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# A preliminary investigation into a rationally designed catalytic system for the epoxidation of alkenes based on a bipyridyl core

Gennadiy Ilyashenko, David Sale, Majid Motevalli, Michael Watkinson*

*The Walter Besant Building, School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK*

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ABSTRACT

A novel series of enantiomerically pure ligands, containing both pyridyl and 2,2′-bipyridyl moieties, derived from 2,6-dibromopyridine is reported, together with the synthesis of a number of manganese(II) complexes of the ligand library, four of which have been structurally characterised by single crystal X-ray diffraction. The efficacy of these complexes in the epoxidation of a range of alkene substrates is investigated principally using per acetic acid as the oxidant.



## 1. Introduction

The oxidation of organic substrates is fundamental to contemporary synthesis, however, despite the vast array of methods that are known for performing synthetic oxidative transformations their application in industrial processes remains surprisingly limited [1]. This is due to a number of factors, including heavy metal product contamination, the need for high catalyst loadings and poor turn over frequencies and the use of environmentally damaging solvents and oxidants. Within the broad spectrum of oxidative transformations, asymmetric epoxidation is particularly appealing as it can generate up to two stereogenic centres in one step from widely available alkene substrates. Thus significant efforts have been directed towards this area in recent years [2]. Amongst the catalytic asymmetric methods that have been developed, of greatest prominence are the metal-based Sharpless [3] and Jacobsen-Katsuki epoxidations [4], as well as the organocatalytic methods of Shi and Julia-Colonna, which represent rare examples of systems that have found industrial applications [5]. Nonetheless these systems have some limitations, including a lack of substrate generality, and for the metal-based systems, the oxidants used are not atom-economical and the solvents undesirable. Consequently great effort has focussed on the development of alternative methods that employ more environmentally benign oxidants and solvents. Of the oxidants investigated hydrogen peroxide is undoubtedly the most desirable due to its high atom economy (47%), low toxicity and cost, as well as its operational ease, but until very recently its use as an oxidant in catalytic asymmetric epoxidation was extremely limited. Elegant reports from the laboratories of Katsuki [6], Beller [7] and Strukul [8] have now shown that high chemical yields in addition to excellent levels of asymmetric induction can be attained using metal-based catalysts with many substrates. Despite the fact that these systems satisfy the industrial requirement for a low environmentally impacting oxidant that provides epoxides in high yield and enantiomeric excess, some issues remain concerning the solvents used, the catalyst loading, and in some cases the ease of ligand synthesis and substrate scope. There is consequently ongoing interest in the development of alternative catalytic systems.

Peracetic acid is a less-studied oxidant than hydrogen peroxide but is a very attractive alternative [9]. Although it is less atom economic than hydrogen peroxide (25%) it is generated from hydrogen peroxide [10] and in principle the acetic acid by-product could be recycled, thus reducing its environmental impact. Moreover, the use of hydrogen peroxide with many transition metal catalysts is hampered by their catalase-like activity which results in its rapid decomposition, a problem not suffered by peracetic acid [11]. Stack and co-workers have reported the use of peracetic acid

* Corresponding author.
*E-mail address:* m.watkinson@qmul.ac.uk (M. Watkinson).

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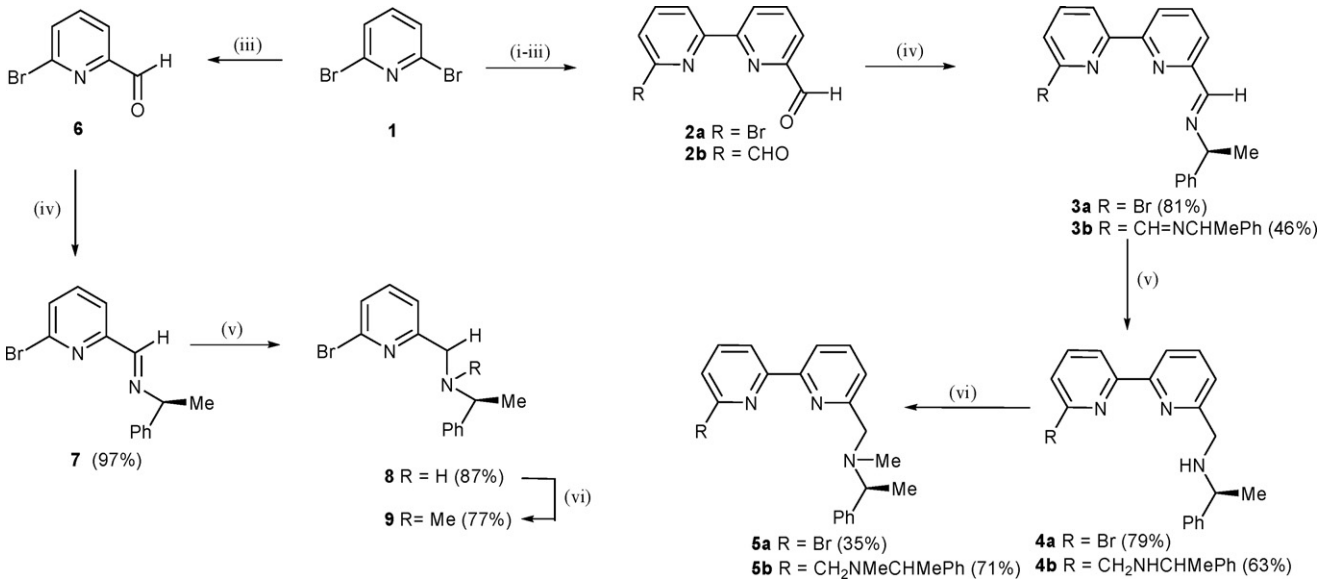



