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PAPER

Influence of *N*-donor bases and the solvent in oxodiperoxomolybdenum catalysed olefin epoxidation with hydrogen peroxide in ionic liquids†

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Biphasic catalytic olefin epoxidation systems consisting of oxodiperoxomolybdenum catalysts in 1-*n*-alkyl-3-methylimidazolium hexafluorophosphate ionic liquid (IL) media with aqueous hydrogen peroxide oxidant were optimised by tuning the molecular structure of the IL and employing *N*-heterocyclic donor base additives to inhibit hydrolysis and enhance the activity of the catalyst. The latter study was only made possible by the solubilising properties of the IL media. Of the bases investigated, pyrazoles were identified as the most efficient additive species and the best results were obtained using 3,5-dimethylpyrazole. Immobilisation of the catalyst in the IL allowed for very efficient catalyst recycling. Finally, the compound $[MoO(O_2)_2(3\text{-}Mepz)_2]$ (3-Mepz = 3-methylpyrazole) was characterised and its structure determined by X-ray crystallography.

Introduction

Industrially the epoxidation of the light olefins ethylene and propylene is carried out on a vast scale *via* processes including oxidation over supported silver,[1] the chlorohydrin process[2] and the HPPO process.[3] In fine chemicals, heavier epoxides are important intermediates in many syntheses, and are typically generated efficiently from olefins by reaction with a stoichiometric organic oxidant, such as *meta*-chloroperbenzoic acid.[4] Such oxidants are efficient and selective in performing epoxidations, but generate substantial quantities of waste which is increasingly considered undesirable due to environmental considerations.[5] Metal catalysed epoxidations offer the possibility of using more benign oxidants such as hydroperoxides.[6] The most active homogeneous catalysts for olefin epoxidation are based on methyltrioxorhenium (MTO),[7] employing hydrogen peroxide as the oxidant.[8] However, even the most stable catalysts in this class[9] ultimately undergo irreversible decomposition to inorganic rhenium oxide species following cleavage of the M–C bond, thus limiting the maximum achievable turnover numbers.[10] Additionally rhenium is scarce and expensive, raising both environmental and economic issues.[11] Amongst the other transition metal catalyst complexes active in this transformation, molybdenum based catalysts have produced some effective systems.[12] Oxodiperoxomolybdenum complexes were first studied in this capacity by Mimoun *et al.*[13] and several groups have since studied these systems.[14,15] The simplicity, stability, facile preparation and low cost of these compounds make them attractive options as catalysts. Oxodiperoxomolybdenum is most typically used in conjunction with organohydroperoxide oxidants, but a limited number of systems utilising hydrogen peroxide have been described.[16] Amongst these the $NaHCO_3$ co-catalysed systems of Bhattacharyya and coworkers stand out as the most active so far developed.[17]

Ionic liquids have received a great deal of investigative attention over the past couple of decades for a variety of applications.[18] As reaction solvents they are often considered interesting as media for green chemistry, particularly because their non-volatility eliminates issues with VOC emissions that would typically be associated with an organic solvent in such a process.[19] However their actual use in this capacity as reaction solvents for industrial processes is very limited.[20] Many of the major classes of IL compound are moderately toxic, they are expensive and synthetically complex compared to traditional organic solvents, in some reaction systems the fluorinated anions can potentially decompose, liberating HF and their elevated viscosities, not an issue at laboratory level, would present a significant problem in process scale-up.[21] Whilst their commercial application is therefore significantly complicated, their novel properties can still make them interesting reaction solvents in laboratory experimental investigations. They can be very powerful solvents, able to solubilise even substrates which typically display very poor solubility in all standard media. Additionally the solvent properties of any particular IL compound may be tuneable to an extent, through modification and functionalisation of the molecular structure, enabling desired solvent parameters to be achieved as required. Catalytic oxidations of organic compounds in IL solvents have been reported,[22] including

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processes utilising hydrogen peroxide as the oxidant.[23] Several authors have investigated ILs as reaction media for Mo catalysed epoxidations,[24] though only dioxomolybdenum complexes have been reported in this capacity.

Forming part of our recent investigations into catalysed oxidations in non-conventional media,[25] we previously described the first oxodiperoxomolybdenum catalysed epoxidation system in an ionic liquid media, wherein *cis*-cyclooctene was efficiently epoxidised in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate by mixing with the catalyst precursor molybdenum trioxide and the crystalline adduct of urea–hydrogen peroxide (UHP), which acted as the oxidant.[26] Here, we report a complete study of the influence of *N*-base additives on the efficiency of this Mo-catalysed epoxidation system and how tuning the IL medium can also affect catalyst activity. To our knowledge, no other examples of oxodiperoxomolybdenum catalysed epoxidation in ILs with hydrogen peroxide are known. Part of these results have been previously communicated.[27]

Experimental

Synthetic reactions were performed under a dry, oxygen-free, nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified appropriately prior to use. Chemicals were obtained from commercial sources and used as supplied or purified by distillation prior to use, as appropriate. The ionic liquids $C_n$mim–PF_6 were prepared according to literature procedures.[28] Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer (as either liquid films supported on KBr discs or in pressed KBr pellets). NMR spectra were recorded using a Bruker AMX-300 spectrometer with $^{13}C\{^1H\}$ and ^1H shifts referenced to the residual solvent signals. All data are reported in ppm downfield from Me_4Si. Gas chromatography (GC) was carried out using a Varian CP-3800, equipped with the automatic injector CP-8410, a capillary column Varian CP-8741 and with a flame ionization detector (dinitrogen gas carrier was supplied by Air Liquide España). Elemental analyses (C, H, N) were conducted by the Microanalytical Service of the Universidad de Sevilla (CITIUS) on an Elemental LECO CHNS 93 analyser. For Mo determination, a Jobin–Yvon S.A. model ULTIMA 2 ICP atomic emission spectrometer was used at the same service (CITIUS).

