New Approaches to Develop Recyclable Catalyst for the Synthesis of Chiral Epoxides

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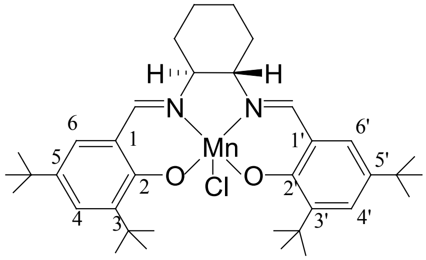
Abstract

Chiral epoxides are useful intermediates for the synthesis of various chiral drugs, fine chemicals and chiral building blocks. Chiral epoxides are prepared from their respective non-functionalized olefin precursors using chiral transition metal complexes such as Jacobsen's Mn(III)salen complexes with various oxidants under homogeneous condition but separation and recycling of the expensive catalyst is problematic making the entire process economically non-viable on an industrial scale. To overcome this problem, the various strategies to make these catalysts recyclable include tuning the solubility of the catalyst by controlling its molecular weight so that catalyst is easily recovered by precipitation in the post epoxidation work-up; heterogenization of the catalyst on an organic and inorganic polymeric support. Besides, enantiomerically pure epoxides can also be achieved by kinetic resolution of inexpensive racemic epoxides by using recyclable hydrolytic kinetic resolution catalyst. These strategies indeed have yielded more efficient catalysts and would be discussed in detail in the present article.

Introduction

Chiral epoxides are extremely valuable chiral synthons useful for the synthesis of many drugs and fine chemicals [1,2] because their facile ring opening allows the introduction of various substituents in a stereospecific manner. As a result, there has been a great interest in developing methods for enantioselective epoxidation of non-functionalized alkenes. Mn(III)salen based catalytic system (salen= bis(salicylidine)ethylenediamine) (**1**) represents one of the most elegant and effective methods developed for the synthesis of chiral epoxides with high yields and chiral purity [3-9]. These catalyst systems are known to be sensitive to a dissymmetric diamine bridge derived from a C_2 symmetric 1,2-diamine as well as bulky substituents at the 3,3'-position of the salicylide ligand. Further, the presence and nature of the substituents at 5,5'-positions of the salicylide ligand can also influence enantioselectivity during epoxidation [10]. Besides, in Mn(III)salen based catalyst, addition of a *N*-oxides as axial bases are observed to improve both catalyst turnover and enantioselectivity[10]. The selection of the *N*-oxide additive largely depends upon the reaction conditions that include the choice of oxidant and solvent. Despite their excellent features in terms of yield and enantioselectivity, these epoxidation catalysts are known to degrade during the epoxidation reaction under homogeneous conditions which limits their re-use.



(1)

Therefore, attempts are made to develop recyclable Mn(III)salen complexes so as to minimize the degradation of the catalyst, allowing easy recovery and re-usability of the catalyst for a number of cycles. The present article discusses the various strategies adopted to develop recyclable Mn(III)salen based catalysts for the epoxidation of non-functionalized alkenes.

The various strategies adopted to develop recyclable enantioselective epoxidation catalysts include

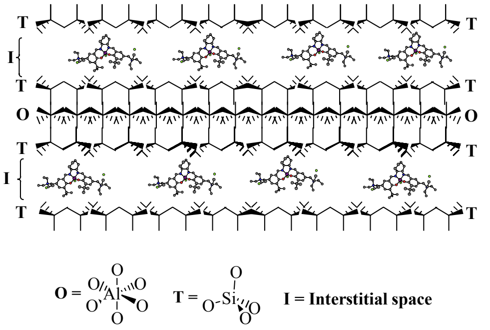
- **On clay**
- **Inorganic support**
- **Organic support**
- **Ionic liquids**
- **Other methods**

These approaches are discussed in the present article with an emphasis in Mn(III)salen based catalysts used for epoxidation of non-functionalized alkenes.

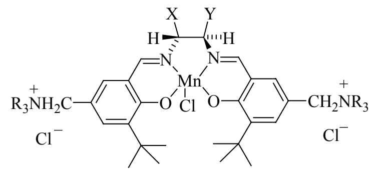
Clay-supported Mn(III)salen complexes

Clays due to their large surface area, lamellar structure and cation exchange capacity, makes them ideal candidate to support suitably tailored complexes by ion exchange process [11,12].

