Journal of Molecular Catalysis A: Chemical 338 (2011) 111–120

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Olefin epoxidation in solventless conditions and apolar media catalysed by specialised oxodiperoxomolybdenum complexes

Matthew Herbert, Francisco Montilla*, Agustín Galindo*

Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, Aptdo 1203, 41071 Sevilla, Spain

ARTICLE INFO

Article history:
Received 11 November 2010
Received in revised form 1 February 2011
Accepted 6 February 2011
Available online 15 February 2011

Keywords:
Catalysis
Molybdenum
Epoxidation
Hydrogen peroxide

ABSTRACT

The epoxidation of olefin substrates, in both apolar organic media and under solventless conditions, with aqueous hydrogen peroxide and catalysed by molybdenum complexes has been investigated. The catalysts compounds employed were the oxodiperoxomolybdenum complexes of several pyridine, 2,2′-bipyridine and pyrazole ligands with apolar functions (alkyl chains, alkyl-trimethylsilyl groups and polydimethylsiloxanyl polymer), which showed enhanced solubility in relatively apolar organic media. Both the isolated complexes and *in situ* preparations were catalytically active. The solubility of the new catalyst complexes appears to facilitate the catalytic activity in these systems, since activity was not observed for the analogous, insoluble complexes of unfunctionalised ligands. In these systems, the oxidant, aqueous hydrogen peroxide, forms a separate phase and the catalyst resides in the organic phase. From a green chemistry and economic perspective the elimination of organic solvents and co-catalysts from a reaction system would present advantages and, consequently, the epoxidation reaction was also investigated under solventless conditions. The 3-hexyl-5-methylpyrazole and 3-hexyl-5-heptylpyrazole complexes were found to show heightened activities, the latter being particularly efficient in these conditions, whilst bipyridines apparently inhibit the epoxidation. In addition, the mechanism of the epoxidation reaction was studied through DFT calculations for the model olefin substrate ethylene with the oxodiperoxomolybdenum complex of 3-hexyl-5-heptylpyrazole. The oxo-transfer reaction occurred by interaction of the ethylene with the peroxo ligand via the spirocyclic transition state proposed by Sharpless.

1. Introduction

The selective oxidation of olefins to the corresponding epoxides is a highly important industrial transformation in the synthesis of many fine and bulk chemical intermediates. Generally efficient oxidative technologies have been developed for the epoxidation of light olefins [1] but for heavier, more complex substrates, stoichiometric quantities of organic oxidants are typically employed [2], resulting in the production of substantial quantities of hazardous by products and poorer atom economies [3]. For these reasons the investigation of catalytic epoxidations for heavier olefins has been an important area of research for several decades. Epoxidations facilitated by transition metal catalyst compounds can employ hydroperoxide oxidants including H_2O_2 as oxidant, resulting in more benign waste products (small alcohols or water) and improved atom economies [4]. In homogeneous epoxidations methyltrioxorhenium based catalysts have been generally found to give the highest activities [5]. However, due to the expense of such catalysts and the relative scarcity of rhenium, catalysts based on more common transition metal elements would be preferable [6]. Molybdenum(VI) compounds have produced some of the more active catalysts to be studied in this capacity [7] and amongst these oxodiperoxomolybdenum type complexes stand out as attractive options due to their facile and cheap preparation, chemical simplicity and robustness [8,9]. Homogeneous molybdenum catalysed epoxidations typically employ organohydroperoxide reagents (most commonly *tert*-butylhydroperoxide) as oxidant but a limited number of systems have been reported employing "greener" hydrogen peroxide [10], most notably including the highly active $NaHCO_3$ co-catalysed systems developed by Bhattacharyya et al. [11].

Continuing our research into metal catalysed oxidations in apolar media [12] we have now investigated oxodiperoxomolybdenum catalysed epoxidations in solventless systems and in low-polar organic solvents. A difficulty which is encountered when trying to use these compounds as catalysts under such conditions is their poor solubility, particular in more apolar organic media including halocarbon, aromatic and hydrocarbon solvents. The role that appropriate ligands can play in solubilising the catalyst complex is crucial to achieving an efficient catalytic system [13]. Previously reported systems in such media typically employed catalyst com-

* Corresponding authors. Fax: +34 954 557153.
E-mail addresses: montilla@us.es (F. Montilla), galindo@us.es (A. Galindo).

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doi:10.1016/j.molcata.2011.02.004

plexes incorporating ligands functionalised with long alkyl chains, such as the alkyl functionalised pyrazolylpyridine ligands used by Thiel et al. [9] or trialkylphosphine oxide ligands [14]. These functional groups help to solubilise the catalyst and thus permit effective homogeneous catalysis. In our own previous studies we have investigated the use of ionic liquids to solubilise oxodiperoxomolybdenum catalysts with simpler unfunctionalised ligands to investigate and compare their catalytic efficiency in epoxidation reactions [15]. As a result we determined that pyrazole type ligands produce a significant enhancement in the catalytic activity of these catalysts [16]. Developing on these precedents the study to be presented here investigated oxodiperoxomolybdenum catalysed olefin epoxidations in relatively apolar media employing specialised alkyl, trimethylsilyl and polydimethylsiloxane functionalised N-donor base ligands in order to solubilise the catalyst complexes. As well as pyridine and bipyridine based ligands, 3,5-dialkylpyrazole species were investigated under solvent-free conditions to see if pyrazole species would again induce enhanced catalytic activity, as previously observed in ionic liquids [16].

2. Experimental

2.1. General

Synthetic reactions were performed under a dry, oxygen-free, nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified appropriately prior to use, using standard procedures. Chemicals were obtained from commercial sources and used as supplied or purified by distillation prior to use, as appropriate. Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer (as either liquid film 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 $Si(CH_3)_4$. Gas chromatography was carried out using a Varian CP-3800. Elemental analysis (C, H, N) was conducted by the Microanalytical Service of the Universidad de Sevilla (CITIUS) on an Elemental LECO CHNS 93 analyser. The synthesis and characterisation of both **A** and **B** have been described previously by us [12b]. The syntheses of compounds **E** and **H** have been communicated previously [17], but the experimental procedures employed vary slightly and are here described. Although the use of **D** has been described previously [18] its synthesis was not been reported in detail and thus is here included.

2.2. Synthesis of ligands

2.2.1. 4-(2,2-Bis-trimethylsilanyl-ethyl)pyridine (*C*)

To a solution of $^iPr_2NH$ (1.05 equiv., 447 μL, 3.15 mmol) in dry THF (~25 mL) at −78 °C was added ^{n}BuLi 1.6 M in hexanes (1.05 equiv., 1.88 mL, 3.15 mmol), resulting in the *in situ* formation of lithium diisopropylamide (LDA). A solution of 4-picoline (1.00 equiv., 291 μL, 3.0 mmol) in THF (15 mL) was then added and the solution warmed to 0 °C in an ice bath, stirring at this temperature for 5 min. Next, 1-chloro-2,2-bis(trimethylsilanyl)methane (1.00 equiv., 650 μL, 3.0 mmol) was added, stirring at 0 °C for a further 5 min before allowing it to warm to room temperature and leaving it to stir for 36 h. The solution was then concentrated to approximately 10 mL, dissolved in dichloromethane (50 mL), and washed with water (3× 25 mL). To prevent significant loss of product in the washes, the aqueous fractions were then themselves extracted with dichloromethane (3× 25 mL), and all of the organic solutions were then combined. The resulting solution was dried ($MgSO_4$), filtered, and evaporated on a rotary evaporator (rotavap), leaving the crude product as an oil. This was purified by column chromatography employing silica gel and 0.5% NEt_3 in 1:1 hexane–ethyl acetate as eluent. The final product **C** was a yellow oil (440 mg, 1.75 mmol, 58%). IR (NaCl, cm^{-1}): 500, 685, 755, 774, 839, 981, 1036, 1251, 1415, 1595, 1558, 1598, 2851, 2898, 2952, 3024, 3067. ^1H NMR ($CDCl_3$): δ 0.00 (br s, 18H, $Si(CH_3)_3$), 0.32 (t, J_{HH} = 6.8 Hz, 1H, C*H*), 2.77 (d, J_{HH} = 6.7 Hz, 2H, CH_2), 7.13 (br m, 2H, *m*-NC_5H_4), 8.46 (br s, 2H, *o*-NC_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.0 (s, $Si(CH_3)_3$), 14.6 (s, *C*H), 31.4 (s, CH_2), 123.7 (s, *m*-NC_5H_4), 149.4 (s, *o*-NC_5H_4), 153.7 (s, *p*-NC_5H_4). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 3.8 (s, $Si(CH_3)_3$). Elemental analysis, calculated for $C_{13}H_{25}NSi_2$: C, 62.08; H, 10.02; N, 5.57. Experimental: C, 58.45; H, 9.79; N, 4.95%.

