

# The dinuclear manganese complex $\text{Mn}_2\text{O}(\text{OAc})_2(\text{TPTN})$ as a catalyst for epoxidations with hydrogen peroxide†

Jelle Brinksma,<sup>a</sup> Ronald Hage,<sup>b</sup> Judith Kerschner<sup>c</sup> and Ben L. Feringa<sup>\*a</sup>

<sup>a</sup> Laboratory of Organic Chemistry, Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: B.L.Feringa@chem.rug.nl

<sup>b</sup> Unilever Research Laboratory Vlaardingen, PO Box 114, 3130 AC Vlaardingen, The Netherlands

<sup>c</sup> Unilever Research US, 45 River Road, Edgewater, New Jersey 07020, USA

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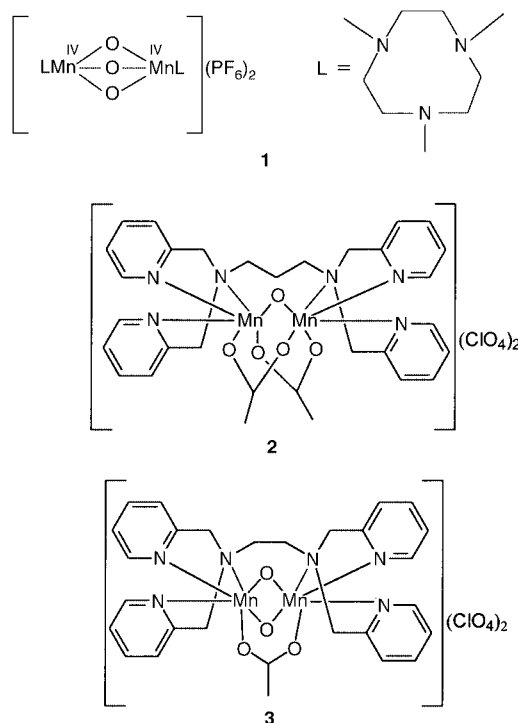
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In acetone and at ambient temperature, the dinuclear manganese complex of TPTN is able to catalyse the oxidation of several alkenes to the corresponding epoxides with high turnovers numbers (up to 900) using  $\text{H}_2\text{O}_2$  as oxidant.

Selective oxidation of alcohols to aldehydes and the formation of epoxides from olefins are among the key reactions in organic chemistry. In the ongoing pursuit to develop environmentally benign synthetic methodology there is currently great interest in new and more efficient catalytic versions of these oxidations. Compared to catalytic methods that require oxidants like NaOCl and ammonium periodates the use of  $\text{H}_2\text{O}_2$  offers the advantage that it is a cheap, environmentally friendly and a readily available reagent. Since water is the only expected byproduct, synthetic applications of this reagent are undoubtedly appealing provided efficient catalysis is accomplished.

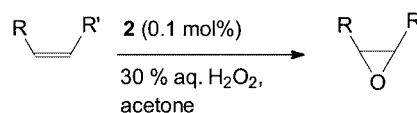
Recently a number of metal complexes have been found to be suitable catalysts for selective epoxidation reactions with  $\text{H}_2\text{O}_2$  as oxidant.<sup>1–4</sup> Noyori and coworkers reported a catalytic system based on  $\text{Na}_2\text{WO}_4$  dihydrate for the epoxidation of terminal olefins and turnovers numbers (TON) were found in the range 150–200 per W atom by using 150 mol%  $\text{H}_2\text{O}_2$  and 0.2–2 mol% of the catalyst.<sup>1</sup> Methyltrioxorhenium (MTO) is also emerging as a highly suitable epoxidation catalyst.<sup>2</sup> A remarkable acceleration effect on the epoxidation rate was found by Sharpless and coworkers by using pyridine and pyridine derivatives for the MTO catalysed epoxidation of terminal and internal olefins.<sup>3</sup> The Jacobsen catalyst<sup>5</sup> and the related Katsuki catalyst<sup>6</sup> are commonly applied for asymmetric epoxidation reactions of *cis*-olefins. However, with a few exceptions<sup>7</sup> NaOCl is used as oxidant for which TON values in the range of 35–40 were found. Recently it was found that a manganese(IV) complex based on the *N,N',N''*-1,4,7-trimethyl-1,4,7-triazacyclononane (MeTACN) ligand is a highly active oxidation catalyst.<sup>4</sup>