Kureshy et al. [13,14] (**2**) have synthesized the dicationic form of Mn(III)salen complexes and immobilized these in the interlayer space of montmorillonite type clay by cation exchange process. This simple method for heterogenization of Mn(III)salen complexes avoided the multi-step grafting reported [15-17] for other inorganic supported systems. These clay-immobilized Mn(III)salen complexes when used as catalysts for the epoxidation of styrene could be recycled up to four cycles with significant enhancement in the enantiomeric excess (70%) as compared to its homogeneous counterpart (ee's, 41-52%) (Table 1). Besides, this system worked well even for bulkier alkenes such as indene and 6-nitro-2,2-dimethyl chromene vis-à-vis other solid supports such as MCM-41 containing Mn(III)salen complex, which failed to epoxidize bulkier and non-planar substrates [15]. The authors have attributed this feature to the flexible nature of T-O-T layers of clay that allowed the bulkier substrates to diffuse in the clay interlayer space.



Mn(III)salen in the interlayer of the clay matrix



1=X=Y= Ph, R= iso-octyl; **2**=X----Y= $(CH_2)_4$, R= iso-octyl
3=X=Y= Ph, R= Ethyl, **4**= X---Y= $(CH_2)_4$ R= Ethyl

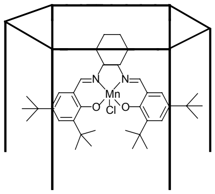
2

Fraile et al. [12] have however, carried out immobilization of Mn(III)salen complex on commercially available Bentonite, Laponite, and K-10 Monmorillonite in two steps. In the first step, these clays were treated with manganese ions to prepare Mn-exchanged clays, which were then reacted with salen ligands to achieve clay supported Mn(III)salen complexes. These complexes were used as catalyst for the epoxidation of 1,2-dihydronaphthalene with PhIO as an oxidant and gave turn over numbers (TON) similar to the homogeneous catalyst but there was a loss in the ee's of the product epoxide. The supported catalyst was recovered and recycled for the above epoxidation however, there was a significant decrease in TON and ee's.

Mn(III)salen complexes on inorganic support

It is known from the literature that the catalytic activity of the Mn(III)salen complexes is significantly influenced by the substituents on the salen ligand, solvents and presence of a co-catalyst [10, 18, 19]. Therefore, it is prudent that during heterogenization process the microenvironment of the active homogeneous catalyst is not disturbed to retain its activity and enantioselectivity. Further, the supported catalyst must allow the substrate to have easy access to the catalytic sites.

Frunza et al. [20] and Piaggio et al. [21] have reported Mn(III)salen complex embedded in the channel of MCM-41 (**3**) either by supporting the complex on mesoporous Al-, Ga-, and Fe-substituted MCM-41 silica by impregnation where the catalyst was thought to be maintained inside the channel through strong host/guest interactions [20] or by reacting the chiral salen ligand with Mn-exchanged Al-MCM-41 by ionic interaction. The former complex gave the comparable results for enantioselective epoxidation of 1,2-dihydronaphthalene with that of homogeneous system suggesting that the reactant had free access to the embedded Mn salen complex. While calcined Mn-Al-MCM-41 with salen ligand [21] gave 70% ee for *trans* stilbene oxide in dichloromethane at 25°C. In both the cases leaching of the metal was not observed.



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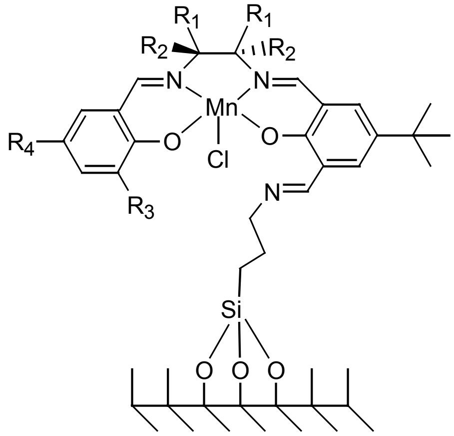
Kim et al. [22] have immobilized a salen complex on the surface of mesoporous MCM-41 in stepwise manner using different chiral diamines and various substituents on the benzene ring (**4**). These catalysts were used for asymmetric epoxidation of styrene at -78^{0}C using *m*-CPBA/NMO as oxidant and were found to give 89% to 92% conversion to epoxide in 4h. However, the conversion of epoxide 97% with ee 86% was observed when the reaction was conducted under homogeneous conditions.



