Enantioselective epoxidation of olefins catalyzed by two novel chiral poly-salen–Mn(III) complexes

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Abstract

Two novel chiral poly-salen–Mn(III) complexes **1** and **2**, derived from (*R,R*)-1,2-diaminocyclohexane and the disalicylaldehydes **5** and **6** were synthesized and employed in the enantioselective epoxidation of olefins. A range of 30–92% ee and 75–97% yield was achieved in NaClO/4-PPNO and *m*-CPBA/NMO oxidant systems when substituted styrenes and substituted 2,2-dimethylchromenes were used as substrates. Furthermore, the poly-salen–Mn(III) complexes could be recovered easily and recycled efficiently several times by a simple catalysis/separation method. After five reactions, an 82% ee and 78% yield of epoxide were obtained using 2,2-dimethylchromene as substrate. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: enantioselective epoxidation; unfunctionalized olefins; chiral poly-salen–Mn(III) complexes.

Enantioselective epoxidation of unfunctionalized olefins catalyzed by chiral salen–Mn(III) complexes has proved to be one of the most useful reactions discovered in the last decade.[1] The classic salen–Mn(III) catalysts show high activities and enantioselectivities for the reaction, but the separation and recycling of the catalyst are still major problems. The interest in the reaction has encouraged some authors to develop supported salen–Mn(III) catalysts, including polymer-bound catalysts[2–5] and inorganic-supported catalysts,[6–9] so as to minimize the degradation of the catalysts allowing recovery of the catalysts and use for a large number of cycles. However, the utilization of insoluble polymer-bound catalysts solved the separation problem but usually suffered from lowered catalytic activity and/or stereoselectivity. Herein, we report two new poly-salen–Mn(III) complexes **1** and **2** (Scheme 1) for the enantioselective epoxidation of unfunctionalized olefins. Using a simple catalysis/separation method, moderate to good catalytic activities and enantioselectivities were achieved, and the catalysts could be recycled effectively several times.

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Poly-Salen-Mn(III) 1　　　　**Poly-Salen-Mn(III) 2**
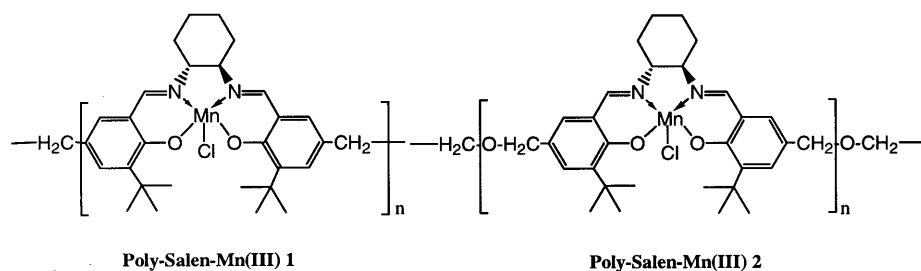
Scheme 1. Two novel poly-salen–Mn(III) complexes

In contrast to most reports on organic polymer-bound chiral salen–Mn(III) catalysts in which the monomer of a chiral salen–Mn(III) complex bearing two vinyl groups is copolymerized with other suitable monomers,[2–5] the chiral poly-salen ligands **3** and **4** were obtained by the condensation of a slight excess of (*R,R*)-1,2-diaminocyclohexane with the corresponding disalicylaldehydes **5** and **6** in ethanol,[10] and the precipitated Schiff bases were then collected and washed with water, ethanol and hexanes in sequence to remove the unreacted diamine and the low molecular weight Schiff bases. The structures of the chiral poly-salen ligands **3** and **4** were confirmed by ^{1}H NMR and ^{13}C NMR, no free aldehyde proton being observed. The average molecular weight of the two ligands was around 5400 ($M_n = \sim 5400$, $n = \sim 12$) based on VPO analysis. The poly-salen–Mn(III) complexes **1**, **2** were synthesized by inserting the manganic ion according to literature procedures (Scheme 2).[11,12] It was found that the two poly-salen–Mn(III) complexes, **1** and **2**, were very soluble in dichloromethane, but almost insoluble in hexanes and diethyl ether.
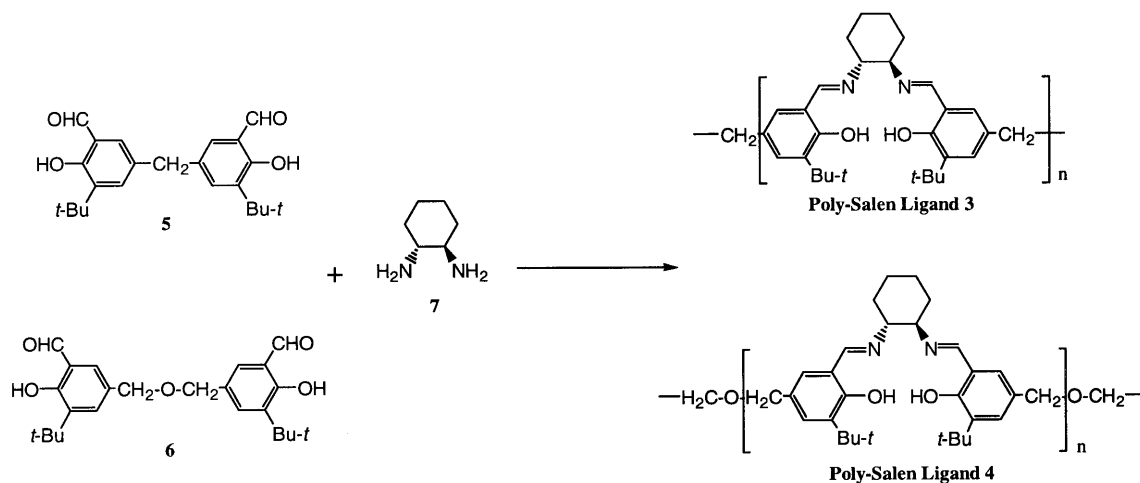
Scheme 2. The synthesis of poly-salen ligands **3** and **4**