Syntheses

[Mo(O)(O₂)₂(H₂O)ₙ] solution in aqueous hydrogen peroxide. Solutions of the aqua complex of oxodiperoxomolybdenum, [Mo(O)(O₂)₂(H₂O)ₙ] in aqueous hydrogen peroxide used both in synthesis and catalytic studies were prepared as follows. A suspension of MoO_3 (2.52 g, 17.5 mmol) in 12 mL 30% aqueous hydrogen peroxide was heated at 55 °C with continuous stirring for approximately 1 h after which complete dissolution of the molybdenum resulting in a clear yellow solution was observed. At this point the solution was cooled to 0 °C and several drops of hydrogen peroxide were added and the solution was then made up to 25 mL with distilled water and stored in a sealed volumetric flask at 4 °C. Occasional venting of this solution is advised upon prolonged storage due to the accumulation of pressure following catalytic decomposition of hydrogen peroxide.

A solution of [Mo] with concentration 834 mM is thus obtained. The solution should actually consist of several molybdenum oxide species in equilibria which are dependent on factors including the concentration, pH and temperature of the solution.[29] For the purpose of simplicity the solution is referred to in this work simply as aqueous [Mo(O)(O₂)₂(H₂O)ₙ].

[Mo(O)(O₂)₂(bipy)][30]. MoO_3 (5.0 g, 35 mmol) and 30% aqueous hydrogen peroxide (14 equiv., 50 mL, 490 mmol) were stirred at 55 °C until complete dissolution was observed. The solution was then cooled to 0 °C and a solution of 2,2′-bipyridine (1 equiv., 5.47 g, 35 mmol) in methanol (10 mL) slowly added. After stirring for ten minutes the resulting yellow precipitate was separated by filtration, washing with cold distilled water and dried under vacuum for a few hours. The product was isolated as a powdery, yellow solid (10.9 g, 94%). IR (KBr, cm⁻¹): 536, 581, 651, 668, 729, 770, 858, 939, 1021, 1032, 1045, 1065, 1103, 1160, 1175, 1220, 1245, 1314, 1444, 1472, 1495, 1569, 1599, 3081. Anal. calc. for $MoC_{10}H_8O_5N_2$: Mo, 28.89; C, 36.16; H, 2.43; N, 8.43. Found: Mo, 24.67; C, 36.11; H, 2.51; N, 8.44%.

[Mo(O)(O₂)₂(bipyO₂)]. MoO_3 (0.155 g, 1.06 mmol) and 30% aqueous hydrogen peroxide (16 equiv., 1.6 mL, 15.6 mmol) were stirred at 55 °C until complete dissolution was observed. The solution was then cooled to 0 °C and a suspension of 2,2′-bipyridine-*N*,*N*′-dioxide (1 equiv., 0.200 g, 1.06 mmol) in methanol (3 mL) slowly added. After stirring for ten minutes the resulting yellow precipitate was separated by filtration, washing with cold distilled water and drying under vacuum for a few hours. The product was isolated as a powdery, pale yellow solid (0.335 g, 92%). IR (KBr, cm⁻¹): 486, 523, 543, 581, 651, 720, 736, 777, 837, 847, 859, 952, 1035, 1100, 1119, 1158, 1200, 1228, 1243, 1258, 1295, 1425, 1445, 1475, 1606, 1622, 3056, 3088. Anal. calc. for $MoC_{10}H_8O_7N_2$: Mo, 26.35; C, 32.98; H, 2.21; N, 7.69. Found: Mo, 28.86; C, 31.77; H, 2.25; N, 7.48%.

[MoO(O₂)₂(3-Mepz)₂]. To 15 mL 0.23 M aqueous [Mo(O)(O₂)₂(H₂O)ₙ] (3.45 mmol) was added 3-methylpyrazole (3-Mepz) (1137 μl, 13.8 mmol). The mixture, which has a very intense yellow colour, was stirred for 30 min at room temperature. The solution was then left to slowly evaporate resulting, after 24 h, in the formation of yellow crystals of [MoO(O₂)₂(3-Mepz)₂], which were collected by filtration, washed with water, acetone and diethyl ether and dried in air. An additional crop of crystals were collected from the mother liquors (0.820 g, 70% yield). IR (cm⁻¹, NaCl, nujol): 649, 663, 695, 755, 803, 858, 873, 894, 951, 1019, 1068, 1109, 1279, 1304, 1378, 1456, 1563, 3145, 3368. Anal. calcd. for $MoC_8H_{12}O_5N_4$: C, 28.25; H, 3.56; N, 16.47. Found: C, 28.63; H, 3.69; N, 16.33%.

General procedure for catalytic olefin epoxidation

The reactor (a 50 mL vial equipped with a Young valve and containing a stirrer flea) was charged with 0.5 M aqueous [Mo(O)(O₂)₂(H₂O)ₙ] (50 μL, 0.025 mmol), *N*-donor base additive (typically 0.1 mmol) as appropriate, reaction solvent (2 mL), oxidant (typically H_2O_2, 350 μL, 3 mmol) and the olefin substrate (1 mmol) in the aforementioned order. The reactor was sealed and heated at 60 °C, maintaining constant stirring in a thermostatted oil bath for the duration of the reaction. Upon completion the reactor was immediately cooled to 0° C and the products extracted

with petroleum ether (3×3 mL). The resulting solution was dried (MgSO$_4$) and analysed by GC (Galaxie Workstation software).

Recycling the [Mo]–IL mixture

Studies were run with both 4 h cycles, which give effectively complete conversion on the first cycle thus allowing assessment of the maximum achievable TONs, and 2 h cycles, which give incomplete conversion and permit clearer analysis of changes in catalytic efficiency. In each case the importance of refreshing the 3,5-dimethylpyrazole additive in-between cycles was also investigated. Up to the product extraction, the experimental procedure for each cycle was conducted as detailed above (aqueous [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] 0.025 mmol, 3,5-dimethylpyrazole 0.1 mmol, 30% aqueous H$_2$O$_2$ 3.0 mmol, *cis*-cyclooctene 1.0 mmol, C$_8$mim–PF$_6$ 2.0 mL, $T = 60$ °C). Extraction with pentane (3×3 mL) was carried out after each cycle and yields calculated by GC. Afterwards the reactor was stirred and heated at 60 °C and vacuum was applied for around 30 min to remove any volatile residues remaining in the reaction mixture. The reactor was then cooled and 30% aqueous hydrogen peroxide (350 µL, 3 mmol) and olefin substrate (1 mmol) were again charged to the reactor which was sealed before repeating the epoxidation reaction in the manner detailed above. In some experiments 3,5-dimethylpyrazole (0.1 mmol) was also added between cycles at the same time as the oxidant and substrate.

