Asymmetric Epoxidation of Olefins Using Novel Chiral Dinuclear Mn(III)-Salen Complexes with Inherent Phase-Transfer Capability in Ionic Liquids

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ABSTRACT Two new chiral dinuclear Mn(III)-Salen complexes with inherent phase-transfer capability have been synthesized, which serve as catalysts in the asymmetric epoxidation of nonfunctionalized alkenes. Experimental results show these complexes are effective catalysts for the asymmetric epoxidation of some cyclic alkenes and the catalysts have certain inherent phase-transfer capability during the epoxidation because of their weak water solubility. In general, good enantioselectivity and acceptable yields were achieved when NaClO was used as oxidant under three different reaction systems. Among these alkenes, the catalyst **6a** gave the highest ee (94%) for 6-chloro-2,2-dimethylchromene in the presence of ionic liquid **2**. Additionally, the recovery and recycling of one dimeric Mn(III)-Salen complex were tested to investigate atom efficiency of the catalyst in different reaction systems on the alkenes epoxidations. The catalyst **6a** could be recovered and recycled for six times without losing activity and selectivity. *Chirality 23:69–75, 2011.*

KEY WORDS: dinuclear Mn(III)-salen; asymmetric catalysis; ionic liquids; epoxidation; phase-transfer; recyclable

INTRODUCTION

Chiral epoxides have two stereocenters and can be converted into a variety of compounds by means of regioselective ring opening, so epoxides are useful synthetic intermediates for the synthesis of chiral pharmaceuticals and fine chemicals.[1–5] It is still a challenge to get excellent enantioselectivity epoxides in high yield. Among several previously reported catalytic systems, chiral Mn(III)-Salen complexes have received considerable attention in recent years in asymmetric epoxidation of alkenes due to their availability and wide usefulness. Since Jacobsen and Katsuki first reported these key findings, much attention has been devoted to expand this system. It is demonstrated that cooperation of steric factors, electronic effects, catalytic centers, and cocatalysts play an important role in the asymmetric catalysis.[6,7] Consequently, the design of novel chiral catalysts constitutes an important strategy in asymmetric catalysis.[8,9] To enhance atom efficiency and develop environmentally friendly technology, many efforts have been devoted to investigate chiral salen complexes in the asymmetric catalysis,[10–14] an important strategy is the recycle of the salen metal complexes due to the high cost of chiral salen ligands. Therefore, the immobilizations of Salen catalysts on polymer, organic or inorganic, and ionic liquids have been developed.[15–19] In these recycling systems, it is presumed that increasing the molecular weight of the catalysts would lead to recycle the catalysts more easily. Additionally, increasing catalytically active metal centers of the catalysts could enhance the catalytic activities and catalyst recovery.[20,21] Many attempts have been made to use ionic liquids in asymmetric epoxidation of alkenes because ionic liquids as green reaction media can improve the separation, activity, and recycling of the catalysts.[22–26] On the basis of these views, we have synthesized two new chiral dinuclear Mn(III)-Salen complexes with two catalytically active metal centers and investigated their activities in asymmetric epoxidation of alkenes in the presence of ionic liquids. Since the transportation of HOCl from water to oil phase is required for salen Mn(III) complexes catalyzed epoxidation, the design of the water soluble salen Mn(III) complexes become an attractive target.[27] To enhance the solubility of dimeric salen Mn(III) complexes in water, we used *N,N*-dibutylamine to substitute other groups of salicylaldehyde at the 5,5′positions.[28,29] Herein, we have extended the application of chiral dimeric salen Mn(III) complexes in the asymmetric epoxidation

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using NaOCl as an terminal oxidant with various reaction solvents. The catalysts showed high chiral induction in the epoxidation of bulkier olefins with short reaction time, and the dimeric salen Mn(III) complex **6a** can be effectively recycled for six times. To the best of our knowledge, this is the first report of dimeric Mn(III)-salen complexes with inherent phase-transfer capability as recyclable catalysts for the asymmetric epoxidation of nonfunctionalized alkenes in the presence of ionic liquids.

EXPERIMENTAL SECTION

General Remarks

^{1}H NMR spectra were recorded on a Mercury Plus 400 spectrometer with **TMS** as internal standard. **IR** spectra were obtained on a Nicolet 170SX **FTIR** spectrophotometer as KBr discs. **ESI-HRMS** were performed on a Bruker Daltonics APEXII47e mass spectrometer. **LC-MS** were performed on a Bruker Daltonics Esquire6000 mass spectrometer. Elemental analyses were taken using a Perkin Elmer 240C analytical instrument. All reactions were monitored by **TLC**. **TLC** was performed on glass plates coated with silica gel 60F254. The crude products were purified by flash chromatography. High-performance liquid chromatograph with Daicel Chiralcel OD-H chiral column was used for the measurements (hexane:i-PrOH = 99:1).

