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Short Communication

A biomimetic tris-imidazole/Mn(II) system for homogeneous catalytic epoxidation of olefins with H_2O_2

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ABSTRACT

A biomimetic tris-imidazole ligand, herein called L_{3imid}, has been synthesized. The complexes formed by its association with Mn(II) have been evaluated for catalytic alkene epoxidation with H_2O_2. The catalytic efficiency of Mn(II)/L_{3imid} system was shown to be switched on by ammonium acetate, with remarkable effectiveness and selectivity towards epoxides. The incorporation of the biomimetic ligand L_{3imid} which combines structural features as Schiff base imine-groups and imidazole rings is considered to be related with the enhanced catalytic activity of the Mn(II)/L_{3imid} system.

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1. Introduction

Olefin epoxidation with H_2O_2 catalyzed by non-heme manganese complexes has received considerable attention because a) H_2O_2 is inexpensive, readily available with relatively high oxygen content and environmentally friendly and b) non-heme manganese complexes are often easily prepared and handled [1].

Activation of H_2O_2 by non-heme manganese-enzymes is well known [2,3]. Thus, the challenge in the field of synthetic biomimetic chemistry is to construct optimized functional, low-cost biomimetic catalysts.

Mn-salen-type complexes have been extensively studied as epoxidation catalysts, with special attention to asymmetric catalysis [4–7]. For the epoxidation of simple olefins, the Jacobsen-type catalysts with *in situ* addition of imidazole or N-methylimidazole have been also evaluated [8,9]. The use of Mn-Me_3TACN complexes (TACN:1,4,7 triazacyclononane), as promising oxidation catalysts has been explored for commercial application e.g. by Unilever for washing detergents [10]. This system was further improved by the work of Bein et al. [11]. Very recently, it was shown that the high activity and selectivity of these systems is due to the *in situ* formation of bis(μ-carboxylato)-bridged dinuclear manganese(III) complexes [12,13]. An efficient dinuclear manganese catalyst based on polypyridine ligands has been also synthesized [14].

Our group has developed imidazole based-acetamide/Mn(II) systems [15,16] and acetylacetone-based Schiff bases/Mn(II) systems [17–19] as homogeneous catalysts for alkene epoxidation with H_2O_2. These systems showed considerable effectiveness in an acetone–methanol mixture at room temperature in the presence of ammonium acetate as additive.

In the context of optimizing the oxidation reactions of olefins by manganese and iron catalysts, we present here the synthesis of a new biomimetic ligand which a) bears three imidazole residues and b) offers exclusively nitrogen atoms for association with manganese (II) centers. The derived tris-imidazole/Mn(II) system, which was evaluated as homogeneous catalyst for alkene epoxidation with H_2O_2, is found to be ammonium acetate-dependent and shows remarkable effectiveness and selectivity.

2. Experimental

All substrates were purchased from Aldrich, in their highest commercial purity, stored at 5 °C and purified by passing through a column of basic alumina, prior to use. Hydrogen peroxide was 30% (w/w) aqueous solution.

Elemental analyses (C, H, N) were obtained using a Perkin Elmer Series II 2400 elemental analyzer. Infrared spectra were recorded on a Spectrum GX Perkin Elmer FT-IR System and UV–Vis spectra were recorded using a UV/VIS/NIR JASCO Spectrophotometer. Mass spectra were measured on an Agilent 1100 Series LC-MSD-Trap-SL spectrometer and solution NMR spectra were recorded with a Bruker AMX-400 MHz spectrometer with external TMS as reference. GC analysis was performed using an 8000 Fisons chromatograph with a flame ionization detector and a Shimadzu GC-17A gas chromatograph coupled with a GC-MS-QP5000 mass spectrometer.

