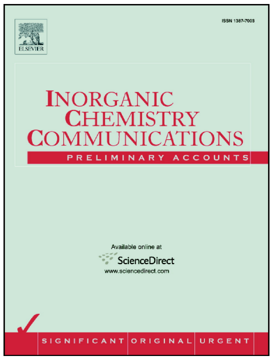

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Asymmetric Epoxidation of unfunctionalized olefins with C_2-Symmetrical Diphenol-derived Axially Coordinated Homogeneous Chiral Bi-Mn(III) Salen Complexes

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Abstract: A novel type of C_2-symmetrical diphenol-derived and axially coordinated homogeneous chiral bi-Mn(III) salen complexes are synthesized and their catalytic effects in asymmetric epoxidation of unfunctionalized olefins are investigated in details. The results show that excellent enantioselectivities and high activities are achieved (enantioselectivities up to >99% in less than 10 min, and conversions up to >99.9%) in the absence of expensive NMO. Compared with Jacobsen's catalyst, the configuration of C_2-symmetrical homogeneous chiral bi-Mn(III) salen complex contribute to the catalytic reactivity and stability. Furthermore, these new homogeneous catalysts could be easily recovered and reused for 5 cycles without significant loss of their properties.

Keywords: Bi-Mn(III) salen Complexe; O-coordinating axial bases; Jacobsen's catalyst; Recycle; Asymmetric epoxidation

Introduction

Asymmetric epoxidation of unfunctionalized olefins holds a considerable interest in organic synthesis because the resulting enantiomerically pure epoxides are versatile intermediates in the preparation of several classes of compounds [1-5]. For industrial purposes, the chiral Mn(III) salen complexes are preferred since manganese itself is a relatively nontoxic metal, and manganese complexes are superior to iron complexes for the selective epoxidation of olefins by virtue of fewer side reactions over manganese complexes[6]. Homogeneous catalysis often provides the superior results in achieving high levels of enantioselectivity, but the recycle of the expensive homogeneous catalysts is so difficult that may limit the practical applications of chiral Mn(III) salen catalysts in both synthetic chemistry and industrial processes[7]. However, heterogeneous catalyst could offer the advantages of simplified product purification and the potential for recycling the catalyst. For the purpose of recycling, a number of supported catalysts with big molecular weights have been synthesized and studied. Among them, the type of Jacobsen's complexes are immobilized onto different types of supports such as MCM-41, SBA-15, ZPS-IPPA, ZPS-PVPA, ZSPP [8-11]. Unfortunately, some of the heterogeneous complexes are generally confronted with intricate synthesis procedure, high costs, poor activity, lower conversion, poor recyclability, as well as leaching of the active species [12]. In fact, precipitating the catalyst by means of solvent is still the most convenient and economical method for both product isolation and catalyst recovery. A new recyclable oligomeric or dimeric homochiral Mn(III) salen complex are synthesized and empolyed as catalysts by Janssen [13], Yao[14], Song[15], Kureshy [16], and Tang [17] for asymmetric epoxidation of unfunctionalized olefins and superior properties have also been achieved. Furthermore, these oligomeric or dimeric homochiral Mn(III) salen catalysts indicate different solubilities in different solvents, which provide a reasonable explanation for its easy recovery and reuse several times without any loss of enantioselectivity.

It is also interesting to note that axial bases play an important role in asymmetric epoxidation reaction. It is reported that the use of excess and expensive axial bases could stabilize the active intermediate species Mn(V)-oxo, such as 4-phenyl pyridine N-oxide (PPNO)[18], 4-phenylpropyl pyridine N-oxide (PPPNO) [19], methylmorphline-Noxide (NMO)[20] and imidazole compounds [21]. On account of the axial bases in the epoxidation systems catalyzed by Mn(III) salen, the presence of NMO in the m-CPBA oxidant system contributes to high enantioselectivity and rate acceleration. And then, NMO is expensive and degraded gradually during the epoxidation procedure [20]. However, chiral Jacobsen's catalyst immobilized on diphenol-modified zirconium poly (syrene-phenylvinylphosphonate)-phosphate (ZPS-PVPA) indicates superior conversions and ee values in the absence of NMO for asymmetric epoxidation of unfunctionalized olefins [22]. We have deduced that the phenomenon of NMO is ascribed to not the support ZPS-PVPA, but the diphenol axial coordinating group. Moreover, List's group have also revealed that adding NMO as the axial base to alkene epoxidation systems with Mn(III) salen phosphate complexes as catalysts could lead to a dramatic decrease of enantioselectivity and reactivity[23]. The Mn (III) salen phosphate complexes could be formed quickly when the corresponding phosphoric acids and the Mn(III) salen chloride complex are mixed together in the presence of NaOH. Unfortunately, these catalysts not only couldn't be recycled, but also could not apply to acidic oxidant systems.

