

# Highly selective olefin epoxidation with manganese triazacyclononane complexes: impact of ligand substitution<sup>1</sup>

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## Abstract

Manganese complexes of 1,4,7-triazacyclononane with different substituents catalyze the selective epoxidation of a large number of olefins to epoxides with  $H_2O_2$ . The activities of complexes with methyl ( $L_1$ ), 2-hydroxybutyl ( $L_2$ ) and acetato ( $L_3$ ) substituents are compared. The effects of solvent and temperature on the epoxide yield are very different for the three complexes. It is proposed that these differences are related to the binding of the pendant arms in Mn- $L_2$  and Mn- $L_3$  complexes. In general, acetone or methanol are preferred solvents. Variations of stereoretention are also observed: with Mn- $L_1$  in acetone, isomer scrambling occurs, while with Mn- $L_1$  in methanol, the epoxidation is almost stereospecific. UV-visible and electron spin resonance spectroscopy are used to characterize the state of manganese under oxidizing conditions.

**Keywords:** Manganese; Functionalized triazacyclononane; Epoxidation; Hydrogen peroxide; Stereoselectivity; Solvent effects

## 1. Introduction

The Mn- or Fe-catalyzed oxyfunctionalization of olefins and alkanes has been the subject of intense research over the past 15 years [1–3]. It is now well-documented that substitution of the metal complexes with various groups can have profound effects on the catalytic activity, such as a higher reactivity of the metal site, a greater resistance against oxidative degradation, enhanced chemo- or regioselectivities, or even chiral induction [4–7].

Recently, the catalytic characteristics of Mn complexes of the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane ( $L_1$ ) have been explored [8,9]. It was shown that under specific solvent and temperature conditions, catalyst turnover numbers up to 1000 can be obtained while retaining high epoxide selectivity [9]. We now report on the reaction of a series of olefins with  $H_2O_2$  in the presence of Mn complexes of 1,4,7-tris(2-hydroxybutyl)-1,4,7-triazacyclononane ( $L_2$ ) or 1,4,7-tris(acetato)-1,4,7-triazacyclononane ( $L_3$ ) (Scheme 1). In these potentially hexadentate ligands, three oxy-

gen donor atoms, in alcohol or carboxylate groups, can coordinate to the metal, in combination with the three nitrogen atoms of the macrocycle. In this paper, this class of hexadentate ligands is shown to confer a high catalytic activity to the chelated Mn. Substantial differences between the activities of complexes of  $L_1$ ,  $L_2$  and  $L_3$  are uncovered. The different solvent effects and selectivities are related to the structure of the catalyst molecules.

## 2. Results and discussion

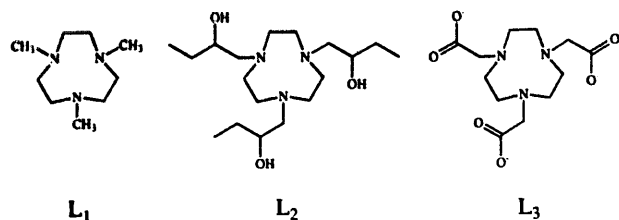
The ligands  $L_2$  and  $L_3$  are obtained readily by reaction of the 1,4,7-triazacyclononane macrocycle with 1,2-epoxybutane or bromoacetate, by modification of previously described procedures. The complexations were performed in situ by adding subsequently the ligand in a concentrated aqueous ( $L_2$ ) or organic ( $L_1$ ,  $L_3$ ) solution, and  $MnSO_4 \cdot H_2O$ , dissolved in water, to the reaction mixture. Reactions were started by addition of  $H_2O_2$ , diluted in the appropriate organic solvent.

### 2.1. Effects of ligand, solvent and temperature on epoxide yield

In view of the temperature and solvent effects that have been observed previously in Mn- $L_1$  catalysis [9],

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<sup>1</sup> Dedicated to Professor Hidemasa Takaya.