**Scheme 1.** *Reagents and conditions*: (i) *n*-BuLi, diethyl ether; (ii) $CuCl_2$, air; (iii) *n*-BuLi, THF, DMF; (iv) (*S*)-α-methylbenzylamine, EtOH, Δ; (v) $NaBH_4$, EtOH, Δ (vi) $HCO_2H$, $CH_2O$, $H_2O$.

in combination with iron and manganese-based catalysts in the rapid epoxidation of a wide-range of alkene substrates, albeit with no useful levels of asymmetric induction when chiral ligands were used [9,11]. Subsequently Chang and co-workers also reported its efficacy in manganese-catalysed epoxidation [12]. Since these first reports a number of other studies have appeared [13], including the first examples of effective asymmetric epoxidation catalysts by Costas and co-workers [13a], which prompts us to report our preliminary findings in this area.

## 2. Results and discussion

### 2.1. The rationale behind the ligand design

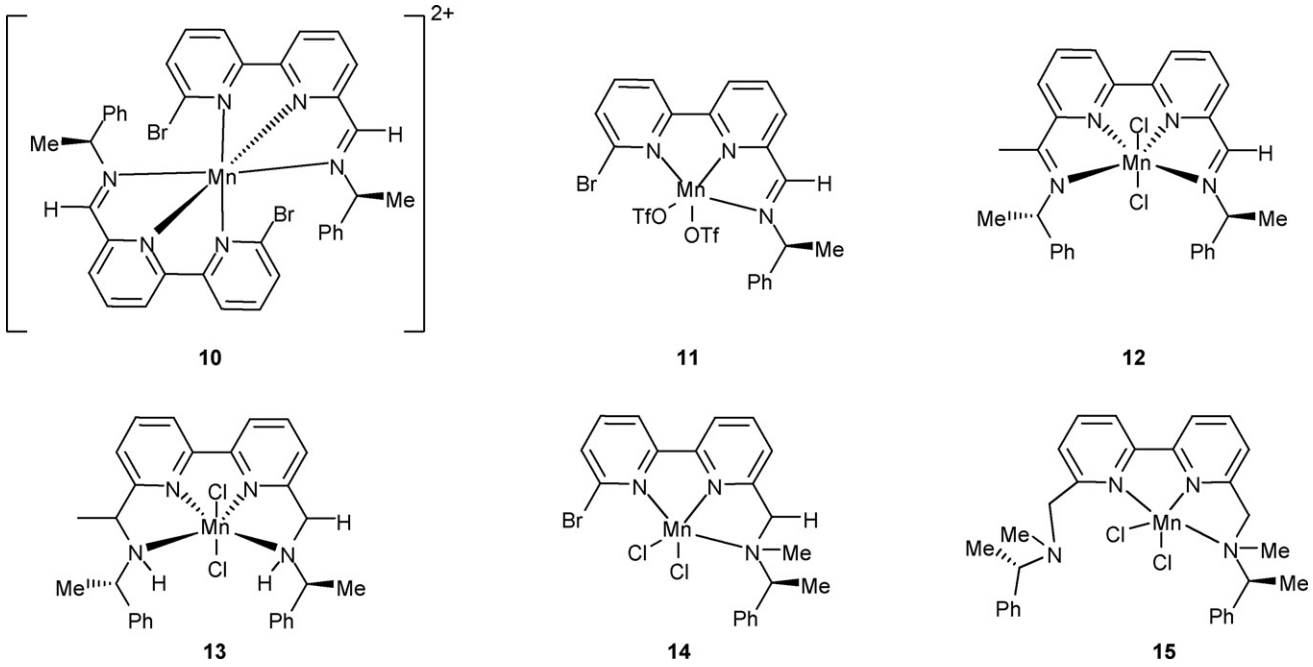
When an oxidative catalytic system is being designed several aspects must be taken into account: (i) the ease of ligand synthesis and the facility to undertake modular structural and electronic changes; (ii) the oxidative stability of the ligand and its complexes; (iii) the coordination properties of the ligand; (iv) the thermodynamic stability of the metal complex; and (v) the ligand's ability to effect the transfer of chirality. We thus sought to develop a ligand library commensurate with these requirements and features. Given the activity of the structurally related 1,10-phenanthroline core in Stack's epoxidation system [9,11], the bipyridine (bipy) core appeared to be an ideal candidate about which to develop an asymmetric variant, as outlined in Scheme 1. The advantages of this approach are numerous: (i) its synthesis has precedent in literature [14–19]; (ii) Schiff bases have been previously used in asymmetric catalysis with considerable success [4]; (iii) a large pool of commercially available chiral amines could be used to tune chirality transfer; (iv) various substituents could replace the bromide moiety, e.g. via palladium-catalysed reactions, thus allowing further fine-tuning of any active catalysts; (v) there is considerable potential for controlling the substitution around the aromatic rings and therefore adjusting electronic and steric effects; (vi) the imine bond can be reduced and the resultant secondary amine alkylated providing further steric and electronic modularity in the library. Given this, allied to the well-defined coordination chemistry of 2,2′-bipyridine, it would appear that this should be an attractive ligand around which an asymmetric catalytic system could be developed. We thus established effective methods for the synthesis of ligands **3**–**5** and **7**–**9** and a number of their manganese complexes **10**–**15** (see Supplementary Information for experimental procedures).

