for 22 h.
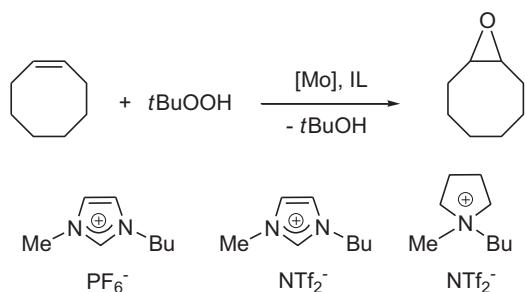
Scheme 3. Mo-catalysed cyclooctene epoxidation in different ionic liquids, [BMI][PF$_6$], [BMI][NTf$_2$] and [BMP][NTf$_2$].
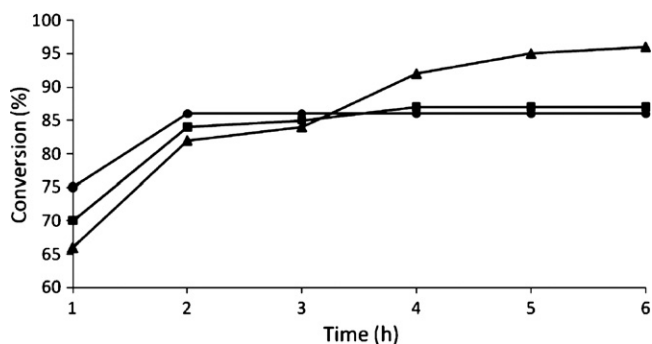
Fig. 3. Cyclooctene epoxidation monitoring using the catalyst **1** in [BMI][PF$_6$]/CH$_2$Cl$_2$ (●), [BMI][NTf$_2$]/CH$_2$Cl$_2$ (■) and [BMP][NTf$_2$]/CH$_2$Cl$_2$ (▲); conversions based on the substrate.

Fig. 5. Cyclooctene epoxidation monitoring using complexes **1** (●), **2** (■) and **3** (▲) as catalysts in [BMP][NTf$_2$]/CH$_2$Cl$_2$; conversions based on the substrate.

due to the lower activity of NHC–molybdenum species formed in the imidazolium-based ionic liquid (see below).

Mono-metallic complexes containing the neutral bis(oxazoline) ligand **B**, [MoO$_2$Cl$_2$(κ^2-N,N-**B**)] (**2**), and the anionic tridentate oxazolinyl-pyridine ligand **C**, [MoO$_2$Cl(κ^3-N,N′,O-**C**)] (**3**), were also tested in cyclooctene epoxidation using [BMP][NTf$_2$] as ionic liquid. These catalytic systems exhibited higher activity than that observed using **1** (entries 2–3 vs 1, Table 3), obtaining nearly full substrate conversion for catalyst **2** after 1 h of reaction (entry 2, Table 3). The activity observed in dichloromethane for **2** and **3** (entries 4 and 5, Table 3) was somewhat higher than that in [BMP][NTf$_2$]/CH$_2$Cl$_2$, as stated for complex **1** (see above). When the molybdenum precursor used for the synthesis of **2** and **3**, [MoO$_2$Cl$_2$(DME)], was used as catalyst, full substrate conversion was obtained after 1 h of reaction, giving 15% of alcohol (entry 6, Table 3). The presence of oxazoline-based ligands in the catalyst avoids the epoxide aperture. Effectively, [MoO$_2$Cl$_2$(DME)] in the absence of oxazoline ligand gave formation of the corresponding diol even at short times of reaction (after 10 min of reaction, 7% of the diol was observed), showing a lower chemoselectivity than that exhibited by complexes **1–3** which exclusively gave the epoxide.