With the purpose of having clearer insight into the performance of bi-catalytic center, we have developed a novel type of C_2-symmetrical diphenol-derived axially coordinated homogeneous chiral bi-Mn(III) salen complexes under mild conditions. The catalytic properties of the catalysts and the reusability as well as the factors such as the amount of catalyst, the reaction time, are also investigated in details.

Scheme 1

The C_2-symmetrical diphenol-derived homogeneous chiral bi-Mn (III) salen catalysts (3a-d) are characterized by FT-IR, DR UV-Vis. The amount of grafted chiral Jacobsen's catalyst is 1.109, 1.106, 1.109, 1.090 mmol/g, respectively by means of atomic absorption spectroscopy (AAS). This confirms that 87.4, 87.2, 95.7, 95.3% of the total diphenol-derived is axially coordinated by chiral Jacobsen's catalyst, respectively.

On account of UV-Vis spectra, the absorption spectrum of homogeneous Jacobsen's catalyst indicates a broad peak near 440 nm, due to the d-d transition of Mn(III). Whereas, chiral bi-Mn(III) salen catalysts (3a-d) show a peak near 415 nm, which confirms the successful grafting of the Jacobsen's catalyst (Fig. S1).

In view of IR spectra (Fig. S2) in the regions of (4000-400 cm^{-1}), the appearance of a strong band at 1631 cm^{-1} owing to stretch of C=N (azomethine), and a medium intensity band due to the band of Mn–N at 515-562 cm^{-1} confirms the grafting of the Jacobsen’s catalyst on the diphenol-derived compounds successfully.

Table 1

The catalytic activity and selectivity of catalysts 3a-d are explored for asymmetric epoxidation of unfunctionalized olefins using m-CPBA as an oxidant system and Jacobsen’s catalyst as the reference (Table 1). All reactions proceeds smoothly, and the bi-Mn(III) salen catalysts 3a-d indicate higher ee values than Jacobsen's catalyst (indene, up to 99.7% vs 65, entry 6 vs 1; α-methylstyrene, up to 97.4% vs 52, entry 15 vs 10) except styrene.

It is also observed that the enantioselectivities increase with the lengths of diphenol-deriveds axial coordinating group (indene, 93.6 vs 99.7%, entry 2 vs 6; α-methylstyrene, 94.5 vs 97.4%, entry 11 vs 15; styrene, 29.5 vs 32.1, entry 20 vs 24), which is similar to Li’s group [24]. The reason might be that olefins toward the Mn-oxo center more expediently with the increase of linkage. While for the catalyst 3d, there is a slight decrease in ee values (entries 8, 17, 26), owing to the steric hindrance of 3d which could lead to a twist against each other, shielding and interfering with their active catalytic centers and further lowering their catalytic performance. In addition, the performance of the catalyst 3b is poorer than the catalyst 3a, which is due to an increase of steric hindrance and a weaker electron-donating properties from diphenol-deriveds axial coordinating group 2b.

Another noteworthy activities of our catalysts is that superior performance also could be obtained in the absence of additional O-coordinating axial base NMO. In fact, adding such a ligand NMO to our reaction system could result in a dramatic decrease of enantioselectivity, for instance indene (ee%: 99.7 vs 54.4; entry 6 vs 7); α-methylstyrene (ee%: 97.4 vs 79.5, entry 15 vs 16) and styrene (ee%, 32.1 vs 27.5, entry 24 vs 25). In our previous work, we have deduced that the special phenomenon is ascribed to the synergistic effect of organic-inorganic hybrid support ZPS-PVPA and the phenoxide axial coordinating group [22]. But in this context, this research has verified that these phenomenon still exist whether diphenol-derived axial coordinating group is immobilized onto ZPS-PVPA or not. In a sense, the role of diphenol-derived group in this paper is similar to that of O-coordinating axial bases such as NMO, owing to similar properties in electronic structure and steric configuration. The addition of NMO may contribute to the competition with diphenol-derived axial coordinating group, and further refraining from the formation of transition-state or intermediates with well-defined configuration. When NMO is added to our reaction system, chiral recognition of catalysts 3a-d may decrease significantly. Further studies concerning the mechanism of NMO phenomenon for the C_2-bi-Mn (III) salen complex are currently in progress.

Fig. 1

Fig. 2

We also have explored the relationship of catalytic performance and different time with the catalyst 3c as the representative (Fig. 1-2). In practice, it is found that most of the catalytic reactions have been carried out rapidly and indicate superior performance (ee%, 99.2; conv%, 96.5; Fig. 1-2) in less than 10 min. However, the similar result for Jacobsen's catalyst would last more than 25 min. On account of the results, it could be deduced that the type of C_2- bi-Mn(III) salen complexes show superior activity and that the two metal active centers of the catalysts are not working in isolation but indicate synergetic effects.

