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Asymmetric Hydrolytic Kinetic Resolution with Recyclable Macrocyclic Co^{III}–Salen Complexes: A Practical Strategy in the Preparation of (*R*)-Mexiletine and (*S*)-Propranolol

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Abstract: A chiral cobalt(III) complex (**1e**) was synthesized by the interaction of cobalt(II) acetate and ferrocenium hexafluorophosphate with a chiral dinuclear macrocyclic salen ligand that was derived from 1*R*,2*R*-(−)-1,2-diaminocyclohexane with trigol bis-aldehyde. A variety of epoxides and glycidyl ethers were suitable substrates for the reaction with water in the presence of chiral macrocyclic salen complex **1e** at room temperature to afford chiral epoxides and diols by hydrolytic kinetic resolution (HKR). Excellent yields (47% with respect to the epoxides, 53% with respect to the diols) and high enantioselectivity (*ee* > 99% for the epoxides, up to 96% for the diols) were achieved in 2.5–16 h. The Co^{III} macrocyclic salen complex (**1e**) maintained its performance on a multigram scale and was expediently recycled a number of times. We further extended our study of chiral epoxides that were synthesized by using HKR to the synthesis of chiral drug molecules (*R*)-mexiletine and (*S*)-propranolol.

Keywords: asymmetric synthesis · cobalt · kinetic resolution · macrocycles · salen ligands

Introduction

By the year 2015, the global market for chiral technology is expected to reach $4.9 billion (Global Industry Analysts Inc.; February 18, 2011) to meet the ever-increasing demand from the pharmaceutical sector for optically pure molecules that are utilized as the framework for enantiomerically pure drugs.[1] With the increase in stress-related ailments, the demand for cardiovascular drugs is growing rapidly, and has fuelled the research into economically viable syntheses of these drugs. To meet these demands, chiral epoxides are valuable intermediates in the syntheses of a large variety of pharmaceutical compounds. Because racemic epoxides are widely available at competitive prices, they have been used in the synthesis of several chiral drugs, in particular (*R*)-mexiletine[2] and (*S*)-propranolol.[3] Hence, the kinetic resolution of racemic epoxides has become one of the most-prevailing methods in the synthesis of chiral epoxides. Jacobsen and co-workers introduced the very powerful and 100% atom-efficient strategy of hydrolytic kinetic resolution (HKR), which used a chiral Co^{III}–OAc salen complex as a catalyst. This process provided direct access to unreacted epoxides and 1,2-diols (also valuable) in high enantiomeric excess and yield.[1b,4] Since then, many variants on the salen catalyst have been developed to fine tune the performance of this system and make this strategy more profitable. The groups of Jacobsen,[1b,4a5] Weck and Jones,[6] and Kim,[7] among others[8] have significantly contributed to the catalyst design and optimization of the HKR reaction parameters, including mechanistic investigation. Fluorous biphase systems[9] and ionic liquids[10] have also been used in these reactions. Mechanistically, a bimetallic pathway for the HKR of epoxides is the most-accepted reaction path and has led to the design of bimetallic[5g,11] and poly-metallic catalysts,[5d,6b,-d,e,h,7a,8a–c]oligomeric catalysts,[5a,b,6c] and dendrimeric catalysts,[5c] which have also addressed the issue of catalyst recyclability. Building upon these discoveries and our own desire to develop recyclable catalysts, herein, we report a the use of a macrocyclic Co^{III}–salen catalyst for the asymmetric HKR of terminal epoxides and its application in the synthesis of chiral drug molecules, such as (*R*)-mexiletine, (*S*)-propranolol, on the gram scale.