2.2.2. 2,6-(Bis-trimethylsilanylmethyl)pyridine (*D*)

The same experimental procedure was followed for this derivative but in place of 4-picoline, 2,6-lutidine (0.50 equiv., 463 μL, 4.0 mmol) was doubly deprotonated by two equivalents of LDA before reacting with chlorotrimethylsilane (1.00 equiv., 1.02 mL, 8.0 mmol). Compound **D** was obtained as a pale yellow oil (520 mg, 2.07 mmol, 52%). IR (NaCl, cm^{-1}): 722, 806, 841, 948, 978, 1030, 1093, 1105, 1153, 1184, 1203, 1311, 1378, 1398, 1444, 1466, 1588, 1600, 1622, 2098, 2427, 2489, 2567, 2720, 2760, 2850, 2923, 2960, 3400. ^1H NMR ($CDCl_3$): δ 0.00 (br s, 18H, $Si(CH_3)_3$), 2.41 (s, 4H, CH_2), 6.68 (d, J_{HH} = 7.5 Hz, 2H, *m*-NC_5H_3), 7.27 (t, J_{HH} = 7.5 Hz, 1H, *p*-NC_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.1 (s, $Si(CH_3)_3$), 32.8 (s, CH_2), 117.3 (s, *m*-NC_5H_4), 135.4 (s, *p*-NC_5H_4), 157.0 (s, *o*-NC_5H_4). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 2.0 (s, $Si(CH_3)_3$). Elemental analysis, calculated for $C_{13}H_{25}NSi_2$: C, 62.08; H, 10.02; N, 5.57. Experimental: C, 60.37; H, 10.16; N, 4.97%.

2.2.3. 4,4′-Di(tridecyl)-2,2′-bypiridine (*E*)

To a solution of $^iPr_2NH$ (1.05 equiv., 950 μL, 6.7 mmol) in dry THF (~30 mL) at −78 °C was added ^{n}BuLi 1.6 M in hexanes (1.05 equiv., 4.0 mL, 6.7 mmol), resulting in the *in situ* formation of lithium diisopropylamide (LDA). A solution of 4,4-dimethyl-2,2-bipyridine (1.00 equiv., 590 mg, 3.20 mmol) in THF (15 mL) was then added and the solution warmed to 0 °C in an ice bath, stirring at this temperature for 5 min. 1-Iodododecane (1.65 mL, 6.7 mmol) was then added, stirring at 0 °C for a further 5 min. The reaction was then allowed to warm to room temperature before leaving to stir for 36 h. The solution was concentrated to a volume of approximately 10 mL on a rotavap before adding dichloromethane (50 mL) and washing with distilled water (3× 25 mL). The aqueous wash fractions were then themselves extracted with dichloromethane (3× 25 mL) before combining all organic fractions, drying the solution over $MgSO_4$, filtering and evaporating the solvent on a rotavap to leave the crude product as a cream coloured solid. This was recrystallised from methanol to give the final product as a colloidal white solid (900 mg, 70%). The ^1H NMR data correlate to those previously reported [17]. IR (NaCl, cm^{-1}): 834, 1110, 1547, 1597, 1964. ^1H NMR ($CDCl_3$): δ 0.80 (t, J_{HH} = 6.4 Hz, 6H, CH_3), 1.18 (v br m, 40H, intermediate CH_2), 1.62 (m, 4H, bipy-$CH_2CH_2CH_2$), 2.61 (t, J_{HH} = 7.8 Hz, 4H, bipy-CH_2CH_2), 7.05 (d, J_{HH} = 4.5 Hz, 2H, 5-C*H* and 5′-C*H* of bipy), 8.16 (s, 2H, 3-C*H* and 3′-C*H* of bipy), 8.48 (d, J_{HH} = 4.5 Hz, 2H, 6-C*H* and 6′-C*H* of bipy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 (s, CH_3), 22.7, 29.4, 29.5, 30.5, 31.9 (s, intermediate CH_2), 35.6 (s, bipy-CH_2), 121.3, 123.9 (s, C-3 and C-5 of bipy), 149.0, 152.9, 156.2 (s, C-2, C-4 and C-6 of bipy). Elemental analysis, calculated for $C_{36}H_{60}N_2$: C, 83.01; H, 11.61; N, 5.38. Experimental: C, 84.23; H, 12.25; N, 5.59%.

2.2.4. 4,4′-Bis-(bistrimethylsilanylmethyl)-2,2′-bipyridine (*F*)

A method analogous to that described for compound **E** was used with chlorotrimethyilsilane (1.00 equiv., 770 μL, 5.9 mmol) in place of 1-iodododecane and the molar proportions of all other reagents adjusted accordingly. Compound **F** was obtained as fine white crystals (310 mg, 24%). IR (KBr, cm^{-1}): 451, 558, 620, 654, 691, 724, 756, 778, 839, 862, 914, 990, 1035, 1069, 1159, 1217, 1247, 1404, 1540,

1580, 3047. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 36H, Si(CH_3)$_3$), 1.72 (s, 4H, C*H*), 6.88 (d, J_{HH} = 5 Hz, 2H, 5-C*H* and 5′-C*H* of bipy), 8.01 (s, 2H, 3-C*H* and 3′-C*H* of bipy), 8.42 (d, J_{HH} = 5 Hz, 2H, 6-C*H* and 6′-C*H* of bipy). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.0 (s, Si(CH_3)$_3$), 30.6 (s, C*H*), 121.5, 123.4 (s, C-3 and C-5 of bipy), 148.4, 153.9, 155.7 (s, C-2, C-4 and C-6 of bipy). ^{29}Si{^{1}H} NMR $CDCl_3$): δ 2.2 (s, *Si*(CH_3)$_3$). Elemental analysis, calculated for $C_{24}H_{44}N_2Si_4$: C, 60.95; H, 9.38; N, 5.92. Experimental: C, 59.90; H, 10.12; N, 6.07%.

*2.2.5. 4,4′-Bis-(2,2-bis-trimethylsilanyl-ethyl)-2,2′-bipyridine (**G**)*

A method analogous to that described for compound **E** was used with 1-chloro-2,2-bis-trimethylsilanyl-ethane (1.00 equiv., 1.00 g, 5.13 mmol) in place of 1-iodododecane and the molar proportions of all other reagents adjusted accordingly. The product was obtained as cream coloured crystals (290 mg, 23%). IR (KBr, cm^{-1}): 839, 1036, 1250, 1551, 1590. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 18H, Si(CH_3)$_3$), 0.47 (t, J_{HH} = 7.0 Hz, 2H, CH_2C*H*), 2.87 (d, J_{HH} = 7.0 Hz, 4H, CH_2CH), 7.14 (d, J_{HH} = 5 Hz, 2H, 5-C*H* and 5′-C*H* of bipy), 8.27 (s, 2H, 3-C*H* and 3′-C*H* of bipy), 8.54 (d, J_{HH} = 5 Hz, 2H, 6-C*H* and 6′-C*H* of bipy). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.0 (s, Si(CH_3)$_3$), 14.3 (s, C*H*), 31.6 (s, CH_2), 121.1 (s, C-5 of bipy), 123.6 (s, C-3 of bipy), 148.7, 154.6, 155.8 (s, C-2, C-4 and C-6 of bipy). ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 3.9 (s, *Si*(CH_3)$_3$). Elemental analysis, calculated for $C_{26}H_{48}N_2Si_4$: C, 62.33; H, 9.66; N, 5.59. Experimental: C, 62.28; H, 10.46; N, 5.84%.