It is interesting that the diphenol-derived compounds 2a-d are slightly soluble in chloroform and almost insoluble in other organic solvent. After assembling with the Jacobsen's catalyst, the diphenol-derived chiral bi-Mn(III) salen complexes 3a-d are completely dissolved in dichloromethane but almost insoluble in hexane, cyclohexane, and diethyl ether. In view of these results, it could be deduced that the catalyst could be easily precipitated and separated from the reaction system by means of the simple usage of solvents.

Furthermore, the recovered catalyst could be recycled for catalytic reactions without further purification. The results after recycling with indene as the substrate are shown in Table 2.

Table 2

After five cycles, the catalyst 3c still indicate favorable reusability (ee%, 83.2; yield%, 90.5), which confirms the good stability. The activity of the catalyst gradually decrease upon successively recycling, which indicates some degradation of the catalyst 3c under the conditions for epoxidation.

In conclusion, a novel type of C_2-symmetrical diphenol-derived chiral bi-Mn(III) salen complexeshave been synthesized and indicate superior properties (ee%, up to >99; conv%, >99.9) in the absence of NMO in asymmetric epoxidation of unfunctionalized olefins. Moreover, the performance of the catalyst 3c is so superior that asymmetric epoxidation reactions could be terminated in less than 10 min. In addition, the catalyst could be conveniently separated from the reaction system by simple precipitation and be recycled five times without significant loss of activity. The novel phenomenon of NMO is remarkable, which could prompt the study on the mechanism and pave the way for the potential application in industry.

Acknowledgements

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Figures captions:

Scheme 1 Synthesis of C_2-symmetrical diphenol-derived axially coordinated chiral bi-Mn(III) salen catalysts(1a–d)

Fig 1 The enantioselectivity versus reaction time plot for epoxidation of indene catalysed by 1c with m-CPBA as oxidant system in CH_2Cl_2 at 0℃

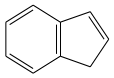
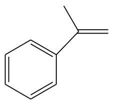
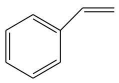
Fig 2 The conversion versus reaction time plot for epoxidation of indene catalysed by 1c with m-CPBA as oxidant system in CH_2Cl_2 at 0℃

Table captions:

Table 1 Enantioselective epoxidation of alkenes catalyzed by 1a–1d with m-CPBA as oxidant

Table 2 Enantioselective epoxidation of indene with recycled catalysts 1c with m-CPBA as oxidant

Table 1. Enantioselective epoxidation of alkenes catalyzed by 3a–3d with m-CPBA as oxidant.[a]

Entry	Substrate	Catalyst	Oxidant	Time(h)	Temp[℃]	ee(%)[b]	conv(%)[c]
1		Jacobsen	m-CPBA/NMO	1	0	65.0[d]	99.9
2		3a	m-CPBA	1	0	93.6[d]	94.0
3		3a	m-CPBA/NMO	1	0	35.3[d]	96.9
4		3b	m-CPBA	1	0	83.8[d]	96.7
5		3b	m-CPBA/NMO	1	0	21.9[d]	97.6
6		3c	m-CPBA	1	0	99.7[d]	96.8
7		3c	m-CPBA/NMO	1	0	54.4[d]	97.3
8		3d	m-CPBA	1	0	98.0[d]	99.9
9		3d	m-CPBA/NMO	1	0	35.4[d]	97.9
10		Jacobsen	m-CPBA/NMO	1	0	52 .0[e]	99.9
11		3a	m-CPBA	1	0	94.5[e]	99.9
12		3a	m-CPBA/NMO	1	0	48.0[e]	96.0
13		3b	m-CPBA	1	0	78.1[e]	99.9
14		3b	m-CPBA/NMO	1	0	40.1[e]	99.9
15		3c	m-CPBA	1	0	97.4[e]	>99.9
16		3c	m-CPBA/NMO	1	0	79.5[e]	91.4
17		3d	m-CPBA	1	0	96.4[e]	99.9
18		3d	m-CPBA/NMO	1	0	48.5[e]	92.3
19		Jacobsen	m-CPBA/NMO	1	0	47.0[f]	99.9
20		3a	m-CPBA	1	0	29.5[f]	>99.9
21		3a	m-CPBA/NMO	1	0	15.3[f]	>99.9
22		3b	m-CPBA	1	0	11.7[f]	>99.9
23		3b	m-CPBA/NMO	1	0	10.7[f]	97.2
24		3c	m-CPBA	1	0	32.1[f]	99.4
25		3c	m-CPBA/NMO	1	0	27.5[f]	99.4
26		3d	m-CPBA	1	0	30.8[f]	>99.9
27		3d	m-CPBA/NMO	1	0	21.4[f]	97.1

[a] Reactions were carried out at desired temperature in CH_2Cl_2 (3 mL) with alkene (0.5 mmol), NMO (337.5 mg, 2.5 mmol, if necessary), nonane (internal standard, 56 µL, 0.5 mmol) and catalysts (0.025 mmol, 5.0 mol%).