Results and Discussion

Co^{III}-complex **1a** was obtained in quantitative yield from the reaction of chiral macrocyclic ligand **1**[12a,b] with cobalt acetate in MeOH/toluene (1:1). Catalysts **1b**–**1e** were obtained by the addition of solutions of *p*-toluene sulfonic

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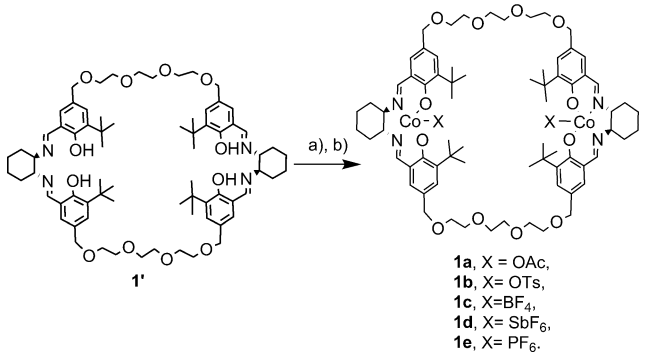


Scheme 1. Synthesis of the macrocyclic catalysts. a) $Co(OAc)_2$ in MeOH/toluene, RT, 30 min. b) Counterion source, 3 h.

acid, ferrocenium tetrafluoroborate, ferrocenium hexafluoroantimonate, and ferrocenium hexafluorophosphate in CH_2Cl_2, respectively, under aerobic conditions (Scheme 1; also see the Supporting Information). The change in counterion was necessary because of its decisive role in HKR reactions.[5f,7e] First, we screened the efficacy of catalysts **1a**–**1e** (0.008 mol%) in the HKR of racemic epichlorohydrin as a model substrate under solvent-free conditions.[11] Catalysts **1a**, **1b**, and **1e** were able to resolve the epoxide with *ee* > 99%, but with different activities (Figure 1). Macrocyclic

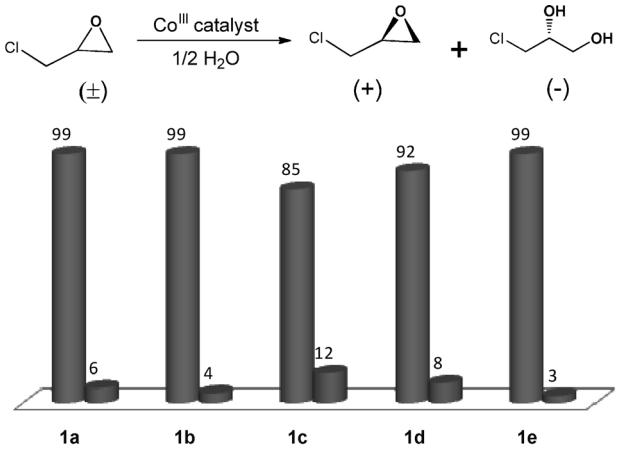
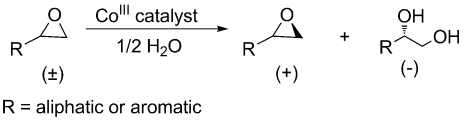
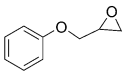
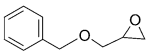
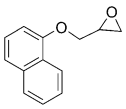


Figure 1. Screening of catalysts **1** for the HKR of (±)-epichlorohydrin at RT. Reaction conditions: racemic epoxide = 10 mmol, H_2O = 5 mmol, catalyst = 0.008 mol%. Left-hand columns: *ee* of epoxide (%); right-hand columns: time (h).

Co^{III} catalyst **1e** with PF_6^- as the counterion was more-active towards HKR, and afforded the desired enantiopure epichlorohydrin in 3 h (see **1a**; OAc^- counterion) and **1b** (OTs^-) afforded epichlorohydrin in 6 and 4 h, respectively). Although it was unclear why PF_6^- was better for the HKR of epichlorohydrin, a similar trend was also reported by Kim et al.[7e] Catalysts, **1a**, **1b**, and **1e**, were then applied to the HKR of various other terminal epoxides (Table 1). A catalyst loading of 0.008 mol% was found to be optimal for the HKR of epichlorohydrin and propene oxide. However, styrene oxide and aryloxy-substituted epoxides required rel-

Table 1. HKR of epoxides catalyzed by macrocyclic Co^{III} catalysts.[a]



