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Pentacoordinated manganese complexes as biomimetic catalysts for asymmetric epoxidations with hydrogen peroxide

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Abstract

Chiral pentadentate dihydrosalen ligands, carrying an imidazole group as a fifth, axial donor have been synthesized in racemic and enantiomerically pure form. All of these ligands afforded mononuclear manganese(III) complexes in good yields. The complexes catalyzed the epoxidation of olefins with a variety of terminal oxidants, but most importantly, with dilute (1%) aqueous hydrogen peroxide and without any added co-ligands. With 1,2-dihydronaphthalene as substrate and 10 mol% of catalyst, enantiomeric excesses up to 64% were achieved. Control experiments using a tetradentate chelate lacking the axial imidazole donor showed that the pentacoordination of the manganese ion is crucial for the peroxidase activity.

1. Introduction

As a part of our studies on biomimetic catalysts for selective oxyfunctionalizations [1,2], we are trying to find new catalysts that can utilize hydrogen peroxide as the terminal oxidant [1]. Its advantages are obvious: It is a cheap and mild reagent, with only water being formed as waste product [4]. The main challenge associated with this oxidant, however, is favoring the heterolytic O–O bond cleavage — with concomitant formation of the reactive metal–oxene species — over destructive radical pathways [5]. In many peroxidases, i.e. hydrogen peroxide utilizing enzymes, the catalytically active iron center is coordinated by the four pyrrole nitrogen atoms of its heme ligand plus an axial imidazole donor [6–8]. This proximal donor is believed to facilitate O–O heterolysis. Not surprisingly, imidazole and derivatives thereof have proven beneficial as co-ligands for manganese-complex catalyzed epoxidations [9], especially with hydrogen peroxide as the source of oxygen [3,10,11]. For the efficient utilization of this oxidant in the enantioselective epoxidation of unfunctionalized olefins, it appeared desirable to combine the features of a peroxidase-like coordination sphere and a (chiral) manganese(III) salen complex (**A**, Fig. 1). In such an arrangement, a fifth, axial donor — preferably an imidazole group — should be

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[1] The application of hydrogen peroxide in manganese-catalyzed asymmetric epoxidations has been described for salen-type catalysts in the presence of large amounts of external co-ligands, see [3].

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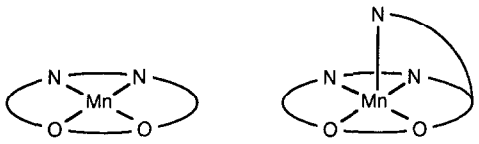


Fig. 1. Pentadentate dihydrosalen complexes of manganese as peroxidase models.

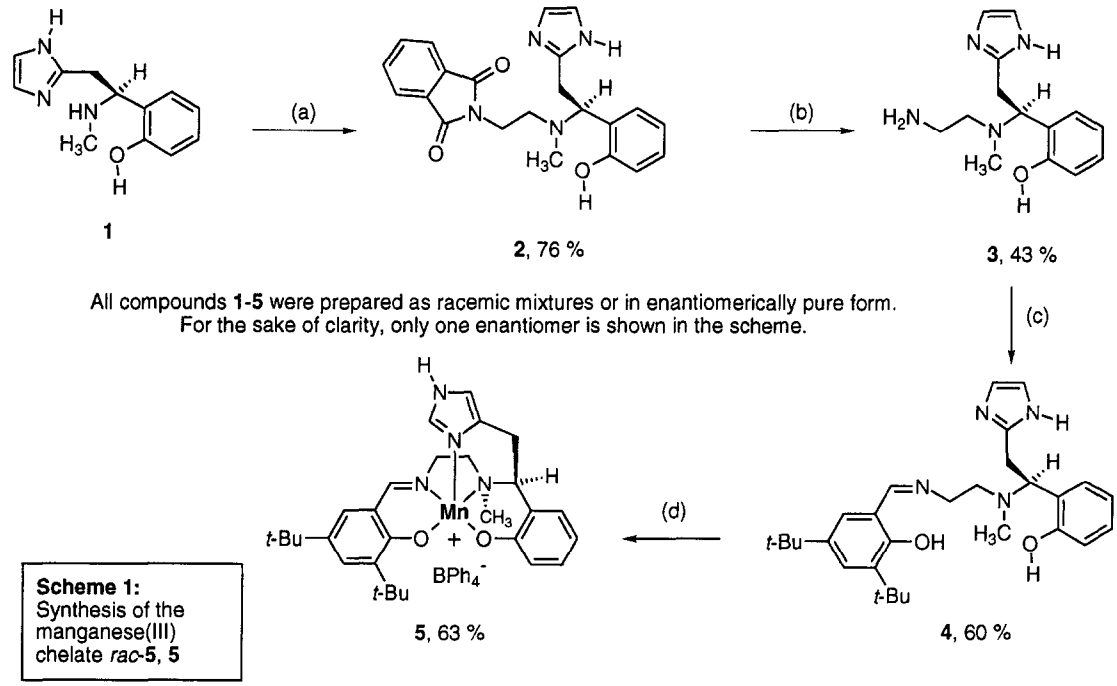
covalently attached [2] to a salen-type complex (**B**, Fig. 1). Herein we describe the synthesis of one representative pentadentate ligand of the dihydrosalen [1], [2], [12](b) type, the conversion of such ligands to manganese(III) complexes of the type **B** (Scheme 1), the X-ray crystal structure of one of these chelates and their catalytic performance.