Preparation of Two Chiral Half-Unit Ligands (4a and 4b)

Synthesis of (1*R*,2*R*)-*N*-[2-hydroxyl-3-*tert*-butyl-5-(*N*,*N*-dibutylmethylene)]-1-amino-2-cyclohexaneimine (4a). The $CHCl_3$ (10 ml), solution of 2-hydroxyl-3-*tert*-butyl-5-(*N*,*N*-dibutylmethylene)benzaldehde[3] (1 mmol) was added slowly to the $CHCl_3$ (10 ml) solution of (1*R*,2*R*)-(−)-diaminocyclohexane (1 mmol) with vigorous stirring at 0°C. The reaction mixture was stirred for 48 h before stirring was discontinued, then the solvent was removed under reduced pressure affording the crude product. The crude product was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 4:1) to generate a yellow oil (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.82 (1H, s, OH); 8.35 (1H, d, CHN); 7.06 (1H, s, ArH); 6.92 (1H, s, ArH); 4.12 (1H, d-d, CH); 3.38 (1H, s, CH); 3.47 (2H, s, CH_2); 2.92–2.74 (2H, m, NH_2); 2.40–2.36 (4H, m, CH_2); 2.06–1.60 (8H, m, CH_2); 1.43 (4H, s, CH_2); 1.39 (9H, s, $C(CH_3)_3$); 1.30–1.24 (4H, m, CH_2); 0.90–0.82 (6H, m, CH_3). LC-MS: m/z 416.1 $[M + H]^+$. Anal. Calcd for $C_{26}H_{45}N_3O$: C, 75.13; H, 10.91; N, 10.11. Found: C, 75.21; H, 10.87; N, 10.93.

Synthesis of (1*R*,2*R*)-*N*-(2-hydroxyl-3-*tert*-butyl-5-(*N*,*N*-dibutylmethylene)]-1-amino-1,2-diphenylethaneimine (4b). The ethanol (10 ml) solution of 2-hydroxyl-3-*tert*-butyl-5-(*N*,*N*-dibutylmethylene)benzaldehde[3] (1 mmol) was added slowly to the ethanol (10 ml) solution of (1*R*,2*R*)-(+)-diphenyldiamine (1 mmol) with vigorous stirring at 0°C. The reaction mixture was stirred for 48 h before stirring was discontinued, then the solvent was removed under reduced pressure affording the crude product. The crude product was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 2:1) to generate a yellow oil (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.72 (1H, s, OH); 8.39 (1H, d, CHN); 7.28–7.15 (10H, m, ArH); 7.06 (1H, s, ArH); 6.94 (1H, s, ArH); 4.73 (1H, s, CH); 4.37 (1H, d-d, CH); 3.74–3.69 (2H, m, NH_2); 3.48 (2H, s, CH_2); 2.40–2.33 (4H, m, CH_2); 1.46 (4H, s, CH_2); 1.41 (9H, s, $C(CH_3)_3$); 1.38–1.20 (4H, m, CH_2); 0.89–0.82 (6H, m, CH_3). LC-MS: m/z 514.0 $[M + H]^+$. Anal. Calcd for $C_{34}H_{47}N_3O$: C, 79.49; H, 9.22; N, 8.18. Found: C, 79.54; H, 9.16; N, 8.16.

Preparation of Two Chiral Dinucleating Ligands and Corresponding Mn(III) Complexes

Synthesis of 5,5-methylenedi-[(*R*,*R*)-{*N*-(3-*tert*-butyl-salicylidine)-*N*′-(3′-*tert*-butyl-5′-(*N*,*N*-dibutylmethylene) salicyladhyde)}-1,2-cyclohexanediamine] (5a). The ethanol (10 ml) solution of (1*R*,2*R*)-*N*-(2-hydroxyl-3-*tert*-butyl-5-(*N*,*N*-dibutylmethylene)-1-amino-2-cyclohexaneimine **(4a)** (2 mmol) was added slowly to the ethanol (10 ml) solution of 5,5′-methylene-di-3-*tert*-butylsalicyladehyde (1 mmol). The mixture was stirred under refluxing for 8 h, and then solvent was removed under reduced pressure to afford the crude product. The crude product was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 10:1) to generate a yellow oil (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.74 (2H, s, OH); 13.70 (2H, s, OH); 8.28 (2H, s, CHN); 8.22 (2H, s, CHN); 7.21 (2H, s, ArH); 7.05 (2H, s, ArH); 6.93 (2H, s, ArH); 6.74 (2H, s, ArH); 3.67 (2H, s, CH_2); 3.39 (4H, s, CH_2); 3.33 (4H, s, CH); 2.36 (8H, s, CH_2); 1.88 (8H, s, CH_2); 1.70 (8H, s, CH_2); 1.60 (8H, s, CH_2); 1.42 (18H, s, $C(CH_3)_3$); 1.39 (18H, s, $C(CH_3)_3$); 1.28–1.23 (8H, m, CH_2); 0.96–0.78 (12H, m, CH_3). ESI-HRMS: m/z 1163.8974 $[M + H]^+$. Anal. Calcd for $C_{75}H_{114}N_6O_4$: C, 77.41; H, 9.87; N, 7.22. Found: C, 77.49; H, 9.81; N, 7.31. FTIR (KBr): 3345, 2929, 2862, 1631, 1441, 1385, 1266, 1205, 1181, 1094, 1023, 963, 750, 689 cm^{-1}.