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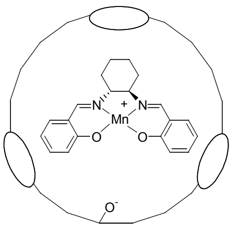
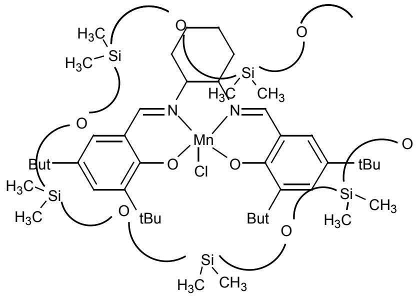
T. Bein et al. (**5**) [23] and A. Corma et al. [24] have reported heterogenization of Jacobsen complex by a ship-in-a-bottle strategy in two ways. The former group has encapsulated the chiral salen ligand in EMT zeolite, followed by its complexation with Manganese. This encapsulated complex was used as catalyst in enantioselective epoxidation of *cis-β*-methyl styrene using NaOCl as oxidant in presence of Py*N*-O as axial base and resulted in to 88% ee's in the product epoxide. While the latter has carried out a direct synthesis of encapsulated Mn salen complex by intrazeolite assembling condensation of chiral 1,2-diaminocyclohexane with salicylaldehyde around Mn(II) metal ion. This catalytic system showed inferior results as compared to homogeneous system due to diffusion problem.



5

Jacobs et al. [25] have reported immobilization of Jacobsen's catalyst in a polydimethylsiloxane membrane (PDMS) (**6**) for the epoxidation of terminal alkenes. In the case of styrene epoxidation using NaOCl, styrene oxide was obtained with nearly same activity and enantioselectivity (52%) as that in homogeneous system.



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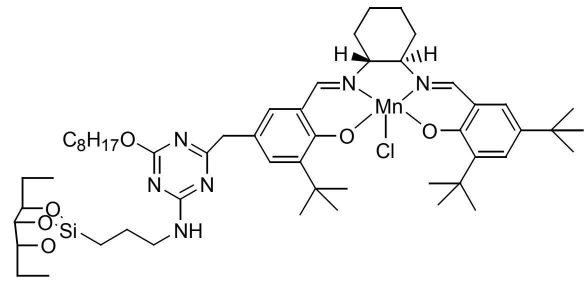
In order to overcome the problem of leaching of the supported catalyst, Mn(III)salen complexes were covalently bonded to the various inorganic supports. To this effect, Bigi et al. [16] have synthesized unsymmetrical Mn(III)salen complex immobilized on MCM-41 through triazine based linker (**7**). High ee up to 84% was achieved with the supported complex for 1-phenylcyclohexene. Xiang et al. [15] have reported immobilization of chiral Mn(III)salen complex on modified MCM-41 at axial position by phenoxyl group (**8**). The immobilized complex worked effectively for enantioselective epoxidation of non-functionalized alkenes and gave significantly higher ee's than the free complex.



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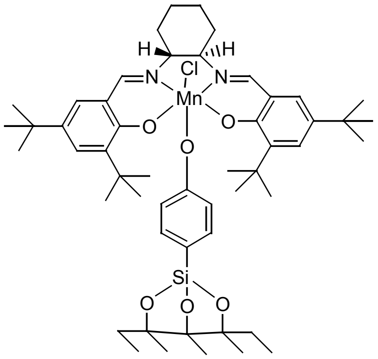
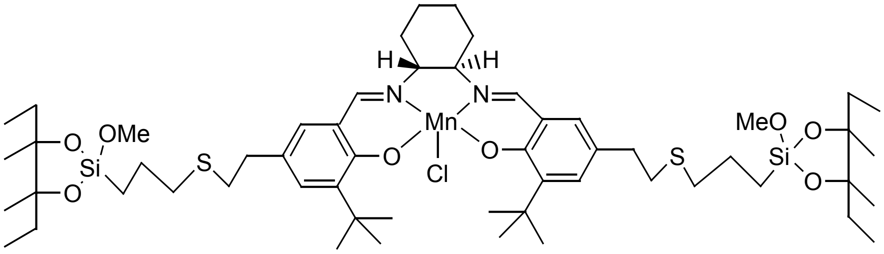


8

Salvadori at al. [17] have reported a silica gel grafted Jacobsen Mn(III)salen complex (**9**), however the supported complex was found to be inferior in performing the epoxidation of 1,2 dihydronaphthalene and indene than in homogeneous condition. Inferior performance of this catalyst was mainly attributed to rigidity imparted to the complex through covalent bonding to the highly cross-linked silica network from 5 and 5' end of the salen ligand.