Given the efficacy of a number of closely related manganese complexes in the catalytic epoxidation of alkenes [9,11,13] we were keen to establish what activity, if any, the complexes of the new ligands possessed. However, rather than resorting to an *in situ* screening method to establish activity from the outset we first sought to investigate the coordination chemistry of the ligand library in order to develop a better understanding of any underlying catalytic activity. We also wished to ascertain whether the potentially meridionally coordinating ligands, **3a**–**5a**, were able to support the formation of di-μ-oxo bridged dimers as we felt that these might provide highly active catalysts. Indeed Brudwig and Crabtree have recently demonstrated the efficacy of exactly such a dimer in the selective C–H oxidation of ibuprofen [20].

Several manganese(II) complexes of ligands **3**–**5** were thus prepared in moderate to good yields (Scheme 2 and also see Supplementary Information Table S1), however, we were unable to prepare any complexes of ligands **7**–**9**, despite very extensive attempts to do so. Whilst molecular models suggested that the conformation of amines **8**–**9** might make them unsuitable bidentate donors, our failure to isolate complexes of ligand **7** is perplexing as complexes of very similar ligands have been reported [21–23].

All complexes were satisfactorily characterised by ESMS, infrared spectroscopy and where possible elemental analysis (see also Supplementary Information). The electrochemistry of all of the authenticated complexes was also investigated which only revealed an irreversible reductive wave at ca. −1.7 V (versus Fc+/Fc with $[(n\text{Bu})_4\text{NCl}]$ as the supporting electrolyte) in both DCM and $CH_3CN$, which we attribute to a ligand-centred process [24]. The structures of **10**, **12**, **13** and **15** were established by single crystal X-ray diffraction (see also Supplementary Information).

Reaction between ligand **3a** and manganese(II) chloride yielded a novel complex **10** comprising a coordinatively saturated cationic centre, $[\text{Mn}(\mathbf{3a})_2]^{2+}$, in which the two ligands adopted the expected meridional mode of coordination, Fig. 1. The cationic charge is balanced by the presence of a nearly perfectly tetrahedral $[MnCl_4]^{2-}$ anion with average Mn—Cl bond lengths of 2.361(9) Å and Cl–Mn–Cl




**Scheme 2.** Schematic representation of the complexes prepared. Full characterisation data is provided in ESI.

angle values of 109.47(9)° (other selected bond lengths and angles are presented in Table S2).

Rather surprisingly a search of the Cambridge Crystallographic Database revealed that no complexes of this type have been structurally characterised and that the only analogous species all contain terpy ligands [26–29] However, analysis of one of these complexes, that of ligand **16** [29], allows some important structural features in **10** to be highlighted (Fig. 2). Both complex **10** and the manganese complex of ligand **16** exhibit a highly distorted octahedral environment. As expected the ligands are meridionally chelating, but the geometry in both complexes is severely distorted from idealised octahedral geometry. However, whilst **16** remains essentially planar on coordination to the metal centre, ligand **3a** is severely distorted from planarity adopting an umbrella configuration which is reflected in the relationship between *trans*-oriented nitrogen donors, e.g. N(1)–Mn–N(3) (see also Table S2). This presumably results from the higher steric demand of the bromide and imine groups in **3a** and is further reflected in the elongation of the Mn—N bonds.

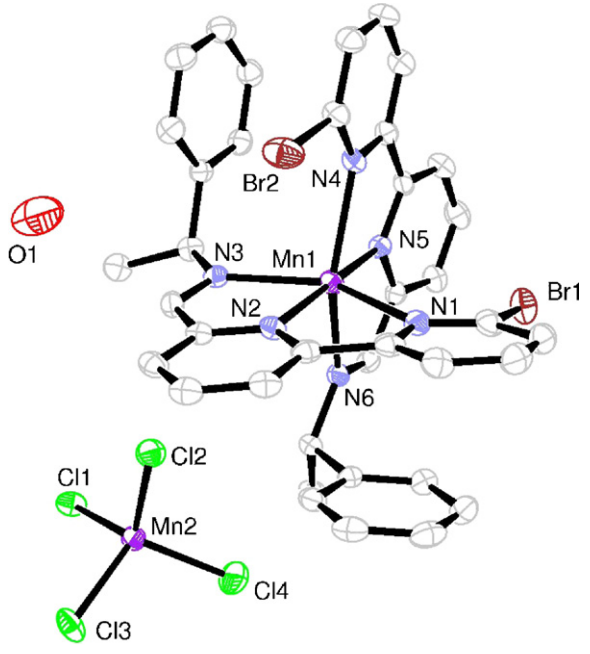



**Fig. 1.** ORTEP [25] view of **10** with labelling scheme for non-carbon atoms (50% probability of displacement ellipsoids).