The cyclooctene epoxidation was monitored during 1 h of reaction for the three catalysts, **1–3** (Fig. 5). During the first 30 min, complexes **1** and **3** showed a similar catalytic activity (after 10 min of reaction: TOF for **1**, 82 h^{-1}; for **3**, 74 h^{-1}), while catalyst **2** was clearly less active (TOF for **2**, 12 h^{-1}). However, the activity of **2** increased faster at longer times (after 1 h, 98% conversion) than that observed for the other two systems, in particular for **1**. It is important to note that the catalytic system **2** preserved its activity after the recharge of olefin and oxidant after 1 h of reaction (90% conversion without formation of by-products).
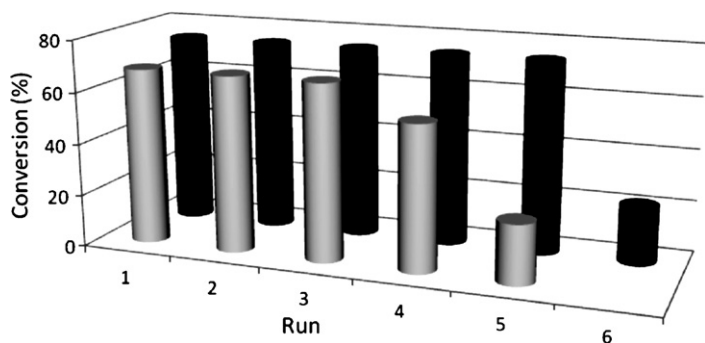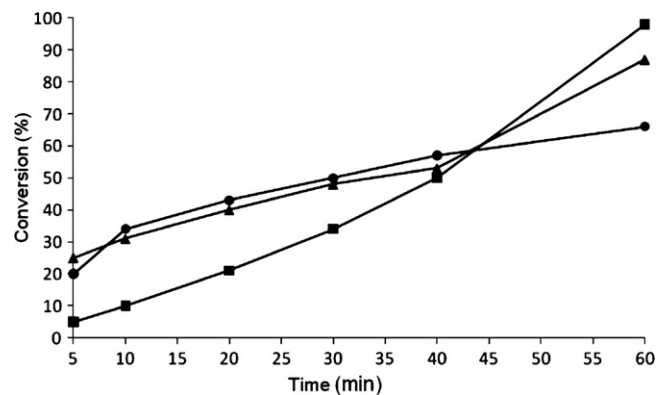

Fig. 4. Recycling experiments using complex **1** as catalyst in [BMP][NTf$_2$]/CH$_2$Cl$_2$ (grey) and [BMI][PF$_6$]/CH$_2$Cl$_2$ (black). For reaction conditions, see entries 8 (grey) and 6 (black) of Table 1.

(R)-limonene and trans-β-methylstyrene epoxidations were chosen to evaluate the diastereo- and enantio-selectivity induced by the dioxomolybdenum(VI) complexes **1–3**, which contain optically pure ligands.

Concerning (R)-limonene epoxidation (Scheme 4), complex **1** led to the formation of the corresponding 1,2-epoxide with 42% conversion in [BMP][NTf$_2$] at 30 °C for 22 h (entry 2, Table 4). This activity is lower than that observed in dichloromethane (entry 2 vs 1, Table 4). However, the diastereoselectivity is remarkably higher in [BMP][NTf$_2$] than in the organic solvent, obtaining exclusively the trans isomer in IL. Increasing the catalyst load (olefin/Mo = 20), the activity remained practically invariable, but the formation of the diol clearly increased (entry 3, Table 4). This behaviour can be associated to the increase of the rate for the epoxide ring-opening in the presence of higher amount of catalyst. In [BMI][PF$_6$], the activity was similar to that obtained in dichloromethane, but with a low diastereoselectivity induction (entry 4, Table 4). However, in [BMI][NTf$_2$] the activity and diastereoselectivity are similar to those found in the pyrrolidinium-based ionic liquid (entry 5 vs 1, Table 4), but the chemoselectivity is lower (ca. epoxide:diol ratio = 1:1). This fact points to a higher rate of the epoxide ring-opening for the cis isomer than for the trans one.

Mono-metallic complexes **2** and **3** were highly active, giving more than 80% olefin conversion, but with a very low diastereoselectivity (entries 6 and 7, Table 4); at shorter times, no changes in the selectivity were observed. The addition of free ligand in the catalytic mixture for the system containing complex **2**, did not lead to a selectivity improvement, giving an activity decrease (entry 8 vs 6, Table 4). This behaviour points to a coordination competition between the olefin and/or oxidant and ligand towards the metal; partial or total ligand dissociation during the epoxidation in the absence of ligand excess could not be observed by the NMR monitoring (see below).

In relation to the chemoselectivity, mono-metallic catalytic systems only gave the 1,2-epoxide, in contrast to the bimetallic system **1** which also led to alcohol formation even if in low yield (up to 6%, entries 2 and 4, Table 4). It is important to note that alcohol formation is more favoured in dichloromethane than in ionic liquid
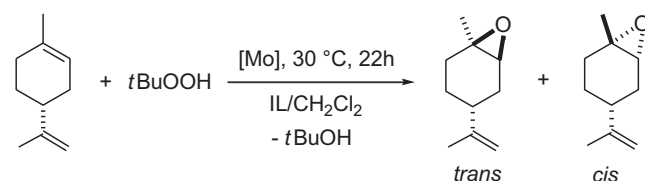
Scheme 4. Mo-catalysed (R)-limonene epoxidation in IL using dichloromethane as co-solvent.