*2.2.6. 4-Methyl-4′-tridecyl-2,2′-bipyridine (**H**)*

To a dry solution of diisopropylamine (461 μL, 3.26 mmol) in THF (30 mL) was added ^{n}BuLi 1.6 M in hexanes (2.04 mL, 3.26 mmol). This was stirred for 15 min after which a solution of 4,4-dimethyl-2,2′-bipyridine (601 mg, 3.26 mmol) in dry THF (25 mL) was added dropwise over 30 min. This solution was then stirred for 90 min before it was cooled to 0 °C and 1-iodododecane (804 μL, 3.26 mmol) was added. The solution was stirred for another 90 min at 0 °C and then quenched with water/ice (25 mL) and the mixture was subsequently extracted with diethyl ether (3× 50 mL) which was then dried ($MgSO_4$), filtered and evaporated to leave the crude product. This was recrystallised from ethyl acetate to leave the product as a white solid (380 mg, 33%). The ^{1}H NMR data correlate to those previously reported [17]. IR (KBr, cm^{-1}): 534, 583, 729, 824, 898, 992, 1043, 1107, 1245, 1374, 1462, 1551, 1596, 2849, 2916, 3054. ^{1}H NMR ($CDCl_3$): δ 0.81 (t, J_{HH} = 6.6 Hz, 3H, CH_2CH_3), 1.18 (br m, 20H, intermediate CH_2), 1.62 (quintet, 2H, bipy-4′-$CH_2CH_2CH_2$), 2.37 (s, 3H, bipy-4-CH_3), 2.62 (t, J_{HH} = 7.8 Hz, 2H, bipy-4′-$CH_2CH_2CH_2$), 7.07 (m, 2H, 5-C*H* and 5′-C*H* of bipy), 8.17 (br s, 2H, 3-C*H* and 3′-C*H* of bipy), 8.48 (m, 2H, 6-C*H* and 6′-C*H* of bipy). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.0 (s, CH_2CH_3), 21.1 (s, bipy-4-*C*H_3), 22.5 (s, *C*H_2CH_3), 29.1–29.5 (several s, intermediate CH_2), 30.3, 31.8 (s, intermediate CH_2), 35.4 (s, bipy-4′-CH_2), 121.3 (s, C-5′ of bipy), 122.0 (s, C-5 of bipy), 123.8 (s, C-3′ of bipy), 124.5 (s, C-3 of bipy), 148.6 (s, C-4 and 4′ of bipy), 153.0 (s, C-6 and 6′ of bipy), 155.6 (s, C-2 and 2′ of bipy). Elemental analysis, calculated for $C_{24}H_{36}N_2$: C, 81.76; H, 10.29; N, 7.95. Experimental: C, 80.94; H, 9.95; N, 7.80%.

*2.2.7. 3-Hexyl-5-methylpyrazole (**I**)*

1-Octyne (3.8 mL, 25 mmol) was degassed, dissolved in dry THF (25 mL), cooled to −78 °C and 1.6 M *n*-BuLi in hexanes (18.75 mL, 30 mmol) was added. The solution was allowed to warm to room temperature and stirred for 5 min. The reaction was again cooled to −78 °C and 1.0 M $ZnCl_2$ in diethyl ether (25 mL, 25 mmol) carefully added. The reaction was warmed to 0 °C. Acetyl chloride (2.0 mL, 27.5 mmol) was then added and the reaction was stirred for 6 h. Working now under air, the resulting solution was washed with saturated NH_4Cl (25 mL) and the phases separated. The aqueous phase was washed twice with ether (25 mL) and all of the organic phases were then combined and the solvents evaporated on a rotavap. The crude intermediate was then dissolved in methanol (50 mL) and $NH_2NH_2{\cdot}H_2O$ (1.75 mL, 35 mmol) added. The reaction was left stirring overnight at room temperature. The solvent was then evaporated to leave the crude product as a brown oil. This was purified by elution through a silica gel column obtaining the product as a clear, pale yellow oil (2.16 g, 13.0 mmol, 52%). IR (NaCl, cm^{-1}): 725, 792, 1008, 1027, 1148, 1315, 1378, 1467, 1580, 2857, 2927, 3033, 3103, 3134, 3196. ^{1}H NMR ($CDCl_3$): δ 0.88, (t, J_{HH} = 6.3 Hz, 3H, CH_2CH_3), 1.31 (br, 6H, intermediate CH_2), 1.60 (br quintet, 2H, pz-5-$CH_2CH_2CH_2$), 2.28 (s, 3H, pz-5-CH_3), 2.60 (t, J_{HH} = 7.7 Hz, 2H, pz-5-CH_2CH_2), 5.83 (s, 1H, C*H* of pz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 12.2 (s, *C*H_3), 13.9 (s, *C*H_3), 22.4, 26.7, 28.9, 29.3, 31.5 (s, intermediate CH_2), 102.8 (s, C*H* of pz), 144.4 (s, *C*CH_3 of pz), 148.9 (s, *C*CH_2 of pz). Elemental analysis, calculated for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91; N, 16.85. Experimental: C, 80.24; H, 11.21; N, 14.10%.

*2.2.8. 3-Hexyl-5-heptylpyrazole (**J**)*

The synthetic procedure was identical to that performed for **I** but using an equal molar quantity of octanoyl chloride in place of acetyl chloride. This product was obtained as a yellow oil (2.56 g, 10.3 mmol, 41%). IR (NaCl, cm^{-1}): 724, 797, 887, 1003, 1027, 1093, 1163, 1259, 1378, 1465, 1577, 1671, 1737, 2853, 2927, 2953, 3103, 3138, 3200. ^{1}H NMR ($CDCl_3$): δ 0.80 (br t, J_{HH} = 6.5 Hz, 6H, CH_3), 1.22 (br, 14H, CH_2), 1.55 (m, 4H, pz-$CH_2CH_2CH_2$), 2.52 (t, J_{HH} = 7.7 Hz, 4H, pz-CH_2CH_2), 5.76 (s, 1H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.0 (s, two alkyl *C*H_3), 21–31 (several s, intermediate CH_2), 100.9 (s, C*H* of pz), 148.2 (s, *C*CH_2 of pz). Elemental analysis, calculated for $C_{16}H_{30}N_2$: C, 76.74; H, 12.07; N, 11.19. Experimental: C, 80.10; H, 12.76; N, 9.45%.

2.3. Synthesis of metal complexes

2.3.1. [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] solution in aqueous hydrogen peroxide

Solutions of the aqua complex of oxodiperoxomolybdenum, [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] 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 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 [19]. For the purpose of simplicity the solution is referred to in this work simply as aqueous [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$].