Synthesis of 5,5-methylenedi-[(*R*,*R*)-{*N*-(3-*tert*-butyl-salicylidine)-*N*′-(3′-*tert*-butyl-5′-(*N*,*N*-dibutylmethylene) salicyladhyde)}-1,2-diphenylethylenediamine] (5b). The ethanol (10 ml) solution of (1*R*,2*R*)-*N*-(2-hydroxyl-3-*tert*-butyl-5-(*N*,*N*-dibutylmethylene)-amino-1,2-diphenylethaneimine **(4b)** (2 mmol) was added slowly to the ethanol (10 ml) solution of 5,5′-methylene-di-3-*tert*-butylsalicyladehyde (1 mmol) with vigorous stirring at room temperature The reaction mixture was stirred for 16 h, then solvent was removed under reduced pressure affording the crude product. The crude product was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 8:1) to generate a yellow oil (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.63 (2H, s, OH); 13.59 (2H, s, OH); 8.33 (2H, s, CHN); 8.25 (2H, s, CHN); 7.23–7.09 (20H, m, ArH); 7.08 (2H, s, ArH); 7.04 (2H, s, ArH); 6.97 (2H, s, ArH); 6.70 (2H, s, ArH); 4.74–4.67 (4H, m, CH); 3.67 (2H, s, CH_2); 3.48 (4H, s, CH_2); 2.40 (8H, s, CH_2); 1.58 (8H, s, CH_2); 1.42 (18H, s, $C(CH_3)_3$); 1.37 (18H, s, $C(CH_3)_3$); 1.29–1.23 (8H, m, CH_2); 0.98–0.82 (12H, m, CH_3). ESI-HRMS: m/z 1359.9287 $[M + H]^+$. Anal. Calcd for $C_{91}H_{118}N_6O_4$: C, 80.37; H, 8.75; N, 6.18. Found: C, 80.46; H, 8.86; N, 6.11. FTIR (KBr): 3318, 2955, 2865, 1627, 1440, 1384, 1264, 1208, 1159, 1094, 1062, 908, 734, 700 cm^{-1}.

Synthesis of 5,5-methylenedi-[(*R,R*)-{*N*-(3-*tert*-butylsalicylidine)-*N*′-(3′-*tert*-butyl-5′-(*N,N*-dibutylmethylene)salicyladhyde)}-1,2-cyclohexanediaminato(2-)manganese(III)chloride] (6a). The ethanol solution of **5a** (1 mmol) was stirred under reflux with the ethanol solution of $Mn(OAc)_2{\cdot}4H_2O$ (3 mmol) under nitrogen atmosphere for 6 h. The reaction mixture was cooled to room temperature. Lithium chloride (6 mmol) was added and the resulting mixture was refluxed for additional 2 h while exposed to air. Then solvent was removed under reduced pressure and the residue was extracted with dichloromethane (3 × 10 ml). The extract was washed with water (2 × 10 ml) and brine and dried over anhydrous Na_2SO_4, and then concentrated to give the crude product. The crude product was recrystallized with petroleum ether affording the desired complex **6a** (yield 85%) as dark brown powder. LC-MS: m/z 1304.3 $[M - Cl]^+$, 635.9 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{75}H_{110}Cl_2Mn_2N_6O_4$: C, 67.20; H, 8.27; N, 6.27. Found: C, 67.31; H, 8.34; N, 6.19. FTIR (KBr): 3400, 2953, 2866, 2362, 1613, 1541, 1435, 1387, 1342, 1311, 1169, 1028, 830 cm^{-1}.

Synthesis of 5,5-methylenedi-[(*R,R*)-{*N*-(3-*tert*-butylsalicylidine)-*N*′-(3′-*tert*-butyl-5′-(*N,N*-dibutylmethylene) salicyladhyde)}-1,2-diphenylethylenediaminato(2-)manganese(III)chloride] (6b). Complex **6b** was prepared as a brown solid (yield 87%) according to the same procedure as **6a**. LC-MS: m/z 1500.5 $[M - Cl]^+$, 732.7 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{91}H_{114}Cl_2Mn_2N_6O_4$: C, 71.12; H, 7.48; N, 5.47. Found: C, 71.20; H, 7.43; N, 5.52. FTIR (KBr): 3409, 2954, 2867, 2364, 1610, 1539, 1420, 1386, 1343, 1308, 1169, 1006, 828 cm^{-1}.

General Procedure in Epoxidation Reactions

Substrate (2 mmol), 0.3 mmol PyNO, and ionic liquids were added to the dichloromethane (2 ml) solution of dinuclear Mn(III)-Salen complex **6a**/**6b** (0.1 mmol). The mixture was stirred vigorously at 0°C, then NaOCl which was combined with Na_2HPO_4 (0.05 mol/l) as oxidant was added to the solution. The pH of the oxidant was adjusted to 11.3 by the instillation of 1 mol/l HCl and 1 mol/l NaOH solutions. After the reaction was totally finished, the mixture was diluted with CH_2Cl_2 (2 × 10 ml). The organic layer was separated, washed with water and brine, and then dried with $MgSO_4$. The solvent was removed under reduced pressure affording the crude product, which was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2 = 2:1) to yield the epoxide. Additionally, the dinuclear catalysts can be precipitated by adding *n*-hexane after partial concentration of the solvent for recycling.

