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

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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 H$_2$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 H$_2$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 H$_2$O$_2$ as oxidant.†‡ Noyori and coworkers reported a catalytic system based on Na$_2$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% H$_2$O$_2$ and 0.2–2 mol% of the catalyst.† Methyltrioxorhenium (MTO) is also emerging as a highly suitable epoxidation catalyst.‡ 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.§ The Jacobsen catalysts and the related Katsuki catalysts are commonly applied for asymmetric epoxidation reactions of cis-olefins. However, with a few exceptions? NaOCl is used as oxidant for which TON values in the range 35–40 were found. Recently it was found that a manganese(tiv) complex based on the N,N,N’,N’’,N”-1,4,7-trimethyl-1,4,7-triazacyclononan (MeTACN) ligand is a highly active oxidation catalyst.¶

This dinuclear manganese complex 1 is capable of the epoxidation of alkenes with TON usually below 100 but in some cases up to 1000 have been reported using H$_2$O$_2$ as oxidant.†⁵ 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).†⁶ 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 metal/TACN ratio often leads to completely inactive Mn-complexes. Therefore a challenge is the design of novel dinucleating ligands featuring the three N-donor sets 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† featuring H$_2$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) oxidation activity. 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 H$_2$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 H$_2$O$_2$ was used as oxidant (1 ml of 30% aqueous H$_2$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 the H$_2$O$_2$ disproportionates to O$_2$. An increase of the catalyst TON was obtained by performing the reaction in acetone at room temperature gas bubbles developed rapidly when the excess of oxidant was added. As for the reactions using 1 the H$_2$O$_2$ disproportionates to O$_2$. An increase of the catalyst TON was obtained by performing the

† Abbreviations TPTN = N,N,N’,N’”,N”-tetraakis(2-pyridylmethyl)propane-1,3-diamine, TPEN = N,N,N’,N”-tetraakis(2-pyridylmethyl)ethane-1,2-diamine.

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Table 1 Oxidation of selected olefins with Mn₃O(OAc)₃(TPTN) complex

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Producta</th>
<th>TONb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 h</td>
</tr>
<tr>
<td>1</td>
<td>Styrene</td>
<td>Styrene oxide</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>Cyclohexene</td>
<td>Cyclohexene oxide</td>
<td>247</td>
</tr>
<tr>
<td>2</td>
<td>Cyclooctene</td>
<td>Cyclooctene oxide</td>
<td>193</td>
</tr>
<tr>
<td>3</td>
<td>Cinnamyl alcohol</td>
<td>Cinnamyl oxide</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>trans-2-Octene</td>
<td>trans-Oct-2-ene oxide</td>
<td>118</td>
</tr>
<tr>
<td>4</td>
<td>styrene</td>
<td>cis-β-Methyl-styrene oxide</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>trans-4-Octene</td>
<td>trans-Oct-2-ene oxide</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>1-Decene</td>
<td>1-Decene oxide</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Benzaldehyde</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Benzaldehyde</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cinnamyl aldehyde</td>
<td>85</td>
</tr>
</tbody>
</table>

a Experimental conditions, see text. b All products were identical to those corresponding epoxides, with H₂O₂ as oxidant. Further studies revealed the elucidation of the mechanism and introduction of chirality in the ligand are in progress.

Notes and references
§ L. Fraisse, J. J. Girerd, F. Perie, A. Rabion, D. Tetard, J. B. Verlhac and A. Nivrozvitch, PCT WO 97/18035 Elf-Aquitaine. Oxidation catalysis with various Mn and Fe complexes based on amine-heterosaromatic ligands has been claimed recently (e.g. cyclohexene oxidation, polyaromatic oxidation). No epoxidation activity was given however.
¶ Catalytic reactions were started by mixing 1.0 ml of a 1.2 μM 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 H₂O₂, 9.8 mM, 8 equiv. 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.