*2.3.2. [Mo(O)(O$_2$)$_2$(**E**)] (**1e**)*

To a solution of 4,4′-di(tridecyl)-2,2′-bypiridine (**E**) (0.19 mmol) in methanol (15 mL) was added aqueous [Mo(O)(O)$_2$(H$_2$O)$_n$] (1 equiv., 273 μL, 0.191 mmol) and the resulting solution was left stirring for 30 min. After this time the resulting precipitate was isolated by filtration, washed with cold distilled water and dried for several hours under vacuum. The product **1e**, the oxodiperoxomolybdenum complex of **E**, was obtained as a yellow powder. IR (KBr, cm^{-1}): 660, 723, 764, 836, 861, 948, 1031, 1420, 1467, 1610, 2850, 2920, 3058, 3117, 3432. ^{1}H NMR ($CDCl_3$): δ 0.81 (br t, J_{HH} = 6.3 Hz, 6H, CH_3), 1.18 (v br, 40H, intermediate CH_2), 1.55 (br m, 2H, bipy-$CH_2CH_2CH_2$), 1.73 (br m, 2H, bipy-$CH_2CH_2CH_2$), 2.62 (t, J_{HH} = 7.7 Hz, 2H, bipy-CH_2CH_2), 2.85 (t, J_{HH} = 7.8 Hz, 2H, bipy-CH_2CH_2), 7.19 (d, 1H, 5- or 5′-C*H* of bipy), 7.61 (d, 1H, 5- or 5′-C*H*

of bipy), 7.81 (s, 1H, 3- or 3′-C*H* of bipy), 8.10 (s, 1H, 3- or 3′-C*H* of bipy), 8.21 (d, 1H, 6- or 6′-C*H* of bipy), 9.36 (d, 1H, 6- or 6′-C*H* of bipy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 (s, *C*H_3), 22.7 (s, intermediate *C*H_2), 29–30.5 (several s, intermediate *C*H_2), 31.9 (s, intermediate *C*H_2), 35.6, 36.0 (s, bipy-*C*H_2), 121.0, 122.8, 126.7, 126.8 (s, C-3 and C-5 of bipy), 147.4, 147.8, 154.1, 155.1, 156.4, 160.8 (s, C-2, C-4 and C-6 of bipy). Elemental analysis, calculated for $MoC_{36}H_{60}O_5N_2$: C, 62.05; H, 8.68; N, 4.02. Experimental: C, 61.56; H, 8.75; N, 3.97%.

2.3.3. *[Mo(O)(O$_2$)$_2$(**F**)] (**1f**)*

This product was synthesised following the same experimental method as for **1b** but with **F** in place of **B**. The product **1f**, the oxodiperoxomolybdenum complex of **F**, was obtained as a yellow powder. IR (KBr, cm^{-1}): 622, 655, 691, 776, 843, 866, 946, 1030, 1219, 1252, 1420, 1603, 2899, 2954, 3447. ^1H NMR ($CDCl_3$): δ 0.00, 0.12 (s, 36H, Si(*C*H_3)$_3$), 1.68, 1.95 (s, 2H, *C*H), 6.82, 7.22 (d, J_{HH} = 6 Hz, 2H, 5-*C*H and 5′-*C*H of bipy), 7.38, 7.64 (br s, 2H, 3-*C*H and 3′-*C*H of bipy), 8.00, 9.14 (d, J_{HH} = 6 Hz, 2H, 6-*C*H and 6′-*C*H of bipy). Elemental analysis, calculated for $MoC_{24}H_{44}O_5N_2Si_4$: C, 44.42; H, 6.83; N, 4.32. Experimental: C, 43.67; H, 6.66; N, 4.32%.

2.3.4. *[Mo(O)(O$_2$)$_2$(**G**)] (**1g**)*

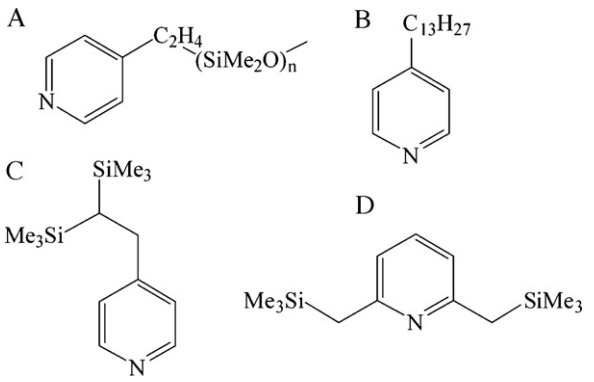
This product was synthesised following the same experimental method as for **1b** but with **G** in place of **B**. The product **1g**, the oxodiperoxomolybdenum complex of **G**, was obtained as a yellow powder. IR (KBr, cm^{-1}): 689, 758, 778, 842, 866, 942, 988, 1036, 1250, 1420, 1610, 2899, 2952, 3447. ^1H NMR ($CDCl_3$): δ 0.00, 0.08 (s, 36H, Si(*C*H_3)$_3$), 0.11, 0.28 (t, J_{HH} = 6.3, 6.4 Hz, respectively, 2H, CH_2*C*H), 2.75, 2.97 (d, J_{HH} = 6.3, 6.4 Hz, respectively, 4H, *C*H_2CH), 7.11, 7.53 (d, J_{HH} = 6 Hz, 2H, 5-*C*H and 5′-*C*H of bipy), 7.69, 7.97 (s, 2H, 3-*C*H and 3′-*C*H of bipy), 8.10, 9.25 (d, J_{HH} = 6 Hz, 2H, 6-*C*H and 6′-*C*H of bipy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.0, 0.1 (s, Si(CH_3)$_3$), 14.6, 15.0 (s, CH), 31.8, 32.4 (s, CH_2), 120.6, 122.4 (s, C-5 of bipy), 126.2, 126.5 (s, C-3 of bipy), 147.3, 147.5, 153.7, 158.6, 154.9, 163.1 (s, C-2, C-4 and C-6 of bipy). Elemental analysis, calculated for $MoC_{26}H_{48}O_5N_2Si_4$: C, 46.13; H, 7.15; N, 4.14. Experimental: C, 47.13; H, 7.14; N, 4.50%.

2.3.5. *[Mo(O)(O$_2$)$_2$(**H**)] (**1h**)*

This product was synthesised following the same experimental method as for **1b** but with **H** in place of **B**. The product **1h**, the oxodiperoxomolybdenum complex of **H**, was obtained as a yellow powder. IR (KBr, cm^{-1}): 661, 723, 836, 863, 947, 1032, 1242, 1308, 1420, 1467, 1610, 2850, 2920, 2956, 3448. ^1H NMR ($CDCl_3$): two isomers, δ 0.88 (t, J_{HH} = 6 Hz, 6H, *C*H_3 terminal), 1.25 (v br, 20H, intermediate *C*H_2), 1.58 (m, 2H, bipy-4′-CH_2*C*$H_2$$CH_2$), 1.79 (m, 2H, bipy-4′-$CH_2$*C*$H_2$$CH_2$), 2.46 (s, 3H, py-4-*C*$H_3$), 2.68 (t, J_{HH} = 7.7 Hz, 2H, bipy-4′-*C*$H_2$$CH_2$), 2.70 (s, 3H, py-4-*C*$H_3$), 2.91 (t, J_{HH} = 7.7 Hz, 2H, bipy-4′-*C*$H_2$$CH_2$), 7.18, 7.61 (m, 2H, 5-*C*H and 5′-*C*H of bipy), 7.82, 7.85, 8.10, 8.14 (s, 1H, 3-*C*H and 3′-*C*H of bipy), 8.19, 9.34 (m, 2H, 6-*C*H and 6′-*C*H of bipy). Elemental analysis, calculated for $MoC_{24}H_{36}O_5N_2$: C, 54.54; H, 6.87; N, 5.30. Experimental: C, 55.15; H, 6.80; N, 5.22%.

2.4. 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)(O)$_2$(H_2O)$_n$] (50 μL, 0.025 mmol), the base additive as specified (typically 0.1 mmol monodentate, 0.05 mmol bidentate), the reaction solvent if required (2 mL), the oxidant (30% aqueous 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.



Scheme 1. Pyridine-based ligands.