This dinuclear manganese complex **1** is capable of the epoxidation of alkenes with TON usually below 100<sup>8,9</sup> but in some cases up to 1000 have been reported using  $\text{H}_2\text{O}_2$  as oxidant.<sup>10‡</sup> This complex was also shown by us to be a highly active and selective catalyst for the oxidation of benzyl alcohols to benzaldehydes (TON up to 1000).<sup>11</sup> Synthesis and modifications of the MeTACN ligand are, however, not easily accomplished due to lengthy and tedious preparation whereas the sensitivity of the corresponding metal complexes to changes in the MeTACN structure often leads to completely inactive Mn-complexes. Therefore a challenge is the design of novel dinuclear ligands featuring the three N-donor set for each Mn-site and retaining the high oxidation activity. We present here, high catalytic epoxidation activity for the manganese complex **2** based on the ligand TPTN† using  $\text{H}_2\text{O}_2$  as oxidant.



Advantages of this type of ligands are the accessibility and the possibility for ligand modification. The ligands and manganese complexes examined here were synthesised following literature procedures and complexes **2** (and **3**) have been reported as mimics for the photosystem II (PS II).<sup>12–15</sup> Preliminary screening in a number of different catalytic epoxidations showed that complex **3** based on TPEN,† featuring a two-carbon spacer between the three N-donor sets in the ligand, was unreactive in epoxidation reactions.§ In sharp contrast, complex **2**, based on TPTN with a three-carbon spacer, is able to catalyse the oxidation of various alkenes to the corresponding epoxides, with  $\text{H}_2\text{O}_2$  as oxidant in acetone and at ambient temperature (Scheme 1).

Catalytic reactions were performed under a nitrogen atmosphere using 1 equiv. of complex **2**, 1000 equiv. substrate and  $\text{H}_2\text{O}_2$  was used as oxidant (1 ml of 30% aqueous  $\text{H}_2\text{O}_2$ , 9.8 mM, 8 equiv. with respect to substrate).¶ During the oxidation reaction in acetone at room temperature gas bubbles developed rapidly when the excess of oxidant was added. As for the reactions using **1**,<sup>11</sup> part of the  $\text{H}_2\text{O}_2$  disproportionates to  $\text{O}_2$ . An increase of the catalyst TON was obtained by performing the



† Abbreviations TPTN = *N,N,N',N'*-tetrakis(2-pyridylmethyl)propane-1,3-diamine, TPEN = *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethane-1,2-diamine.

**Table 1** Oxidation of selected olefins with Mn<sub>2</sub>O(OAc)<sub>2</sub>(TPTN) complex **2**<sup>a</sup>

Entry	Substrate	Product <sup>b</sup>	TON			
			2 h, 298 K <sup>c</sup>	4 h, 298 K <sup>c</sup>	2 h, 273 K <sup>d</sup>	4 h, 273 K <sup>d</sup>
1	Styrene	Styrene oxide	157	208	176	271
		Benzaldehyde	5	75	2	14
2	Cyclohexene	Cyclohexene oxide	247	563	328	868
		Cyclooctene				
3	Cyclooctene	Cyclooctene oxide	193	636	262	575
		<i>cis</i> -Diol	49	93	61	48
4	Cinnamyl alcohol	Cinnamyl oxide	208	219	219	321
		Cinnamyl aldehyde	69	85	70	86
5	<i>trans</i> -2-Octene	Benzaldehyde	22	47	21	46
		<i>trans</i> -Oct-2-ene oxide	118	188	178	248
6	<i>trans</i> -4-Octene	<i>trans</i> -oct-2-ene oxide	97	148	153	210
		1-Decene	28	34	80	97
8	<i>cis</i> - $\beta$ -Methylstyrene	1-Decene oxide	19	84	23	115
		<i>cis</i> -oxide	43	104	44	147