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2.1. Synthesis and characterization of L_{3imid}

(1H-Imidazol-4-ylmethylene)-[2-(3-{2-[(1H-imidazol-4-ylmethylene)-amino]-ethyl}-2,3,4,5-tetrahydro-1′H-[2,4′]biimidazolyl-1-yl)-ethyl]amine ($C_{18}H_{24}N_{10}$, L_{3imid}): a solution of triethylentetramine (0.774 ml, 5.2 mmol) in methanol (50 ml) was added to an ice-cold solution of 4(5)-imidazolecarboxaldehyde (1.0 g, 10.4 mmol) in methanol (100 ml). The resulting pale-yellow solution was stirred for 15 min at 0 °C. Then a new solution of 4(5)-imidazolecarboxaldehyde (0.5 g, 5.2 mmol) in methanol (50 ml) was added into the reaction mixture. The yellow solution was stirred at 0 °C for 15 min, and finally at 30 °C for 23 h. The solution was then evaporated to dryness. The crude product was treated with hexane and acetone, and finally the yellow solid was dried under reduced pressure over fused $CaCl_2$. Yield 81%. m. p. 72–75 °C. Anal. Calcd. for $C_{18}H_{24}N_{10}.CH_3OH$ (%): C, 55.3; N, 34.0; H, 6.8. Found (%): C, 55.0; N, 34.4; H, 7.1.

IR (KBr, cm^{-1}, selected peaks) 3120: $\nu(NH)$; 1649: $\nu(C{=}N)$; 1558: $\delta(NH)$; 1496: $\nu(C{=}C)$; 1447: ring stretching modes (imidazole); 625: $\delta(NH)$. ^1H NMR ($(CD_3)_2SO$, δ) 2.2 (m, 4H): $CH_2NC\mathbf{H_2}CH_2$; 3.2 (m, 4H): $C\mathbf{H_2}NCH_2CH_2$; 3.48 (m, 4H): $HCNC\mathbf{H_2}CH_2NCH_2$; 3.9 (H): N–**C**–N; 6.95 (H): C=C**H**–N; 7.3 (m, H): N=C**H**–NH; 7.56 (H): C–N**H**–CH; 8.13(H): **C**=N. ^{13}C NMR ($(CD_3)_2SO$, δ) 51.6: $CH_2N\mathbf{CH_2}CH_2$; 54.3: $\mathbf{CH_2}NCH_2CH_2$; 60.5: $HCN\mathbf{CH_2}CH_2NCH_2$; 82.6: N–**C**–N; 130: C=**C**H–N; 136: N=**C**H–NH; 138: CO–**C**H_2–C C=**C**–NH N; 154: **C**=N. UV (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})) 251 (119000); 308 (19900); 437 (5900). ESI-MS (*m/z*) 381.3 ($[MH]^+$); 403.3 ($[M+Na]^+$).

2.2. Catalytic reactions

Manganese catalysts were prepared *in situ*, by mixing appropriate amounts of $MnCl_2$ or $Mn(CH_3COO)_2$ with L_{3imid} ligand. A 0.055 M stock solution of the catalysts was prepared by dissolving 1.1 mmol of L_{3imid} in a 0.110 M solution of $MnCl_2 \cdot 4H_2O$ or $Mn(CH_3COO)_2 \cdot 4H_2O$ in 20 ml CH_3OH.

Typical conditions employed in catalytic reactions were: 1 equiv. of catalyst, 2000 equiv. of H_2O_2 30% (w/w) and 1000 equiv. of substrate and additive. The alkene (1 mmol), acetophenone or bromobenzene (internal standard, 1 mmol), catalyst solution (1 μmol) and CH_3COONH_4 (additive, 1 mmol) in a acetone/MeOH (450 μl/400 μl) solvent mixture were cooled to 0 ° C. H_2O_2 (2 mmol) was added by a digitally controlled syringe pump, type SP101IZ WPI, over 1 h under stirring. 10 min later, the test tube was removed from the ice bath and allowed to warm to room temperature 26 ± 1 °C.