The average bond length between the central manganese and the 'inner' nitrogen donors, i.e. N(2) and N(5), is 2.184(5) Å which is 0.019 Å longer than those reported in analogous complexes [30,31]. Moreover, the distance between the metal ion and the 'outer' nitrogen donors, i.e. N(1), N(3), N(4) and N(6) are markedly longer than the equivalent Mn—N bonds in $[Mn(\mathbf{16})_2]^{2+}$. It is only appropriate to directly compare Mn(1)–N(1) and Mn(1)–N(4) with $[Mn(\mathbf{16})_2]^{2+}$ whose average length of 2.335 Å is 0.046 Å longer, however, the metal centre and the imine nitrogens are also substantially longer 2.283(7) Å. Thus, given the apparent requirement for vacant *cis*-sites at the manganese centre in potent epoxidation catalysts [9] we were pessimistic of the potential of **10** as an active catalyst, fears that were subsequently substantiated (*vide infra*).

Reaction between ligand **3b** and manganese(II) chloride afforded yellow crystals of complex **12** which revealed the structure to contain an extremely distorted octahedrally coordinated manganese centre with the ligand occupying the equatorial plane, Fig. 3, and the two chloride anions occupying the axial *trans*-positions (for selected bond lengths and angles see Supplementary Information Table S3).

The majority of previously reported ligands with four nitrogen donors form manganese complexes in which the chloride anions have a *cis*-relationship to each other [32–50], which as already discussed is a desirable feature in potential epoxidation catalysts. With the exception of porphyrins, there is only one example of a complex that is structurally similar to the one reported here where labile ligands bear a *trans*-relationship, **16** [24]. Comparison of **12** with this structure reveals that the Mn(1)–N(2) and Mn(1)–N(3) pyridyl nitrogen bonds in **12** are on average longer by 0.062 Å. The Mn(1)–N(1) and Mn(1)–N(4) imine distances in complex **8** are on

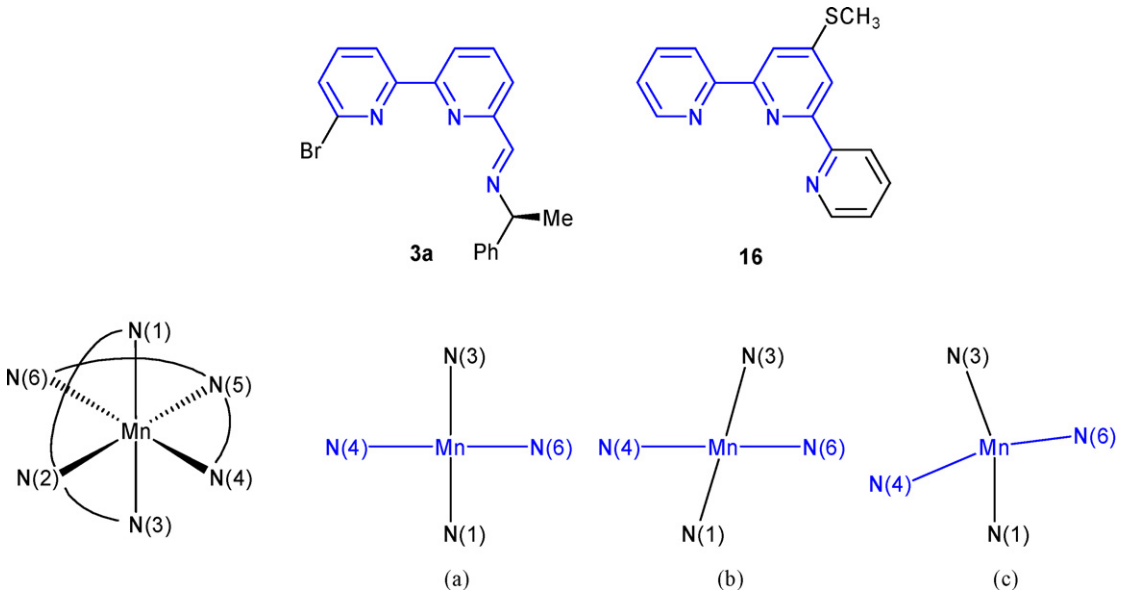



**Fig. 2.** Representations of the structures observed in (a) a perfect octahedron; (b) $[Mn(\mathbf{16})_2]^{2+}$; (c) $[Mn(\mathbf{3a})_2]^{2+}$ when viewed along N(2)–Mn–N(5) axis.

