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Poly(styrene)-Supported Co–Salen Complexes as Efficient Recyclable Catalysts for the Hydrolytic Kinetic Resolution of Epichlorohydrin

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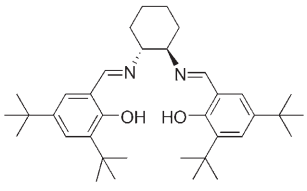
Abstract: Here we describe an unprecedented synthetic approach to poly(styrene)-supported chiral salen ligands by the free radical polymerization of an unsymmetrical styryl-substituted salen monomer (H_2salen = bis(salicylidene)ethylenediamine). The new method allows for the attachment of salen moieties to the polymer main chain in a flexible, pendant fashion, avoiding grafting reactions that often introduce ill-defined species on the polymers. Moreover, the loading of the salen is controlled by the copolymerization of the styryl-substituted salen monomer with styrene in different ratios. The polymeric salen ligands are metallated with cobalt(II) acetate to afford the corresponding supported Co–salen complexes, which are used in the hydrolytic kinetic resolution of racemic epichlorohydrin, exhibiting high reactivity and enantioselectivity. Remarkably, the copolymer-supported Co–salen complexes showed a better catalytic performance (>99% *ee*, 54% conversion, one hour) in comparison to the homopolymeric analogues and the small molecule Co–salen complex. The soluble poly(styrene)-supported catalysts were recovered by precipitation after the catalytic reactions and were recycled three times to afford almost identical enantiomeric excesses as the first run, with slightly reduced reaction rates.

Keywords: asymmetric catalysis · cobalt · kinetic resolution · polymerization · supported catalysts

Introduction

Chiral salen complexes (H_2salen = bis(salicylidene)ethylenediamine) represent a powerful family of catalysts for a spectrum of important asymmetric organic transformations,[1–5] including the epoxidation of olefins,[6,7] the hydrolytic kinetic resolution of epoxides,[8–10] other epoxide ring-opening reactions,[11–13] hetero Diels–Alder reactions,[14] and conjugate addition reactions.[15–17] Among the many catalytic reactions that salen complexes can promote, the asymmetric epoxidation and the hydrolytic kinetic resolution (HKR) of epoxides are of particular value, given the fact that enantiopure epoxides are versatile intermediates for asymmetric organic syntheses. Since Jacobsen's salen **1** has been recognized as a universal ligand for many of those transformations,[1–5] the development of immobilized salens with a scaffold mimic to **1** has drawn considerable attention in the past decade.[18–23] In addition to the potential of reusing catalysts many times and the ease of separating metals from products, immobilization of salens onto supports of desirable morphologies may potentially lead to the discovery of more efficient supported catalysts for asymmetric catalysis. While the litera-



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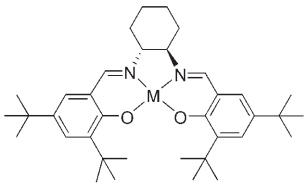

2a M = Co
2b M = Co(OAc)

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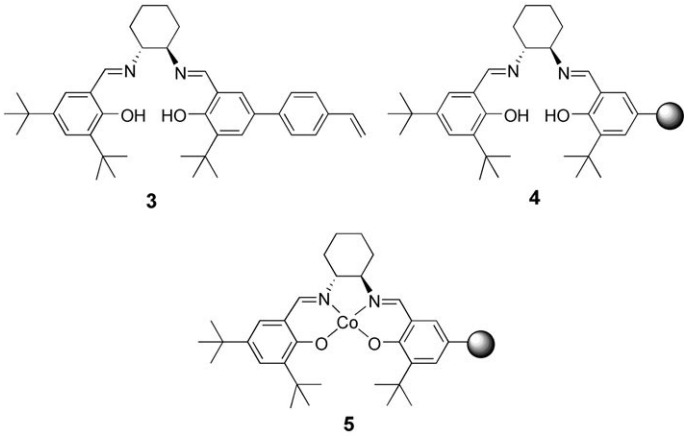
ture in this field has mainly focused on the immobilization of salen complexes for epoxidation reactions,[18–32] the development of dendrimer,[33] oligomer,[34–36] and polymer-supported[37–42] Co–salen catalysts for the HKR has been reported in recent years. Inorganic supports including silica[42–44] and zeolite[45] and liquid-immobilization methods, such as the fluorous biphasic system (FBS)[46] and ionic liquids,[47] were also applied to investigate recyclable HKR catalysts. Interestingly, kinetic studies of the HKR reactions with the homogeneous Co–salen catalyst **2** indicated a second-order dependence of the reaction rates on the Co–salen species; this dependence strongly supports a cooperative bimetallic mechanism for the ring-opening step.[8,48] In this context, supported Co–salen catalysts may possess a higher local concentration of metal catalysts and, if the neighboring catalytic sites can cooperate with each other, could exhibit improved catalytic reactivity in comparison with their homogeneous analogues.