Table 3

Cyclooctene epoxidation catalyzed by dioxomolybdenum complexes **1**–**3**[a].

Entry	Catalyst	Solvent	Conv. (%)[b]	Epoxide yield[b,c]
1	**1**	[BMP][NTf$_2$]/CH$_2$Cl$_2$	81	81 (0)
2	**2**	[BMP][NTf$_2$]/CH$_2$Cl$_2$	98	98 (0)
3	**3**	[BMP][NTf$_2$]/CH$_2$Cl$_2$	87	87 (0)
4	**2**	CH$_2$Cl$_2$	100	100 (0)
5	**3**	CH$_2$Cl$_2$	94	94 (0)
6	[MoO$_2$Cl$_2$(DME)]	[BMP][NTf$_2$]/CH$_2$Cl$_2$	100	85 (15)

[a] Results obtained from duplicated tests. Reaction conditions: 1 mmol cyclooctene, 1.5 mmol tBuOOH in decane (ca. 5.5 M) and 0.025 mmol Mo in 1 mL of [BMP][NTf$_2$] and 1.5 mL of CH$_2$Cl$_2$, at 55 °C for 1 h.
[b] Determined by GC.
[c] In brackets, diol yield.

Table 4

(R)-limonene epoxidation catalysed by dioxomolybdenum complexes **1**–**3**[a].

Entry	Catalyst	Solvent	Conv. (%)[b]	Epoxide yield (%)[b,c]	Trans/cis ratio[b]
1	**1**	CH$_2$Cl$_2$	87	62 (18)[d]	80/20
2	**1**	[BMP][NTf$_2$][e]	42	38 (4)	100/0
3	**1**	[BMP][NTf$_2$][e]	37[f]	18 (19)	100/0
4	**1**	[BMI][PF$_6$][g]	64	58 (6)	54/46
5	**1**	[BMI][NTf$_2$][e]	44	24 (20)	100/0
6	**2**	[BMP][NTf$_2$][e]	89 (47)[h]	89 (0)	60/40(60/40)[h]
7	**3**	[BMP][NTf$_2$][e]	82 (57)[h]	82 (0)	60/40(60/40)[h]
8[i]	**2**	[BMP][NTf$_2$][e]	57	57 (0)	50/50

[a] Results obtained from duplicated tests. Reaction conditions: 1 mmol (R)-limonene, 1.5 mmol tBuOOH in decane (ca. 5.5 M) and 0.025 mmol Mo in 1 mL of solvent, at 30 °C for 22 h.
[b] Determined by GC.
[c] In brackets, diol yield.
[d] 18% diol and 7% double epoxide.
[e] 1 mL of [BMP][NTf$_2$] and 1.5 mL of CH$_2$Cl$_2$ at 30 °C for 22 h.
[f] 0.050 mmol Mo used.
[g] 1 mL of [BMI][PF$_6$] and 2.5 mL of CH$_2$Cl$_2$.
[h] In brackets, data at 3 h of reaction.
[i] Reaction in the presence of 0.10 mmol of free ligand (Mo/B ratio = 1/5).

Table 5

Trans-β-methylstyrene epoxidation catalysed by dioxomolybdenum complexes **1**–**3** in [BMP][NTf$_2$]/CH$_2$Cl$_2$[a].

Entry	Catalyst	Conv. (%)[b]	Epoxide yield (%)[b,c]
1	**2**	76	74 (2)
2	**3**	30	27 (3)
3	**1**	16	0 (10)[d]

[a] Results obtained from duplicated tests. Reaction conditions: 1 mmol trans-β-methylstyrene, 1.5 mmol tBuOOH in decane (ca. 5.5 M) and 0.025 mmol Mo in 1 mL of [BMP][NTf$_2$] and 1.5 mL of CH$_2$Cl$_2$; 30 °C for 22 h.
[b] Determined by GC.
[c] In brackets, benzaldehyde yield.
[d] 6% of benzylmethylketone was also obtained.

(entry 1 vs 2 and 4, Table 4). The corresponding 8,9-epoxide (or the double epoxide) was never observed, in contrast to that obtained in organic solvents [25a].