	Substrate	Catayst	Catalyst [mol%]	*t* [h]	Epoxide Yield [%][b]	Epoxide *ee* [%][c]	Diol Yield [%][b]	Diol *ee* [%][c]
1		**1a**	0.008	6	44	>99	51	95
2		**1b**	0.008	4	45	>99	50	96
3		**1e**	0.008	3	45	>99	53	96
4		**1a**	0.008	5	45	96	47	94
5		**1b**	0.008	4	45	98	48	94
6		**1e**	0.008	2.5	43	>99	50	95
7		**1a**	0.075	24	46	91	41	90
8		**1b**	0.075	18	46	94	48	92
9		**1e**	0.075	16	47	99	48	92
10		**1a**	0.03	24	45	96	46	94
11		**1b**	0.03	18	46	98	46	93
12		**1e**	0.03	12	44	99	50	96
13		**1a**	0.03	24	45	97	47	94
14		**1b**	0.03	18	46	98	51	94
15		**1e**	0.03	12	45	99	51	95
16[d]		**1a**	0.03	24	45	96	50	94
17		**1b**	0.03	24	45	97	48	95
18		**1e**	0.03	18	46	99	50	95

[a] Reaction conditions: racemic epoxide = 10 mmol, H_2O = 5 mmol, catalyst = 0.008–0.03 mol%; [b] yield of isolated product; [c] *ee* values were determined by GC and HPLC analysis of the reaction mixture; [d] reaction conditions: racemic epoxide = 10 mmol, H_2O = 5 mmol, catalyst = 0.03 mol%, THF = 1 mL.

atively higher catalyst loadings (0.075 and 0.03 mol%, respectively) for comparable results. Nevertheless, these catalyst loadings are among the lowest reported so far for these compounds. Furthermore, irrespective of which substrate was used, catalyst **1e** afforded higher activity and enantioselectivity than catalysts **1a** and **1b**.

Jacobsen and co-workers investigated the mechanistic aspects of the HKR and the related epoxide ring-opening reactions by using monomeric (salen) metal catalysts, and reported second-order kinetic dependence on the catalyst concentration,[13] which led to a cooperative mechanism of the catalysis.

Based on this report, a possible mechanism for the HKR of terminal epoxide is proposed herein. Accordingly, the two metal centers that were in close proximity to one another (energy-minimized structures A and B),[6a,14k] owing to cyclic nature of the ligand (Figure 2, top), worked in a cooperative manner (Scheme 2).[5a,b,7d,g,14] Jones et al. proposed a cooperative interaction between two salen units that were in close proximity to one another, based on density func-

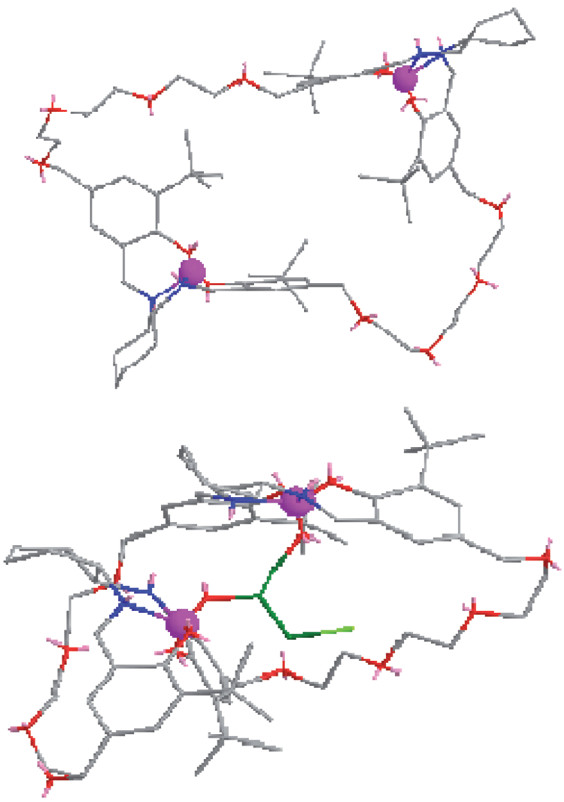
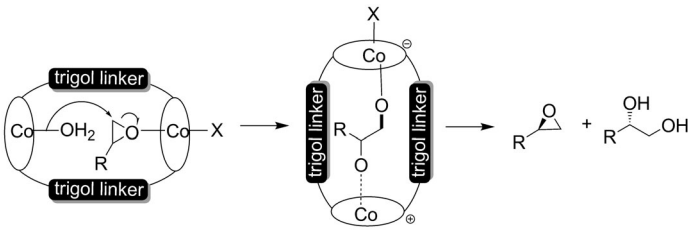