Oxidation of 4-tridecylpyridine

4-Tridecylpyridine (500 mg, 1.9 mmol) in chloroform (5 mL) was stirred for 5 min with a mixture of 0.5 M aqueous [Mo(O)(O)$_2$(H$_2$O)$_n$] (190 µL, 9.6 µmol) and 30% aqueous hydrogen peroxide (420 µL, 3.8 mmol). The organic phase was then separated and concentrated until precipitation of a cream coloured solid was observed. This was separated by filtration, washed with cold water (2 mL), recrystallised from dichloromethane, and dried by applying vacuum for a few hours. The product was obtained as a cream coloured, powdery solid (285 mg, 55%). IR (NaCl, cm^{-1}): 719, 790, 845, 866, 898, 936, 1037, 1126, 1180, 1212, 1239, 1377, 1470, 1487, 1637, 2850, 2919, 3038, 3374, 3500. ^{1}H (CDCl$_3$): δ 0.88 (t, 3H, $J_{HH} = 6.6$ Hz, CH_3), 1.00–1.75 (m, 22H, CH_2), 2.60 (q, 2H, $J_{HH} = 7.7$ Hz, CH_2-CH$_3$), 7.08 (d, 2H, $J_{HH} = 6.6$ Hz, m-NC$_5H_4$), 8.13 (d, 2H, $J_{HH} = 6.6$ Hz, o-NC$_5H_4$).

X-Ray structural study of [MoO(O$_2$)$_2$(3-Mepz)$_2$]

The X-ray data were collected at 173 K on a Bruker–Nonius X8APEX-II CCD diffractometer equipped with a graphite monochromator and Mo-K$_\alpha$ radiation.‡ The data were reduced[31a] and corrected for Lorentz polarisation effects and absorption by a multiscan method applied by SADABS.[31b] The structure was solved by direct methods (SIR-2002)[32] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-

6.12).[31c] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters, except the hydrogen atoms bonded to the nitrogen atoms in both 3-Mepz rings, which were detected from a difference Fourier map and refined isotropically with both N–H distances retrained to 0.85(2) Å.

Results and discussion

Concerning our previous results with the aforementioned MoO$_3$–UHP–IL system,[26] besides its simplicity and the absence of a volatile reaction solvent, a particular advantage was the fairly efficient immobilisation of the catalyst in the ionic liquid phase, which meant that after product extraction the reaction media and catalyst could be recycled several times, allowing higher turnover numbers to be achieved. However, a problem which arose during this process was the accumulation of urea resulting from the oxidant in the ionic liquid, which had to be eliminated by means of a time consuming procedure utilising significant quantities of organic solvents. The use of aqueous hydrogen peroxide as the oxidant would be preferable in this respect, since the residing moisture could be far more easily removed by evaporation and constitutes a more benign waste product than urea. Aqueous hydrogen peroxide is also considerably cheaper. However, when aqueous hydrogen peroxide was used in this system, whilst complete conversion was observed there was no selectivity for the epoxide product after 18 h due to complete hydrolysis of the product to the diol. Using the dry§ oxidant UHP was the only strategy by which this unwanted decomposition was avoided. It is interesting to note how analogous problems have been recorded in the development of MTO catalysed epoxidations with hydrogen peroxide in organic solvents. Strategies employed to reduce hydrolysis of epoxide products in these systems have included the use of drying agents to remove moisture from the reaction medium[33] and the use of dry oxidants to prevent hydrolysis simply by ensuring the absence of moisture.[34] However, a more popular and far easier means of inhibiting hydrolysis is to employ coordinating base species which block access of the epoxide to the acidic metal centre,[35] thus inhibiting the mechanism of hydrolysis.[36] Additionally these bases are also found to accelerate the rate of the epoxidation step, improving the efficiency of the catalysis.[37,38]

With these precedents, in our continued study of oxodiper-oxomolybdenum catalysed epoxidations in ionic liquids we decided to investigate strategies by which hydrolytic decomposition of the epoxide product might be inhibited, thus permitting a switch from the UHP oxidant to aqueous hydrogen peroxide. In the investigations to be discussed here two possibilities have been examined: (a) modification of the ionic liquid structure to reduce water miscibility and thus its concentration in the reaction media, reducing hydrolysis; and, (b) the use of several classes of simple coordinating bases to block the mechanism of hydrolysis. For the purposes of these studies a series of

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‡ Crystal data for [MoO(O$_2$)$_2$(3-Mepz)$_2$]: C$_8$H$_{12}$MoN$_4$O$_5$, Mw = 340.16, monoclinic, a = 11.4740(3) Å, b = 13.3115(4) Å, c = 8.5537(3) Å, β = 104.148(2)°, V = 1266.83(7) Å^3, T = 173(2) K, space group $P2_1/c$, Z = 4, D_{calc} = 1.783 Mg m^{-3}, μ(Mo Kα) = 1.055 mm^{-1}, $F(000)$ = 680, 39044 reflections measured, 3882 independent reflections (R_{int} = 0.0300). 171 refined parameters, final $R_1(F^2)$ = 0.0190, for reflections with $I > 2\sigma(I)$, and $wR_2(F^2)$ = 0.0515 (all data), GOF = 1.066.

§ When urea–hydrogen peroxide adduct is used as an oxidant 1 equivalent of H$_2$O is produced as a by-product. However, in these systems the resulting concentrations are apparently too low for any significant hydrolysis to take place.

Table 1 Effects of varying alkyl chain lengths, aqueous H_2O_2 and addition of pyridine[a]

Entry	Solvent	Oxidant	Base	Conversion (%)	Yield (%)	Selectivity (%)
1	C_4mim–PF_6	UHP	—	99	99	100
2		H_2O_2	—	97	0	0
3		H_2O_2	Pyridine[b]	75	48	64
4	C_8mim–PF_6	UHP	—	77	77	100
5		H_2O_2	—	97	21	22
6		H_2O_2	Pyridine[b]	97	97	100
7	C_{12}mim–PF_6	H_2O_2	—	95	95	100
8		H_2O_2	Pyridine[b]	93	93	100
9	C_8mim–PF_6–C_{18}mim–PF_6	H_2O_2	—	32	15	47
10		H_2O_2	Pyridine[b]	31	15	48

[a] Aqueous [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] 0.025 mmol, oxidant (30% aqueous H_2O_2 or UHP) 3.0 mmol, *cis*-cyclooctene 1.0 mmol, solvent 2.0 mL, 18 h, 60 °C. Extraction with pentane (3 × 3 mL), yields and conversions calculated by GC. [b] Pyridine 0.20 mmol.