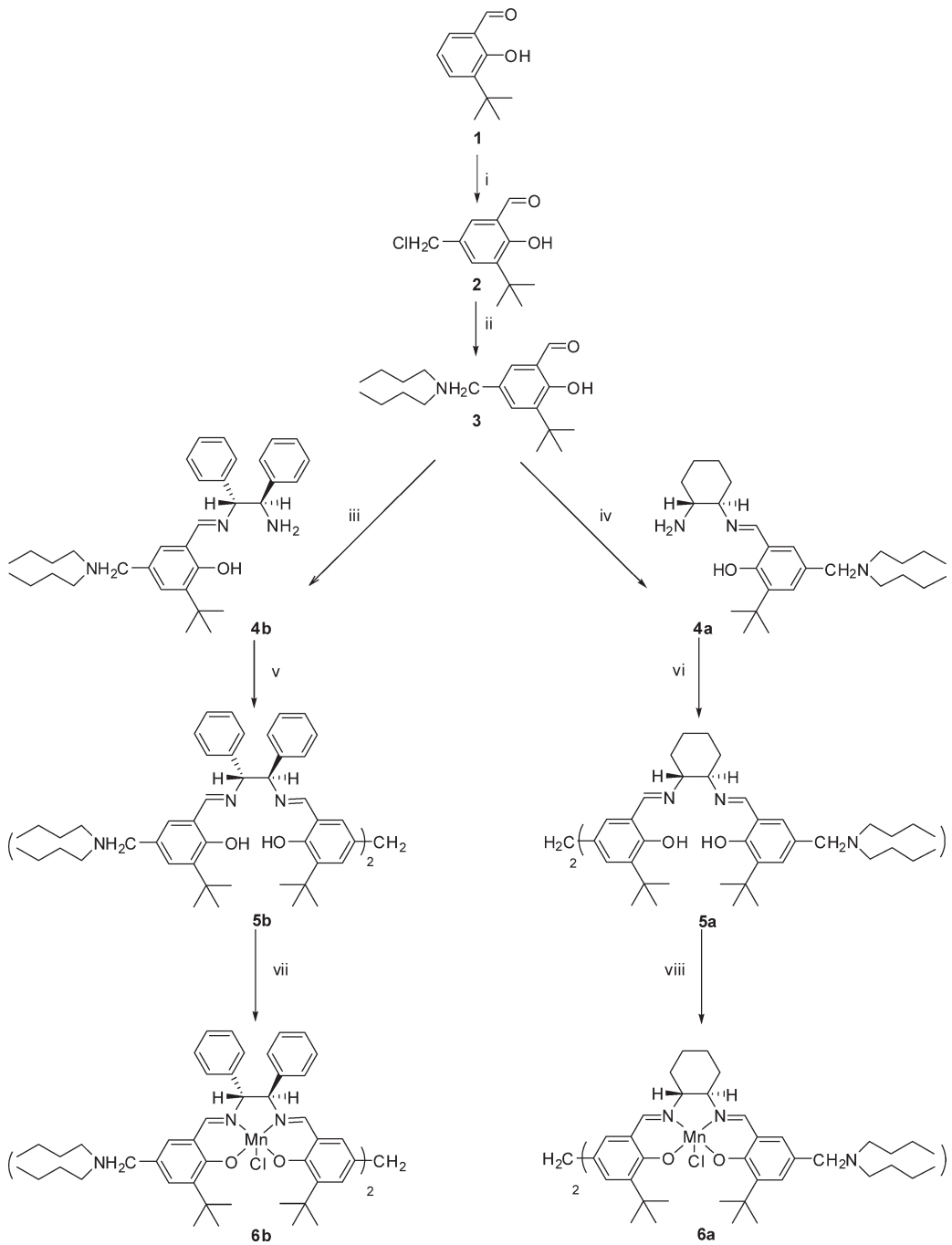
RESULTS AND DISCUSSION

The Synthesis of the Novel Chiral Dimeric Mn(III) Complexes

According to the previous studies, two chiral dinucleating ligands (**5a** and **5b**) and corresponding Mn(III) complexes (**6a** and **6b**) were prepared (as show in Scheme 1). Additionally, in a stepwise manner, 3-t-butylsalicyladhyde was chloromethylated[30] and reacted with *N*,*N*-dibutylamine giving 2-hydroxy-3-t-butyl-5-(*N*,*N*-dibutylmethylene)-salicyladhyde **3** with high yield.[31] Compound **3** reacted with (*1R,2R*)-(−)-diaminocyclohexane and (*1R,2R*)-(+)-diphenyldiamine, respectively, in a 1:1 molar ratio affording half-unit ligands **4a** and **4b**. The synthetic procedure of **4b** was carried out with some modification following the reported method.[32] Dinucleating ligands (**5a** and **5b**) were synthesized by condensation of 5,5′-methylene-di-3-t-*tert*-butylsalicylaldehyde with **4a** and **4b**, respectively.[33] The synthetic produce of dinucleating ligands have different reaction conditions because the ligand **4b** reacted with 5,5′-methylene-di-3-t-*tert*-butylsalicylaldehyde can rearrange to monomeric salen ligand without any dinucleating ligand **5b** when the mixture were heated to reflux. Finally, ligands **5a** and **5b** reacted with manganese yielding 5,5-methylenedi-[(*R,R*)-{*N*-(3-*tert*-butylsalicylidine)-*N*′-(3′-*tert*-butyl-5′-(*N,N*-dibutylmethylene)salicyladhyde)}-1,2-cyclohexanediaminato(2-)manganese(III)chloride] **6a** and 5,5-methylenedi-[(*R,R*)-{*N*-(3-*tert*-butylsalicylidine)-*N*′-(3′-*tert*-butyl-5′-(*N,N*-dibutylmethylene)salicyladhyde)}-1,2-diphenylethylenediaminato (2-)manganese(III)chloride] **6b**, respectively. Chiral dinuclear Mn(III)-Salen complexes **6a** and **6b** were characterized by **LC-MS**, **FTIR**, and Elemental analyses.