2. Results

2.1. Synthesis of the catalysts

Our three-step sequence used for the synthesis of the pentadentate dihydrosalen ligands is depicted in Scheme 1. The secondary amine *rac*-**1** served as starting material. It was prepared in racemic form by reductive amination of the corresponding ketone (see Ref. [13] for the synthesis of *rac*-**1**). The reductive alkylation of the secondary amine *rac*-**1** using 2-(N-phthalimido)acetaldehyde and sodium cyanoborohydride afforded the N-protected derivative of ethylene diamine *rac*-**2** in good yield. In the next step, the N-protecting group was removed by hydrazinolysis. The subsequent condensation of

[2] For an achiral Mn–Porphyrin with a pendant imidazole group, see [12](a), for examples of tetradentate dihydrosalen complexes, see [12](b)–(c).



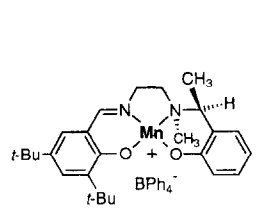
Scheme 1: Synthesis of the manganese(III) chelate *rac*-**5**, **5**

Reagents and conditions: (a) 2-(N-phthalimido)acetaldehyde, $NaBH_3CN$, methanol; (b) hydrazine hydrate, methanol; (c) 3,5-di-*tert*-butylsalicylaldehyde, methanol; (d) $MnCl_2 \cdot 4\,H_2O$, $NaBPh_4$, air, methanol.

Scheme 1. Synthesis of the pentadentate manganese(III) chelate *rac*-**5**, **5**.

the ethylene diamine derivative *rac*-**3** with 3,5-di-*tert*-butylsalicylaldehyde gave the Schiff's base ligand *rac*-**4**. The enantiomerically pure ligand **4** was prepared from the *S*-configurated amine **1** in just the same way (see Ref. [13] for the preparation of **1** in enantiomerically pure form). Finally, the ligand *rac*-**4** was reacted with manganese(II) chloride tetrahydrate in methanol in the presence of air and sodium tetraphenyl borate, affording the dark brown manganese(III) complex *rac*-**5** as microcrystalline powder (Scheme 1). Besides *rac*-**5**, the enantiomerically pure complex **5** was obtained from the Schiff's base **4**.

For comparison, the tetradentate dihydrosalen complex *rac*-**9**, lacking the axial imidazole donor, was prepared, too. Its synthesis closely paralleled that of the pentadentate manganese chelate discussed so far: In the first step, ortho-hydroxyacetophenone was reductively aminated with methyl amine, affording the secondary amine (*RS*)-2-[1-(methylamino)ethyl]phenol in 92% yield. The subsequent N-alkylation, hydrazinolysis, condensation with 3,5-di-*tert*-butylsalicylaldehyde and metallation as described above gave the dark brown manganese(III) chelate *rac*-**9**.