average longer by the more considerable 0.097 Å, although this is probably largely due to the strained nature of the ligands when coordinated to the metal as both complexes display 'outer' Mn—N bond lengths that are longer than the two 'central' bonds. Nevertheless, Mn—N distances are comparable to previously reported Mn—N bond lengths in the aforementioned structures. As can be seen from the crystal structure, Fig. 3 (see also Supplementary Information Table S3), the angles about the metal centre deviate substantially from the ideal values for a regular octahedron. However, these are comparable to those observed in the other related structure and deviations of only 2 or 3 degrees are observed for example the Cl(1)–Mn–Cl(2) angle of 153.31° *cf.* 150.02° for the equivalent $H_2O$–Mn–$OH_2$ angle. Thus, whilst **12** does not display the desired *cis*-vacant sites the distorted nature of the structure gave us cause for optimism, particularly given its structural similarity to other potent manganese-based catalysts [4]. Despite several different attempts to isolate satisfactory crystals of complex **13** for single crystal X-ray diffraction studies these always proved to be twinned. Nonetheless we were able to establish that the coordination mode of **4b** and the general geometry of the complex is essentially identical to **3b** (see Supplementary Information Figure S1).

The reaction between ligand **5b** and manganese(II) chloride yielded yellow crystals of complex **15**, Fig. 4 (selected bond lengths and angles are listed in Table S4).

In contrast to the structures already described, the manganese ion in **15** is five coordinate with a $\tau$ value of 0.31 [51] which indicates that the structure is closer to square-based pyramidal geometry than trigonal bipyramidal. Although the data for complex **13** are poor, the planar $N_4$ coordination mode of the ligand

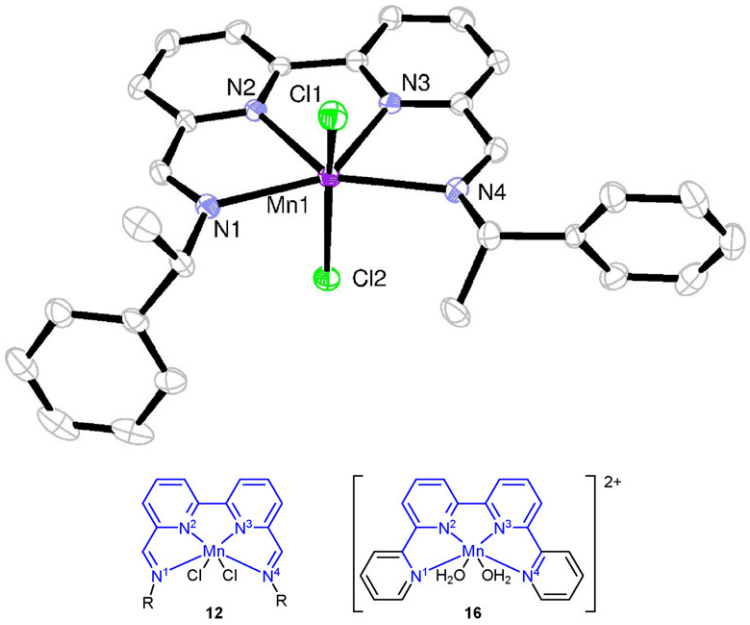



**Fig. 3.** ORTEP [25] view of complex **12** with labelling scheme for non-carbon atoms (50% probability of displacement ellipsoids) and similarities between complexes **12** and **16**.

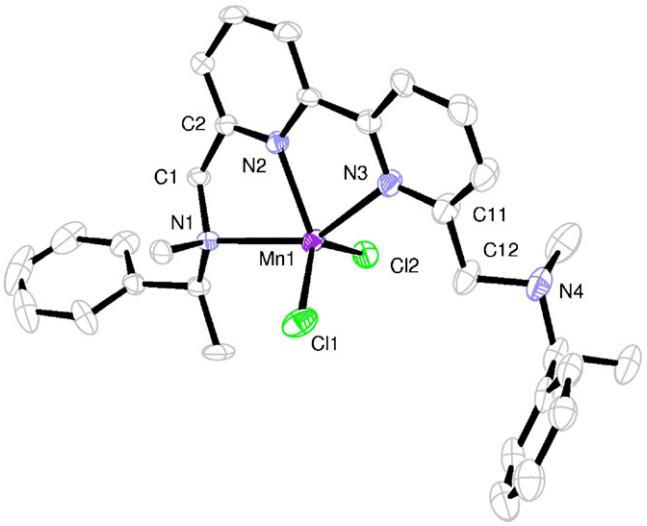



**Fig. 4.** ORTEP [25] view of manganese complex **15** showing the labelling scheme for the non-carbon atoms (40% probability of displacement ellipsoids).

is clear and suggests that the change in the coordination mode of the ligand observed in **15** is not just due to the increased flexibility of the ligand backbone that results from the reduction of the $sp^2$-hybridised imine carbon atoms in **3b**, but that the steric interaction between the methyl group of the tertiary amine and the (*S*)-α-methylbenzylamine derived residue is also important. This is reflected in the Mn(1)–N(4) distance which is the longest observed in this series and perhaps suggests that the steric strain is too great for both tertiary amines to coordinate and we were encouraged by the presence of *cis*-sites at the manganese centre allied with the potential of the uncoordinated nitrogen donor N(4) to participate in hydrogen bonding. Other bond lengths and angles are comparable to those previously reported values [32–50].