Scheme 1. Triazacyclononane-derived ligands.

four different solvents were selected for a screening of the catalytic properties of Mn–L<sub>2</sub> and Mn–L<sub>3</sub>: tetrahydrofuran (THF), acetonitrile, acetone and methanol. All of these are capable of dissolving even high concentrations of the substrate and the oxidant, H<sub>2</sub>O<sub>2</sub>, in a single phase. Large differences between the different solvents are observed in the oxidation of cyclohexene and styrene (Tables 1 and 2).

With Mn–L<sub>1</sub>, considerable epoxide yields are only obtained in acetone, especially at subambient temperature. With all other solvents, a more or less vigorous oxidant decomposition is observed, together with a poor epoxide yield. This peculiar behavior of acetone can be rationalized based on the known nucleophilic addition of H<sub>2</sub>O<sub>2</sub> on acetone, resulting in the formation of 2-hydroxy-2-hydroperoxypropane (HHPP) [10]:



The formation of this perhemiketal in our reaction mixtures was confirmed via <sup>1</sup>H NMR spectroscopy [11]. Equilibrium constants for this hemiketalisation are  $K = 0.23 \text{ M}^{-1}$  (at 273 K) and  $K = 0.078 \text{ M}^{-1}$  (at 300 K). From these data, we estimate that at room temperature about 66% of the peroxide is present as HHPP, whereas this fraction increases to 85% at 273 K. The high epoxide yield in the acetone reaction seems, therefore, primarily a consequence of the reduced concentration of H<sub>2</sub>O<sub>2</sub>. This raises the [olefin]/[oxidant] ratio, and ap-

Table 1  
Effects of temperature and solvent on the epoxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub> in the presence of Mn–L<sub>1</sub>, Mn–L<sub>2</sub> or Mn–L<sub>3</sub>. Cyclohexene oxide yields are given in per cent <sup>a</sup>

Solvent	T (K)	Epoxide yield (%)		
		Mn–L <sub>1</sub>	Mn–L <sub>2</sub>	Mn–L <sub>3</sub>
THF	298	2.0	4.9	1.0
	273	0.9	2.0	1.3
Acetonitrile	298	6.2	18.8	3.4
	273	1.8	10.6	2.2
Acetone	298	25.2	13.5	9.6
	273	79.2	38.5	18.0
Methanol	298	6.1	34.2	32.3
	273	3.4	40.8	29.3

<sup>a</sup> Conditions: 1 mmol olefin, 2 mmol H<sub>2</sub>O<sub>2</sub>, 1.1 g of solvent, 7.5 μmol of L<sub>2</sub> or L<sub>3</sub>, and 5 μmol Mn, 10 h (or 1.5 μmol of L<sub>1</sub>, 1 μmol Mn, 3 h).

Table 2

Effects of temperature and solvent on the epoxidation of styrene with H<sub>2</sub>O<sub>2</sub> in the presence of Mn–L<sub>1</sub>, Mn–L<sub>2</sub> or Mn–L<sub>3</sub>. Styrene oxide yields are given in per cent. Conditions as in Table 1

Solvent	T (K)	Epoxide yield (%)		
		Mn–L <sub>1</sub>	Mn–L <sub>2</sub>	Mn–L <sub>3</sub>
THF	298	1.4	12.8	nd
	273	0.5	5.7	nd
Acetonitrile	298	5.4	16.0	1.3
	273	1.4	10.2	1.5
Acetone	298	32.7	29.6	14.7
	273	98.0	53.4	32.9
Methanol	298 <sup>a</sup>	4.5	48.1	14.0
	273	3.4	60.0	15.2

<sup>a</sup> Methanolysis of styrene oxide was observed.

parently favors epoxidation over peroxide disproportionation. Especially at low temperatures, HHPP thus functions as an oxidant reservoir, slowly releasing H<sub>2</sub>O<sub>2</sub> as the reaction proceeds.