2.5. Computational details

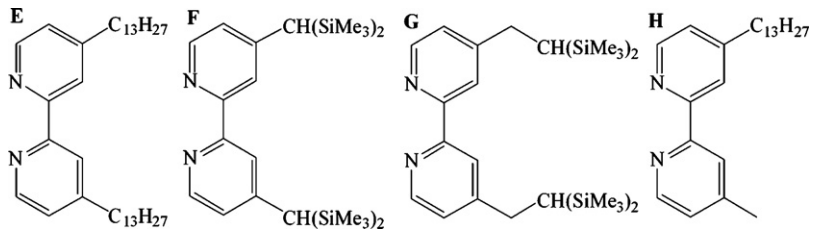
The electronic structure and geometries of the model compounds were computed using density functional theory at the B3LYP level [20,21]. The Mo atom was described with the LANL2DZ basis set [22] whilst the 6-31G(d,p) basis set was used for the C, O, N and H atoms. The DFT calculations were performed using the Gaussian 03 suite of programs [23]. The nature of the optimised geometries of all the compounds were characterised by the calculated number of imaginary frequency at the same level of theory, *i.e.*, energy minimum structures without imaginary frequencies (NImag = 0). Transition states were located using the quadratic synchronous transit (QST2) approach [24] and frequency calculations were performed in order to check the stationary states (NImag = 1).

3. Results and discussion

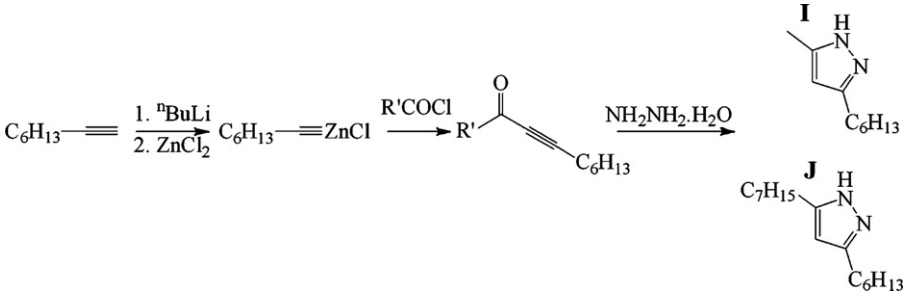
3.1. Ligand synthesis and preparation of metal complexes

A series of ligand species consisting of pyridine, 2,2′-bipyridine or pyrazole functionalised with various alkyl chains, trimethylsilyl groups or polydimethylsiloxane polymer was synthesised (Schemes 1–3). The preparations of 4-polydimethylsiloxanylethylpyridine (**A**) and 4-tridecylpyridine (**B**) have been previously reported by us and are not repeated here [12b]. The synthesis of the other pyridine ligands (Scheme 1), 4-(2,2-bis-trimethylsilanyl-ethyl)pyridine (**C**) and 2,6-(bis-trimethylsilanylmethyl)pyridine (**D**), were based on a previously described procedure for the synthesis of related substituted bipyridines [25] and the synthetic method was analogous to that which we previously described for the preparation of **B** [12b]. The methyl groups of 4-picoline and 2,6-lutidine were deprotonated by lithium diisopropylamide and reaction with chloro-bistrimethylsilanyl-methane or chlorotrimethylsilane as appropriate subsequently gave the products (see details in Section 2). The use of compound **D** in experimental studies has been previously described elsewhere, though without details concerning its synthesis [18].

In the same manner, the functionalised 2,2-bipyridines (Scheme 2), 4,4′-di(tridecyl)-2,2′-bipyridine (**E**), 4,4′-bis-(bistrimethylsilanylmethyl)-2,2′-bipyridine (**F**), 4,4′-bis-(2,2-bis-trimethylsilanyl-ethyl)-2,2′-bipyridine (**G**) and 4-methyl-4′-tridecyl-2,2′-bipyridine (**H**) were prepared by deprotonation of 4,4′-dimethyl-2,2′-bipyridine and subsequent reaction with appropriate organo or silano halides (see details in Section 2). The synthesis and ^1H NMR data of compounds **E** and



Scheme 2. 2,2′-Bipyridine-based ligands.



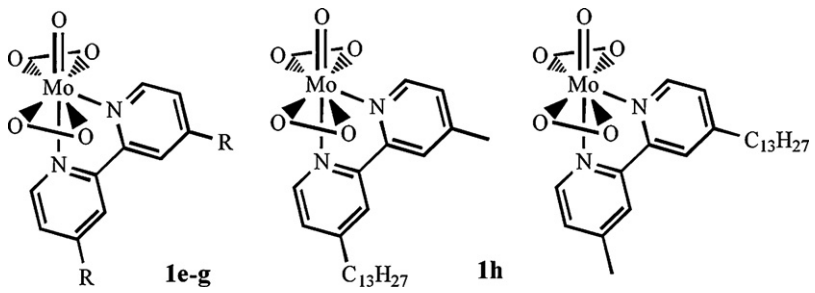
Scheme 3. Synthesis of alkyl substituted pyrazole ligands.

H have been communicated previously [17]. Complete spectroscopic characterisation of these and of the new substituted bipyridines **F** and **G** has been performed (see Section 2 and Figure S1 in Supplementary data).

Functionalised pyrazoles were synthesised by first coupling an alkyne, as an organometallic intermediate, with the appropriate acid chloride, followed by reaction with hydrazine to form the pyrazole ring (Scheme 3). In this manner both 3-hexyl-5-methylpyrazole (**I**) and 3-heptyl-5-hexylpyrazole (**J**) were prepared and characterised.

The corresponding complexes of oxodiperoxomolybdenum were subsequently prepared. Generally, this was achieved fairly easily by dissolving molybdenum trioxide in excess aqueous hydrogen peroxide and reacting this solution appropriately with the ligands. The monodentate complexes of the pyridines took the form of viscous yellow coloured oils whilst the bipyridines gave pale yellow, colloidal solids. The isolation and spectroscopic characterisation of the complexes of the bidentate bipyridine ligands, **1e**–**h**, was both significant and interesting as oxodiperoxomolybdenum complexes of bipyridines are usually very insoluble in apolar organic solvents making it difficult to record their NMR spectra in solution. The solubilising functions of these species render them highly soluble in $CDCl_3$ such that well defined spectra were easily achieved. The ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes are relatively simple since the only signals arise exclusively from the ligands. As an example, in the spectra of $[Mo(O)(O_2)_2(\mathbf{G})]$ (**1g**), in the ^1H NMR spectrum two separate triplet signals at 0.11 and 0.28 ppm are observed corresponding to the CH hydrogen atom of the $-CH_2CH(SiMe_3)_2$ groups, the signals shifted slightly upfield with respect to the corresponding signal on the spectrum of the free ligand **G**. In the same way, the CH signals of the aromatic hydrogen atoms, which for the free **G** ligand display a doublet + singlet + doublet pattern typical of 4,4′-substituted-2,2′-bipyridines, are clearly split into two set of signals due to coordination to the $\{Mo(O)(O_2)_2\}$, demonstrating the non-equivalence of the pyridine rings. The $^{13}C\{^1H\}$ NMR spectrum of **1g** affords complimentary information, with ten distinct singlets observable for the aromatic carbon atoms in the pyridine rings, rather than the five that would be expected if the rings were equivalent. Analogous observations were made in the NMR spectra of all of the complexes of the symmetrical bipyridine ligands **E**–**G** (compounds **1e**–**g**), with two distinct sets of signals visible for each aromatic ring. These observations would seem to indicate that these complexes adopt the structure shown in Scheme 4, with the split signals resulting from the electronic difference between the axially and equatorially coordinated rings in the complex. An analogous structure has previously been ascertained by X-ray analysis of $[Mo(O)(O_2)_2(bipy)]$ [26] and has also been seen in related complexes with substituted bipyridine ligands [27] and other bidentate N-ligands [9b,c,28].

For the complex of the unsymmetrically substituted bipyridine **H**, $[Mo(O)(O_2)_2(\mathbf{H})]$ (**1h**), the ^1H NMR spectra indicate that both of the two possible isomers corresponding to the two alternative coordination modes **H** can adopt with the $\{Mo(O)(O_2)_2\}$ core (Scheme 4) were present, in a ratio at least approximately 1:1, indicating that neither was formed more favourably. Illustrating this, the ^1H NMR



Scheme 4. Structures of molybdenum complexes **1e**–**g** and the two isomers of **1h**.