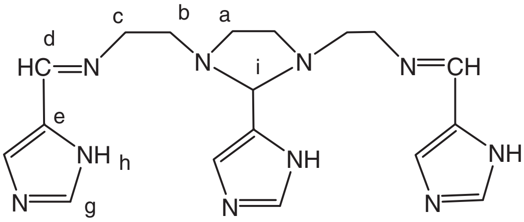
The progress of the reaction was monitored by GC–MS, by removing small samples of the reaction mixture. GC analysis of the solution provided the substrate conversion and product yield relative to the internal standard integration. To establish the identity of the epoxide product unequivocally, the retention time and spectral data were compared to those of an authentic sample. Blank experiments showed that without Mn-catalyst or CH_3COONH_4, epoxidation reactions do not take place.

3. Results and discussion

3.1. Synthesis of the ligand

The biomimetic ligand L_{3imid} was prepared by a stepwise condensation of trien with three equivalents of 4(5)-imidazolecarboxaldehyde (Fig. 1).

The five-member imidazolyl ring was formed at the ethylenediamine backbone by imidazolecarboxaldehyde mediation. Thus, a fully symmetrical molecule was synthesized bearing three imidazole residues. In the mass spectra, the molecular peaks for $[MH]^+$ and $[M+Na]^+$ appear at m/z 381.3 and 403.3 (Supporting information). The IR band at 1649 cm^{-1} was attributed to the imine-stretching bands, $\nu(C{=}N)$. ^1H and ^{13}C NMR spectral assignments were consistent with the proposed formulation. For example, in the ^{13}C NMR spectrum, the signal at 154 ppm was attributed to the imine-carbon atoms. In the ^1H NMR spectrum the imine N=CH resonance was located at 8.13 ppm.



L_{3imid}

Fig. 1. The ligand (1H-imidazol-4-ylmethylene)-[2-(3-{2-[(1H-imidazol-4-ylmethylene)-amino]-ethyl}-2,3,4,5-tetrahydro-1′H-[2,4′]biimidazolyl-1-yl)-ethyl]amine (L_{3imid}) used herein.

3.2. Catalytic epoxidation with H_2O_2

According to the data in Table 1, the $MnCl_2/L_{3imid}$, and $Mn(acet)_2/L_{3imid}$ systems showed significant catalytic activity within 3 h. Epoxidation of a wide range of olefins proceeded with high conversion and selectivity for the epoxide product (the mass balance is 98–100%) in most of the cases (Table 1).

Oxidation of cyclooctene, catalysed by $MnCl_2/L_{3imid}$ and Mn $(acet)_2/L_{3imid}$, provided a 100% selectivity for *cis*-cyclooctene epoxide with 77.7% and 74.9% yield corresponding to 777 and 749 TONs and 259 and 250 TOF respectively (Figs. 2 and 3). Hexene-1, which is a rather hard oxidation substrate, showed maximum epoxide yield 21.3% and 100% selectivity for the *cis*-epoxide. Cyclohexene oxidation

Table 1

Alkene epoxidations catalyzed by $MnCl_2/L_{3imid}$ and $Mn(acet)_2/L_{3imid}$ systems in the presence of H_2O_2.