A very different picture is obtained when Mn–L<sub>2</sub> or Mn–L<sub>3</sub> are used. First, reactions are markedly slower than with Mn–L<sub>1</sub>. Therefore, reaction times and Mn concentrations were somewhat increased. Second, peroxide decomposition is much less prominent than with Mn–L<sub>1</sub>. Third, considerable epoxide yields are obtained not only in acetone, but also with other solvents. For Mn–L<sub>3</sub>, methanol is an excellent solvent, while very low yields are obtained with THF and acetonitrile. The solvent effects are less pronounced in the case of Mn–L<sub>2</sub>-catalyzed reactions.

Although it might be difficult to account fully for this complex pattern of solvent dependency of the reaction yield, several factors are of obvious importance. For both Mn–L<sub>2</sub> and Mn–L<sub>3</sub>, substantial spectroscopic evidence proves (vide infra) that in catalytic conditions, a major fraction of the Mn is chelated in a hexadentate fashion. However, catalytic reaction at the Mn center implies that at least one or possibly more of the pendant ligand arms are removed from the metal ion, thus opening a coordination site for an incoming peroxide or substrate molecule. We tentatively propose that, for example, methanol may assist in the partial deligation of Mn by forming hydrogen bonds with a dissociated carboxylate group in Mn–L<sub>3</sub>, thus facilitating the access of reagents to the Mn center [12]. Solvents that are poor hydrogen bond donors, such as THF or CH<sub>3</sub>CN, are therefore less suitable as reaction media when Mn–L<sub>1</sub> is used. As the dissociated hydroxyl groups in the Mn–L<sub>2</sub> system are less polar than the carboxylate groups in L<sub>3</sub>, solvent effects can be expected to be less dramatic, as is indeed observed in Tables 1 and 2.

A model in which the flipping of the pendant arms of L<sub>2</sub> and L<sub>3</sub> controls the activity of Mn also explains the much reduced H<sub>2</sub>O<sub>2</sub> decomposition in Mn–L<sub>2</sub> and

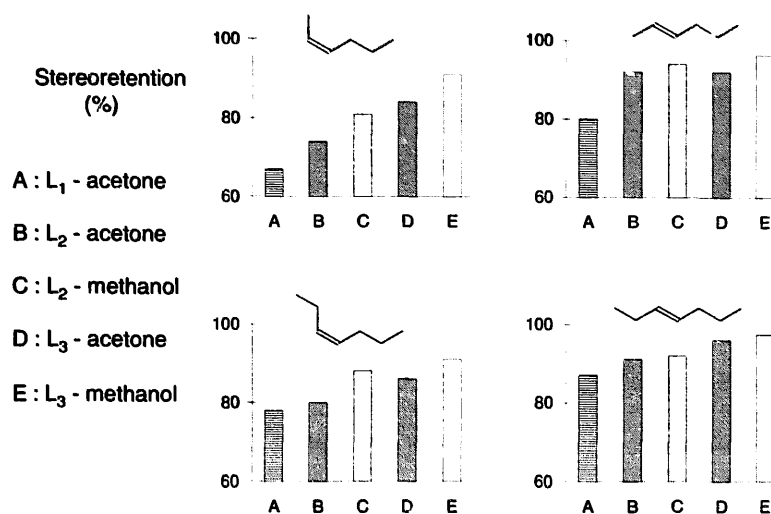


Fig. 1. Stereoretention (%) in the epoxidation of *cis* and *trans* 2-hexenes and 3-heptenes. Conditions as in Table 1.

Mn-L<sub>3</sub> catalysis. Peroxide decomposition occurs when a second peroxide reacts with the oxidized Mn species to ultimately form O<sub>2</sub>. In Mn-L<sub>2</sub> and Mn-L<sub>3</sub> chelates, most of the coordination sites are blocked by the ligand. As a consequence, coordination of a second peroxide molecule to these complexes is much less likely than for Mn-L<sub>1</sub> complexes, which contain three labile coordination sites. We note that in reaction conditions Mn-L<sub>1</sub> complexes are oxidized to  $\mu$ -oxo or  $\mu$ -hydroxy bridged dimers [13]; these bridging groups are probably easily displaced by the rather nucleophilic peroxide.