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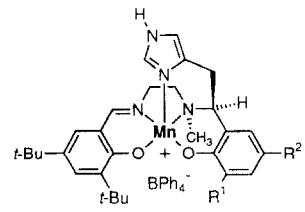


10: $R^1 = CH_3$, $R^2 = H$
11: $R^1 = H$, $R^2 = OCH_3$

2.2. X-ray crystal structure of the manganese(III) dihydrosalen complex rac-5

Single crystals suitable for X-ray structural analysis could be obtained by slow cooling of hot, saturated solutions of the chelate *rac*-**5** in ethanol. The result is shown in Fig. 2. The metal ion is coordinated equatorially by the oxygen (phenolate) and nitrogen (amine and imine) donor atoms of the dihydrosalen ligand. Furthermore, the fifth imidazole donor occupies an axial position. The sixth coordination site is vacant and may thus be expected to bind and

Table 1
Asymmetric two-phase epoxidation with 1% aqueous hydrogen peroxide, catalyzed by the manganese chelate **5**; molar ratio of olefin:oxidant:catalyst 10:100:1

Entry	Olefin	Oxidant	Reaction time (h)	Olefin consumed (%)	Epoxide formed (%) [b,c]	ee (%) [a,b]
1	**6**	30% H_2O_2	12 [d]	87	60 (69)	34
2	**6**	30% H_2O_2	1	88	68 (77)	45
3	**6**	30% H_2O_2	1 [e]	93	73 (78)	45
4	**6**	1% H_2O_2	1	92	77 (84)	48
5	**6**	1% H_2O_2	1 [e]	91	65 (71)	50
6	**6**	1% H_2O_2	1 [e]	93	72 (77)	64 [f]
7	**7**	1% H_2O_2	2 [e]	n.d.	24 [g]	63 [f,g]
8	styrene	1% H_2O_2	2 [e]	51	51	46

[a] The catalyst **5** was prepared from the ligand **4** of 81% ee.
[b] Yield and ee determined by capillary GC [heptakis(2,6-di-O-methyl-3-O-pentyl)-β-cyclodextrin column], employing 1,2-dibromobenzene as internal standard. Absolute configurations of the major enantiomers were determined by comparison with authentic samples: epoxidation of **6**: (1*R*, 2*S*)-epoxide, epoxidation of styrene: (*R*)-epoxide, epoxidation of **7**: not determined.
[c] Values in parentheses are corrected for incomplete conversion of the olefin (selectivity).
[d] In this experiment, acetonitrile was used as solvent. The oxidant was added as a solution in acetonitrile by means of a syringe pump over a period of 12 h.
[e] Epoxidation was carried out at 0°C.
[f] Catalyst **5** prepared from ligand **4** of > 98% ee.
[g] Isolated yield, ee determined by HPLC on a CHIRALCEL OD-H column.

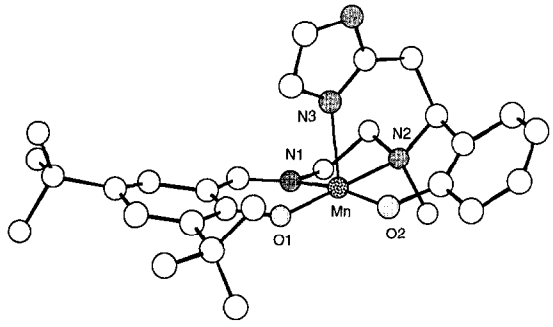


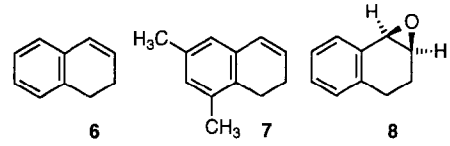
Fig. 2. X-Ray crystal structure of the manganese(III) chelate *rac*-5 (only the (*S*)-enantiomer is shown, H-atoms are omitted for clarity). Selected bond lengths (Å): Mn–O1 1.82(2); Mn–O2 1.81(2); Mn–N1 1.95(2); Mn–N2 2.06(2); Mn–N3 2.20(3).

activate a hydrogen peroxide molecule — just as in heme peroxidases. As could be expected, the dihydrosalen ligand is not planar. Both the tetrahedral amine nitrogen atom and the tetrahedral carbon atom carrying the (2-imidazolyl)methyl side-chain induce significant distortion. The planes of the two benzene rings intersect at an angle of ca. 45°. Since the substituent at the amine nitrogen atom is pointing 'downward', i.e. towards the face of the complex where the oxygenation of a substrate is expected to take place, significant asymmetric induction may be anticipated.