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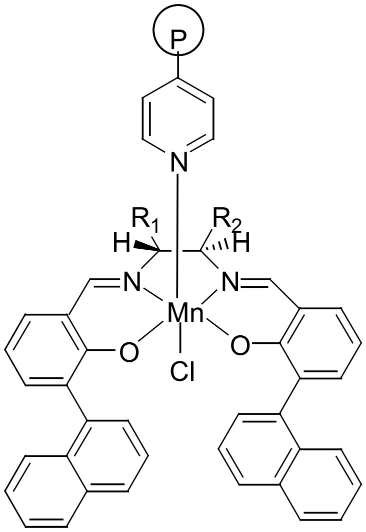
Mn(III)salen complexes on organic polymer supports

The use of organic co-polymers as support for transition metal complexes allows one to conjugate a controllable flexibility of the polymeric matrix with the possibility to fine tune the physical properties such as polarity, ability to swell, morphology etc. of the material by suitable combination of co-monomers and cross linkers.

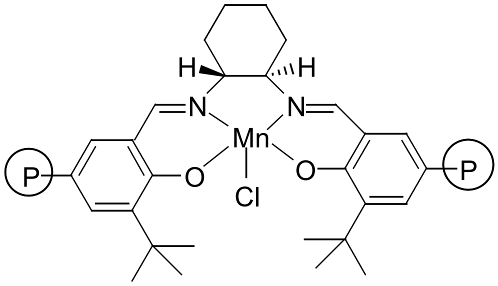
Kureshy et al. [26] reported a polymer based chiral Mn(III)salen complex via coordinative approach of co-polymerization of styrene divinyl benzene and 4-vinyl pyridine generated highly cross-linked 50% porous beads loaded with pyridine ligand at 3.4 mmmol/g (**10**). The resulting catalyst was employed in the epoxidation of styrene and 4-substituted styrene using PhIO as oxidant. The reaction carried out in dichloromethane at 4°C gave the product in 16-46% ee's (Table 2). The catalyst was recycled up to 10 times indicating strong binding between manganese and the pyridine in the polymer.



1= R_1=R_2= $(CH_2)_4$
2= R_1= H,R_2= CH_3
3= R_1=R_2= C_6H_5

10

Other notable work on polymer supported Mn(III)salen complex for the asymmetric epoxidation of non-functionalized alkenes include the work of De et al. [27] whose work started from the synthesis of appropriate vinyl monomer of salen via the reaction of 5-vinyl salicylaldehyde with 1,2-diaminocyclohexane (**11**). Thus heterogenized Jacobsen's catalysts were shown to epoxidize non-functionalized alkenes in good yield (65-72%) but low enantioselectivity (1-26%) with an excess of PhIO as the oxygen source and without additives. However, the heterogeneous catalyst containing a spacer arm between active site and the polymeric backbone induced better enantioselectivity (14-62% ee). The poorer enantiomeric purity obtained relative to that found with the homogeneous system may be well explained by the structural rigidity of these immobilized catalysts. The salen ligands used in these studies are attached through both the aromatic rings to the support and the resultant manganese complex may be forced to adopt a flatter geometry compared to that of homogeneous counterpart. This resultant rigid system may well be responsible for the poor asymmetric induction observed and the better result obtained with the complexes which are more flexible tend to confirm this.



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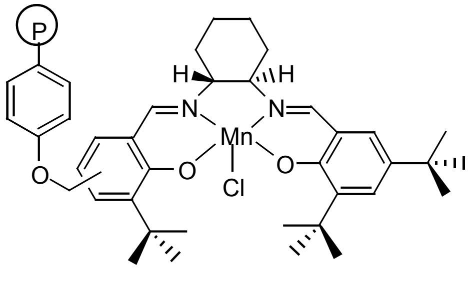
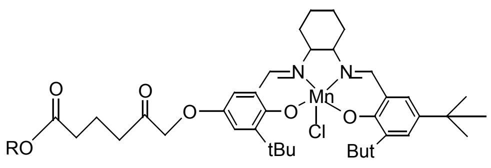
Sherrington et al. (**12**) [28] and Salvadori et al. [29] have reported a series of polymer-supported complexes where the Mn(III)salen moiety was immobilized in pendent fashion by only one of its aromatic rings to polystyrene and poly methacrylate resin beads of various morphologies. The attachment was achieved at different positions on the aromatic group relative to the hydroxy functional group. The Mn(III)salen containing polymer allowed the oxidation of 1-phenyl cyclohexene with enantioselectivity in the range of 61-91%