### 2.2. Catalytic activity

The manganese complexes of ligands **3**, **4b** and **5** were screened for activity in the catalytic epoxidation of cyclooctene and styrene substrates in acetonitrile using hydrogen peroxide and commercial peracetic acid ($PAA_C$). In all but one case the use of hydrogen peroxide as the oxidant did not result in the formation of any epoxide and the decomposition of the oxidant dominated through catalase-like activity despite very extensive attempts to develop effective conditions similar to those previously reported [52]. In one case however (the catalytic epoxidation of styrene in acetone 10 mol% **14**, 0 °C with 1 equiv. NaOAc) (*S*)-styrene oxide was isolated in 33% yield and 83% ee. Unfortunately we were subsequently unable to reproduce this exciting preliminary result.

Given the extreme sensitivity to hydrolysis of all of the imine ligands reported herein, especially under mildly acidic conditions, we were rather surprised to see the catalytic epoxidation activity of complexes of closely related imine ligands under acidic conditions reported [12]. We therefore decided to test our imine complexes in the epoxidation reaction using peracetic acid. Unsurprisingly, all complexes of the imine ligands were completely unsuitable when this oxidant was used and they rapidly decomposed (indicated by a rapid colour change from yellow to brown and formation of brown precipitated) to the corresponding amine and aldehyde which could be isolated from the reaction mixture. All other complexes, with the exception of **14** and **15** were similarly unproductive. In contrast the combination of peracetic acid and **15** did produce a positive hit in the epoxidation of both styrene and cyclooctene. For

**Table 1**
The pH dependence of the catalytic epoxidation of *cis*-cyclooctene using catalyst **15**

| Entry | pH | Catalyst loading (mol%) | % Yield[a] | % Conversion[b] | TON |
|---|---|---|---|---|---|
| 1 | 2 | 10 | 32 | 65 | 3.2 |
| 2 | 3 | 10 | 35 | 83 | 3.5 |
| 3 | 4 | 5 | 22 | 55 | 4 |
| 4 | 5 | 10 | 10 | 47 | 1 |

An ice-cold solution of catalyst **15** and *cis*-cyclooctene (1.0 equiv.) and internal standard in acetonitrile were treated with buffered $PAA_R$ (1.2 equiv.).

[a] Yields obtained from GC analysis.

[b] Conversion defined as a % of substrate consumed during the reaction.

cyclooctene our initial screen at room temperature using 10 mol% of the catalyst in acetonitrile gave average conversions of 45% and epoxide yields of 17% after only 5 min, whereupon the reaction mixture turned brown, which coincided with a cessation of activity. Cooling the same mixture on ice prolonged the lifetime of the catalyst with both conversion and epoxide yield increasing (to 57 and 25% respectively) as well as the period before the brown precipitate was observed (to 20 min). Stack and co-workers have recently reported that the use of peracetic acid prepared using resin, $PAA_R$, as an effective oxidant in metal-catalysed epoxidation [11] due to its higher pH (2–3) than commercial peracetic acid, $PAA_C$ (pH 1). As the epoxidation reaction appeared to be pH dependent a series of reactions using carbonate buffer and $PAA_R$ was carried out to establish the optimum pH value. It must be noted that the addition of buffer directly to the reaction mixture prior to the addition of the oxidant quenches catalysis completely. However, pre-treating $PAA_R$ with carbonate buffer to adjust its pH to that stated in Table 1, prior to its addition to the reaction mixture resulted in higher yields and conversions. Similar activities were observed when the catalyst was made *in situ*.

Though higher yields and conversions were obtained when the $PAA_R$ was adjusted to pH 3, the TON was marginally higher at pH 4. Therefore it appeared that establishing a careful balance between reaction rate and catalyst stability might be the key to the optimisation of the system. Disappointingly, when the system was tried with styrene neither epoxidation nor substrate conversion were observed.

Manganese complex **14** showed improved activity compared to **15** under the same reaction conditions. When the reaction was carried out on an ice-bath, epoxide yields of up to 50% with a TON of 10 could be achieved, which were decreased slightly when the reaction was performed at room temperature (to 45% and 4.5 respectively). Although this complex proved to be more active than **15** we decided that the more challenging and low yielding synthesis of **2a** would make its optimisation more problematical and therefore decided to focus our initial efforts on the optimisation of catalysts employing ligand **5b**.

As the *in situ* system developed is rather complex (manganese(II) chloride, ligand, carbonate buffer, peracetic acid, acetic acid and hydrogen peroxide (the last two remaining from the preparation of $PAA_R$) it was decided to simplify it. We therefore changed the source of the metal to manganese(II) acetate and buffered the solutions with sodium acetate rather than carbonate. Initial studies of this system in the epoxidation of cyclooctene at 0 °C were very promising. After only 20 min a 68% conversion of the substrate with a 60% yield of the epoxide were recorded. In contrast to the original system this combination was also found to be active in the catalytic epoxidation of styrene with 65% conversion and 52% yield (TON = 5.2) after less than 1 h. Moreover, the epoxidation of styrene occurred with 20% ee ((*S*)-styrene oxide).