Table 1
Oxobisperoxomolybdenum catalysed *cis*-cyclooctene epoxidations in apolar organic solvents with a selection of base additives[a].

Entry	Solvent	Ligand	Conversion	Yield
1	Hexane	Pyridine	5	1
2		4-(Polydimethylsiloxanyl-ethyl)-pyridine (**A**)	4	2
3		2,6-Bis-trimethylsilanylmethyl-pyridine (**D**)	9	1
4		2,2′-Bipyridine	0	0
5		4,4′-Ditridecyl-2,2′-bipyridine (**E**)	0	0
6	$CHCl_3$	–	0	0
7		Pyridine	2	2
8		4-(Polydimethylsiloxanyl-ethyl)-pyridine (**A**)	86	86
9		4-Tridecylpyridine (**B**)	99	99
10		4-(2,2-Bis-trimethylsilanyl-ethyl)-pyridine (**C**)	72	71
11		2,6-Bis-trimethylsilanylmethyl-pyridine (**D**)	38	38
12		2,2′-Bipyridine	12	2
13		4,4′-Ditridecyl-2,2′-bipyridine (**E**)	17	17
14		4,4′-Bis(bistrimethylsilanylmethyl)-2,2′-bipyridine (**F**)	17	17

[a] Experimental conditions: Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, ligand 0.1 mmol for monodentate and 0.05 mmol for bidentate, 30% $H_2O_{2(aq)}$ 3.0 mmol, *cis*-cyclooctene 1.0 mmol, solvent 10 mL, t = 18 h, T = 60 °C. Yields and conversions calculated by GC.

of **1h** shows two pairs of distinct singlets and triplets corresponding to the 4-CH_3 and 4′-CH_2 groups respectively, both shifted slightly downfield with respect to the free **H** ligand. Similarly, a pair of multiplets corresponding to the 4-CH_2CH_2 groups and pairs of signals are apparent for the aromatic protons.

3.2. Mo-catalysed epoxidation reactions

Subsequently, the catalytic activity of these complexes in the epoxidation of olefins in apolar media was investigated, studying first of all the oxidation of *cis*-cyclooctene (Scheme 5) in organic solvent media; chloroform and hexane (see Table 1). In these reactions the molybdenum catalyst complex formed *in situ* from an aqueous solution of oxodiperoxomolybdenum, $[Mo(O)(O_2)_2(H_2O)_n]$, and the respective base additive, mixing them together at the start of the reaction. Other experimental details are included in the corresponding table footnotes.

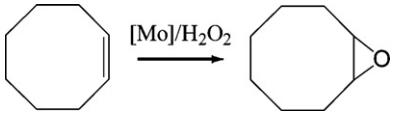
This preliminary study focussed only on the functionalised pyridine and bipyridine ligands, which were compared with their unfunctionalised analogues. In chloroform, all of the functionalised ligands solubilised the catalyst sufficiently to result in reaction systems wherein the catalyst and olefin substrate were dissolved in the reaction solvent with the aqueous hydrogen peroxide oxidant forming a separate phase. When the unfunctionalised analogues were used however, the molybdenum complexes were always observed to precipitate as a yellow solid, leaving no detectable colouration in the organic phase. In hexane there was never any observable solubility even for the functionalised ligands.

Significant conversion in hexane was never achieved (entries 1–5, Table 1), probably attributable to the insolubility of the catalysts in such a highly apolar solvent. Following these results we discontinued studies in hydrocarbon solvents. In chloroform, when no base or the unsubstituted analogue bases (entries 6, 7 and 12, Table 1) were employed there was never any significant conversion to the epoxide product, again probably due to the insolubility of the catalyst complexes. Low, but significant conversions were observed when 4,4′-dialkyl substituted bipyridines were used (entries 13 and 14, Table 1). However, the yields with these bidentate ligands were found to be markedly lower than those obtained with their monodentate counterparts (entries 8–11, Table 1). Previously we had made a similar observation in epoxidation reactions in ionic liquids [16b,c].

The two 4-substituted monopyridyl ligands 4-(polydimethylsiloxanyl-ethyl)pyridine (**A**) (entry 8, Table 1) and 4-tridecylpyridine (**B**) (entry 9, Table 1) afforded high yields within the 18 h, with complete conversion to the epoxide observed in the latter.[1] Use of the solubilising ligands seems to result in complete dissolution of the metal catalyst complex in the organic phase of a biphasic system and the oxodiperoxomolybdenum complexes of the monodentate pyridine ligands are apparently reasonably efficient catalysts. The other monodentate pyridine ligands tested, the structural isomers 4-(2,2-bis-trimethylsilanyl-ethyl)pyridine (**C**) and 2,6-bis(trimethylsilanylmethyl)pyridine (**D**) (entries 10 and 11, Table 1), afforded significant epoxidation, though with a marked difference in the observed yields indicating that steric hindrance due to the proximity of the 2,6-functions to the metal centre in the former may influence the epoxidation, resulting in slower oxidation. However, the benefits from the solubilising effect of the methyl-trimethylsilanyl substituents still clearly outweigh this hindrance compared with unsubstituted pyridine (entry 7, Table 1), showing that solubilisation of the catalyst complexes is a crucial factor.

Investigations of epoxidation in systems employing **A** and **B** were subsequently extended to other olefin substrates (see Table 2). Six substrates were tested in this study, cyclohexene which is relatively active to epoxidation, the inactive terminal alkene 1-octene, one *cis* and two *trans* secondary alkenes which should be more activated and also styrene, the oxide of which is very vulnerable to decomposition through hydrolysis.

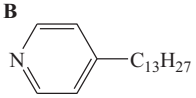
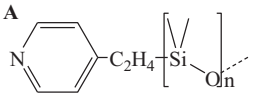
A brief examination of the results is sufficient to conclude that neither of the base additives investigated induced a catalytic system which was active in the epoxidation of this wider range of substrates. Thus, the high activities observed in the preliminary investigation with *cis*-cyclooctene seem to be limited to only this sterically and electronically activated substrate. In the epoxidation of cyclohexene, **A** produced the most active system, (entry 7, Table 2) with a reduced level of conversion observed for **B** (entry



Scheme 5. Selected test reaction.

[1] It should be noted that certainly some of the pyridine coordinating species that were investigated here probably converted *in situ* to their corresponding N-oxides, a reaction that we have demonstrated for **B**. In fact, IR and elemental analysis of the product from the reaction of **B** with oxodiperoxomolybdenum indicated that the N-oxide complex, $[Mo(O)(O_2)_2(\mathbf{B}O)(H_2O)]$, had been isolated [16c]. Additionally, oxidation of 4-tridecylpyridine by oxodiperoxomolybdenum species in ionic liquid medium has been also demonstrated [16b].

Table 2
Oxobisperoxomolybdenum catalysed olefin epoxidations in chloroform[a].

Entry	Ligand	Olefin	Conversion	Yield
1	**B** 	Cyclohexene	23	5
2		1-Octene	0	0
3		*trans*-2-Octene	15	13
4		*trans*-4-Octene	25	22
5		*cis*-2-Heptene	29	29
6		Styrene	60	0
7	**A** 	Cyclohexene	75	75
8		1-Octene	0	0
9		*trans*-2-Octene	2	3
10		*trans*-4-Octene	2	2
11		*cis*-2-Heptene	1	1
12		Styrene	100	0

[a] Experimental conditions: Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, base additive 0.10 mmol, 30% $H_2O_{2(aq)}$ 3.0 mmol, olefin substrate 1.0 mmol, chloroform 10 mL, t = 18 h, T = 60 °C. Yields and conversions calculated by GC.