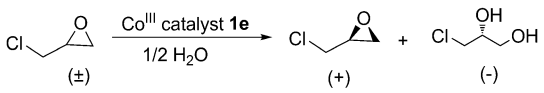
Figure 2. Energy-minimized structure of complex **1** (top) and plausible intermediate with epichlorohydrin in the HKR reaction (bottom).



X = PF_6^-, BF_4^-, OTs^-, OAc^- and SbF_6^-.

Scheme 2. Cooperative mechanism of the HKR of racemic epoxides.

Table 2. Recyclability of the macrocyclic Co^{III} catalyst **1e**.[a]



Run	t [h]	Epoxide		Diol	
		ee[b] [%]	Yield [%]	ee[b] [%]	Yield [%]
1	3	>99	45	96	53
2	3	>99	43	96	53
3	4	99	43	96	52
4	6	99	42	95	52
5	6	99	42	95	52
6	6	99	42	95	52

[a] Reaction conditions: racemic epichlorohydrin = 10 mmol, H_2O = 5 mmol, catalyst **1e** = 0.008 mol%; [b] *ee* values were determined by GC and HPLC analysis of the reaction mixture.

tional theory calculations.[6a] Thus, one Co center coordinated with a nucleophile ($^-$OH in this case), whilst the other activated the epoxide through weak coordination. Consequently, the diol was formed through an intermediate (Figure 2, bottom). The best-performing catalyst (**1e**) was then investigated for its recyclability in the HKR of racemic epichlorohydrin. After completion of the catalytic reaction, the catalyst was recovered in quantitative yield and successfully recycled five times without any apparent loss in activity or enantioselectivity (Table 2). To ascertain the stability[6i] of complex **1e**, kinetic experiments for the HKR of epichlorohydrin (21.6 mmol scale) were performed with fresh catalyst and catalyst that had been recovered from two consecutive cycles (Figure 4). The kinetic data clearly showed that complex **1e** was stable under the HKR conditions. Furthermore, the IR spectrum of the recovered catalyst was the same as that of the fresh catalyst. After recovery of the catalyst, the reaction mixture showed no trace of Co metal, which ruled out leaching of Co that might happen as a consequence of partial degradation of the catalyst during the HKR reaction. This result led us to attribute the prolonging of the reaction time (from the fourth cycle onward) to the loss of the catalyst during the recovery process. Notably, catalyst **1e** did not require a reactivation step during the catalyst-reuse experiments, which was attributed to the presence of the PF_6^- counterion[7e] (for the experimental details, see the Supporting Information), which also diminished the possibility of