2.3. Catalytic activity of the manganese chelate 5

2.3.1. Asymmetric epoxidation with hydrogen peroxide catalyzed by the enantiomerically pure manganese chelate 5

As expected, the manganese chelate **5** showed catalytic activity in the epoxidation of olefins with hydrogen peroxide. The results for the epoxidation of 1,2-dihydronaphthalene **6**, 6,8-dimethyl-1,2-dihydronaphthalene **7** and styrene are summarized in Table 1.



6 **7** **8**

As it turned out, hydrogen peroxide could either be used in homogeneous solution using acetonitrile as solvent, or in a two-phase system. In the latter case, both the olefin and the catalyst were dissolved in dichloromethane, and this solution was then layered with aqueous hydrogen peroxide — at the temperatures and concentrations stated in Table 1. Typically, 10 eq. of the oxidant were used, and 10 mol% of the catalyst (rel. to the olefin). In the case of the epoxidation of 1,2-dihydronaphthalene **6**, using the enan-

Table 2
Asymmetric epoxidation catalyzed by the manganese chelate **5**, using terminal oxidants other than hydrogen peroxide

Entry	Olefin	Oxidant	Reaction time (h)	Olefin consumed (%)	Epoxide formed (%) [b,c]	ee (%) [a,b]
1	**6**	$(H_2N)_2CO \cdot H_2O_2$	1	94	70 (74)	48
2	**6**	$Na_2CO_3 \cdot 1.5\ H_2O_2$	29	87	66 [d] (76)	53
3	**6**	Ph–IO [e]	1	83	68 (82)	52
4	**6**	NaOCl [f]	24	95	76 (80)	56
5	**6**	*m*CPBA [g]	1	14	11 (79)	23
6	trans-stilbene	Ph–IO [h]	14	n.d.	39 [i]	33 [i]

[a] The catalyst 5 was prepared from the Schiff's base **4** of 81% ee.
[b] Yield and ee determined by capillary GC [heptakis(2,6-di-O-methyl-3-O-pentyl)-β-cyclodex-trin column], employing 1,2-dibromobenzene as internal standard. Absolute configurations of the major enantiomers as in Table 1, epoxidation of trans-stilbene: not determined.
[c] Values in parentheses are corrected for incomplete conversion of the olefin (selectivity).
[d] The yield of isolated, chromatographically purified material could be raised to 77% by driving the reaction to full conversion of the olefin.
[e] Two equivalents of iodosylbenzene (rel. to olefin) were added at once.
[f] Four equivalents of sodium hypochlorite (rel. to olefin) were added.
[g] Epoxidation carried out at 0°C, using 1 eq. of oxidant (rel. to the olefin).
[h] Three equivalents of iodosylbenzene (rel. to olefin) were added at once, 8 mol% of catalyst 5 were used.
[i] Isolated yield, ee determined by HPLC on a CHIRALCEL OD-H column.

tiomerically pure complex **5** (Table 1, entries 1–6), the best results were achieved under two phase conditions: Using 1%-hydrogen peroxide and dichloromethane at 0°C, the (1*R*, 2*S*)-epoxide **8** was obtained in high yield (72%) and enantiomeric excess (64%, Table 1, entry 6). When the substrate olefin was changed to 6,8-dimethyl-1,2-dihydronaphthalene **7**, a similar ee was achieved (63%, Table 1, entry, 7), but at significantly lower yield. Finally, when styrene was subjected to the epoxidation procedure, 51% of the (*R*)-epoxide were obtained at 46% ee (Table 1, entry 8).