1-*n*-alkyl-3-methylimidazolium hexafluorophosphate ($C_n$mim–PF_6) type ionic liquids were employed, with *n*-butyl (C_4mim–PF_6), *n*-octyl (C_8mim–PF_6), *n*-dodecyl (C_{12}mim–PF_6) and *n*-octadecyl (C_{18}mim–PF_6) alkyl groups (Scheme 1).
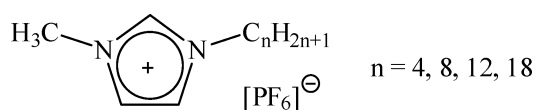
Scheme 1 $C_n$mim–PF_6 structure.

Of these compounds, the first two are liquids at room temperature and C_{12}mim–PF_6 has a melting point <60 °C (the previously established optimum temperature for this epoxidation). C_{18}mim–PF_6 however has a higher melting point, being solid at 60 °C, and would be unusable as a solvent under the reaction conditions. A 1:1 volumetric mixture of C_{18}mim–PF_6 and C_8mim–PF_6 is liquid at 60 °C however, and this composite media was thus also investigated. Increasing the length of the 1-alkyl chain on the imidazolium cation of these ILs reduces miscibility with water and thus the concentration of water in the reaction media. By limiting the availability of water, the rate of the hydrolysis reaction should be reduced and the desired increase in selectivity might be achieved. As we stated before, another means by which hydrolysis could be inhibited is to employ base ligands which will bind strongly to vacant coordination sites on the metal complex. By blocking access of the epoxide to the metal selectivity the mechanism of hydrolysis may be inhibited, resulting in improved selectivity in spite of the presence of moisture. A particular problem affecting the application of this strategy in homogeneous catalysis involving oxodiperoxomolybdenum complexes is the poor solubility of the resulting coordination complexes. The role that appropriate ligands can play in solubilising the catalyst complex is crucial to achieving an efficient catalytic system.[39] The ionic liquid media employed here are useful in this respect, since their novel solvent properties lead to very effective dissolution of these normally poorly soluble complexes, thus facilitating this study. The investigation here aimed to focus specifically on simple *N*-heterocyclic bases: pyridines, 2,2′-bipyridines, imidazoles and pyrazoles.

Tuning the cation 1-alkyl chain and preliminary investigation of *N*-donor bases

The first study investigated conversion and selectivity in the catalytic epoxidation of *cis*-cyclooctene after 18 h in each of the IL media with 30% aqueous hydrogen peroxide (Scheme 2). In each an experiment was also run with 20 mol% pyridine, as a preliminary investigation into the effect of a base ligand additive, and comparative studies with UHP as the oxidant were also run where appropriate. Other experimental details are included in the corresponding table footnotes. These results are collected in Table 1.
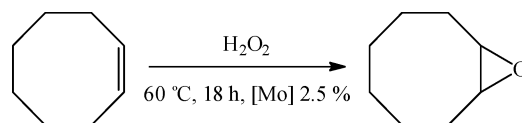
Scheme 2 Catalytic epoxidation of *cis*-cyclooctene.

The results obtained in the composite C_{18}mim–PF_6–C_8mim–PF_6 media (entries 9 and 10, Table 1) are markedly poorer than those in the monospeciatic ILs with only a low level of conversion even after 18 h and no effect attributable to pyridine, in contrast to the other results. Both of the reactions performed in this mixture had a very turbid appearance throughout the course of the reaction and solubility issues seemingly prevented a smooth, homogeneous catalysis. No further investigations regarding this reaction were subsequently carried out in this media. In the monospeciatic IL media, considering first only the reactions performed without pyridine, a clear pattern of increasing selectivity as the length of the 1-*n*-alkyl chain increases was observed (Entries 2, 5 and 7, Table 1). In all cases conversion was virtually complete, but the selectivity for the epoxide, which is 0% in C_4mim–PF_6, is partial in C_8mim–PF_6 and complete in C_{12}mim–PF_6. Slight modification of the IL structure to reduce water miscibility was therefore shown to inhibit the undesirable hydrolysis side reaction,[¶,40] an example of how ionic liquid media can be tuned to obtain desired solvent properties for a specific process. In both C_4mim–PF_6 and C_8mim–PF_6, when UHP was used as the oxidant, complete selectivity

¶ The possible hydrolysis, under the catalytic conditions, of the PF_6^- anion of IL was discarded on the basis of the ^{19}F NMR analysis of the reaction medium. This fact is in agreement with the recent study reported in reference 54.

Table 2 Comparing the effect of pyridine additives in the molybdenum catalysed epoxidation of *cis*-cyclooctene in IL solvents over 2 h[a]

Entry	Base additive [pK_a]	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	None	Cl$_3$CH	17	1	6
2		C$_4$mim–PF$_6$	29	9	31
3		C$_8$mim–PF$_6$	38	25	66
4		C$_{12}$mim–PF$_6$	40	40	100
5	Pyridine [5.25]	C$_8$mim–PF$_6$	29	29	100
6		C$_{12}$mim–PF$_6$	49	49	100
7	4-Picoline [5.98]	C$_4$mim–PF$_6$	31	18	58
8		C$_8$mim–PF$_6$	54	54	100
9		C$_{12}$mim–PF$_6$	46	46	100
10	4-Picoline-*N*-oxide [1.4]	C$_4$mim–PF$_6$	32	23	72
11		C$_8$mim–PF$_6$	39	39	100
12		C$_{12}$mim–PF$_6$	48	48	100

[a] Aqueous [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] 0.025 mmol, base additive 0.10 mmol (where appropriate), 30% H$_2$O$_2$ (aq) 3.0 mmol, *cis*-cyclooctene 1.0 mmol, solvent 2.0 mL, $T = 60\,°C$, $t = 2$ h. Extraction with pentane (3×3 mL), yields and conversions calculated by GC.

for the epoxide was observed. This can be attributed to using a dry oxidant, limiting the availability of water (entries 1 and 4, Table 1). A slightly lowered conversion was observed in C$_8$mim–PF$_6$. 20 mol% pyridine was shown to greatly increase selectivity for the epoxide product (entries 3 and 6, Table 1) compared to equivalent reactions in its absence. Even in C$_4$mim–PF$_6$, where selectivity for the epoxide was 0% in the absence of pyridine, a good yield of product was recovered and in C$_8$mim–PF$_6$ and C$_{12}$mim–PF$_6$ complete selectivity for the product was now observed. It was therefore apparent that the base was able to inhibit hydrolysis and facilitate selective epoxidation even in the presence of some moisture.