12

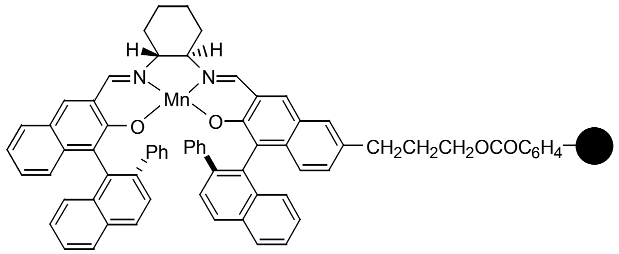
Janda et al. **(13)** [30] have described the synthesis of both soluble and insoluble polymer supported chiral Mn(III)salen complexes and their use in asymmetric epoxidation of styrene, *cis-β*-methyl styrene and 1,2 dihydronaphthalene. Best results (86-90%) were obtained for *cis-β*-methyl styrene.



R= different resins

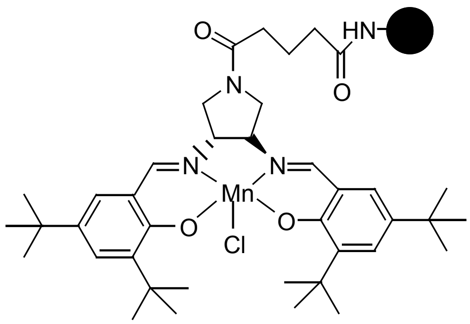
13

Smith et al. **(14)** [31] reported the preparation and application of Merrifield resin-supported. Katsuki type Mn(III)salen complex in the asymmetric epoxidation of alkenes. The catalytic activity and stereoselectivity of the immobilized catalyst were evaluated in epoxidation of 1,2-dihydronaphthalene using NaOCl as oxidant and 4-phenyl pyridine *N*-oxide as activator. The reaction gave 94% ee's and 37% yield of the epoxide. Re-use of the catalyst showed no loss of enantioselectivity for the first three runs while a little drop of enantioselectivity was observed from the fourth run and thereafter.



14

Song et al. [32] has reported chiral Mn(III)salen catalyst connected to the polymer support by amido functionality using a proper spacer (**15**) that showed activity and enantioselectivity comparable to that of homogeneous system.

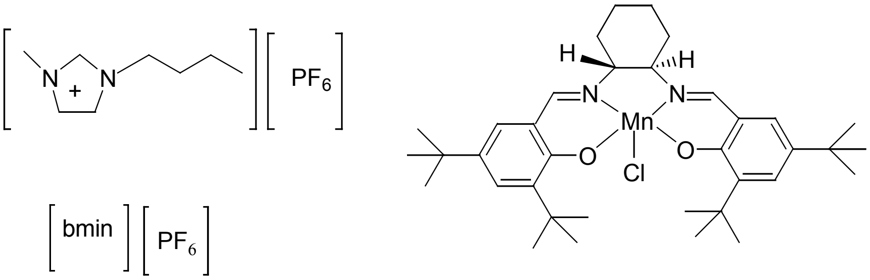


15

Use of Ionic liquids to recycle Mn(III)salen complexes

Recently, few examples of ionic liquids have been reported to have supportive role in various catalytic processes. These ionic liquids are easy to synthesise and posses peculiar properties, in terms of thermal and chemical stability, high vapor pressure, miscibility with water and common organic substrates.

The asymmetric epoxidation of alkenes with Jacobsen's Mn (III)salen catalyst was examined in ionic liquids by Song et al. [33] (**16**). The chiral catalyst was immobilized in [bmim][PF_6]. The reaction occurred at 0°C using NaOCl as an oxidizing agent. Since [bmim][PF_6] was solid at this temperature, the reaction was performed in a homogeneous medium formed with [bmim][PF_6]/CH_2Cl_2 (1/4). Performances of the reaction in terms of enantioselectivity (up to 96%) was comparable to those obtained in pure CH_2Cl_2. However, an enhanced reactivity of the catalyst was noticed in the ionic liquid medium. Both catalyst and ionic liquid could be recovered and re-used five times. However, enantioselectivity and activity decreased slightly after each cycle presumably because of a minor degradation of the catalyst.