In order to understand the effect of the ionic liquid in the epoxidation selectivity, a ^{95}Mo NMR study was carried out. Complex **1** was stable at 35 °C for a long period (at least for one week) in [BMP][NTf$_2$]/dichloromethane, even in the presence of (R)-limonene (see Fig. S3 in Supplementary Information), exhibiting one signal at −66.5 ppm (width at middle height: 1100 Hz; the large width is due to the presence of several isomers due to the relative position of the two oxazolinyl-pyridine ligands (**A**)

in the bimetallic structure; see Ref. [25a] for a detailed structural discussion). However, in [BMI][PF$_6$]/dichloromethane, a new broad signal can be distinguished at ca. 120 ppm which becomes more intense after the olefin addition (+123 ppm, width at middle height: 600 Hz) (see Fig. S4 in Supplementary Information). This low-fielded shift points to an electronic density increase around the metallic centre [35]. This behaviour, in contrast to that observed using pyrrolidinium-based ionic liquid [BMP][NTf$_2$], can be due to the formation of Mo–NHC carbene bond by partial de-coordination of the chiral ligand; the presence of the olefin favours the de-coordination of the isothiocyanate group in agreement with that observed in neat dichloromethane [25b]. With the aim to evidence the formation of Mo–carbene bond, ^{13}C NMR spectrum for complex **1** was recorded in [BMI][NTf$_2$], observing the appearance of new signals in the region 170–165 ppm corresponding to the C=N and plausible Mo–C(NHC) bonds [37] (see Fig. S5 in Supplementary Information), in agreement with the low-fielded signal observed by ^{95}Mo NMR (see Fig. S4). This fact also explains the higher activity of the catalyst at relative long times in [BMP][NTf$_2$], in contrast to that observed in imidazolium-based ionic liquids for the cyclooctene epoxidation (see above kinetics profile, Fig. 3).

The lack of selectivity induced by complex **2** in pyrrolidinium-based ionic liquid can be due to a ligand de-coordination, in agreement with the large signal observed by ^{95}Mo NMR, both in the presence and in the absence of (R)-limonene (see
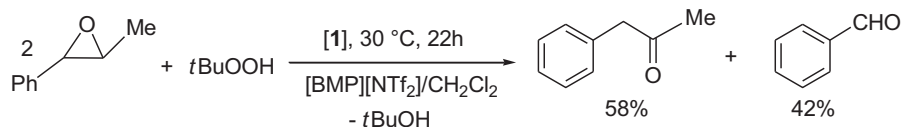

Scheme 5. Catalytic decomposition of trans-β-methylstyrene epoxide by complex **1** in [BMP][NTf$_2$]/CH$_2$Cl$_2$.

Fig. S6 in Supplementary Information), as previously observed for dioxomolybdenum complexes containing hemi-labile ligands [24].

Relative to trans-β-methylstyrene epoxidation, monometallic complexes **2** and **3** mainly led to the formation of the expected epoxide, being noticeably more active the complex containing the bis(oxazoline) ligand, **2** (entries 1 and 2, Table 5); less than 5% of benzaldehyde was observed in each case. Unfortunately, no asymmetric induction was observed. However, the bimetallic molybdenum system **1** was scarcely active, giving a mixture of benzaldehyde and benzylmethylketone instead of the corresponding epoxide (entry 3, Table 5). Starting with trans-β-methylstyrene epoxide in the presence of complex **1**, benzaldehyde and benzylmethylketone were quantitatively obtained (Scheme 5); this result points to that the epoxide is formed but it quickly decomposes towards the formation of achiral by-products.

4. Conclusions

In summary, bimetallic (**1**) and monometallic (**2**, **3**) complexes bearing chiral oxazoline ligands have led to active and chemoselective catalytic systems in ionic liquids, in contrast to the behaviour exhibited by [MoO₂Cl₂(DME)] for the cyclooctene epoxidation which gave an important amount of the corresponding diol. In particular, complex **1** allowed the recycling of the catalytic system up to 5 times without activity loss.

In relation to the diastereoselectivity, catalyst **1**, in contrast to monometallic systems **2** and **3**, led to the exclusive formation of trans-1,2-(R)-limonene epoxide in the pyrrolidinium-based ionic liquid [BMP][NTf₂]. However, this diastereoselectivity induction was lost when imidazolium ionic liquid was used due to the plausible formation of Mo–NHC carbene complex by partial decoordination of the oxazolinyl-pyridine ligand A, in agreement with the NMR observations.