The epoxidation reactions catalyzed by the poly-salen–Mn(III) complexes **1** and **2** were carried out in dichloromethane, styrene being used initially as a typical substrate. When sodium hypochlorite (NaClO) was used as oxidant in an aqueous-oil biphasic system without additive, the reaction time for total conversion was so long, usually more than 24 hours, that most of the poly-salen–Mn(III) complexes **1** and **2** were degraded, and the enantioselectivity of styrene oxide formation was low (entries 1 and 2 in Table 1).[13] When 0.2 equivalents of 4-phenylpyridine-*N*-

Table 1
The chiral poly-salen–Mn(III) complexes **1** and **2** catalyzed enantioselective epoxidation with NaClO/4-PPNO[a]
and *m*-CPBA/NMO[b] as oxidants

Entry	Substrate	Catalyst	Oxidant	Temp. (°C)	Ee (%)[c]	Yield (%)[d]
1[e]	Styrene **8**	**1**	NaClO	Rt	25	61
2[e]		**2**	NaClO	Rt	28	64
3		**1**	NaClO/4-PPNO	0	31	84
4		**2**	NaClO/4-PPNO	0	36	75
5		**1**	*m*-CPBA/NMO	0	43	96
6		**1**	*m*-CPBA/NMO	−78	45	91
7		**2**	*m*-CPBA/NMO	0	41	91
8		**2**	*m*-CPBA/NMO	−78	42	89
9	*cis*-β-Methyl-styrene **9**	**1**	NaClO/4-PPNO	0	56	74
10		**2**	NaClO/4-PPNO	0	58	69
11		**1**	*m*-CPBA/NMO	0	70	85
12		**2**	*m*-CPBA/NMO	0	68	86
13	2,2-Dimethyl-chromene **10**	**1**	NaClO/4-PPNO	0	91	82
14		**2**	NaClO/4-PPNO	0	92	81
15		**1**	*m*-CPBA/NMO	0	91	87
16		**2**	*m*-CPBA/NMO	0	91	85
17	6-Cyano-2,2-dimethyl-chromene **11**	**1**	NaClO/4-PPNO	0	86	95
18		**2**	NaClO/4-PPNO	0	89	96
19	6-Nitro-2,2-dimethyl-chromene **12**	**1**	NaClO/4-PPNO	0	85	96
20		**2**	NaClO/4-PPNO	0	88	97
21	6-Bromo-2,2-dimethyl-chromene **13**	**1**	NaClO/4-PPNO	0	88	95
22		**2**	NaClO/4-PPNO	0	91	94

[a] The enantioselective epoxidation reactions were carried out at 0°C in dichloromethane (2 mL) with 1 mmol of olefin substrate, using TLC to detect the total conversion, usually in 2–3 h. The mole ratio of substrate/poly-salen–Mn(III) complex was from 1:0.02 to 1:0.04.

[b] The enantioselective epoxidation reactions were carried out in dichloromethane (5 mL) with 1 mmol of olefin substrate, using TLC to detect the total conversion, usually in 10 min at 0°C and 0.5–1 h at −78°C. The mole ratio of substrate/poly-salen–Mn(III) complex was 1:0.04.