Effect of pyridines on the Mo catalysed model epoxidation

With the capacity of pyridine to enhance selectivity over 18 h thus established, a more detailed study subsequently aimed to investigate the manner and efficiency of its effect. By reducing the reaction time to 2 h the reactions did not run to completion allowing a fair comparison of activity. The epoxidation of *cis*-cyclooctene was thus investigated over 2 h in a selection of IL media in the presence of 10 mol% of pyridine, 4-picoline and the *N*-oxide of 4-picoline. These results are shown in Table 2.

In the absence of base a significant yield was only recovered in the IL media (entries 2–4, Table 2), with only a trace of product recorded in chloroform (entry 1). Selectivity was again dependent on the alkyl chain length with complete selectivity observed in C$_{12}$mim–PF$_6$ and partial selectivities in C$_4$mim–PF$_6$ and C$_8$mim–PF$_6$, although it is notable that over the shorter reaction time there was now a partial yield in the C$_4$mim–PF$_6$ (compare entry 2, Table 2 and entry 2, Table 1) presumably since part of the epoxide product had not resided long enough to yet undergo decomposition. It is worth noting that the conversions fall into the 30–50% range, as was observed in many of the subsequent studies with base additives, indicating similar activities. Additionally the activity seems to increase as the 1-alkyl chain length is enlarged, a trend which was again generally observed in many of the subsequent studies. The reason for this latter observation is not clear, solubilities, solvent polarity or even some participation by the IL in the mechanism are all possibilities, but this will not be discussed here.

When the pyridine additives were employed (entries 5–12, Table 2) there was generally no notable change in the activity compared to the reactions in the absence of additive, with the conversions still falling approximately into the 30–50% range. However the selectivities were markedly improved, with 100% selectivity always observed in C$_8$mim–PF$_6$ and C$_{12}$mim–PF$_6$, and elevated selectivity in C$_4$mim–PF$_6$. Interestingly there is little difference observed between the results obtained with pyridine (entries 5 and 6), 4-picoline (entries 7–9) and even 4-picoline-*N*-oxide (entries 10–12). This is significant as it would seem to indicate that the *in situ* catalytic species in each case is electronically similar, with the logical conclusion being that the unoxidised pyridine species were rapidly oxidised to their *N*-oxides within the reaction systems, an oxidation which many metal–peroxo complexes are known to efficiently catalyse.[41,42] This is not surprising, the addition of pyridine to oxodiperoxomolybdenum solutions in hydrogen peroxide results in the formation of *N*-oxide complexes,[43] and we made analogous observations when attempting to prepare molybdenum–peroxo complexes of picolines,[26b] lutidine and collidine.[44] To specifically demonstrate the catalytic oxidation of a pyridine by oxodiperoxomolybdenum, 4-tridecylpyridine in chloroform was mixed with a catalytic amount of [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] in aqueous hydrogen peroxide for a few minutes at room temperature, after which 4-tridecylpyridine-*N*-oxide was isolated from the organic phase and easily identified by IR and ^{1}H-NMR (Scheme 3).
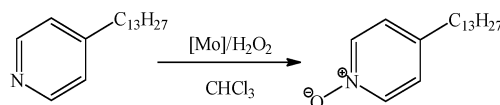
Scheme 3 Catalytic oxidation of 4-tridecylpyridine to its *N*-oxide.

Effect of bipyridines on the Mo catalysed model epoxidation

Investigation of the influence of simple bipyridine compounds as additives was carried out in an analogous manner, using 5 mol% of these bases since they form bidentate complexes (see data in Table 3). In all cases (entries 1-4, Table 3) the bipyridine additives were found to inhibit the catalytic activity with barely significant yields of epoxide recovered. We do not think that catalyst solubility was a factor in these poor conversions as the

Table 3 Comparing the effect of bipyridine additives in the molybdenum catalysed epoxidation of *cis*-cyclooctene in IL solvents over 2 h[a]

Entry	Base additive [pK_a]	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	2,2′-Bipyridine [4.30]	C_4mim–PF_6	18	5	28
2		C_{12}mim–PF_6	19	1	5
3	4,4′-Dimethyl-2,2′bipyridine [5.9]	C_4mim–PF_6	16	6	38
4		C_{12}mim–PF_6	19	4	21

[a] Aqueous [Mo(O)(O_2)$_2$(H_2O)$_n$] 0.025 mmol, base additive 0.05 mmol, 30% H_2O_2 (aq) 3.0 mmol, *cis*-cyclooctene 1.0 mmol, solvent 2.0 mL, $T = 60\,°C$, $t = 2$ h. Extraction with pentane (3×3 mL), yields and conversions calculated by GC.

catalyst was visually observed to have completely dissolved at the loadings employed in this study and the results therefore seem to indicate that bipyridines inhibit the mechanism of epoxidation without affecting the hydrolysis. These results lead to some discrepancy with results previously published by us, where 5 mol% [Mo(O)(O_2)$_2$(bipy)] in C_4mim–PF_6 with UHP as oxidant completely epoxidised *cis*-cyclooctene after 18 h,[26] however this result was found to be reproducible which indicates that the long reaction time and dry reaction are sufficient to allow an efficient conversion even with a less active catalyst. It is likely that the bipyridine species coordinated to the oxodiperoxomolybdenum centre as bidentate *N*-donors rather than *N*-oxides, reaction between aqueous oxodiperoxomolybdenum and bipyridine is known to produce such a complex.[30,44,45] It is interesting that 2,2′-bipyridines and their oxides are not found to produce an analogous retardation of epoxidation activity in MTO catalysts.[46]

Further investigations were subsequently carried out into the influence of bipyridine in these epoxidation systems, investigating the effect that an excess of base, a dry oxidant and starting with the *N*-oxide complex would have over an 18 h reaction in C_8mim–PF_6 (data included in Table 4).