It is remarkable that the epoxide yields for Mn-L<sub>2</sub> and Mn-L<sub>3</sub> are not very dependent on temperature in methanol, whereas in acetone, a sharp yield increase is observed upon cooling, similar to the situation with Mn-L<sub>1</sub>. This strongly suggests that the formation of HHPP has an important impact on the epoxide yield when acetone is used as a solvent.

## 2.2. Epoxide selectivities and stereoretention

In all cases where high epoxide yields are obtained, the epoxides are by far the major product, especially

with Mn-L<sub>2</sub> and Mn-L<sub>3</sub> [14]. With these catalysts, products other than the epoxide are often too little to be detected (i.e. less than 0.5–1.0%). Whereas a small amount of allylic oxidation can be detected with cyclohexene and Mn-L<sub>1</sub> (epoxide selectivity, 89%), these allylic products are almost absent from the reactions in methanol with Mn-L<sub>2</sub> or Mn-L<sub>3</sub> (epoxide selectivity 95% and 99% respectively). These differences are even more pronounced in the case of cyclooctene. With Mn-L<sub>1</sub> in acetone, the cyclooctene oxide selectivity is rather limited (71%), but it increases in the order Mn-L<sub>2</sub> (90%, methanol) < Mn-L<sub>3</sub> (96%, methanol).

In reactions performed at room temperature and in methanol, solvolysis of the more reactive epoxides was observed. This was specifically the case for styrene oxide and the isoprene epoxides, whereas cyclohexene oxide was unaffected. However, this methanolysis is efficiently suppressed when reactions are conducted at 273 K, and high epoxide yields (90%) are obtained even for styrene in methanol.

An important issue is whether or not epoxides are obtained in a stereoselective way. Therefore, *cis*-*trans* epoxide isomer distributions were determined in the

Table 3  
Competitive oxidation of olefin pairs with H<sub>2</sub>O<sub>2</sub> in the presence of Mn-L<sub>1</sub>, Mn-L<sub>2</sub> or Mn-L<sub>3</sub><sup>a</sup>

Olefin 1	Olefin 2	Epoxide 1 : epoxide 2				
		Mn-L <sub>1</sub> acetone	Mn-L <sub>2</sub> acetone	Mn-L <sub>2</sub> methanol	Mn-L <sub>3</sub> acetone	Mn-L <sub>3</sub> methanol
<i>cis</i> -2-Hexene	1-hexene	5.2	6.5	4.5	5.3	4.2
<i>trans</i> -2-Hexene	1-hexene	1.1	1.9	2.0	2.3	2.2
<i>cis</i> -2-Hexene <sup>b</sup>	<i>trans</i> -2-hexene <sup>b</sup>	4.7	3.4	2.3	2.3	1.9
<i>cis</i> -3-Heptene	1-hexene	3.8	3.7	3.3	3.5	3.0
<i>trans</i> -3-Heptene	1-hexene	0.8	0.9	1.0	1.2	1.3
<i>cis</i> -3-Heptene <sup>b</sup>	<i>trans</i> -3-heptene <sup>b</sup>	4.8	4.0	3.3	2.9	2.4
Cyclohexene	1-hexene	12.2	10.1	9.6	8.2	6.6
1-CH <sub>3</sub> -cyclohexene	cyclohexene	0.8	0.9	0.8	1.2	1.1

<sup>a</sup> Conditions: 0.5 mmol of olefin 1, 0.5 mmol of olefin 2, 2 mmol H<sub>2</sub>O<sub>2</sub>, 1.1 g of solvent, 7.5  $\mu$ mol of L<sub>2</sub> or L<sub>3</sub> and 5  $\mu$ mol Mn, 10 h (or 1.5  $\mu$ mol of L<sub>1</sub>, 1  $\mu$ mol Mn, 3 h). <sup>b</sup> Calculated from the competitive reactions of the *cis* and *trans* alkenes with 1-hexene.