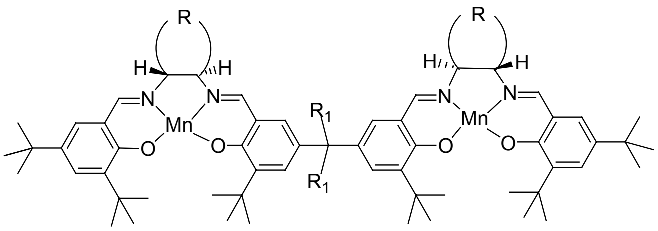


(16)

Tuning the solubility of Mn(III)salen complex by altering its molecular weight

An alternative strategy to recycle the catalyst is to increase the molecular weight of the catalyst that would lower its solubility, aiding product isolation and product recovery. The potential of this approach is highlighted by the preparation of dimeric, polymeric Mn(III) salen complexes as efficient recyclable catalysts for enantioselective epoxidation reaction.

Dimeric Mn(III) salen complex Kureshy et al. have reported chiral dimeric Mn(III)salen complexes [34-37] as catalyst for enantioselective epoxidation of non-functionalized alkenes [Table 3] with oxidants such as aqueous NaOCl, $KHSO_5$, UHP adduct as oxidants (**17**). In all the cases the catalyst could be recyclable up to 5 times except in case of aqueous H_2O_2. The results obtained with these dimeric complexes as catalyst were either at par with Jacobsen's catalyst [3-5] or better with added advantage of its recycling capability.



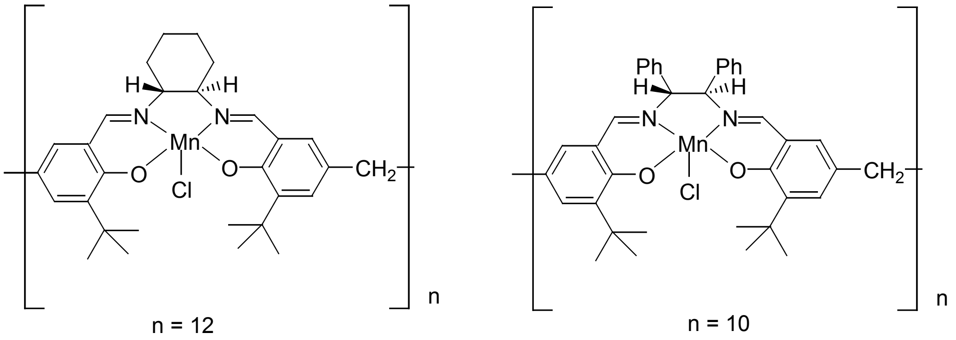
R = cyclohexyl; **1**, R = diphenyl; **2**

R_1=H, CH_3

(17)

Polymeric Mn(III) salen complex:

Polymeric chiral Mn(III)salen complexes (**18**) with number of repetitive units and molecular weight of the polymeric ligands between 10 to 12 and M_n=~5200 to ~5400 have been reported [38] to catalyze enantioselective epoxidation of chromenes, indene and styrene using NaOCl as an oxidant that gave >99% epoxide yields except for cyclochromene where the yield was found in the range of 50-61% in 2.5-12h. The enantiomeric excess (ee) for the product epoxide was found to be in the range of 75 to >99%, except for styrene (ee, 32-56%) (Table 4). The catalysts were easily recovered by precipitation method and were re-used up to five times with some loss of activity while there was no loss of enantioselectivity in the product epoxide.



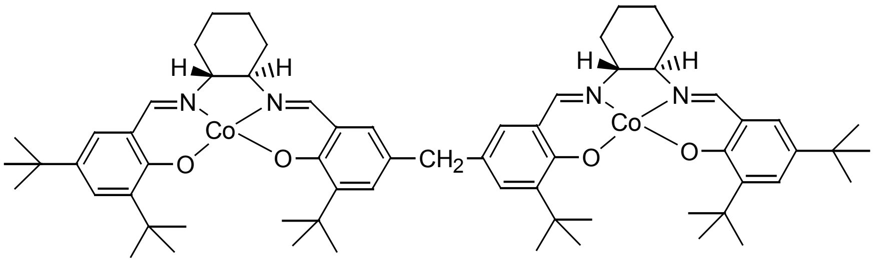
1a **18** **1b**

Other Methods

Recyclable Co(III)salen complexes as hydrokinetic resolution-catalyst for the production of chirally pure epoxides

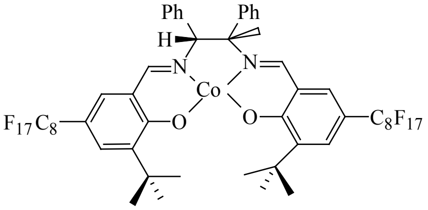
Hydrokinetic resolution (HKR) of racemic epoxides is another interesting technique for the simultaneous preparation of chirally pure diol and epoxide of terminal and smaller alkenes whose racemic epoxides are easily available at low-costs. For the efficient resolution the reaction rates of the two enantiomers must be unequal and the reaction must be stopped when only one enantiomer reacts to give a maximum of 50% product leaving behind the other enantiomer unreacted.