1, Table 2). However, given the long reaction time the incomplete conversion for such an active substrate still indicates fairly limited efficiency. In neither system was any trace of epoxidation detected for the terminal olefin 1-octene (entries 2 and 8, Table 2). In spite of its markedly elevated efficiency in the epoxidation of cyclohexene, the system using **A** generated only trace yields for all of the other substrates tested (entries 9–12, Table 2). In the conversion of the secondary alkenes **B** did show a moderate level of activity however (entries 3–5, Table 2). In neither system was any unreacted styrene detected after reaction (entries 6 and 12, Table 2), although the high conversions indicate that whilst the styrene was probably oxidised to the epoxide it was subsequently transformed. In both cases GC analysis showed low levels of benzaldehyde which may therefore be an intermediate breakdown product.

The study subsequently moved to solventless epoxidations, similar to those we previously studied using methyltrioxorhenium catalysts [12b]. In the same way as in the solvent based studies this began with an investigation of the influence of the various ligands in the epoxidation of *cis*-cyclooctene (see Table 3). The bipyridine type ligands were not investigated in this study but we introduced the alkyl functionalised pyrazoles 3-hexyl-5-methylpyrazole (**I**) and 3-hexyl-5-heptylpyrazole (**J**), having witnessed in related studies that pyrazole ligands can produce more activated oxodiperoxomolybdenum catalysts for epoxidations [16], sulphide oxidation [29], and alkylbenzene oxidation [30].

Only minor epoxide yields (less than 10%) were generated in the absence of any ligand or where unfunctionalised pyridine was used (entries 1 and 2 respectively, Table 3). Pyrazole was found to produce a slightly more active system and 3,5-dimethylpyrazole gave an even higher yield of 31% (entries 3 and 4, Table 3). This additional enhancement may be due to the solubilising influence of the methyl groups but we have previously observed that the more basic 3,5-dimethylpyrazole seems to produce a greater activating effect than unfunctionalised pyrazole in similar systems [16] and this may also be a factor. Moving on to the functionalised ligands, both **A** and **B** gave enhanced yields when compared to unfunctionalised pyridine (entries 5 and 6, Table 3), but yields were well short of complete unlike in chloroform. When the functionalised pyrazoles **I** and **J** were tested however, complete conversion of the olefin substrate was observed within 18 h (entries 7 and 8, Table 3). Selectivity was lower for **I** (63%) than **J** (95%) however, indicating that there was a greater extent of epoxide hydrolysis in the former. By reducing the reaction time to 4 h these selectivities could be improved so that with **J** a 100% conversion with complete selectivity for the epoxide was achieved. The reactions were also analysed after 66 h, finding that the hydrolysis slowly continues over time, although in the case of **J** the yield still remained above 90%. The heightened activity of these latter two pyrazole based systems when compared to unfunctionalised pyrazole analogues is presumably due to the enhanced solubility of the metal complexes, whilst compared to the functionalised pyridines the use of a pyrazole type ligand as opposed to a pyridine results in a more active catalyst. As previously mentioned we have made similar observations in ionic liquid based systems and the resistance of the pyrazole species to oxidation may well be the reason for this enhancement [16]. Pyridines are fairly quickly converted to their corresponding N-oxides under the oxidising conditions but pyrazoles do not undergo any such oxidation with the result that, *in situ*, pyrazoles are the stronger donor ligands, being N- rather than O-donor ligands. This may result in an electronically enhanced catalyst complex and subsequently more efficient epoxidation.

The epoxidation systems utilising pyrazoles **I** and **J** were monitored over a 2 h period to observe the profile and progress of the epoxidation (see data in Table S1 in Supplementary data). Fig. 1 shows the solventless epoxidation reaction where **J** is the base additive used and Figure S2 displays the same reaction for **I**. These experiments demonstrated that epoxidation in these systems proceeds relatively rapidly, with almost all of the substrate consumed

Table 3
Oxobisperoxomolybdenum catalysed solventless epoxidation of *cis*-cyclooctene[a].

Entry	Ligand	Conversion (yield)		
		t = 4 h	t = 18 h	t = 66 h
1	None	–	12 (5)	–
2	Pyridine	–	8 (8)	–
3	Pyrazole	–	16 (12)	–
4	3,5-Dimethylpyrazole	–	31 (31)	–
5	**A**	–	25 (23)	–
6	**B**	–	31 (31)	–
7	**I**	99 (88)	100 (63)	100 (29)
8	**J**	100 (100)	100 (95)	100 (91)

[a] Experimental conditions: Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, base additive 0.10 mmol, 30% $H_2O_{2(aq)}$ 3.0 mmol, olefin substrate 1.0 mmol, T = 60 °C. Conversions and yields calculated by GC.

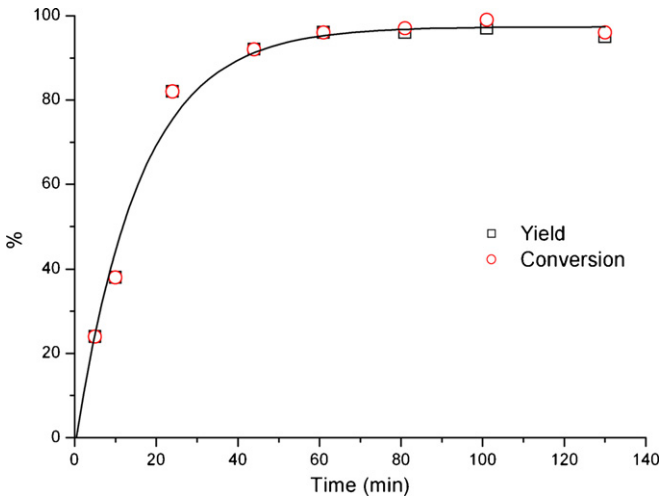


Fig. 1. Reaction profile of the oxobisperoxomolybdenum catalysed solventless epoxidation of *cis*-cyclooctene with **J** as ligand. Experimental details in Table S1.

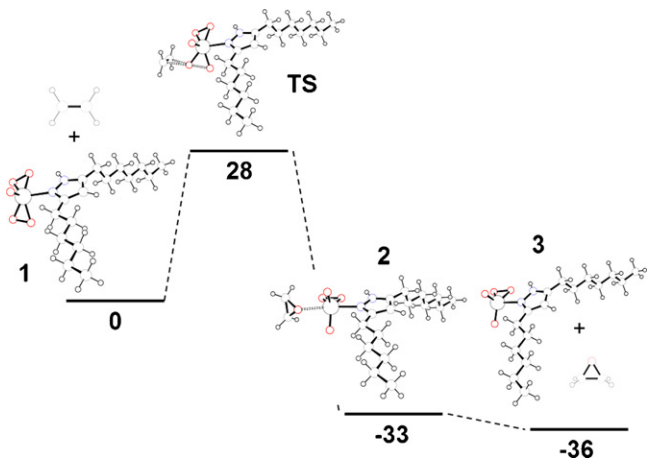


Fig. 2. Calculated Gibbs free energy profile of the model epoxidation reaction with $[Mo(O)(O_2)_2(J)]$ (kcal mol^{-1}).

within little over half an hour. In the system utilising **I** the epoxide subsequently begins to hydrolyse whilst where **J** was used there was no substantial evidence of this within the 2 h. It is not clear why the hydrolysis reaction was so much more rapid in the system using **I**, it may be attributable to differences in the solubilities of the respective complexes of **I** and **J** but this is entirely speculative. The TON and TOF calculated for the reaction with **J** are 9.6 and 115 h^{-1} (for 5 min), respectively. These values are lower than those previously reported by us for a rhenium catalysed solventless epoxidation system [12b] though this is unremarkable as methyltrioxorhenium derivatives are typically much more active epoxidation catalysts than oxomolybdenum compounds [31]. The values are also far lower than those reported for the Mo catalysed olefin epoxidation system developed by Bhattacharyya and co-workers, which constitutes one of the optimal examples of an oxomolybdenum catalysed epoxidation [11,32]. However the solventless systems reported here are advantageous in that neither a co-catalyst, such as $NaHCO_3$, nor any organic solvent is required. Finally, a further study was conducted using a much lower catalyst:substrate ratio (0.25 mol% catalyst), under the same experimental conditions, raising the achievable TON to 1820, but with a lower TOF value.