reactions of *cis* and *trans* 2-hexenes and 3-heptenes. The results are presented in Fig. 1. As expected, stereoretention is in general higher for the thermodynamically more stable *trans* olefins than for the corresponding *cis* alkenes. The most pronounced isomer scrambling is observed in reactions with Mn–L<sub>1</sub> in acetone; for instance, 33% *trans*-2,3-epoxyhexane is obtained from *cis*-2-hexene. Better results are obtained with the hexadentate ligands; the stereoretention increases in the order L<sub>1</sub> < L<sub>2</sub> < L<sub>3</sub>. Moreover, for the same complex catalyst, the olefin configuration is better preserved in methanol than in acetone. As a result, for Mn–L<sub>3</sub> in methanol, the stereoretention ranges from 90% (for *cis*-2-hexene) to over 97% for *trans*-3-heptene, where the *cis* oxide is almost below detection. This result compares favorably with the selectivities reported by Kochi and coworkers for the Mn–salen catalyst, used in oxidations with PhIO [4].

### 2.3. Relative reactivity of olefin pairs

Relative reactivities of different olefins can be considered a fingerprint of the catalytic site [6a,6c,15]. Reactivities of *cis*–*trans* pairs were determined via competitions with 1-hexene, because in our system *cis* and *trans* olefins give rise to small but variable amounts of isomerized epoxides (Table 3). The most marked variation in Table 3 is seen in the relative reactivity of the *cis*–*trans* pairs of 2-hexene and 3-heptene. Whereas Mn–L<sub>1</sub> shows a strong preference for *cis* olefins, Mn–L<sub>2</sub> and Mn–L<sub>3</sub> also effect considerable conversion of the *trans* form. These variations are probably to be interpreted as the result of a subtle interplay between the steric approach of the olefin to the reaction site and the nature of the oxidized metal complex [15].

### 2.4. Spectroscopy of catalyst solutions

A brief spectroscopic investigation was performed on the catalyst solutions before and after oxidant addition, and a comparison was made with literature data. Mn complexes of L<sub>2</sub> have not been reported previously, but information is available for the related 2-hydroxyethyl and 2-hydroxypropyl ligands [16]. Chelation of Mn<sup>II</sup> by L<sub>2</sub> was demonstrated unambiguously by the observation in the ESR spectra of a Mn<sup>II</sup> species with a large zero-field splitting ( $D > 0.06 \text{ cm}^{-1}$ ). Upon contact with air, this complex is slowly oxidized, as indicated by the purple coloration (bands at 550 nm, 460 nm). Addition of H<sub>2</sub>O<sub>2</sub> results in a drastic increase of the intensity of these transitions, and in a new intense shoulder at 380 nm. Similar bands have been assigned to charge transfer transitions of Mn<sup>IV</sup> complexes [16]. In the ESR spectrum of the oxidized catalyst, a signal is observed with apparent parameters  $g_{\parallel} \approx 2.0$ ,  $g_{\perp} \approx 4.0$ . This spectrum is assigned to the d<sup>3</sup> ion Mn<sup>IV</sup> [17]. The Mn<sup>IV</sup> signal is

often accompanied by a Mn<sup>II</sup> signal of variable intensity.

ESR shows that upon complexation of Mn by L<sub>3</sub>, Mn remains in the divalent oxidation state, even in the presence of air. The intensity of the Mn<sup>II</sup> ESR signal decreases drastically upon addition of H<sub>2</sub>O<sub>2</sub>, and an intense red color develops. The peaks in the visible spectrum (472 nm; 483 nm, sh) allow us to attribute this color to the formation of Mn<sup>III</sup>–L<sub>3</sub>, the spectrum of which was described by Wieghardt et al. [18]. No ESR evidence was found for formation of Mn<sup>IV</sup>.