Substrate	Products	Yield (%)[a] TON TOF (h^{-1})					
		$MnCl_2/L_{3imid}$			$Mn(acet)_2/L_{3imid}$		
Cyclooctene	*cis*-Epoxide	77.7	*777*	*259*	74.9	*749*	*250*
Hexene_1	*cis*_Epoxide	21.3	*213*	*71*	17.6	*176*	*59*
Cyclohexene	*cis*-Epoxide	49.1			59.9		
	2-Cyclohexenone	4.9			4.7		
	2-Cyclohexenol	3.1			3.4		
	cis-Diol	2.0			1.8		
			591	*197*		*698*	*233*
Styrene	Epoxide	58.1			63.1		
	Phenyl acetaldehyde	1.8			1.5		
			599	*200*		*646*	*215*
trans-β-Methylstyrene	*trans*-Epoxide	62.5			56.3		
	trans-Methyl-ketone	1.4			1.3		
			639	*213*		*576*	*192*
Limonene[b]	1,2-Epoxides	71.7			69.4		
	(*Z*−/*E*−)	(40.3/31.4)			(37.4/32.0)		
	8,9-Epoxides	13.4			14.5		
	-Alcohol	2.2			2.4		
	-Ketone	1.4			1.5		
	di-Epoxide	1.3			1.0		
			900	*300*		*888*	*296*
cis-Stilbene	*cis*-Epoxide	32.0			35.0		
	trans-Epoxide	4.7			5.5		
	-ketone	5.5			6.1		
			422	*141*		*466*	*155*

Conditions-ratio of catalyst: H_2O_2:CH_3COONH_4:substrate = 1:2000:1000:1000; equivalent of catalyst = 1 μmol in 0.85 ml CH_3COCH_3:CH_3OH (0.45:0.40). Italic data corespond to TONs and TOFs numbers.

[a] Yields based on starting substrate and products formed. The mass balance is 98–100%. Reactions were completed within 3 h.

[b] Limonene 1,2-oxide was found as a mixture of Z− and E− isomers and limonene 8,9-oxide as a mixture of two diastereoisomers.

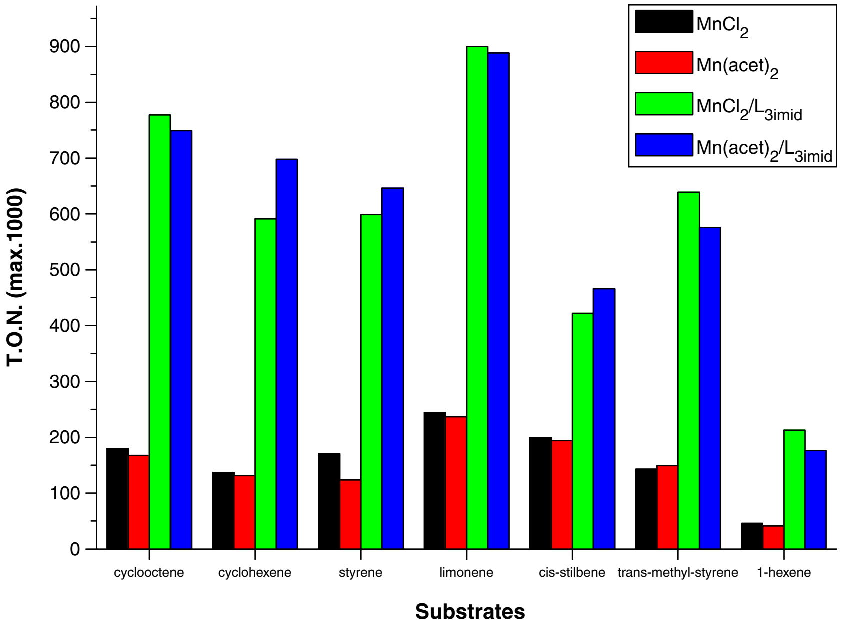


Fig. 2. Total turnover numbers for alkene epoxidations catalyzed by $MnCl_2$, $Mn(acet)_2$, $MnCl_2/L_{3imid}$ and $Mn(acet)_2/L_{3imid}$ in the presence of H_2O_2. Reaction performed in CH_3COCH_3/CH_3OH (0.45:0.40 ml). See Table 1 and Supporting information for details.

provided mainly epoxide with yields from 49.1 to 59.9%. In addition, small amounts of the corresponding diol, probably as epoxide ring opening product, have been also detected (1.8–2.0%). In some extent, allylic oxidation has also occurred forming 2-cyclohexene-1-ol (3.1–3.4%) and 2-cyclohexene-1-one (4.7–4.9%). The total yield of cyclohexene oxidation products was 59.1% for $MnCl_2/L_{3imid}$ and 69.8% for $Mn(acet)_2/L_{3imid}$ system.