In the same way as for the study of epoxidations in chloroform, the efficiency of the solventless systems in the oxidation of alternative olefin substrates was investigated. Dimethylpyrazole, the functionalised pyridines, **A** and **B**, and the functionalised pyrazoles, **I** and **J**, were all studied in this capacity. These results are shown in Table 4. A quick overview of the results reveals that, in common with the study in chloroform, none of the systems investigated had a particularly high activity toward the less activated substrates. Somewhat disappointingly the activity of even the systems using the functionalised pyrazoles **I** and **J** toward the wider range of substrates was limited. Only barely higher than trace yields were recorded for 1-octene in all of the systems. For the secondary *trans* and *cis* olefin substrates the systems using dimethylpyrazole and **A** demonstrated generally lowered activities compared to those using **B**, **I** and **J**. There was no obvious difference in reactivity toward the *cis* and *trans* substrates indicating that neither is more inhibited nor activated than the other. Traces of epoxide were obtained in the epoxidation of styrene, though with significant levels of conversion in all cases, indicating that the epoxidation may well have proceeded but that subsequently the product was largely lost to hydrolysis. In the systems using **I** and **J** a 7% yield of benzaldehyde was detected.

3.3. DFT study of the mechanism of the stoichiometric epoxidation reaction

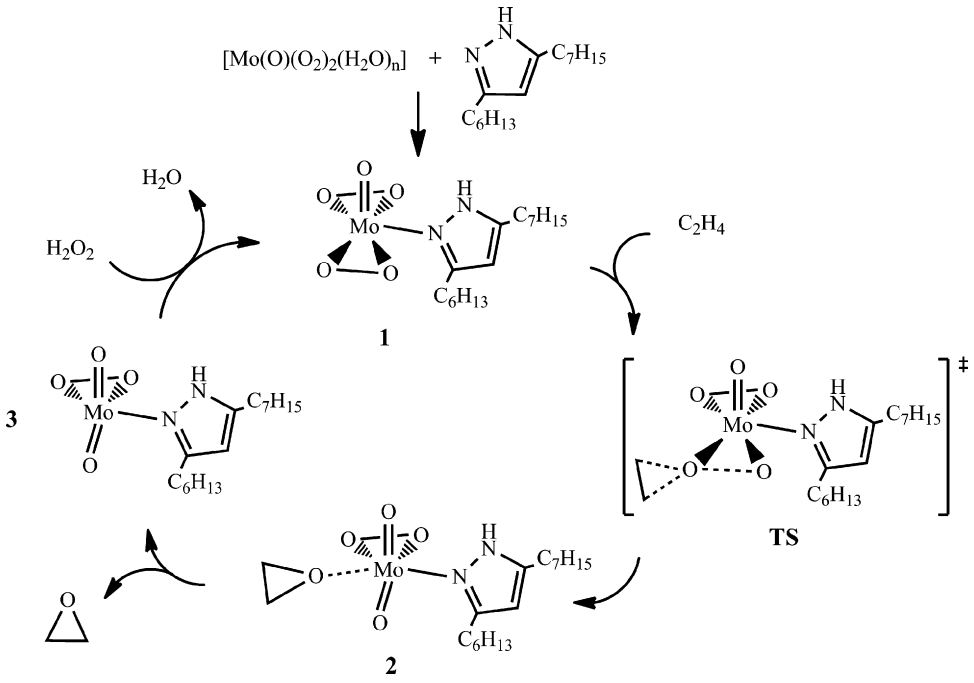
Density functional calculations were carried out to obtain further insight into the mechanism of the epoxidation reaction. Ethylene, the simplest olefin model was selected as the substrate with the oxodiperoxomolybdenum complex of 3-hexyl-5-heptylpyrazole as the oxidising molybdenum species, this complex being the most active under solventless conditions. The starting model compound $[Mo(O)(O_2)_2(J)]$ (**1**), as well as other considered intermediates (see Scheme 6), were optimised without symmetry restrictions at the B3LYP level.

The reaction profile for the epoxidation is shown by Fig. 2, which contains the optimised structures for compounds **1**–**3** and the transition state **TS**. The reaction is exergonic, in common with related studies [33]. The first step is the oxo-transfer reaction from the peroxo ligand of complex **A** to the ethylene substrate which affords the dioxoperoxo complex **2**, wherein the generated epoxide is initially coordinated to the molybdenum centre. This intermediate is characterised by the transition structure **TS** which takes the

Table 4
Oxobisperoxomolybdenum catalysed solventless epoxidations[a].

Ligand	Conversion (yield)				
	1-Octene	*trans*-2-Octene	*trans*-4-Octene	*cis*-2-Heptene	Styrene
3,5-Dimethylpyrazole	3(1)	5(5)	17(10)	87(1)	15(3)
A	1(1)	4(4)	3(3)	13(6)	23(3)
B	5(1)	44(22)	21(18)	51(12)	62(8)
I	1(1)	73(24)	48 (25)	71 (30)	87(1)[b]
J	14(1)	65(23)	68 (32)	49 (36)	83(1)[b]

[a] Experimental conditions: Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, base additive 0.10 mmol, 30% $H_2O_{2(aq)}$ 3.0 mmol, olefin substrate 1.0 mmol, t = 18 h, T = 60 °C. Conversions and yields calculated by GC.
[b] 7% yield of benzaldehyde quantified.



Scheme 6. Catalytic cycle for the epoxidation reaction.

form of the spirocycle originally proposed by Sharpless [34] and theoretically analysed for other [Mo(O)(O$_2$)$_2$(L)] models by several groups [35]. The structural parameters of the **TS** here agree well with those of similar species as previously reported [16a,35]. The calculated energy barrier for **TS** (28 kcal mol^{-1}) is also similar to other computed values and is equivalent to that found for the closely related [Mo(O)(O$_2$)$_2$(dmpz)] compound (dmpz = 3,5-dimethylpyrazol) [16a]. The dissociation of the epoxide from the intermediate **2** is slightly favourable (*ca.* −3 kcal mol^{-1}) and yields the dioxoperoxo complex **3**. The catalytic cycle is closed by the energetically favourable (−9.4 kcal mol^{-1}) reaction of hydrogen peroxide with **3** which regenerates the starting complex **1**. Solvent effects were included in the calculations and no significant influence in the energetic reaction profile was detected (see Table S2 in the Supplementary data).

4. Conclusions

It was shown that low polarity substituents (alkyl chains, trimethylsilane bearing functions, polydimethylsiloxane polymers) attached to the coordinated ligands of oxodiperoxomolybdenum complexes enhance their solubility in low polar organic solvents. In epoxidation reactions the solubility enhancements induced by appropriate ligands lead to high yields in the epoxidation of *cis*-cyclooctene, not attainable with unfunctionalised analogue catalysts due to their insolubility. Pyrazoles were found to induce significantly more efficient epoxidation than pyridines, whilst 2,2′-bipyridines seem to slow the reaction. Of particular interest were the observations made in the epoxidations conducted under solventless conditions, where the oxodiperoxomolybdenum complex of 3-hexyl-5-heptylpyrazole showed markedly enhanced catalytic efficiency in the epoxidation of *cis*-cyclooctene with hydrogen peroxide. The elimination of the necessity for any organic solvent and the absence of any co-catalyst makes this system significantly advantageous in green chemistry terms. However, the substrate range of these systems is limited, whilst the complexes are active in the epoxidation of less active substrates the oxidations proceed too slowly to be of practical use. Surmounting this limitation is a key objective of our continuing research.

Acknowledgements

This research was supported by the Spanish Ministerio de Ciencia e Innovación (CTQ2007-61037 and CTQ2010-15515) and Junta de Andalucía (Proyecto de Excelencia, FQM-2474).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.02.004.

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