These observations indicate that the chemistry of our complexes in oxidative conditions is essentially the same as that reported in previous studies, particularly regarding the relationship between ligand structure and favored oxidation states. With L<sub>3</sub>, Mn<sup>III</sup> is the prevalent state [18]. With L<sub>2</sub> or related ligands, the +III state is less dominant, and Mn<sup>II</sup> and Mn<sup>IV</sup> are simultaneously observed in oxidizing conditions [16]. Oxidation of Mn in the presence of L<sub>1</sub> typically results in formation of dinuclear complexes [13]. In spite of these obvious divergences between the different complexes, the catalytic properties vary only gradually, suggesting that for all three ligands similar active Mn species are involved in the oxygen transfer. It should be noted that with L<sub>2</sub> and L<sub>3</sub>, the active species probably contains a partially dissociated ligand. Although such species have not been described in previous studies of Mn–triazacyclononane-type complexes, the existence of a V=O complex with L<sub>3</sub>, in which one of the COO<sup>−</sup> groups is non-binding, suggests that such a partial deligation is a rather facile process [18].

## 3. Conclusion

The Mn-containing triazacyclononane core preserves its catalytic potential when the substituents on the N atoms are varied. Even when potentially hexadentate ligands are used, partial deligation seems sufficiently facile to allow for high catalytic epoxidation activity. The important solvent effects can be related to the molecular structure of the ligand. In comparison with the methyl-substituted ligand, considerable improvements of epoxide selectivity and configuration retention are observed, especially with the tris(acetato)-substituted ligand.

With the high level of stereoretention that is now possible, it does not seem unrealistic to devise triazacyclononane-based chiral ligands for asymmetric catalytic oxidation. There are numerous sp<sup>3</sup> hybridized carbon atoms in very close vicinity of the active Mn center, which can be replaced with stereogenic chiral carbon centers. Moreover, the well-explored functionalization of the side chains offers interesting perspectives for the attachment of these complexes to support materials.

Efforts in these directions are underway in our laboratory.

## 4. Experimental section

### 4.1. Ligand synthesis and materials

1,4,7-Triazacyclononane trihydrobromide and the free base were synthesized via literature procedures [19]. 1,4,7-tris(2-hydroxybutyl)-1,4,7-triazacyclononane ( $L_2$ ) was prepared by a procedure similar to the one used by Hancock and coworkers in the synthesis of the 2-hydroxyethyl-substituted ligand [20]. 1,4,7-Triazacyclononane (0.0645 g) and 1,2-epoxybutane (0.108 g) were dissolved in absolute ethanol (0.6 g). After 24 h, the solvent was removed by evaporation, and a colorless oily residue was obtained.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ) indicates that the reaction is complete:  $\delta$  0.85 (t, 9 H), 1.38 (m, 6 H), 2.58 (m, 6 H), 2.81 (s, 12 H), 3.69 (m, 3 H).

1,4,7-Tris(acetato)-1,4,7-triazacyclononane ( $L_3$ ) was synthesized by a modification of the method of Wieghardt et al. [18]. 0.371 g of triazacyclononane trihydrobromide was neutralized with 0.12 g of NaOH in 1 ml of water. To this solution was gradually added a 1 ml aqueous solution of bromoacetic acid (0.417 g) and NaOH (0.12 g). After 1 h of stirring, excess NaOH (0.12 g in 0.6 ml water) was added. After 2 h more stirring the reaction was complete, as shown by the  $^1\text{H}$  NMR data ( $\text{D}_2\text{O}$ ):  $\delta$  2.50 (s, 12 H), 3.22 (s, 6 H). The solution containing fully deprotonated  $L_3$  ligand was adjusted to pH 6 with concentrated HBr.

All other products, such as olefin substrates, were from commercial sources and were used as-received.

### 4.2. Spectroscopic measurements

$^1\text{H}$  NMR spectra were recorded with a Varian 200 spectrometer. For UV-vis measurements, an Hitachi U-3501 spectrophotometer was used. ESR spectra of frozen solutions (100 K) were recorded at X-band (9.44 GHz) with a Bruker ESP-300 spectrometer, equipped with a rectangular  $\text{TE}_{104}$  cavity. Methanol solutions were used, as this solvent produces a glass with a maximum dispersion of the ESR-active Mn centers.