[b] Conversions were determined by GC, by integration of product peaks against an internal quantitative standard (nonane), correcting for response factors.

[c] Determined by GC with a chiral capillary column (HP19091G-B233, 30 m×25µm×0.25µm).

[d] Expoxide configuration R.

[e] Epoxide configuration R.

[f] Epoxide configuration 1R, 2S.

Table 2. Enantioselective epoxidation of indene with recycled catalysts 1c[a]

Run	fresh	2	3	4	5
ee[b] (%)	99.9	98.7	92.9	90.6	83.2
Conversion[c] (%)	97.1	95.2	96.1	95.1	90.5
Time (h)	0.5	0.5	1	1.5	3

[a] Reactions were carried out at 0 ℃ in CH_2Cl_2 (3 mL) with indene (1 mmol), n-nonane (internal standard, 1 mmol), m-CPBA (1.6 mmol), the catalyst 1c (5 mol%). The conversions and the ee values were determined by GC with chiral capillary columns HP19091G-B213, 30 m×0.25 μm×0.25 μm.

[b] Same as in Table 1.

[c] Same as in Table 1.

Highlights

Asymmetric Epoxidation of unfunctionalized olefins with C_2-Symmetrical Diphenol-derived Axially Coordinated Homogeneous Chiral Bi-Mn(III) Salen Complexes

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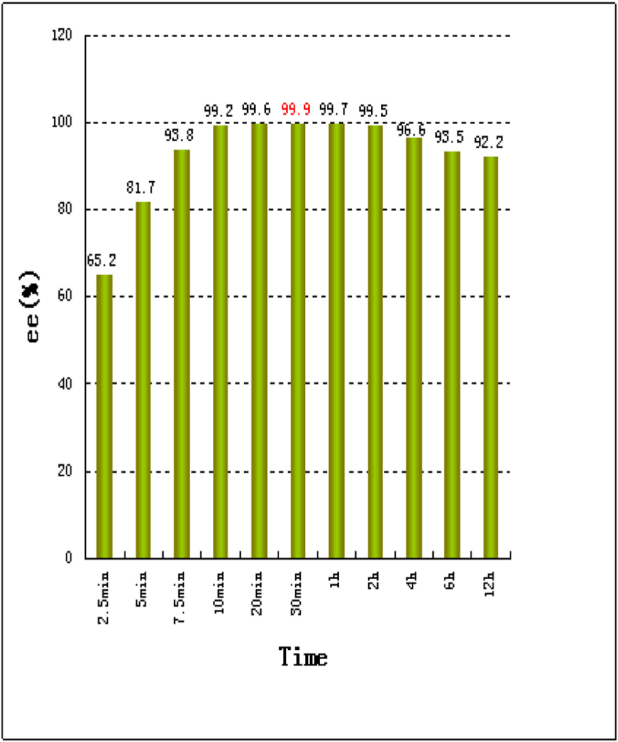
ee (%)
120
100
80
60
40
20
0
65.2
81.7
93.8
99.2
99.6
99.9
99.7
99.5
96.6
93.5
92.2
2.5min
5min
7.5min
10min
20min
30min
1h
2h
4h
6h
12h
Time

Figure 1

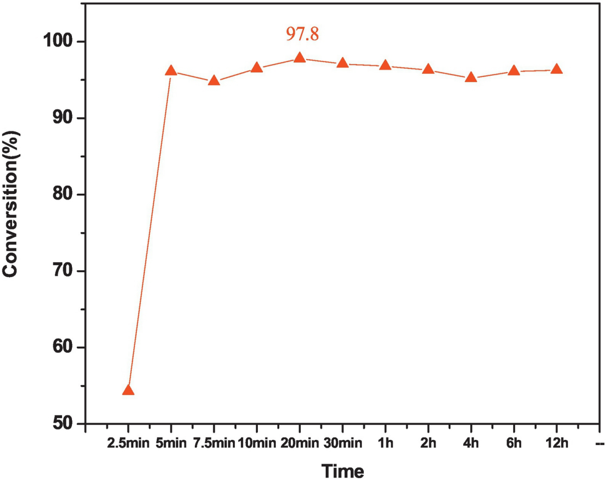
97.8
100
90
80
70
60
50
Conversition(%)
2.5min
5min
7.5min
10min
20min
30min
1h
2h
4h
6h
12h
--
Time

Figure 2