*2.3.2. Asymmetric epoxidation catalyzed by the manganese chelate **5** using terminal oxidants other than hydrogen peroxide*

Solid adducts of hydrogen peroxide and other terminal oxidants were tested, in conjunction with the enantiomerically pure catalyst **5**, too. The results are summarized in Table 2. As it turned out, the urea clathrate of hydrogen peroxide (Table 2, entry 1) or so-called sodium 'percarbonate' (Table 2, entry 2) could be employed as a suspension in dichloromethane, too. The enantiomeric excesses observed were generally comparable to those obtained in the two-phase system (48% and 53%, respectively). In addition, the chemical yields were quite reasonable. As shown in Table 2, entries 3–5, 1,2-dihydronaphthalene **6** could also be epoxidized using a suspension of iodosylbenzene, a two-phase system with sodium hypochlorite, or *meta*-chloroperbenzoic acid in homogeneous solution. In the latter case, both yield and ees were unsatisfactory, whereas both hypochlorite and iodosylbenzene gave chemical yields and ees comparable to hydrogen peroxide. Interestingly, the epoxidation of trans-stilbene (Table 2, entry 6) could be achieved *only* with iodosylbenzene as terminal oxidant.

Table 3
Two-phase epoxidation of 1,2-dihydronaphthalene **6** with 1% hydrogen peroxide, catalyzed by the manganese chelates *rac*-**9**–**11**

Entry	Catalyst	Reaction time (h) [a]	Olefin consumed (%)	Epoxide formed [b,c]
1	*rac*-**10**	2.5	96	82 (86)
2	*rac*-**11**	2.5	69	58 (84)
3	*rac*-**9** [d]	4	0	0

[a] All reactions were carried out at 0°C.
[b] Yields determined by capillary GC [heptakis(2,6-di-O-methyl-3-O-pentyl)-β-cyclodextrin column], employing 1,2-dibromobenzene as internal standard.
[c] Values in parentheses are corrected for incomplete conversion of the olefin.
[d] The addition of 2-methylimidazole (up to 20 eq. rel. to catalyst) did not change this result.

*2.3.3. Variations on the catalyst structure: Epoxidation of 1,2-dihydronaphthalene **6** catalyzed by the manganese chelates rac-**9**–**11***

In the manganese chelate **5**, the 'left' benzene ring is substituted by two *tert*-butyl groups, whereas the 'right' benzene does not carry any further substituents. In the catalyst *rac*-**10**, an additional methyl group is positioned ortho to the 'right' phenolic oxygen atom. In *rac*-**11**, a methoxy group occupies the para position relative to the 'right' phenolic oxygen atom. The synthesis of *rac*-**10**,**11** was carried out analogous to that of *rac*-**5** (Scheme 1). The catalytic performance of these derivatives of the parent system *rac*-**5** was explored under two-phase conditions, using 1%-hydrogen peroxide as terminal oxidant and 1,2-dihydronaphthalene **6** as substrate. The results are summarized in Table 3: The ortho-methylated catalyst *rac*-**10** indeed showed a higher efficiency than the parent system *rac*-**5**; the epoxide *rac*-**8** was formed in 82% yield (Table 3, entry 1). The introduction of a methoxy group (*rac*-**11**, Table 3, entry 2) resulted in a lowering of the epoxide yield. Most importantly, the tetradentate manganese complex *rac*-**9** showed no catalytic activity at all (Table 3, entry 3), even in the presence of a large excess of 2-methylimidazole (up to 20 eq., relative to the complex *rac*-**9**).

*2.3.4. Asymmetric epoxidation of 1,2-dihydronaphthalene **6** using the catalyst **5** under two-phase conditions: Enantiomeric excess of the epoxide **8** as a function of time*

1,2-Dihydronaphthalene **6** was epoxidized under two-phase conditions with 1%-hydrogen

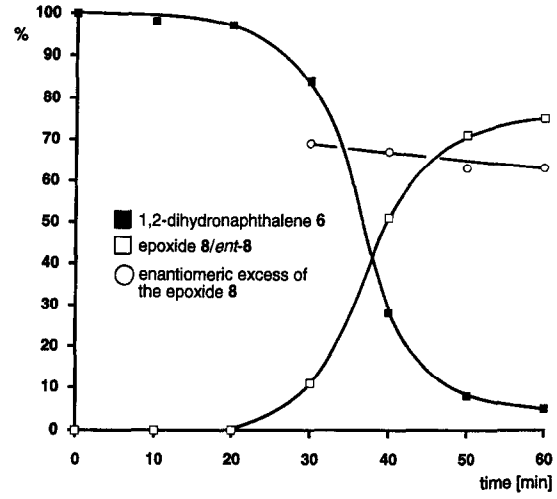


Fig. 3. Time course of the asymmetric epoxidation of 1,2-dihydronaphthalene **6** with hydrogen peroxide using the catalyst **5**.