Further studies are required concerning the catalyst design in order to induce enantioselectivity in the epoxidation reactions; unfortunately, our systems failed in the trans-β-methylstyrene epoxidation.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.03.024.

References

[1] (a) R.A. Sheldon, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, 2nd edition, Wiley-VCH, Weinheim, 2002, pp. 412–426;
(b) Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, Chem. Rev. 105 (2005) 1603–1662;
(c) F.E. Kühn, M. Santos, W.A. Herrmann, Dalton Trans. (2005) 2483–2491;
(d) F.E. Kühn, J. Zhao, W.A. Herrmann, Tetrahedron: Asymmetry 16 (2005) 3469–3479.
[2] J.M. Brégeault, Dalton Trans. (2003) 3289–3302.
[3] (a) J. Kollar, Halcon, US Patents 3,350,422 and 3,351,635 (1967).;
(b) M.N. Sheng, G.J. ZAjaczek, ARCO, GB Patent 1,136,923 (1968).
[4] D. Cole-Hamilton, R. Tooze, Catalyst, Separation, Recovery and Recycling, Springer, The Netherlands, 2006.
[5] S. Zhang, X. Lu, Q. Zhou, X. Li, X. Zhang, S. Li, Ionic Liquids. Physicochemical Properties, Elsevier, Amsterdam, 2009.
[6] For a recent review, see: H. Olivier-Bourbigou, L. Magna, D. Morvan, Appl. Catal. A: Gen. 373 (2010) 1–56.
[7] (a) J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3367;
(b) P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003;
(c) C. Baudequin, J. Baudoux, J. Levillain, D. Cahard, A. Gaumon, J. Plaquevent, Tetrahedron: Asymmetry 14 (2003) 3081;
(d) P.J. Dyson, T.J. Geldbach, Metal Catalysed Reactions in Ionic Liquids, Springer, The Netherlands, 2005.
[8] (a) For selected reviews, see: J. Durand, E. Teuma, M. Gómez, C.R. Chimie 10 (2007) 152–177;
(b) S.V. Malhorta, V. Kumar, V.S. Parmar, Curr. Org. Synth. 4 (2007) 370–380;
(c) K. Bica, P. Gaertner, Eur. J. Org. Chem. (2008) 3235–3250;
(d) M.H.G. Prechtl, J.D. Jackson, B.A.D. Brenno, J. Dupont, Curr. Org. Chem. 13 (2009) 1259–1277.
[9] Y. Chauvin, L. Mussmann, H. Olivier, Angew. Chem. Int. Ed. Engl. 34 (1995) 2698–2700.
[10] C.E. Song, E.J. Roh, Chem. Commun. (2000) 837–838.
[11] C.E. Song, C.R. Oh, E.J. Roh, D.J. Choo, Chem. Commun. (2000) 1743–1744.
[12] A.A. Valente, Z. Petrovski, L.C. Branco, C.A.M. Afonso, M. Pillinger, A.D. Lopes, C.C. Romão, C.D. Nunes, I.S. Gonçalves, J. Mol. Catal. A: Chem. 218 (2004) 5–11.
[13] F.E. Kühn, J. Zhao, M. Abrantes, W. Sun, C.A.M. Afonso, L.C. Branco, I.S. Gonçalves, M. Pillinger, C.C. Romão, Tetrahedron Lett. 46 (2005) 47–52.
[14] D. Betz, A. Raith, M. Cokoya, F.E. Kühn, ChemSusChem 3 (2010) 559–562.
[15] M. Abrantes, P. Neves, M.M. Antunes, S. Gago, F.A. Almeida Paz, A.E. Rodrígues, M. Pillinger, I.S. Gonçalves, C.M. Silva, A.A. Valente, J. Mol. Catal. A: Chem. 320 (2010) 19–26.
[16] (a) M. Herbert, A. Galindo, F. Montilla, Catal. Commun. 8 (2007) 987–990;
(b) M. Herbert, E. Alvarez, D.J. Cole-Hamilton, F. Montilla, A. Galindo, Chem. Commun. 46 (2010) 5933–5935.
[17] S.-F. Cai, L.-S. Wang, C.-L. Fan, Molecules 14 (2009) 2935–2946.
[18] C. Bibal, J.-C. Daran, S. Deroover, R. Poli, Polyhedron 29 (2010) 639–647.