The Catalysis of the Novel Chiral Dimeric Mn(III) Complexes

The asymmetric epoxide reactions catalyzed by the two novel dimeric catalysts were systematically investigated with the substrates of styrene (A), α-methylstyrene (B), *trans*-stilbene (C), indene (D), 1,2-dihydronaphthalene (E), 2,2-dimethylchromene (F), and 6-chloro-2,2-dimethylchromene (G). As is known to all, the organic cocatalyst plays an important role in the Jacobsen epoxidation because it coordinates to the unsaturated Mn(III) species emerging form the first catalytic cycle and prevents this reacting with active Mn(V) oxo species to produce catalytically inactive μ-oxo-Mn(IV) dimmer.[34,35] Based on this point, Pyridine *N*-oxide was used as cocatalyst since it has remarkable effects on both the activity and enantioselectivity of the enantioselcetive epoxidation. To apprehend the effects of the solvent factors on alkenes epoxidation, the asymmetric epoxidation experiments were preformed in pure CH_2Cl_2, mixed solvent of CH_2Cl_2/ionic liquid **1**, and mixed solvent of CH_2Cl_2/ionic liquid **2**, respectively, at 0°C using buffer NaOCl as terminal oxidant with pyridine *N*-oxide as cocatalyst. As expected, reaction solvent plays a crucial role in asymmetric epoxidation of alkenes. After the completion of the reaction, products in ionic liquids system can be easily separated with the extraction by hexane than in pure CH_2Cl_2. It was also observed that the reaction time of ionic liquids system was shorter than the system without ionic liquid, since ionic liquids can stabilize the catalyst or ionic intermediates and enhance the activity of the catalyst.[36,37] The results data were summarized in Table 1. According to these data, in pure CH_2Cl_2 system dimeric salen Mn(III) complex **6a** gives high entantioselectivity and chemical yield of alkenes (yield 76–89%, ee 21–93%) (Table 1, entries 1, 3, 5, 7, 9, 11, and 13).

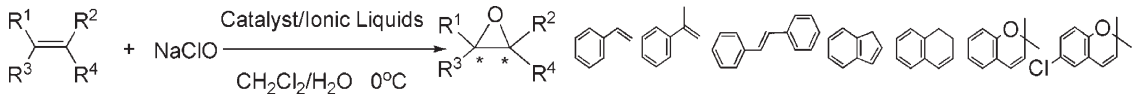


Scheme 1. Reagents and conditions: (i) paraformaldehyde, conc. HCl, tetrabutylammonium bromide, rt, 48 h, 93%; (ii) *N*,*N*-dibutylamine, toluene, Et_3N, reflux, 8 h, 84%; (iii) (1*R*,2*R*)-(+)-diphenyldiamine, EtOH, 0°C, 48 h, 86%; (iv) (1*R*,2*R*)-(−)-diaminocyclohexane, CH_3Cl, 0°C, 48 h, 68%; (v) 5,5′-methylene-di-3-*tert*-butylsalicyladehyde, EtOH, rt, 16 h, 91%; (vi) 5,5′-methylene-di-3-*tert*-butylsalicyladehyde, EtOH, reflux, 8 h, 92%; (vii (1) $Mn(OAC)_2{\cdot}4H_2O$, EtOH, reflux, 6 h, (2) $LiCl{\cdot}H_2O$, EtOH, reflux, 2 h, 87%; and (viii) (1) $Mn(OAC)_2{\cdot}4H_2O$, EtOH, reflux, 6 h, (2) $LiCl{\cdot}H_2O$, EtOH, reflux, 2 h, 85%.

The use of **6b** instead of **6a** led to slightly reduced entantioselectivity and chemical yield (yield 53–80%, ee 15–78%) (Table 1, entries 2, 4, 6, 8, 10, 12, and 14). In general, the salen-Mn(III) complex derived from chiral diaminocyclohexane (**6a**) afforded higher entantioselectivity on alkenes epoxidation than its analogue catalyst from chiral diphenyldiamine (**6b**). This feature may be attributed to the built in phase-transfer capability in the catalytic system.

In the three different solvent systems, in most cases, both catalysts gave the highest ee and the highest chemical yields in the presence of ionic liquid **2**, especially for 6-chloro-2,2-dimethylchromene (yield 93%, ee 94%) (Table 1, entries 1–14). For instance, the reaction of **6a** in ionic liquid **2** gave better enantioselectivity and chemical yield than in ionic liquid **1** (yield 72–93%, ee 29–94%) (Table 1, entries 1, 3, 5, 7, 9, 11, and 13). While **6b** had better enan-

TABLE 1. Asymmetric epoxidation of alkenes using complexes 6a and 6b as catalyst in the presence of ionic liquids[a]