Extending the reaction time from 2 h to 18 h increased the conversions obtained, which in all cases were approximately 60%, inferring that the catalyst was approximately equally active in all of the systems. This represented a marked decrease in conversion from equivalent reactions in the absence of bipyridine (Table 1) again demonstrating that bipyridine retards the catalytic activity. Selectivity was observed to differ between the systems. With 2.5 mol% [Mo(O)(O_2)$_2$(bipy)] as the catalyst only limited selectivity (38%) was observed when aqueous H_2O_2 was used as the oxidant (entry 1, Table 4) but when the dry oxidant UHP was employed (entry 2, Table 4) the selectivity was effectively complete, as would be anticipated in the dry system. Bipyridine seems to do little to inhibit hydrolytic epoxide opening compared to other donor additive species (compare Tables 2, 5 and 6). When the reaction was performed with 1 extra equivalent of bipyridine (entry 3, Table 4) the conversion was unaffected but the selectivity for the epoxide

became complete, indicating that the excess base served to help block the hydrolysis reaction without having any impact on the epoxidation step. Interestingly, and perhaps unexpectedly given the significantly lower donor strength of the ligand, the complex of bipyridine-*N*,*N*′-dioxide (entry 4, Table 4) gave a similar conversion to the bipyridine catalysts but with complete selectivity, despite being used in conjunction with aqueous hydrogen peroxide. This may indicate that the retardation of the rate of epoxidation is linked to common steric or electronic factors resulting from coordination of the bidentate ligands, but that the oxide is for some reason much more efficient in blocking hydrolysis, despite the fact that it would be expected to bond less strongly to the acidic metal centre.

Effect of imidazoles on the Mo catalysed model epoxidation

Imidazoles are more basic than pyridines, and are thus stronger donor ligands. This was anticipated to possibly lead to their being more efficient in blocking access to the metal centre and thus the mechanism of hydrolysis. Studies of their influence on the epoxidation were conducted in the same manner as that described for the pyridines (Table S1 in ESI†). Consistent results were observed in this study, conversion remained in the 30–50% range and in both C_8mim–PF_6 and C_{12}mim–PF_6 complete selectivity was always observed (entries 1-6, Table S1†), indicating that the imidazoles were able to block hydrolysis and had no negative effect on the epoxidation reaction. An aspect of the reaction that we wished to investigate was whether the *in situ* catalyst might be an imidazole-*N*-oxide complex,[47] similar to that formed with pyridine species (Table 2), or an imidazole *N*-donor complex, such as the one characterised by Martín–Zarza *et al.*[48] We therefore attempted to isolate such a species through the reaction of imidazoles with aqueous solutions of oxodiperoxomolybdenum. However, this study revealed that imidazoles actually undergo rapid oxidative decomposition in the presence of molybdenum and hydrogen peroxide, even at low temperature, indicating that imidazole-containing complexes of molybdenum, if formed, probably could

Table 4 The influence of 2,2′-bipyridine on epoxidation[a]

Entry	Catalyst	Oxidant	Conversion (%)	Yield (%)	Selectivity (%)
1	[Mo(O)(O_2)$_2$(bipy)]	H_2O_2 (aq)[b]	61	23	38
2		UHP[c]	59	57	97
3	[Mo(O)(O_2)$_2$(bipy)] + bipy[d]	H_2O_2 (aq)[b]	57	57	100
4	[Mo(O)(O_2)$_2$(bipyO$_2$)]	H_2O_2 (aq)[b]	65	65	100

[a] [Mo(O)(O_2)$_2$(bipy)] 0.025 mmol, *cis*-cyclooctene 1.0 mmol, C_8mim–PF_6 2.0 mL, $T = 60\,°C$, $t = 18$ h. [b] 30% aqueous H_2O_2 3.0 mmol. [c] UHP 1.5 mmol. [d] 2,2′-Bipyridine 0.025 mmol.

Table 5 Comparing the effect of pyrazole additives in the molybdenum catalysed epoxidation of *cis*-cyclooctene in IL solvents over 2 h[a]

Entry	Base additive [pK_a]	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	Pyrazole [2.5]	Cl$_3$CH	16	3	19
2		C$_8$mim–PF$_6$	63	63	100
3		C$_{12}$mim–PF$_6$	73	73	100
4	3-Methylpyrazole [3.3]	C$_8$mim–PF$_6$	62	62	100
5		C$_{12}$mim–PF$_6$	78	78	100
6	3,5-Dimethylpyrazole [4.2]	Cl$_3$CH	23	8	35
7		C$_8$mim–PF$_6$	84	84	100
8		C$_{12}$mim–PF$_6$	99	99	100

[a] Aqueous [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] 0.025 mmol, base additive 0.10 mmol, 30% aqueous H$_2$O$_2$ 3.0 mmol, *cis*-cyclooctene 1.0 mmol, solvent 2.0 mL, $T = 60\,°C$, $t = 2$ h. Extraction with pentane (3 × 3 mL), yields and conversions calculated by GC.

not be stable in the reaction for any significant length of time (see ESI†). The high level of similarity between the results may be due to the fact that rapid decomposition of the imidazoles means that the active catalytic species was identical in each reaction. These reactions were not further investigated.