### 4.3. Catalytic procedure

Catalytic reactions were performed in a 4 ml vessel, containing 1 mmol of substrate, dissolved in 0.6 g of solvent. For the competitive oxidations, 0.5 mmol of each substrate was used. To this mixture were added 7.5  $\mu\text{mol}$  of  $L_2$  or  $L_3$  (dissolved in 0.1 ml of the organic solvent and water respectively) and 5  $\mu\text{mol}$  of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , dissolved in 0.1 ml of water. For reactions with  $L_1$ , 1.5  $\mu\text{mol}$  of the ligand (in 0.1 ml of the organic

solvent) and 1  $\mu\text{mol}$  of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (in 0.1 ml water) were used. Reactions were started by addition of 2 mmol of  $\text{H}_2\text{O}_2$ , 30% in water, diluted in the organic solvent in a 1 : 2 weight ratio. Product identification was performed with GC-MS and  $^1\text{H}$  NMR; quantification was performed with GC on a DB-5 column, using chlorobenzene as the internal standard. Reference epoxides were synthesized by reaction with *meta*-chloroperbenzoic acid.

## 5. Supplementary material

ESR and UV-vis spectra of Mn- $L_2$  and Mn- $L_3$  are available (5 pages).

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## References and notes

- [1] For some reviews, see: (a) K.A. Jørgensen, *Chem. Rev.*, 89 (1989) 431; (b) K.S. Suslick, in C.L. Hill (ed.), *Activation and Functionalisation of Alkanes*, Wiley, 1989; (c) B. Meunier, *Chem. Rev.*, 92 (1992) 1411; (d) T. Katsuki, *Coord. Chem. Rev.*, 140 (1995) 189.
- [2] (a) W. Nam, R. Ho and J.S. Valentine, *J. Am. Chem. Soc.*, 113 (1991) 7052; (b) R.J. Guajardo, S.E. Hudson, S.J. Brown and P.K. Mascharak, *J. Am. Chem. Soc.*, 115 (1993) 7971.
- [3] (a) J.P. Renaud, P. Battioni, J.F. Bartoli and D. Mansuy, *J. Chem. Soc. Chem. Commun.*, (1985) 888; (b) B. Meunier, M.E. de Carvalho, O. Bortolini and M. Momenteau, *Inorg. Chem.*, 27 (1988) 161.
- [4] K. Srinivasan, P. Michaud and J.K. Kochi, *J. Am. Chem. Soc.*, 108 (1986) 2309.
- [5] (a) P.E. Ellis and J.E. Lyons, *Catal. Lett.*, 8 (1991) 45; (b) M.W. Grinstaff, M.G. Hill, J.A. Labinger and H.B. Gray, *Science*, 264 (1994) 1311; (c) T.G. Traylor, K.W. Hill, W. Fann, S. Tsuchiya and B.E. Dunlap, *J. Am. Chem. Soc.*, 114 (1992) 1308.
- [6] (a) J.T. Groves and T.E. Nemo, *J. Am. Chem. Soc.*, 105 (1983) 5786; (b) K.S. Suslick and B.R. Cook, *J. Chem. Soc. Chem. Commun.*, (1987) 200; (c) P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Artiles, M. Fort and D. Mansuy, *J. Am. Chem. Soc.*, 110 (1988) 8462; (d) M.E. de Carvalho and B. Meunier, *New J. Chem.*, 10 (1986) 223; (e) T.G. Traylor, T. Nakano, B.E. Dunlap, P.S. Traylor and D. Dolphin, *J. Am. Chem. Soc.*, 108 (1986) 2782.
- [7] E.N. Jacobsen, W. Zhang, L.C. Muci, J.R. Ecker and L. Deng, *J. Am. Chem. Soc.*, 113 (1991) 7063.
- [8] R. Hage, J.E. Iburg, J. Kerschner, J.H. Koek, E.L.M. Lempers, R.J. Martens, U.S. Racherla, S.W. Russell, T. Swarthoff, M.R.P. van Vliet, J.B. Warnaar, L. van der Wolf and B. Krijnen, *Nature*, 369 (1994) 637.
- [9] D.E. De Vos and T. Bein, *J. Chem. Soc. Chem. Commun.*, (1996) 917.