Entry	Alkene[b]	Catalyst	ee[c] (%) (yield[d] (%), time[e](h)) PyNO	Ionic liquid **1**[g]	Ionic liquid **2**[h]	Configuration[f]
1	A	**6a**	48 (80, 3.5)	32 (85, 3.0)	49 (88, 2.5)	*R*-(+)
2	A	**6b**	33 (63, 3.5)	34 (71, 3.0)	36 (73, 2.5)	*R*-(+)
3	B	**6a**	31 (66, 2.5)	27 (76, 2.0)	30 (82, 2.0)	*R*-(+)
4	B	**6b**	18 (63, 2.5)	21 (74, 2.0)	25 (69, 2.0)	*R*-(+)
5	C	**6a**	21 (84, 4.0)	21 (88, 3.0)	29 (89, 2.0)	1*R*,2*R*-(+)
6	C	**6b**	15 (80, 4.0)	11 (83, 3.0)	16 (86, 2.0)	1*R*,2*R*-(+)
7	D	**6a**	75 (83, 3.0)	68 (79, 2.0)	76 (84, 1.5)	1*R*,2*S*-(−)
8	D	**6b**	64 (74, 3.0)	72 (76, 2.0)	62 (80, 1.5)	1*R*,2*S*-(−)
9	E	**6a**	54 (60, 3.0)	38 (68, 2.5)	55 (72, 2.0)	1*S*,2*R*-(+)
10	E	**6b**	35 (53, 3.0)	33 (53, 2.5)	36 (58, 2.0)	1*S*,2*R*-(+)
11	F	**6a**	90 (78, 2.0)	83 (80, 1.0)	91(89, 1.0)	3*R*,4*R*-(+)
12	F	**6b**	78 (77, 2.0)	87 (80, 1.0)	77 (84, 1.0)	3*R*,4*R*-(+)
13	G	**6a**	93 (89, 2.5)	87 (91, 1.5)	94 (93, 1.0)	3*R*,4*R*-(+)
14	G	**6b**	78 (80, 2.5)	84 (85, 1.5)	79 (86, 1.0)	3*R*,4*R*-(+)

[a]Reaction conditions: substrate (2 mmol), catalyst (5 mol %), NaOCl (4 mmol), PyNO (15 mol %).
[b]A, styrene; B, α-methylstyrene; C, trans-stilbene; D, indene; E, 1,2-dihydronaphthalene; F, 2,2-dimethylchromene; G, 6-chloro-2,2-dimethylchromene.
[c]Determined by HPLC on chiral OD-H column.
[d]Isolated yield.
[e]Monitored by TLC every other 20 min.
[f]Absolute configuration was determined by comparison of the sign of $[\alpha]_D$ with the literature value.
[g]Ionic liquid **1**: [BMIM]PF_6.
[h]Ionic liquid **2**: L-1-ethyl-3-(1′-hydroxy-2′-propanyl)imidazolium bromide [38].

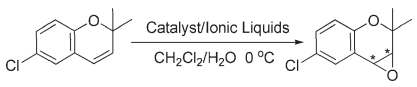
tioselectivity and modest chemical yield in ionic liquid **2** too for the epoxidation of styrene, α-methylstyrene, *trans*-stilbene, and 1,2-dihydronaphthalene than in ionic liquid **1** (ee 16–36%) (Table 1, entries 2, 4, 6, and 10). It is presumed that chiral catalyst cooperates with the ionic liquid **2** which contains one chiral carbon in asymmetric epoxidation reaction. When ionic liquid **1** was used in the epoxidation of A, B, C, D, and E, moderate ee values of alkenes with acceptable chemical yields were observed (Table 1, entries 1–10), but significantly improved ee values and chemical yields were observed in the epoxidation of 2,2-dimethylchromene and 6-chloro-2,2-dimethylchromene (Table 1, entries 11–14). To our surprise, in this system, catalyst **6b** gave better ee values for indene (72%), 2,2-dimethylchromene (87%), and 6-chloro-2,2-dimethylchromene (84%) than other two systems. (Table 1, entries 8, 12, and 14). This result is definitively better than that reported by Kureshy et al.[28] The remarkable improvement in the performance of **6b** can be attributed to the cooperation of catalyst, PyNO, and ionic liquids. When PyNO was used in the asymmetric epoxidation without ionic liquids, although ee values of epoxides were better than ionic liquid **1**, the chemical yields were lower than ionic liquid **1** in most cases. That because ionic liquids have strong coordination action with the metal center of chiral dinuclear Mn(III)-Salen, which occupy the most of coordination sites and strongly influence the catalytically active species.[20]

After the completion of the asymmetric epoxidation, the water phase converted slightly yellow, which indicates the inherent phase-transfer capability of **6a** and **6b** with methylene aminoalkyl groups on their salicylaldehyde moieties. The fact of the epoxidation reaction time was shorten than general Jocobsen Salen Mn(III), also demonstrates the inherent phase-transfer capability of **6a** and **6b**.[13] It was also observed that the reaction time in solvent of CH_2Cl_2/ionic liquid **2** was shorter than in CH_2Cl_2/ionic liquid **1** system. This fact may result from high miscibility of ionic liquid **1** with water and a higher proportion of the catalyst in the aqueous phase, in which the catalyst might be unstable.[25]

The Recovery and the Recycling of the Dimeric Mn(III) Complexes (6a)

To further investigate the atom efficiency of dimeric Mn(III)-Salen complexes with inherent phase-transfer capability, the recycling experiments of catalyst **6a** in three catalytic conditions were examined. Epoxidation of 6-chloro-2,2-dimethylchromene was carried out with catalyst **6a** under optimized reaction conditions for reusability experiments. The catalyst **6a** can be easily separated from the concentrated reaction mixture by the addition of excess of *n*-hexane due to its high molecular weight and lower solubility. The recycled complex was washed with hexane, dried in vacuum, and used for the subsequent run without any purification. The recycling data were listed in Table 2. In CH_2Cl_2 system, 80% yield was achieved in the last reaction with only minor decrease in the entantioselectivity compared with the first run (Table 2, entries 1–6). In ionic liquid **1** system, 72% yield was afforded in the last reaction