peroxide, using the catalyst **5**. When the concentrations of the starting material **6**, the product epoxide **8**/*ent*-**8** and the ratio of **8**/*ent*-**8** were followed by gas chromatography, the time profile shown in Fig. 3 was obtained. The most striking features are the induction period and the fact that the enantiomeric excess of the product epoxide changed only very little with time (initial value: 69%, final value: 64%).

3. Discussion

For the sake of clarity the results presented in this paper shall briefly be summarized again: (a) The synthetic sequence depicted in Scheme 1 allows for the preparation of novel pentadentate dihydrosalen manganese(III) complexes. Depending on whether the starting secondary amines are used in racemic or enantiomerically pure form, the manganese(III) chelates are obtained enantiomerically pure or as racemates. In principle, many other metal ions can be complexes with the ligands. (b) The pentadentate manganese(III) chelates act as peroxidase models. They efficiently epoxidize olefins using dilute aqueous hydrogen peroxide as terminal oxidant. In enantiomerically pure form, the chiral catalysts induce high enantiomeric excesses in the product epoxides. Oxidants other than hydrogen peroxide can be used as well. (c) The pentacoordination of the manganese(III) ion is a prerequisite for peroxidase activity: Omitting the axial imidazole donor eliminates the catalytic activity. (d) The enantiomeric excess of the product epoxide changes only very little in the course of the reaction. Therefore, a secondary stereospecific transformation of the primary epoxidation product appears not to take place.

3.1. Pentadentate manganese(III) complexes of the dihydrosalen type as peroxidase models and as new epoxidation catalysts

In view of the above results, it appears that our initial concept of using pentadentate manganese(III) chelates as peroxidase models (Fig. 1) actually afforded a new class of biomimetic oxidation catalysts. As in heme-peroxidases, it may be assumed that the axial ligand facilitates the O–O bond heterolysis of hydrogen peroxide coordinated to the 'opposite' axial site at the manganese(III) ion [6–8]. The substrate spectrum of the catalyst **5** appears to be similar to that of the manganese(III) salen catalysts described by Jacobsen [14] and Katsuki [15]: *Cis*-1,2-disubstituted, conjugated olefins, like e.g. 1,2-dihydronaphthalene **6** are epoxidized best, whereas trans-olefins or terminal alkenes like 1-octene give at best poor yields of epoxide. In this context, it is interesting to note that our catalyst **5** did epoxidize trans-stilbene (Table 2, entry 6), but only with iodosylbenzene as terminal oxidant, and not with any other. It has been pointed out before [16] that the mechanistic pathway for metal-catalyzed oxygen transfer from iodosylbenzene may be different from other oxygen donors: In the former case, an adduct of the catalyst with intact iodosylbenzene may be the active, oxidizing entity, as opposed to the M=O 'oxene species' usually postulated [15].

3.2. On the mechanism of asymmetric induction

It was recently found that the high enantioselectivity of the epoxidation of 1,2-dihydronaphthalene **6** with Jacobsen's catalysts is in part due to a subsequent, stereospecific hydroxylation of the minor enantiomer of the initially formed epoxide mixture [17]. In other words, the enantiomeric excess of the product epoxide is increased by a subsequent kinetic resolution. As an experimental indicator, the ee of the product increases as the reaction proceeds [17]. In our case, the ee of the product epoxide remains basically constant (Fig. 3), and there is no indication for a secondary process. Consequently, the enantioselectivities observed must occur exclusively at the epoxidation stage. In fact, inspection of space filling models revealed that the enantioselectivity observed can consistently be explained by nonbonding interactions between the approaching substrate olefin and the non-planar catalyst: In the case of 1,2-dihydronaphthalene **6**, the approach of the (3*Re*)-face of the prochiral olefin **6** to the oxygen atom of an intermediate Mn=O species is strongly disfavored. [3] Model studies of this type also indicate that the introduction of substituents on the 'right' benzene ring of the catalyst **5** (Fig. 2) should further direct the approach of the olefin and thus increase the face selectivity of the oxygen transfer.