Jacobsen et al. reported kinetic resolution of a racemic epoxide, using Co(III)salen complex which proved to be extraordinarily general and a powerful method to achieve concurrently enantiomerically pure epoxide and diol [39]. An improvement upon the monomeric Jacobsen's Co(III)salen complex was reported by Kureshy et al. where recyclable dimeric homochiral Co(III)salen complex derived from chiral diamine with 3,5-di-*tert*-butyl salicylaldehyde and 5,5-methylene-di-3-tert-butyl salicylaldehyde (**19**) and used for HKR of racemic styrene oxide, 1-propene oxide and epichlorohydrin using water as resolving agent (Table 5). With a loading <0.3 mol% of the catalyst, the system works well up to three cycles with out any loss in activity and selectivity [40].



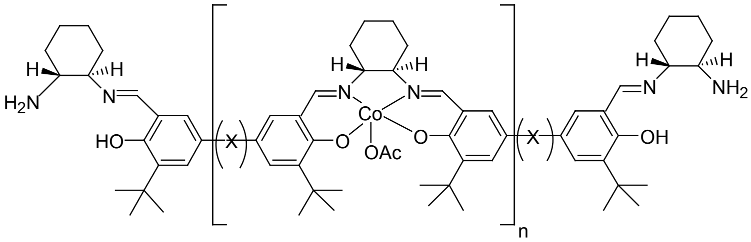
(19)

Later Pozzi et al. [41] reported highly active, enantioselective and recyclable flouro substituted Co(III)salen complex (**20**) for HKR of terminal epoxides. While Kim et al, [42] have used Co(III)salen system bearing PF6, BF4, Br as counter ions for HKR of racemic terminal epoxides.



(**20**)

Zheng et al. [43] have reported poly-salen Co(III) complexes (**21**) as HKR catalyst for terminal alkene epoxides. The polymeric catalysts provided product epoxides in their high chiral purity (ee's, 98%) and could be recycled with retention of activity and enantioselectivity.



(21)

Song et al. recently described the chiral Co(III)salen catalyzed hydrolytic kinetic resolution of racemic epoxide in ionic liquid [44]. Enantiomerically pure epoxides were obtained by reactions performed in [bmim][PF_6] or [bmim][NTF_2]. The recovered ionic liquid phase retained Co(III)salen complex and was re-used up to ten times without any loss of activity and enantioselectivity.

Conclusion

In this chapter, some current examples of the synthesis of chiral epoxides of the non-functionalized alkenes by salen based recyclable catalyst have been described. A high degree of success was achieved using recyclable dimeric form of Mn(III)salen catalysts for the epoxidation of non-functionalized alkenes. Due to their unique tendency to precipitate in low polarity solvents these catalysts are easy to separate and re-used. This strategy has potential for its use in other reaction types. Further, the use of dimeric form of Co(III)salen complexes as HKR catalysts have potential for its application in the production of terminal epoxides and corresponding diols in their high chiral purity and isolated yields. The use of organic and inorganic supports to immobilize epoxidation catalysts has also shown potential for their future application at process scale.

Acknowledgement

RIK is thankful to DST and CSIR, Task force project for financial assistance and also thankful to Dr. P. K. Ghosh, the Director, CSMCRI for providing necessary facilities.

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Table 1. Product yields, Ee's, and TOF for enantioselective epoxidation of non-functionalized alkenes catalyzed by dicationic chiral Mn(III)salen complexes **1-4,** and **1'-4'** shown in **structure (2) ref. [13,14]**

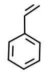
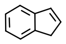
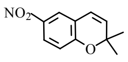
Catalyst	Substrate	Time (h)	Yield (%)	Ee(%)	TOF x10^{-3}
1 (1')		4.0 (7.0)	>99 (70)	45 (70)	3.55(1.41)
2 (2')		4.5(8.0)	99 (72)	44 (69)	3.13(1.29)
3 (3')		4.0 (24)	>99 (68)	52 (70)	3.55(0.41)
4 (4')		4.5 (24)	>99 (74)	>41 (69)	3.13(0.60)
1 (1')		4.0 (10)	>99 (99)	68 (65)	3.55(1.37)
2 (2')		5.0 (9.0)	>99 (99)	67 (62)	2.82(1.56)
3 (3')		4.0 (7.0)	98 (99)	59 (50)	3.50(2.02)
4 (4')		4.0 (10)	99 (99)	72 (69)	3.55(1.41)
1 (1')		0.5(8)	99(99)	>99(89)	28.66(1.77)
2 (2')		4.5(9)	99(99)	>99(99)	3.13(1.56)
3 (3')		5.5(12)	99(99)	84(90)	2.59(1.17)
4 (4')		5.0 (8.0)	99 (99)	89 (91)	2.82(1.77)