Styrene oxidation produces mainly the corresponding epoxide by $MnCl_2/L_{3imid}$, and $Mn(acet)_2/L_{3imid}$ with yields 58.1 and 63.1% respectively, and high selectivities up to 97%; trace amounts of phenyl acetaldehyde as side product have been detected. The catalysts showed analogous ability towards the oxidation of *trans*-β-methylstyrene resulted in 62.5 and 56.3% epoxide yield with >97% retention of its configuration. Traces of the corresponding methyl-ketone have been also observed (~1.3%) (Figs. 4 and 5).

The major products detected from oxidation of limonene, were two epoxides (*Z*- and *E*-) derived from epoxidation of the 1,2-double bond and two diastereoisomers derived from the exocyclic 8,9-double bond. Additionally, small amounts of di-epoxide and products formed by allylic oxidation of the limonene ring have been identified. However, the epoxidation was clearly the main reaction path resulting mainly in 1,2-epoxides. The total yield of epoxides (1,2- plus 8,9-) was 85.1% (ratio 1,2-/8,9- equal to 5.4) by $MnCl_2/L_{3imid}$ and 83.9% (ratio 1,2-/8,9- equal to 4.8) by $Mn(acet)_2/L_{3imid}$; the total yield of oxidation products raised at 90% with 900 TONs and 300 TOF for $MnCl_2/L_{3imid}$ and 88.8% with 888 TONs and 296 TOF for $Mn(acet)_2/L_{3imid}$ system.

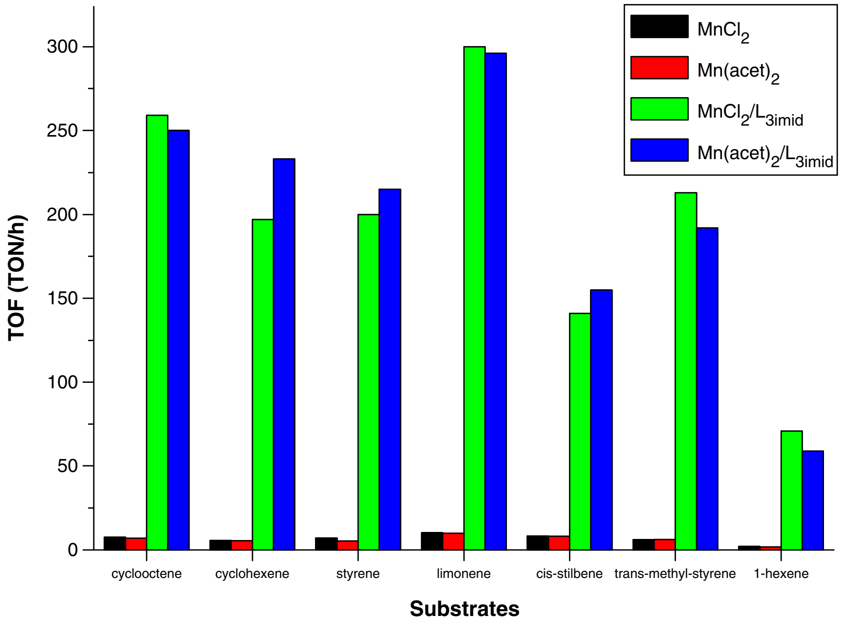


Fig. 3. TOF for alkene epoxidations catalyzed by $MnCl_2$, $Mn(acet)_2$, $MnCl_2/L_{3imid}$ and $Mn(acet)_2/L_{3imid}$ in the presence of H_2O_2. Reaction performed in CH_3COCH_3/CH_3OH (0.45:0.40 ml). See Table 1 and Supporting information for details.