Effect of pyrazoles on the Mo catalysed model epoxidation

Pyrazoles are known to resist oxidation in MTO catalysed systems and this type of ligands was the final class of *N*-donor base to be investigated. The results are shown in Table 5. For pyrazole and 3-methylpyrazole conversions in the 60–80% range were recorded in the ILs C$_8$mim–PF$_6$ and C$_{12}$mim–PF$_6$ with complete selectivity for the epoxide (entries 2–5, Table 5), representing a significant enhancement in the catalytic activity compared to the systems previously tested. Even more remarkable amongst the results were those recorded when 3,5-dimethylpyrazole was used as the additive in ILs (entries 7 and 8, Table 5). In this case complete conversion with complete selectivity was observed within 2 h in C$_{12}$mim–PF$_6$ (entry 8). The capacity of pyrazoles to enhance oxodiperoxomolybdenum catalysed epoxidations with H$_2$O$_2$ as the oxidant is an interesting discovery and the mechanism of the enhancement may well be the same as that observed for similar MTO catalysed epoxidations. The use of pyrazole complexes of oxodiperoxomolybdenum as catalysts for oxidation reactions has a limited number of precedents, though not in olefin epoxidation. Supported [Mo(O)(O$_2$)$_2$(H$_2$O)(pz)] has been used to catalyse the heterogeneous oxidation of sulfides,[49] and [Mo(O)(O$_2$)$_2$(dmpz)$_2$] has been described as a homogeneous alcohol oxidation catalyst.[50]

Recycling the [Mo]–IL mixture

To investigate the efficiency of catalyst immobilisation in the IL phase and, thus, the maximum TON obtainable from the optimum 3,5-dimethylpyrazole system, parallel catalytic studies were carried out wherein the [Mo]–IL mixture was recycled in further catalytic cycles. The selected IL was C$_8$mim–PF$_6$ since this solvent is more easily manipulated than C$_{12}$mim–PF$_6$ due to its lower melting point. Two experiments were initially run with a 4 h reaction time for each cycle. In one, following extraction of the product and elimination of any residing volatiles the system was recycled by addition of only oxidant and substrate. In the other 3,5-dimethylpyrazole was also added along with the reactants, in order to compensate for the partial ligand extraction produced during the epoxide extraction. For other details see the Experimental

section. Within 4 h this system gave almost complete conversion on the first cycle. As repeat cycles were carried out the epoxide yield was observed to slowly decline in the experiment where base additive was not added between cycles. Where the additive was added prior to each reaction however the yields remained effectively complete even after ten complete cycles (Fig. 1).
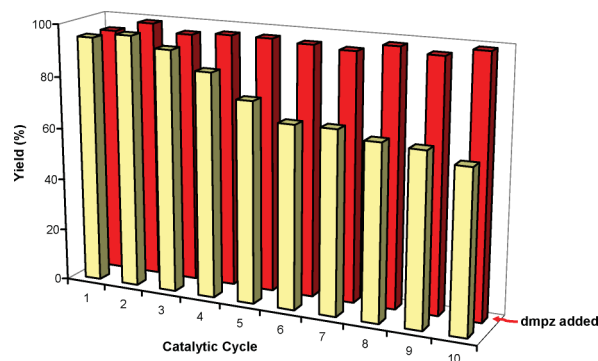

Fig. 1 Epoxide yield for ten catalytic cycles after 4 h reaction time in C$_8$mim–PF$_6$ as solvent in the presence of [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$]–dmpz (dmpz = 3,5-dimethylpyrazole) with added dmpz after each cycle (red) or without (yellow).

To try to ascertain if this system was effectively retaining its entire catalytic potency or simply declining at a lesser rate the experiments were subsequently repeated with only a 2 h reaction time, which gave incomplete conversions (~85%) in the first cycle. In these experiments a steady decline was again witnessed in the reaction where base additive was not added prior to each reaction, as was anticipated. Interestingly the tenth cycle produced a yield slightly lower than the 30–50% observed in single batch reactions in the absence of base (entry 3, Table 2). The reaction where the base additive was added had apparently retained effectively the same catalytic potency even after ten cycles however (Fig. 2). This would seem to indicate that the metal is very well immobilised in the IL phase and does not leach to a significant extent during the product extraction. The 3,5-dimethylpyrazole additive however presumably slowly leaves the system either during the product extraction or when the volatile residues are evaporated and thus must be refreshed in order to retain the same level of activity. Over 4 h, in the experiment where base was added prior to each reaction, after ten catalytic runs 0.025 mmol of molybdenum converted over 95% of 10.0 mmol *cis*-cyclooctene to its epoxide, a TON of
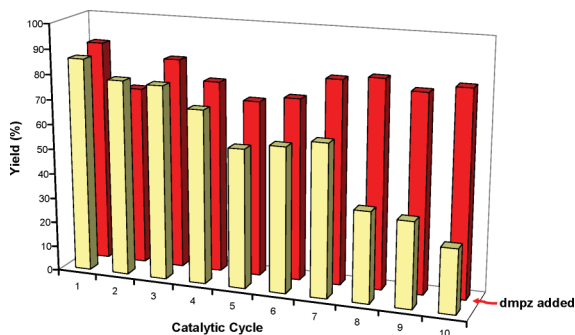
Fig. 2 Epoxide yield for ten catalytic cycles after 2 h reaction time in C_8mim–PF_6 as solvent in the presence of $[Mo(O)(O_2)_2(H_2O)_n]$–dmpz (dmpz = 3,5-dimethylpyrazole) with added dmpz after each cycle (red) or without (yellow).

≥380. In the same experiment over 2 h TOF remained steady at approximately 17 h^{-1}.

Applicability to other olefins

Having studied the recyclability of the system its applicability to other substrates was studied. The reaction conditions used were those that achieved the best results with the *cis*-cyclooctene model reaction and the results were collected in Table 6. Surprisingly, consistently limited yields were observed for all of the substrates that were tested. For 1-octene only around 2% conversion to the epoxide was observed even after 18 h (entries 1 and 2, Table 6).

As a terminal alkyl olefin this is a poorly activated substrate and low conversions were also observed in the related rhenium catalysed reaction.[25b] The secondary olefins, *trans* 2-octene and 4-octene and *cis*-2-heptene also gave only limited yields, even with extended reaction times (entries 3–6, Table 6). No significant difference in activity towards *cis*- or *trans*- substrates was noted.[35b] A higher conversion was observed in the case of styrene, although very little (4%) epoxide was recovered, presumably attributable to hydrolysis and over oxidation (entry 7, Table 6). The ester ethyl acrylate and allyl amine showed no sign of any conversion. This fact was attributable to the effects of their functional groups (entries 8 and 9, Table 6) and was similarly observed in the related rhenium catalysed reaction.[25b] Finally, the enol substrate was cyclohexen-1-ol converted to a limited extent with a 34% yield of epoxide recovered (entry 10, Table 6).