Table 2. Data for Enantioselective epoxidation of styrene derivatives with Mn(III) Schiff base complexes **1-3** anchored on polymeric support **structure (10) ref. [26]**

Catalyst	Substrate	Conversion	Time (h)	Ee	Configuration
1	Styrene	56	3.5	22	R
	4-Chlorostyrene	39	24	30	R
	4-Methylstyrene	48	4.5	20	R
	4-Nitrostyrene	25	24	40	R
2	Styrene	48	24	27	R
	4-Chlorostyrene	74	24	35	R
	4-Methylstyrene	65	4	26	R
	4-Nitrostyrene	40	1.5	46	R
3	Styrene	44	6	18	S
	4-Chlorostyrene	42	24	23	S
	4-Methylstyrene	30	24	16	S
	4-Nitrostyrene	29	0.5	30	S

Table 3. Data for enantioselective epoxidation of non-functionalized alkenes catalyzed by dimeric Mn(III) chiral salen complex in Presence of Py*N*-O/ammonium acetate with NaOCl/UHP/$KHSO_5$ as oxidants **structure (17) ref. [34-36]**

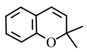
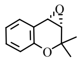
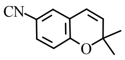
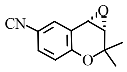
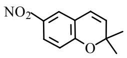
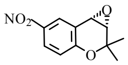
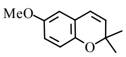
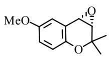
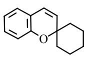
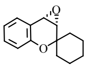
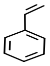
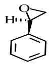
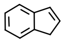
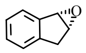
Substrate	Product	Yield (%)	Time (h)	Ee (%)	Absolute configuration
		97/99/99	1/2.5/5	83/84/71	*3R, 4R*
		100/100/99	2.5/5/5	99/100/99	*3R, 4R*
		100/100/99	11/6/5	>99/100/99	*3R, 4R*
		100/100/99	4/2/5	69/91/71	*3R, 4R*
		100/99/99	20/1.3/4	78/67/91	*3R, 4R*
		100/68/-	3/6/-	35 /23/-	*R*
		100/99/-	5.5/5/-	60/64/-	*1R,2S*

Table 4 Data for enantioselective epoxidation of non-functionalized alkenes catalyzed by Polymeric complexes **1a**, **1b** in Presence of Py*N*-O with NaOCl as oxidant structure **(18) Ref. [38]**

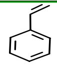
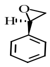
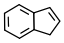
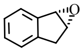
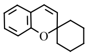
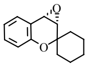
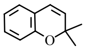
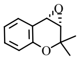
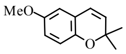
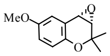
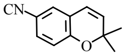
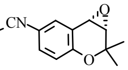
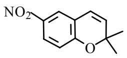
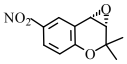
Catalyst	Substrate	Product	Yield (%)	Time (h)	Ee (%)	TOFx10^{-3}
1a(1b)			>99(>99)	10 (12)	32 (56)	1.37(1.14)
1a(1b)			>99(>99)	10(6)	78(79)	1.37(2.29)
1a(1b)			50(61)	10(9)	78(82)	0.70(0.95)
1a(1b)			>99(>99)	10(9.5)	75 (77)	1.37(1.45)
1a(1b)			>99(>99)	6(10)	82(89)	2.29(1.37)
1a(1b)			>99(>99)	6(5.5)	99 (99)	2.29(2.50)
1a(1b)			>99(>99)	2.6(2.5)	99 (99)	5.30(5.51)

Table -5 Data for HKR of racemic terminal alkenes epoxides with water catalyzed by dimeric homochiral Co(III) salen complex structure **(19)** **ref. [40]**

Racemic epoxide	Time	Epoxide		1,2 Diol	
		Yield %	Ee's %	Yield %	Ee's %
Epichlorohydrin	6	49	97	43	92
Propene oxide	6	52	96	44	98
Styrene oxide	40	46	98	39	99