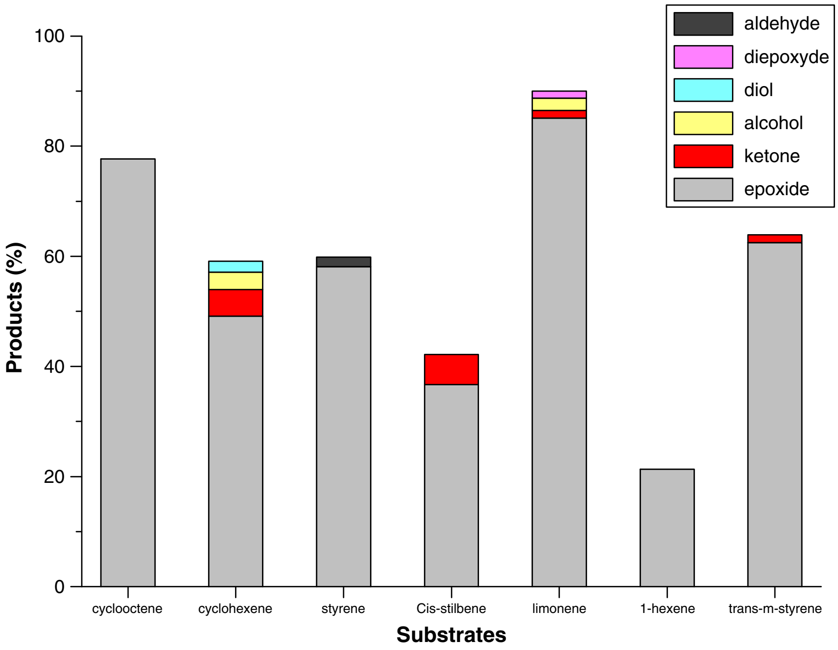


Fig. 4. Distribution of oxidation products catalyzed by $MnCl_2/L_{3imid}$ in the presence of H_2O_2. Reaction performed in CH_3COCH_3/CH_3OH (0.45:0.40 ml). See Table 1 for further details.

In the oxidation of *cis*-stilbene, the major product was cis-epoxide with selectivity ~75% and yield ranging from 32.0 to 35.0%. Moreover, considerable amounts of trans-stilbene epoxide (4.7–5.5%) and 1,2-diphenyl ethanone (5.5–6.1) have been also detected.

Competitive reactions show alkene reactivity to increase with the electron density of the double bond, e.g. hex-1-ene<cyclohexene<1-methylcyclohexene and the electron-rich trisubstituted double bond of limonene in 1,2-position gave several times more epoxides than the more accessible but less electron-rich double bond in 8,9-position (Table 2). These data might be taken as evidence of the electrophilic nature of oxygen transfer from manganese-oxo intermediate to the olefinic double bond. The reactivity of various substrates was screened and the results are listed in Table 2.

At this point is of relevance to compare the present systems with other pertinent catalysts. We have developed two sets of homogeneous Mn(II)-catalytic systems: a) imidazole based-acetamide ligands/Mn(II) [15,16] and b) acetylacetone-based Schiff bases/Mn (II) [17–19]. Generally, the catalytic systems associated with Schiff bases showed higher catalytic reactivity with H_2O_2 for alkene epoxidations. The present catalytic system incorporates a new biomimetic ligand which combines structural features of both previous systems. Thus, it is a Schiff base ligand with two imine-groups and also it bears three imidazole residues. Comparing the present catalytic system with that previously reported [15–19], we observe an enhanced reactivity of the present catalytic system. We consider that this is attributable to the structure of the ligand which