[19] (a) S. Gago, S.S. Balula, S. Figueiredo, A.D. Lopes, A.A. Valente, M. Pillinger, I.S. Gonçalves, Appl. Catal. A: Gen. 372 (2010) 67–72;
(b) P. Neves, C.C.L. Pereira, F.A. Almeida Paz, S. Gago, M. Pillinger, C.M. Silva, A.A. Valente, Romão, I.S. Gonçalves, J. Organomet. Chem. 695 (2010) 2311–2319.
[20] (a) W.R. Thiel, M. Jia, Chem. Commun. (2002) 2392–2393;
(b) M. Jia, A. Steifert, M. Berger, H. Giegengack, S. Schulze, W.R. Thiel, Chem. Mater. 16 (2004) 877–882;
(c) M. Jia, A. Steifert, W.R. Thiel, J. Catal. 221 (2004) 319–324;
(d) A. Castro, J.C. Alonso, P. Neves, A.A. Valente, P. Ferreira, Eur. J. Inorg. Chem. (2010) 602–607.
[21] (a) K.R. Jain, F.E. Kühn, Dalton Trans. (2008) 2221–2227;
(b) K.A. Jain, W.A. Herrmann, F.E. Kühn, Coord. Chem. Rev. 252 (2008) 556–568.
[22] P. Neves, S. Gago, C.C.L. Pereira, S. Figueiredo, A. Lemos, A.D. Lopes, I.S. Gonçalves, M. Pillinger, C.M. Silva, A.A. Valente, Catal. Lett. 132 (2009) 94–103.
[23] M. Abrantes, F.A. Almeida Paz, A.A. Valente, C.C.L. Pereira, S. Gago, A.E. Rodrígues, J. Klinowski, M. Pillinger, I.S. Gonçalves, J. Organomet. Chem. 694 (2009) 1828–1833.
[24] M. Gómez, S. Jansat, G. Muller, G. Noguera, H. Teruel, V. Moliner, E. Cerrada, M. Hursthouse, Eur. J. Inorg. Chem. (2001) 1071–1076.
[25] (a) J.A. Brito, M. Gómez, G. Muller, H. Teruel, J.C. Clinet, E. Duñach, M.A. Maestro, Eur. J. Inorg. Chem. (2004) 4278–4285;
(b) J.A. Brito, H. Teruel, G. Muller, S. Massou, M. Gómez, Inorg. Chim. Acta 361 (2008) 2740–2746.
[26] G. Balavoine, J.C. Clinet, I. Lellouche, Tetrahedron Lett. 30 (1989) 5141–5144.
[27] (a) V.K. Aggarwal, L. Bell, M.P. Coogan, P. Jubault, J. Chem. Soc., Perkin Trans. 11 (1998) 2037–2042;
(b) K. Hallman, A. Frölander, T. Wondimagegn, M. Svensson, C. Moberg, PNAS 101 (2004) 5400–5404;
(c) K.A. Nolin, R.W. Ahn, D. Toste, J. Am. Chem. Soc. 127 (2005) 12462–12463.
[28] B. Kamenar, M. Penaviimage, B. Korpar-imageolig, B. Markoviimage, Inorg. Chim. Acta 65 (1982) L245–L247.
[29] G.M. Sheldrick, SHELXS-97, Acta Crystallogr. A46 (1990) 467–473.
[30] G.M. Sheldrick, SHELXL-97 Program for Crystal Structure Refinement, University of Göttingen, 1997.
[31] ORTEP3 for Windows: L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[32] Only one structure has been previously reported corresponding to a Mo(III) complex containing a bis(oxazoline) derived of oxalic acid: F. Stoffelbach, P. Richard, R. Poli, T. Jenny, C. Savary, Inorg. Chim. Acta 359 (2006) 4447–4453.
[33] F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, J. Organomet. Chem. 621 (2001) 207–217.
[34] H. Arzoumanian, G. Agrifoglio, H. Kretzein, M. Capparelli, J. Chem. Soc., Chem. Commun. (1995) 655–656.
[35] J.A. Brito, H. Teruel, S. Massou, M. Gómez, Magn. Reson. Chem. 47 (2009) 573–577.
[36] D. Betz, W.A. Herrmann, F.E. Kühn, J. Organomet. Chem. 694 (2009) 3320–3324.
[37] For related NHC-based dioxomolybdenum(VI) complexes see: P.M. Mas-Marza, E. Reis, B. Peris, Royo, J. Organomet. Chem. 691 (2006) 2708–2712.