TABLE 2. Recycling experiments of complex 6a for asymmetric epoxidation of 6-chloro-2,2-dimethylchromene using NaOCl/PyNO, NaOCl/ionic liquid 1, and NaOCl/ionic liquid 2



	ee (%) (yield (%), time (h))		
Catalytic cycle	PyNO	Ionic liquid **1**	Ionic liquid **2**
1	93 (89, 2.5)	87 (91, 1.5)	94 (93,1.0)
2	91 (86, 3.5)	87 (90, 2.5)	91 (90, 1.5)
3	90 (83, 3.5)	84 (88, 2.5)	90 (87, 2.0)
4	88 (83, 4.0)	83 (84, 3.0)	90 (86, 2.5)
5	85 (80, 4.5)	81 (77, 3.5)	89 (82, 3.0)
6	83 (80, 5.5)	78 (72, 3.5)	83 (76, 3.0)

with only minor decrease in the entantioselectivity (Table 2, entries 1–6). In ionic liquid **2** system, 83% entantioselectivity was obtained in the last reaction with only modest increasing of the reaction time (Table 2, entries 1–6). According to these data, it is evident that the catalyst **6a** worked well for six times without losing activity and selectivity and gave excellent chemical yields. It is demonstrated that the catalyst can be successfully used as recyclable chiral catalyst for the asymmetric epoxidation of alkenes with high atom efficiency. The results of recycling experiments for catalyst **6b** were the same as **6a**, but catalyst **6b** gave lower chemical yields and enantioselectivity.

CONCLUSIONS

In conclusions, two new chiral dinuclear Mn(III)-Salen complexes with inherent phase-transfer capability have been prepared. They are efficient catalysts for the asymmetric epoxidation of nonfunctionalized alkenes with good-to-excellent chemical yields and enantioselectivity in the presence of ionic liquids, especially epoxidation of 6-chloro-2,2-dimethylchromene (yield 93%, ee 94%) with catalyst **6a**. The chiral catalysts can be recovered easily and reused for six times and still retain its high atom efficiency. The inherent phase-transfer capability of weakly water soluble catalysts had been revealed through the catalytic effect of their collaboration in different solvents and the color change of the upper water at the end of epoxidation. This work emphasizes a combinational strategy to encourage more attempts to explore new effective and recoverable oligomeric catalysts with strongly water solubility to transport HOCl from water to oil phase. However, the asymmetric induction was low in some cases, further optimizations and studies of the scope and mechanisms of the chiral bimetallic catalyst for asymmetric epoxidation of alkenes with the ionic liquids are ongoing in our laboratory.

LITERATURE CITED

1. Fan Q-H, Li Y-M, Chan ASC. Recoverable catalysts for asymmetric organic synthesis. Chem Rev 2002;102:3385–3466.
2. Katsuki T. Asymmetric oxidations and related reactions: asymmetric epoxidation of unfunctionalized olefins and related reactions. In: Ojima I, editor. Catalytic asymmetric synthesis, 2nd ed. New York: Wiley-VCH; 2000. p 287–325.
3. Canali L, Sherrington DC. Utilisation of homogeneous and supported chiral metal (salen) complexes in asymmetric catalysis. Chem Soc Rev 1999;28:85.
4. Zhang W, Jacobsen EN. Asymmetric olefin epoxidation with sodium hypochlorite catalyzed by easily prepared chiral manganese(III) salen complexes. J Org Chem 1991;56:2296–2298.
5. Zhang W, Loebach JL, Wilson SR, Jacobsen EN. Enantioselective epoxidation of unfunctionalized olefins catalyzed by salen manganese complexes. J Am Chem Soc 1990;112:2801–2803.
6. McGarrigle EM, Gilheany DG. Chromium- and manganese-salen promoted epoxidation of alkenes. Chem Rev 2005;105:1563–1602.
7. Brandes BD, Jacobsen EN. Highly enantioselective, catalytic epoxidation of trisubstituted olefins. J Org Chem 1994;59:4378–4380.
8. Zhang W, Lee NH, Jacobsen EN. Nonstereospecific mechanisms in asymmetric addition to alkenes result in enantiodifferentiation after the first irreversible step. J Am Chem Soc 1994;116:425–426.
9. Deng L, Jacobsen EN. A practical, highly enantioselective synthesis of the taxol side chain via asymmetric catalysis. J Org Chem 1992; 57:4320–4323.
10. Gill CS, Venkatasubbaiah K, Phan NTS, Weck M, Jons CW. Enhanced cooperativity through design: pendant CoIII_salen polymer brush catalysts for the hydrolytic kinetic resolution of epichlorohydrin (salen=*N*,*N*′-bis(salicylidene)ethylenediamine dianion). Chem Eur J 2008;14:7306–7313.
11. Ballistreri FP, Brinchi L, Germani R, Savelli G, Tomaselli GA, Toscano RM. Enantioselective epoxidations of alkenes catalyzed by (salen)Mn(III) in aqueous surfactant systems. Tetrahedron 2008;64:10239–10243.
12. Yang HQ, Zhang L, Zhong L, Yang QH, Li C. Enhanced cooperative activation effect in the hydrolytic kinetic resolution of epoxides on [Co(salen)] catalysts confined in nanocages. Angew Chem Int Ed 2007;46:6861–6865.
13. Shitama HK, Katsuki T. Synthesis of metal-(pentadentate-salen)complexes: asymmetric epoxidation with aqueous hydrogen peroxide and asymmetric cyclopropanation (salenH2: *N*,*N*′-bis(salicylidene)ethylene-1,2-diamine). Chem Eur J 2007;13:4849–4858.
14. Ready JM, Jacobsen EN. Highly active oligomeric (salen)Co catalysts for asymmetric epoxide ring-opening reactions. J Am Chem Soc 2001;123:2687–2688.
15. Ready JM, Jacobsen EN. A practical oligomeric [(salen)Co] catalyst for asymmetric epoxide ring-opening reactions. Angew Chem Int Ed 2002;41:1374–1377.
16. Welbes LL, Scarrow RC, Borovik AS. Development of porous materials for heterogeneous catalysis: kinetic resolution of epoxides. Chem Commun 2004;2544–2545.
17. Zhang XL, Jones CW, Weck M. Poly(styrene)-supported Co-sale n complexes as efficient recyclable catalysts for the hydrolytic kinetic resolution of epichlorohydrin. Chem Eur J 2006;12:576–583.
18. Serrano DP, Vargas JAC. A comparison of methods for the heterogenization of the chiral Jacobsen catalyst on mesostructured SBA-15 supports. Appl Catal A 2008;335:172–179.
19. Lou LL, Yu K, Ding F, Peng XJ, Dong MM, Zhang C, Liu SX. Covalently anchored chiral Mn(III) salen-containing ionic species onmesoporous materials as effective catalysts for asymmetric epoxidation of unfunctionalized olefins. J Catal 2007;249:102–110.
20. Mazet C, Jacobsen EN. Dinuclear {(salen)Al} complexes display expanded scope in the conjugate cyanation of a,b-unsaturated imides. Angew Chem Int Ed 2008;47:1762–1765.
21. Egami H, Katsuki T. Nb(salen)-catalyzed asymmetric epoxidation of allylic alcohols with hydrogen peroxide. Angew Chem Int Ed 2008;47:5171–5174.
22. Tan R, Yin DH, Yu NY, Jin Y, Zhao HH, Yin DL. Ionic liquid-functionalized salen Mn(III) complexes as tunable separation catalysts for enantioselective epoxidation of styrene. J Catal 2008;255:287–295.