- [10] M.C.V. Sauer and J.O. Edwards, *J. Phys. Chem.*, **75** (1971) 3004.
- [11] The  $^1\text{H}$  NMR spectra of acetone– $\text{H}_2\text{O}_2$  mixtures show a resonance at  $\delta = 1.33$  ppm, which has previously been ascribed to 2-hydroxy-2-hydroperoxypropane [10]. There is no evidence for the formation of dimethyldioxirane in reaction conditions. Moreover, no products are formed at all when the Mn catalyst is omitted from the reaction mixture, whereas dimethyldioxirane is known to epoxidize olefins spontaneously. For NMR spectra and reactivity of dimethyldioxirane: R.W. Murray and R. Jayaraman, *J. Org. Chem.*, **50** (1985) 2847.
- [12] We cannot exclude the possibility that one of the pendant carboxylate arms of  $\text{L}_3$  assists in the oxygen transfer through intermediate formation of a covalently attached peracid, which reacts with Mn to form the oxygen-transferring metal species. Such a mechanism has been proposed for a Mn-porphyrin substituted with a  $-(\text{CH}_2)_3\text{COOH}$  group: S. Banfi, F. Legrandi, F. Montanari, G. Pozzi and S. Quici, *J. Chem. Soc. Chem. Commun.*, (1991) 1285.
- [13] When mixtures of Mn and  $\text{L}_1$  are exposed to  $\text{H}_2\text{O}_2$ , dinuclear complexes form, such as the  $\text{Mn}^{\text{III}}-\text{Mn}^{\text{IV}}$  dimer with a 16-line ESR signal: (a) K. Wieghardt, *Angew. Chem. Int. Ed. Engl.*, **28** (1989) 1153; (b) K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S.E. Vitols and J.J. Girerd, *J. Am. Chem. Soc.*, **110** (1988) 7398.
- [14] Considerable formation of by-products is only observed for the oxidation of cyclohexene in THF with  $\text{Mn}-\text{L}_1$  and to a lesser extent with  $\text{Mn}-\text{L}_2$ . The by-products are cyclohexenol, cyclohexenone and cyclohexenylhydroperoxide, which together can account for up to 60% of the converted cyclohexene. Moreover, some of the solvent is oxidized in these conditions. These side reactions are not noticed when  $\text{Mn}-\text{L}_3$  is used as a catalyst, nor when another solvent is used.
- [15] (a) K.A. Jørgensen, *J. Am. Chem. Soc.*, **109** (1987), 698; (b) J.F. Kinneary, J.S. Albert and C.J. Burrows, *J. Am. Chem. Soc.*, **110** (1988) 6124; (c) R.D. Arasasingham, G.-X. He and T.C. Bruice, *J. Am. Chem. Soc.*, **115** (1993) 7985.
- [16] A.A. Belal, P. Chaudhuri, I. Fallis, L.J. Farrugia, R. Hartung, N.M. McDonald, B. Nuber, R.D. Peacock, J. Weiss and K. Wieghardt, *Inorg. Chem.*, **30** (1991) 4397.
- [17] (a) R.S. Czernuszewicz, Y.O. Su, M.K. Stern, K.A. Macor, D. Kim, J.T. Groves and T.G. Spiro, *J. Am. Chem. Soc.*, **110** (1988), 4158; (b) M.K. Chan and W.H. Armstrong, *Inorg. Chem.*, **28** (1989) 3779.
- [18] K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B.C. Mehnke and J. Weiss, *Inorg. Chem.*, **21** (1982) 4308.
- [19] (a) K. Wieghardt, W. Schmidt, B. Nuber and J. Weiss, *Chem. Ber.*, **112** (1979) 2228; (b) G.H. Searle and R.J. Geue, *Aust. J. Chem.*, **37** (1984) 959.
- [20] B.A. Sayer, J.P. Michael and R.D. Hancock, *Inorg. Chim. Acta*, **77** (1983) L64.