A preliminary investigation into the sensitivity of this system towards the concentration of the catalyst was then carried out (Table 2), which revealed that it was possible to obtain high conver-

**Table 2**
Investigation into the time dependence on catalyst activity upon lowering catalyst loading in the epoxidation of *cis*-cyclooctene

| Entry | Catalyst loading (mol%) | Time | Conversion[a] (%) | Epoxide yield[b] (%) | TON |
|---|---|---|---|---|---|
| 1[c] | 10 | 20 min | 65 | 52 | 5.2 |
| 2 | 1 | 1 h | 54 | 25 | 25 |
| 3 | 1 | 2 h | 63 | 35 | 35 |
| 4 | 1 | 3 h | 77 | 45 | 45 |
| 5 | 1 | 4 h | 95 | 56 | 56 |

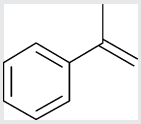
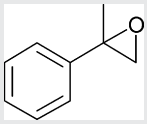
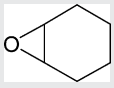
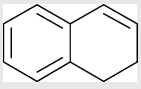
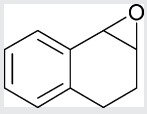
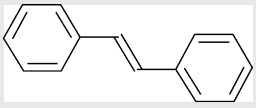
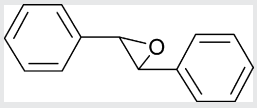
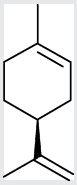
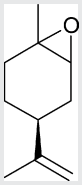
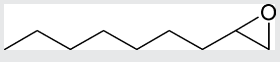
An ice-cold solution of catalyst **15** and *cis*-cyclooctene (1.0 equiv.) and internal standard in acetonitrile were treated with buffered $PAA_R$ (1.2 equiv.).
[a] Conversion defined as a % of substrate consumed during the reaction.
[b] Yields obtained from GC analysis.
[c] Decomposition of catalyst after 20 min was observed.

**Table 3**
Epoxidation of styrene using ligands **5a** and **5b** [a](*S*)-enantiomer

| Entry | Ligand | Reaction time (h) | Conversion[a] (%) | Epoxide yield[b] (%) | TON | ee |
|---|---|---|---|---|---|---|
| 1 | **5a** | 3 | 50 | 15 | 30 | |
| 2 | **5a** | 7 | 58 | 20 | 60 | 0 |
| 3 | **5a** | 16 | 90 | 36 | 71 | 0 |
| 4 | **5b** | 1 | 33 | 21 | 48 | 7[a] |
| 5 | **5b** | 7 | 89 | 43 | 102 | 21[a] |

An ice-cold solution of the appropriate catalyst (0.5 mol%) and styrene (1.0 equiv.) and internal standard in acetonitrile were treated with buffered $PAA_R$ (1.2 equiv.).
[a] Conversion defined as a % of substrate consumed during the reaction.
[b] Yields obtained from GC analysis.

**Table 4**
Epoxidation of various substrates using ligand **5b**

| Entry | Substrate | Conversion[a] (%) | Epoxide | Yield[b] (%) |
|---|---|---|---|---|
| 1[c] |  | 37 |  | 12 |
| 2[d] | | 20 | | 2.5 |
| 3[e] | | 20 | | 3 |
| 4[c] |  | 25 |  | 17 |
| 5[d] | | 75 | | 15 |
| 6[e] | | 55 | | 15 |
| 7[c] |  | 42 |  | 12 |
| 8[d] | | 32 | | 12 |
| 9[e] | | 15 | | 13 |
| 10[c] |  | 23 |  | 22 |
| 11[d] | | 30 | | 25 |
| 12[e] | | 36 | | 14 |
| 13[c] |  | 44 |  | 42 |
| 14[d] | | 57 | | 52 |
| 15[e] | | 40 | | 39 |
| 16[c] |  | –[f] |  | 8 |
| 17[d] | | –[f] | | 7 |
| 18[e] | | –[f] | | 7 |

[a] Conversion defined as a % of substrate consumed during the reaction.
[b] Yields obtained from GC analysis.
[c] 10 mol% catalyst loadings, 20 min reaction times.
[d] 5 mol% catalyst loadings, 6 h reaction times.
[e] 1 mol% catalyst loadings, 12 h reaction times.
[f] Cannot be determined as the substrate coincides with the solvent peak on the GC trace.

sions and adequate yields with lower catalytic loadings, however, this required that the reaction times be extended. Although the increase in reaction times is potentially a disadvantage due to the possibility of the epoxide decomposing, the catalyst lifetime is considerably extended from 5.2 TON to 56 TON. At loadings of 10 mol% of **15**, precipitation of brown materials after 20 min coincided with the termination of catalytic activity. In contrast, at 1 mol% loading, the catalyst retains its activity even after 4 h, suggesting that its concentration has a profound effect on the inactivation pathway. Thus a fine balance between the catalytic loading and reaction times was required.