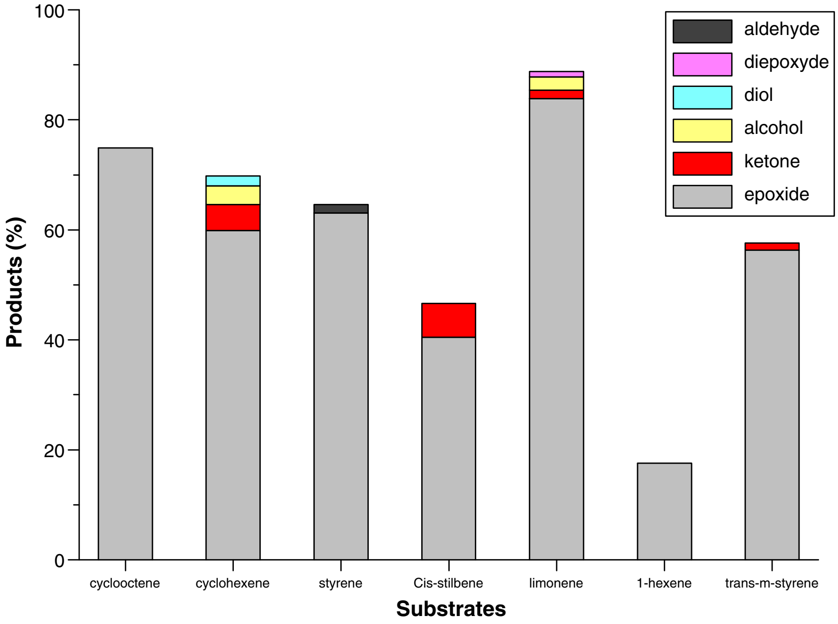


Fig. 5. Distribution of oxidation products catalyzed by $Mn(acet)_2/L_{3imid}$ in the presence of H_2O_2. Reaction performed in CH_3COCH_3/CH_3OH (0.45:0.40 ml). See Table 1 for further details.

Table 2
Chemo- and regio-selectivity in alkene epoxidation with H_2O_2 catalysed by $MnCl_2/L_{3imid}$ and $Mn(acet)_2/L_{3imid}$.

Alkene 1	Alkene 2	Epoxide 1/epoxide 2[a]	
		$MnCl_2/L_{3imid}$	$Mn(acet)_2/L_{3imid}$
Styrene	trans-Methylstyrene	0.73	0.79
Styrene	cis-Stilbene	0.70	0.72
Cyclooctene	Styrene	2.57	2.41
Cyclooctene	Cyclohexene	0.94	1.02
Cyclohexene	Hex-1-ene	12.00	12.21
Cyclohexene	1-Methylcyclohexene	0.93	0.86
Limonene[b]		5.35	4.79

Conditions-ratio of catalyst: H_2O_2:CH_3COONH_4:substrate$_1$:substrate$_2$ = 1:2000:1000:500:500; equivalent of catalyst = 1 μmol in 0.85 ml CH_3COCH_3:CH_3OH (0.45:0.40). Reactions were usually complete within 3 h.

[a] Yields based on starting substrate.

[b] 1,2- vs. 8,9-epoxides.

provides both Schiff base imine-nitrogen atoms and imidazole-nitrogen atoms for association with manganese(II) centers. In this respect the present Mn(II)/L_{3imid} is an optimized system e.g. compared with the previous catalysts.

4. Conclusion

A new biomimetic ligand has been synthesized which bears two imine-groups and three imidazole residues. The obtained tris-imidazole/Mn(II) system was evaluated as oxidation catalyst for the epoxidation of simple olefins with H_2O_2. The results obtained here demonstrate that this homogeneous system is more reactive than imidazole based-acetamide or acetylacetone-based Schiff bases/Mn (II) complexes reported previously. This is due to the incorporation of a biomimetic ligand which combines structural features as Schiff base imine-groups and imidazole rings. Thus the present Mn(II)/L_{3imid} system consists an optimised system of our previous biomimetic Mn (II) systems. Importantly, the Mn(II)/L_{3imid} catalyst is also ammonium acetate-dependent and can activate H_2O_2 favouring productive alkene epoxidations to a remarkable extent with high selectivity.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.10.021.

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