[c] The ee's for the epoxidation product was determined by GC using a chiral capillary column (cyclodex-β,2,3,6-methylated, 30 m × 0.25 mm (i.d.)).

[d] Isolated yield.

[e] The mole ratio of substrate/poly-salen–Mn(III) complex was 1:0.05, NaClO used as oxidant only. The total conversion time was more than 24 hours.

oxide (4-PPNO) was added to the catalytic system as the additive, the reaction was complete in a period of 2–3 hours. Both the yields and the enantioselectivities for the formation of styrene oxide were obviously improved (entries 3 and 4 versus entries 1 and 2, respectively).[14] Under the condition of NaClO as the oxidant with 4-PPNO as the additive, ee's of 56–58% were obtained with *cis*-β-methylstyrene as substrate (entries 9 and 10). Promisingly good results with ee's of 85–92% and yields of 81–97% for epoxide formation were achieved by using substituted 2,2-dimethylchromenes as substrates (entries 13 and 14, 17–22).

The homogeneous oxidation system of *m*-chloroperbenzoic acid (*m*-CPBA) and *N*-methyl-morpholine-*N*-oxide (NMO) in dichloromethane, a highly efficient epoxidation system at low temperature,[15,16] has also been employed in the chiral poly-salen–Mn(III) complex **1** and **2** catalyzed enantioselective epoxidation. The results of the reaction are also summarized in Table 1. When *m*-CPBA/NMO was used as the oxidant, the enantioselectivities and activities for the substituted styrene oxides were better than those obtained using NaClO/4-PPNO. At 0°C, an ee of 43% was obtained for styrene oxide (entry 5). This result is equivalent to that obtained by using Jacobsen's salen–Mn(III) catalyst at the same temperature.[15] When the reaction temperature was lowered to −78°C, the catalysts showed high catalytic efficiency. However, no significant improvement in ee's was observed in our experiments at −78°C, in contrast to other systems in which the ee's increased remarkably.[15,16]

We are also interested in recycling the catalysts as well as in the ee's of the epoxidation. Based on the solubility of our poly-salen–Mn(III) complexes **1** and **2** mentioned above, the catalysts can be recovered easily by using hexanes to precipitate the catalyst from the concentrated reaction mixture. The solid can be conveniently isolated by filtration, and then dissolved in dichloromethane for another reaction. Any small amount of catalyst remaining in the filtrate can be removed through Celite.[17] Either recovered **1** or **2** could be recycled efficiently both in NaClO/4-PPNO and *m*-CPBA/NMO oxidation systems. Table 2 lists the typical results for five cycles using poly-salen–Mn(III) complex **1** as catalyst with 2,2-dimethylchromene as the substrate and NaClO/4-PPNO as the oxidant. As can be seen, a 78% yield was obtained in the fifth reaction with only a small decrease in catalytic activity compared to the fresh catalyst (entry 5 versus entry 1 in Table 2). It was discovered that the enantioselectivities decreased from 91% ee using the fresh catalyst to 87% ee in the first cycle (entry 1 versus entry 2), then to 83% in the fourth cycle (entries 2–5). Considering that the poly-salen–Mn(III) complexes fall behind the Jacobsen's salen–Mn(III) catalysts in term of activity, especially enantioselectivity, we suspected that some lower molecular weight catalysts, which could provide better ee's during the fresh reaction, were being degraded more easily than the higher molecular weight catalysts, which were being recycled without obvious degradation, several times.

Table 2
The recycling experiment for the enantioselective epoxidation of 2,2-dimethylchromene using NaClO/4-PPNO as oxidant catalyzed by complex **1**[a]

Entry	Cycle	Time (h)	Ee (%)[b]	Yield (%)[c]
1	Fresh	3	91	82
2	1	4	87	80
3	2	4.5	85	80
4	3	4.5	84	79
5	4	4.5	83	78

[a] The enantioselective epoxidation reactions were carried out according to the procedure described in Table 1. After the total conversion, the organic phase was separated, washed with saturated NaCl solution (2×5 mL) and dried (Na_2SO_4). The solution was concentrated and hexane (2 mL) was added to precipitate the catalyst. The solid was isolated by filtration and washed with hexane (2 mL), and then dissolved in dichloromethane for another reaction.
[b] The ee's for the epoxidation product were determined by GC using a chiral capillary column (cyclodex-β,2,3,6-methylated, 30 m × 0.25 mm (i.d.)).
[c] Isolated yield.

Acknowledgements

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