These conditions were applied to test the efficacy of both ligands **5a** and **5b** with the catalyst loading further reduced (to 0.5 mol%) in the epoxidation of styrene. Despite earlier indications that **5a** might provide a more active catalytic system, the superiority of **5b** ligand over **5a** quickly became apparent (Table 3, entries 4 and 5). After 7 h the reaction using **5b** was mostly complete, producing epoxide in 43% yield and 21% ee (*S*-enantiomer). However, similar conversions and yields could be obtained when **5a** was used only after 16 h and in this case the final product was a racemate.

Further investigations using ligand **5b** in the epoxidation of a variety of substrates were then carried out (Table 4), although we were unable to assess the enatioselectivity of the epoxide products. The general trend for all substrates is that the consumption of the starting material is greater that the formation of the epoxide which we believe arises as a result of epoxide decomposition under the prolonged reaction times required. Closely related systems with shorter reaction times reported recently by Costas and co-workers do not suffer from this deficiency [13a,b]. In the cases where 10 mol% of catalyst was used (Table 4, entries 1, 4, 7, 10, 13, 16) the reaction times were 30 min, whereas for 5 mol% (Table 4, entries 2, 5, 8, 11, 14, 17) and 1 mol% (Table 4, entries 3, 6, 9, 12, 15, 18) the reactions were allowed to continue for 6 and 12 h respectively. This provided some interesting observations which indicate that the system is also substrate dependant. In some cases higher catalytic loadings and short reaction times are preferred (to the lower catalytic loadings and longer reaction times) giving both higher conversions and epoxide yields (Table 4, entries 1–3), whilst on other occasions the higher conversion at higher catalyst loadings is not translated into a higher epoxide yield (Table 4, entries 7–9). Disappointingly the challenging substrate 1-octene is very unreactive to this system. In contrast *trans*-stilbene shows exclusive selectivity to *trans*-stilbene oxide. Similarly the one epoxide product from (*S*)-limonene detected is formed from the regioselective oxidation of the endocyclic double bond and represents a rare example of such selectivity in related systems that use per acetic acid as the oxidant [53].

Whilst we have not undertaken extensive mechanistic investigations into this system, given the apparent lack of redox activity of the manganese centre in **15** we speculate that the manganese centres is acting as a Lewis acid activating the peracetic acid via a hydrogen bond to the non-coordinated tertiary amine, Fig. 5. An analogous mechanism of activation has very recently been proposed for the activation of hydrogen peroxide in an iron(III) scorpion complex [54] and in a closely related system for the activation of peracetic acid [13b].

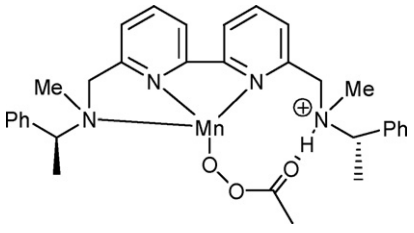



**Fig. 5.** Proposed intermediate species involving Lewis acid activation of the peracid and its orientation via interaction with the non-coordinated amine.

## 3. Conclusions

A series of novel ligands and their manganese complexes has been developed and tested for their efficacy in the catalytic epoxidation of alkene substrates. Despite the generally modest levels of enantioselectivity in the reactions the manganese complexes of ligands **5a** and **5b** have shown good activity in the catalytic epoxidation of various epoxidation substrates. Currently the optimisation of these systems is ongoing in our laboratories to reduce reaction times, increase yields and enatioselectivities and further findings along these lines will be reported in the due course.

## 4. Experimental

### *4.1. Screening of authentic manganese complexes using commercial peracetic acid, $PAA_C$, or freshly prepared peracetic acid, $PAA_R$*

An appropriate manganese(II) complex (10 mol%), substrate (1.0 equiv.), *n*-decane (50 μL) and 1,2-dichlorobenzene (57 μL) were dissolved in the acetonitrile (2.0 $cm^3$). The reaction mixture was cooled on ice prior to the addition of PAA (1.2 equiv.). Once addition of the oxidant was complete the reaction was stirred for a further 20 min, diluted with ether (3.0 $cm^3$) and filtered through a pad of alumina. The reaction was then analysed by Gas Chromatography (GC) and retention times and response values were compared to those obtained using commercial samples. (N.B. When the reactions were investigated for the durability of the catalyst the catalytic loadings were decreased to 1 mol%, however the reaction times were increased to 12 h.) All reports of catalytic activity represent significant acceleration in the product formation when compared to the oxidant alone. Also, the blank reactions containing oxidant and free salt did not yield epoxide products at all and instead caused decomposition of the oxidant. Blank reactions with PAA alone were carried out over period of 48 h at r.t. to give less than 10% conversion and 5% yield. The rate of the blank reaction can be enhanced by the presence of $NaHCO_3$ but not NaAOc. Blank reaction with $MnCl_2$ and PAA did not result in any epoxidation and instead showed decomposition of PAA by $MnCl_2$ to give off oxygen. All catalytic runs were analysed by Gas Chromatography using a Hewlett Packard 5890 apparatus and a Varian, chrompack capillary column (CP-Sil 8 CB, LB/MS # CP5860 30 cm, 025 mm, 0.25 μm). Retention times for the products were compared to those obtained from commercial samples.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.07.011.

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