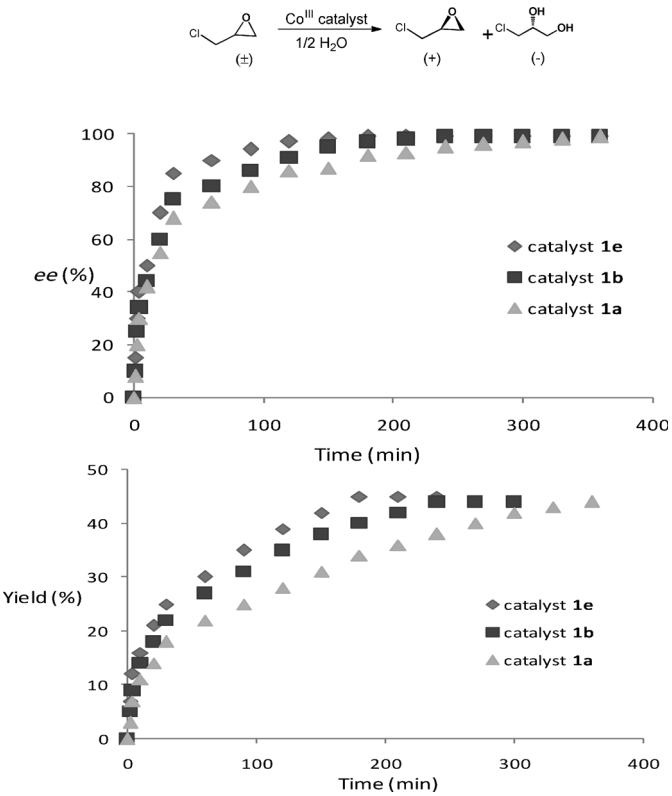


Figure 3. The catalytic activity of Co^{III} catalysts **1e**, **1b**, and **1a** in the asymmetric HKR of (±)-epichlorohydrin at RT: a) *ee* value of the epoxide versus time; and b) yield versus time. Reaction conditions: racemic epoxide = 10 mmol, H_2O = 5 mmol, catalyst = 0.008 mol%.

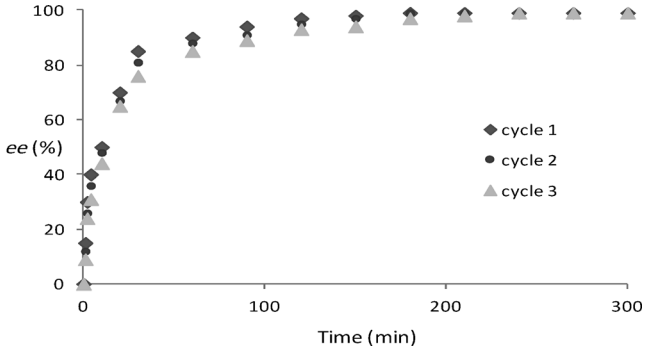
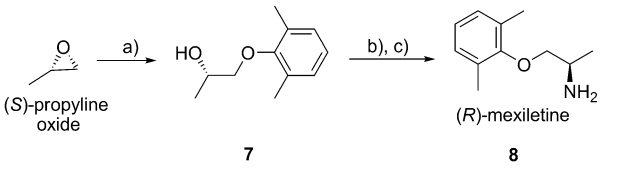


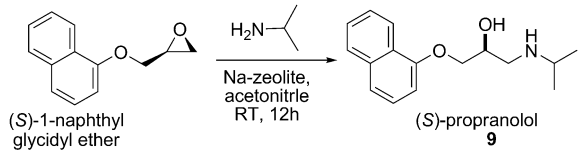
Figure 4. Recycling of catalyst **1e** in the HKR of (±)-epichlorohydrin over 3 cycles. Catalyst = 0.008 mol %.

racemization[7e] during distillation of the product from the reaction mixture (Figure 3a, b).Having established the HKR parameters with catalyst **1e**, this procedure was extended to the synthesis of chiral drugs, (*R*)-mexiletine and (*S*)-propranolol.

Mexiletine (commercially available as Mexitil) is an important I-B anti-arrhythmic agent that is largely used for arrhythmia, allodynia, and myotonic syndromes, etc.[2] (*R*)-Mexiletine is more-potent than *(S)*-mexiletine in experimental arrhythmias and in binding studies on cardiac sodium channels. Moreover, the use of the mexiletine racemate in the treatment of neuromuscular disorder is limited, owing to its possible side-effects.[2] Typically, the synthesis of (*R*)-mexiletine consists of the resolution of racemic intermediates, chemoenzymatic routes, or by using stereospecific procedures. However, most of these methods have several disadvantages, such as tedious and time-consuming experiments, unavailability or expensive chiral starting materials, low yields, low enantiomeric purity, etc. Recently, Muthukrishnan and co-workers reported the synthesis of (*R*)-mexiletine from epichlorohydrin in good *ee*.[15a] Herein, (*S*)-Propene oxide, which that was obtained by the HKR racemic propene oxide using catalyst **1e**, was used as a starting material for the synthesis of (*R*)-mexiletine in 3 steps with high overall yield (80 %) and *ee* (> 98 %; Scheme 3; for details of the experimental procedure, see the Supporting Information).[15b–d] The well-known β-blocker, (*S*)-propranolol, was obtained directly in good yield (95 %) and excellent *ee* (99 %; Scheme 4) from the ring-opening of chirally pure (*S*)-1-naphthyl glycidyl ether with isopropyl amine by using Na-zeolite as a catalyst.[16] (*S*)-1-Naphthyl glycidyl ether was obtained by the **1e**-mediated HKR of racemic 1-naphthyl glycidyl (g).