3.3. Stability of the catalysts

As with other oxidation catalysts, the major weakness of our catalytic system is its limited stability. In fact, the epoxide yields stated in this article reflect the kinetic competition between oxygen transfer to a substrate and oxidative degradation of the catalyst. Experimentally, the brown solutions of the manganese(III) catalysts bleach as the reaction proceeds. Once they are colorless, the catalytic activity is lost. It was already shown by Jacobsen [14] that the catalyst stability is increased when the positions *ortho* and *para* to the phenolic oxygen atoms are blocked. Most likely, substituents at these positions prevent oxidative phenol coupling reactions. Furthermore, sterically demanding substituents at these positions increase the enantioselectivity of the oxygen transfer reactions. In line with this argumentation, we found that the *ortho*-methylated complex *rac*-**10** gives indeed higher epoxidation yields (Table 3, entry 1). As may have been expected, the electron rich methoxylated catalyst *rac*-**11** is degraded even faster than the parent system *rac*-**5** (Table 3, entry 2). Taken together, the above results indicate that a substitution of both the *ortho* and the *para* position (relative to the phenolic oxygen atom) of the 'right' benzene ring in **5** with bulky alkyl substituents should provide higher stability towards oxidative degradation.

In summary, we have shown that pentacoordinate manganese(III) chelates of the dihydrosalen type show peroxidase activity and that they may be used as catalysts for the asymmetric epoxidation of olefins with hydrogen peroxide as terminal oxidant. Their synthetic value is presently limited by their relatively complex synthesis. We are aiming at (a) a significant simplification of the synthesis, and simultaneously at (b) increasing the stability of this promising new class of oxidation catalysts.

4. Experimental

The synthesis of the catalysts and the details of the X-ray structural analysis of the manganese chelate *rac*-**5** will be reported by the authors in *J. Mol. Catal.*, special issue on 'Recent Developments on Biomimetic Oxidation Catalysts'.

[3] Assuming a coordination state of the manganese ion as shown in Fig. 2, with the oxene–oxygen atom bonded trans to the imidazole nitrogen, and a perpendicular attack [14,15] of this intermediate Mn=O species on the C=C double bond.

4.1. General procedure for epoxidations using 1%-hydrogen peroxide under two phase conditions, catalyzed by the manganese chelates ***5*** *and rac-****9–11****:*

A 10 ml flask was charged at room temperature with a solution of the olefin (40.0 μmol), 1,2-dibromobenzene [9.40 mg, 40.0 μmol (as internal standard)] and the manganese catalyst (4.00 μmol, 10 mol%) in 1.5 ml of dichloromethane. Water (1.5 ml) was added and the resulting mixture was stirred vigorously. 30%-Hydrogen peroxide (45.0 mg, 400 μmol, 10 eq.) was then injected by means of a syringe. The course of the reaction was monitored by GC or HPLC. For each olefin, the identity and the yield of the oxidation product was verified by isolation. For example, the isolation of 1,2-epoxy-1,2,3,4-tetrahydronaphthalene ***8****/ent-****8*** was done as follows: The organic phase was filtered through Celite. After evaporation of the solvent, the residue was extracted with *n*-pentane. The extract was flash-chromatographed on silica gel, eluting with *n*-pentane/ethyl ether 40:1.

4.2. General procedure for epoxidations catalyzed by the manganese chelate ***5****, using oxidants other than 1%-hydrogen peroxide*

A 10 ml flask was charged at room temperature with a solution of the olefin (40.0 μmol), 1,2-dibromobenzene [9.40 mg, 40.0 μmol (as internal standard)] and the manganese chelate **5** (3.45 mg, 4.00 μmol, 10 mol%) in 1.5 ml of dichloromethane. With vigorous stirring, the oxidant was added at room temperature. The course of the reaction was monitored by GC or HPLC.

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