23. Maria PDD. "Nonsolvent" applications of ionic liqulids in biotransformations and organocatalysis. Angew Chem Int Ed 2008;47:2–10.
24. Parvulescu VI, Hardacre C. Catalysis in ionic liquids. Chem Rev 2007;107:2615–2665.
25. Smith K, Liu SF, El-Hiti GA. Use of ionic liquids as solvents for epoxidation reactions catalysed bya chiral Katsuki-type salen complex: enhanced reactivity and recoveryof catalyst. Catal Lett 2004; 98:95–101.
26. Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev 1999;99:2071–2084.
27. Senanayake CH, Smith GB, Ryne KM, Fredenburgh LE, Liu J, Roberts FE, Hughes DL, Larsen RD, Verhoeven TR, Reider PJ. The role of 4-(3-phenylpropyl)pyridine *N*-Oxide (P_3NO) in the manganese-salen-catalyzed asymmetric epoxidation of indene. Tetrahedron Lett 1996;37:3271–3274.
28. Kureshy RI, Khan NH, Abdi SHR, Patel ST, Iyer PK, Jasra RV. Enantioselective epoxidation of chromenes using chiral Mn(III)salen catalysts with built-in phase-transfer capability. Tetrahedron Lett 2002; 43:2665–2668.
29. Sun Y, Tang N. Enantioselective epoxidation of olefins catalyzed by chiral dimeric and partially water-soluble monomeric salen-Mn(III) complexes in the presence of novel co-catalysts. J Mol Catal A Chem 2006;255:171–179.
30. Canali L, Coean E, Deleuze H, Gibson CL, Sherrington DC. Polystyrene and polymethacrylate resin-supported Jacobsen's alkene epoxidation catalyst. J Chem Soc Perkin Trans1 2000;13:2055–2066.
31. Fraile JM, Mayoral JA, Serrano J, Pericàs MA, Solà L, Castellnou D. New silica-immobilized chiral amino alcohol for the enantioselective addition of diethylzinc to benzaldehyde. Org Lett 2003;5:4333.
32. Kureshy RI, Khan NH, Abdi SHR, Patel ST, Jasra RV. Enantioselective epoxidation of non-functionalised alkenes usinga urea-hydrogen peroxide oxidant and a dimeric homochiral Mn(III)-Schiff base complex catalyst. Tetrahedron: Asymmetry 2001;12:433–437.
33. Kureshy RI, Khan NH, Abdi SHR, Singh S, Ahmad I, Jasra RV, Vyas AP. Enantioselective epoxidation of nonfunctionalized alkenes catalyzed by recyclable new homochiral dimeric Mn(III) salen complexes. J Catal 2004;224:229–235.
34. Abashkin YG, Burt ST. (Salen)Mn-catalyzed epoxidation of alkenes: a two-zone process with different spin-state channels as suggested by DFT study. Org Lett 2004;6:59–62.
35. Brandt P, Norrby PO, Daly AM, Gilheany DG. Chromium ± salen-mediated alkene epoxidation: a theoretical and experimental study indicates the importance of spin-surface crossing and the presence of a discrete intermediate. Chem Eur J 2002;8:4299–4306.
36. Welton T. Ionic liquids in catalysis. Coord Chem Rev 2004;248:2459–2477.
37. Chowdhury S, Mohan RS, Scott JL. Reactivity of ionic liquids. Tetrahedron 2007;63:2363–2389.
38. Bao WL, Wang ZM, Li YX. Synthesis of chiral ionic liquids from natural amino acids. J Org Chem 2003;68:591–593.