Scheme 3. Synthesis of (*R*)-mexiletine: a) bismuth triflate, 2,5-dimethylphenol, CH_2Cl_2, 6 h, RT, 86 %; b) PPh_3, phthalimide, DIAD, THF, RT, 4 h, 80 %; c) N_2H_4, H_2O, EtOH, reflux, 3 h, 85 %. DIAD = diisopropyl azodicarboxylate.



Scheme 4. Synthesis of (*S*)-propranolol.

Conclusion

A new class of chiral macrocyclic Co^{III}–salen complexes has been used as efficient, recyclable, and scalable catalysts for the HKR of terminal epoxides. In particular, the combination of catalyst **1e** and PF_6^- ions afforded enantioenriched epoxides (up to 47 % yield, *ee* > 99 %) and diols (up to 53 % yields, up to 96 % *ee*) at room temperature under solvent-free conditions. The synthesis of the pre-catalysts (the corresponding macrocyclic ligands) was very convenient and reproducible, to afford the desired dimeric ligands in reasonably high yield. Multigram-scale reactions showed no drop in the performance of these catalysts, which suggested that this procedure is scalable.

Experimental Section

Microanalysis of the products was carried out on Perkin–Elmer 2400 CHNS analyzer, ElementarVario micro, and Perkin–Elmer Optical Emission Spectrometer Optima 2000 DV. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 200 MHz and 500 MHz instruments at ambient temperature. FTIR spectra were recorded on Perkin–Elmer Spectrum GX spectrophotometer in KBr window. The purity of the products were determined by gas chromatography (GC) on a Shimadzu GC 14B instrument with a stainless-steel column (2 m long, 3 mm inner diameter, 4 mm outer diameter) that was packed with 5 % SE30 (mesh size 60–80) and equipped with an FID detector. Ultrapure nitrogen was used as the carrier gas (rate 30 mL min^{-1}). The injection port and detector temperature were kept at 200 °C. The synthetic standards of the products were used to determine the conversions by comparing the peak height and area. Enantiomeric excesses were determined by HPLC (Shimadzu SCL-10AVP and Shimadzu CBM-20 A) by using a Daicel Chiralpak OD column with 2-propanol/*n*-hexane as the eluent and by GC analysis by using a Shimadzu GC 2010 instrument with SupelcoAstec Chiral DEX™ G-TA or ATA columns. Optical rotations of the chiral complexes and their ligand precursors were recorded on an automatic Polari meter (Digipol 781, Rudolph) instrument. Energy-minimized structures were drawn by using ChemDraw version 12.

Recyclability of the catalyst for the HKR of epichlorohydrin: A 10 mL flask equipped with a stirrer bar was charged with epichlorohydrin (2 g, 21.6 mmol) and catalysts **1e** (0.00173 mmol) at RT. The reaction mixture was cooled to 0 °C, and H_2O (11.8 mmol) was added dropwise over 30 min. The reaction was allowed to warm to RT and was stirred for 2.5 h. Subsequently, (*S*)-epichlorohydrin was recovered from the reaction mixture by vacuum distillation. To the remaining solution, was added a mixture of *n*-hexane/Et_2O mixture (5:1). The precipitate was recovered by filtration, washed with *n*-hexane (3 × 5 mL), dried under reduced pressure for 6 h, and was then used in the recycling experiments.

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