<sup>a</sup> Experimental conditions, see text. <sup>b</sup> All products were identical to independent samples and identified by GC (HP 6890, column HP1 15  $\times$  0.3 mm  $\times$  2.65  $\mu$ m, polydimethylsiloxane) and <sup>1</sup>H NMR. <sup>c</sup> Turnover number = mol product per mol catalyst, 8 equiv. H<sub>2</sub>O<sub>2</sub> with respect to substrate. <sup>d</sup> 16 equiv. H<sub>2</sub>O<sub>2</sub> with respect to substrate.

catalytic reactions in acetone at 0 °C suppressing H<sub>2</sub>O<sub>2</sub> decomposition. For the selected olefins generally up to 300 TONs were found. Addition of a further 1 ml of H<sub>2</sub>O<sub>2</sub> (30% aqueous solution in water, 9.8 mmol, 8 equiv. with respect to substrate) resulted in a considerable increase in epoxide yield after 4 h (total TON up to 900, for cyclohexene). These results indicate that the catalyst is very robust under the conditions used. High selectivity is observed and it should be emphasized that in the epoxidation reaction of cyclic alkenes (especially for cyclohexene), besides the epoxides, no allylic oxidation products were found. In control experiments replacing Mn<sub>2</sub>O(OAc)<sub>2</sub>(TPTN) **2** with Mn(OAc)<sub>3</sub>·3H<sub>2</sub>O, strong peroxide decomposition and no epoxide formation was found. Data for the conversion of various alkenes to the corresponding epoxides are compiled in Table 1. Styrene epoxidation is accompanied by the formation of a small amount of benzaldehyde; a feature commonly observed with epoxidation of this substrate. Cinnamyl alcohol also showed some cleavage and alcohol oxidation leading to benzaldehyde and cinnamyl aldehyde, respectively. A substantial amount of *trans*-epoxide is obtained in the reaction of *cis*- $\beta$ -methylstyrene with H<sub>2</sub>O<sub>2</sub> in the presence of catalyst **2** which is usually attributed to the formation of a radical intermediate with a lifetime sufficient for internal rotation before ring closure.<sup>16</sup> Excellent results were also found for internal alkenes *e.g.* entries 5 and 6 whereas slightly lower yields were found for terminal linear alkenes.

In conclusion, we have demonstrated that the manganese complex **2** based on TPTN is a promising catalyst in catalytic epoxidation procedures using H<sub>2</sub>O<sub>2</sub> as the terminal oxidant.

Main advantages of the new catalytic system are the facile synthesis and possibility for ligand modification. In acetone and at ambient temperature the manganese complex of TPTN is able to catalyse the selective oxidation of various alkenes to the corresponding epoxides, with H<sub>2</sub>O<sub>2</sub> as oxidant. Further studies towards the elucidation of the mechanism and introduction of chirality in the ligand are in progress.

## Notes and references

‡ Very recently a co-ligand effect was reported by the groups of De Vos and Berkessel, see: D. E. De Vos, B. F. Sels, M. Reynaers, S. Rao and P. A. Jacobs, *Tetrahedron Lett.*, 1998, **39**, 3221; A. Berkessel and C. A. Sklorz, *Tetrahedron Lett.*, 1999, **40**, 7965

§ L. Fraisse, J. J. Girerd, F. Perie, A. Rabion, D. Tetard, J. B. Verlhac and A. Nivorozhkin, PCT WO 97/18035 Elf-Aquitaine. Oxidation catalysis with various Mn and Fe complexes based on amine-heteroaromatic ligands has been claimed recently (*e.g.* cyclohexane oxidation, polyaromatic oxidation). No epoxidation activity was given however.

¶ Catalytic reactions were started by mixing 1.0 ml of a 1.2  $\mu$ M stock solution of the manganese complex in acetone and 1.0 ml of a 1.2 mM stock solution of substrate at 25 °C under a nitrogen atmosphere. As an internal standard, bromobenzene or 1,2-dichlorobenzene (in the case of cyclooctene) were used. After stirring for 2 min, an excess of hydrogen peroxide (1.0 ml of 30% aqueous H<sub>2</sub>O<sub>2</sub>, 9.8 mM, 8 eq. with respect to substrate) was added. The progress of the reaction was monitored by GC, by removing small samples of the reaction mixture and filtering over a short column of silica. To establish the identity of the epoxides and other products unequivocally, the retention times and spectral data were compared to those of commercially available and independently synthesised compounds.

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