Table 6 Molybdenum catalysed epoxidation of other olefin substrates[a]

Entry	Olefin substrate	Conversion (%)	Yield (%)
1	1-Octene	<1	<1
2[b]	1-Octene	2	2
3	*trans*-2-Octene	5	5
4[b]	*trans*-2-Octene	20	20
5[b]	*cis*-2-Heptene	15	15
6	*trans*-4-Octene	20	20
7	Styrene	60	4
8	Ethyl acrylate	0	0
9	Allyl amine	0	0
10	Cyclohexen-1-ol	66	34

[a] Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, 3,5-dimethylpyrazole 0.1 mmol, 30% H_2O_2 (aq) 3.0 mmol, olefin substrate 1.0 mmol, C_8mim–PF_6 2.0 mL, T = 60 °C, t = 4 h. Extraction with pentane (3 × 3 mL), yields and conversions calculated using GC. [b] t = 18 h.

Synthesis and structural characterisation of $[MoO(O_2)_2(3\text{-Mepz})_2]$

During the catalytic assays with 3-methylpyrazol (3-Mepz), complex $[MoO(O_2)_2(3\text{-Mepz})_2]$ was obtained by reaction of an aqueous solution of $[Mo(O)(O_2)_2(H_2O)_n]$ with an slight excess of 3-Mepz. Compound $[MoO(O_2)_2(3\text{-Mepz})_2]$ was isolated, after appropriate work-up, as yellow crystals in a good yield. The IR spectrum shows strong absorption bands at 951 and 858 cm^{-1}, due to the antisymmetric vibrations of Mo═O and the two peroxide groups, respectively. Its crystal structure was determined by X-ray diffraction (Fig. 3), showing the characteristic features of this type of compounds.[51]
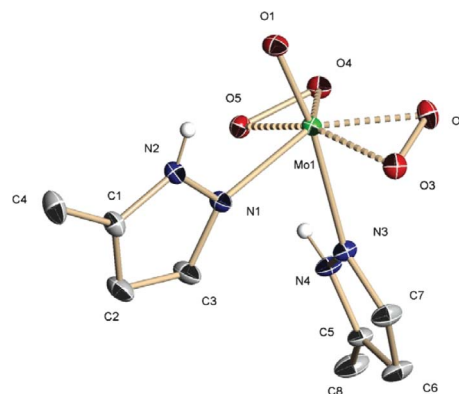

Fig. 3 Molecular structure of $[MoO(O_2)_2(3\text{-Mepz})_2]$ with thermal ellipsoids at 50% probability. The hydrogen atoms are omitted for clarity except those of the N–H moieties.

The structural features of $[MoO(O_2)_2(3\text{-Mepz})_2]$ are analogous to those reported for related oxodiperoxomolybdenum complexes.[15b,c,26b,30,52] The atomic environment of the molybdenum atom is at the centre of a distorted trigonal bipyramid. The axial positions are occupied by the oxo ligand and the nitrogen of one of the 3-Mepz ligands, whilst the two peroxo ligands and the nitrogen atom of the other 3-Mepz ligand are coordinated on the distorted equatorial plane, being bent slightly towards the axis occupied by the axial 3-Mepz (umbrella effect). The Mo═O and O–O bond lengths are 1.6818(10) and 1.4734(15), 1.4714(14) Å, respectively, within the ranges for the oxo (1.61 to 1.71 Å) and peroxo (1.42 to 1.51 Å) bond distances, typically observed in this type of compound.[53] The angles between the oxo ligand and the oxygen atoms of the peroxo groups range between 100.92(5) to 103.69(5)° also falling within the typically observed range (99.5–108.5°).[53] Looking at the bond lengths with the 3-Mepz ligands, the axial Mo–N(3) bond distance was found to be about 0.16 Å longer than the equatorial Mo–N(1). This, along with the distortion of the equatorial plane with the O(oxo)–Mo–O(peroxo) angles greater than 90°, results from the *trans*-influence of the oxo ligand. Other structural parameters are collected in Table 7.

Conclusions

In oxodiperoxomolybdenum catalysed olefin epoxidations employing aqueous hydrogen peroxide as the oxidant in ionic liquids, hydrolysis of the epoxide product can be limited both by tuning the IL media to limit the availability of water and by employing coordinating base species to block the epoxidation. Many

Table 7 Selected bond distances [Å] and angles [°] for [MoO(O$_2$)$_2$(3-Mepz)$_2$]

Mo(1)–O(1)	1.6818(10)	O(1)–Mo(1)–O(3)	100.92(5)
Mo(1)–O(2)	1.9192(10)	O(2)–Mo(1)–O(3)	44.60(4)
Mo(1)–O(3)	1.9622(10)	O(4)–Mo(1)–O(3)	131.80(4)
Mo(1)–O(4)	1.9280(10)	O(5)–Mo(1)–O(3)	157.55(4)
Mo(1)–O(5)	1.9540(10)	O(1)–Mo(1)–N(1)	88.63(5)
Mo(1)–N(1)	2.1754(12)	O(2)–Mo(1)–N(1)	134.15(5)
Mo(1)–N(3)	2.3387(11)	O(4)–Mo(1)–N(1)	131.10(5)
O(2)–O(3)	1.4734(15)	O(5)–Mo(1)–N(1)	86.87(5)
O(4)–O(5)	1.4714(14)	O(3)–Mo(1)–N(1)	89.90(5)
O(1)–Mo(1)–O(2)	103.21(5)	O(1)–Mo(1)–N(3)	170.08(5)
O(1)–Mo(1)–O(4)	103.69(5)	O(2)–Mo(1)–N(3)	83.90(4)
O(2)–Mo(1)–O(4)	89.37(5)	O(4)–Mo(1)–N(3)	83.07(4)
O(1)–Mo(1)–O(5)	101.21(5)	O(5)–Mo(1)–N(3)	78.38(4)
O(2)–Mo(1)–O(5)	131.88(4)	O(3)–Mo(1)–N(3)	79.16(4)
O(4)–Mo(1)–O(5)	44.54(4)	N(1)–Mo(1)–N(3)	81.45(4)

N-heterocyclic base species undergo unfavourable oxidation under the reaction conditions but pyrazoles both resist oxidation and enhance the catalytic activity, particularly 3,5-dimethylpyrazole. For the latter, the immobilisation of the resulting catalyst in the IL allowed for very efficient catalyst recycling and after ten cycles no significant diminution of the yield was observed. However, whilst the system is very efficient for the epoxidation of activated substrates such as *cis*-cyclooctene, the activity toward a wider range of substrates is limited.

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