In general, the syntheses of the polymer-supported salens[18] involve the following two strategies: A) grafting reactions of salen ligands onto insoluble supports such as resins,[30–32,42] or B) polymerizations of salen monomers.[24–29,37–41] Method A, often realized by using a multistep route, suffers from the coexistence of ill-defined species in the polymers and relatively low catalyst loading. Therefore, method B might be considered advantageous with respect to method A, yet it has been practiced only with symmetrical salen ligands as monomers. While salen ligands with C_2 symmetry are readily available from a synthetic point of view, polymerization or copolymerization of such monomers introduces the salen cores along the main chain or as a crosslink of the polymer matrix, respectively, which undesirably hinders the accessibility and flexibility of the catalytic sites. Therefore, in comparison with their homogeneous counterparts, the polymer-bound salen complexes often exhibit poor enantiocontrol and reduced reactivity.

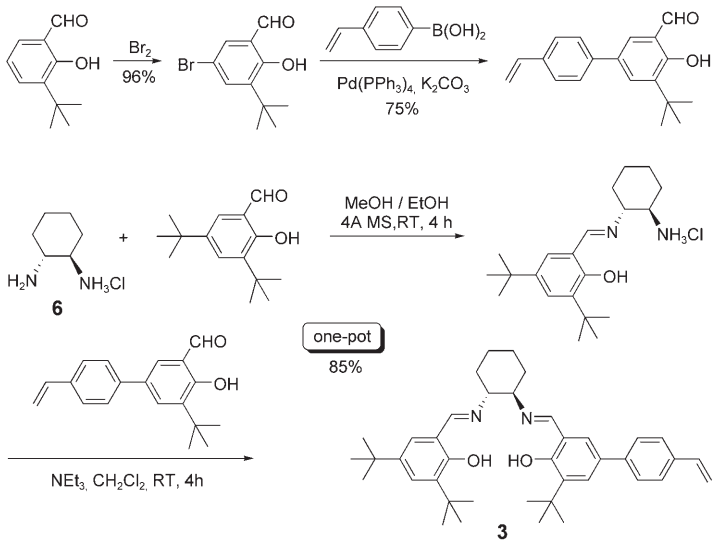
In contrast, the polymerization of unsymmetrical salen monomers can be used to immobilize the salen moieties on the polymer backbone in a flexible, pendant fashion that can overcome the aforementioned drawbacks. There are no reports in the literature of the synthesis of monotethered organic polymer-supported Co–salen derivatives, presumably due to the lack of efficient synthetic pathways to unsymmetrical salens. In this contribution, we report that the free radical homo- and copolymerization of an unsymmetrical monostyryl-substituted salen monomer (**3**) afforded polymers **4** with the salen moieties being bound as side arms with respect to the poly(styrene) backbone. The corresponding supported Co–salen complexes (**5**) exhibited high reactivity and enantioselectivity for the HKR of epichlorohydrin, with the best catalytic performance obtained by the copolymer-immobilized catalysts.



Results and Discussion

One-pot synthesis of unsymmetrical salen 3: The condensation of one equivalent of a diamine and two equivalents of a salicylaldehyde has been established as a standard synthetic methodology for symmetrical tetradentate Schiff base ligands.[4,49] However, it turned out to be very difficult to prepare salen ligands that are unsymmetrical in terms of the substituents on the two aromatic rings.[50–52] Since the condensation reactions of the first and the second amino groups of a diamine often proceed at comparable rates, it becomes almost impossible to control the reaction to stop after a single condensation step. As a result, condensations with two different salicylaldehydes afford inevitably a statistical mixture of three salens, of which one is the targeted unsymmetrical product while the two other byproducts are symmetrical.[42] Recently, we have developed a novel one-pot practical protocol for the synthesis of a variety of unsymmetrical salens.[53] This method was successfully applied to the preparation of the monostyryl-substituted unsymmetrical salen **3** in high yield. The condensation of the ammonium salt **6**[50] with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 3-*tert*-butyl-2-hydroxy-5-(4′-vinylphenyl)benzaldehyde[30] afforded **3** in 85% yield as a bright yellow solid (Scheme 1).

Free-radical polymerization: Having monomer **3** in hand, we set forth to prepare polymer-supported salen ligands **4** by means of free-radical polymerization (Scheme 2). It was anticipated that the presence of phenolic hydroxyl groups in the monomer could present a problem, because it is widely known that phenols are free-radical inhibitors.[54] For example, 2,6-di-*tert*-butylphenol has been used as an antioxidant or a radical trap in polymeric materials.[55] Nevertheless, the free-radical polymerization of **3** with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator readily afforded the target polymers **4**. We propose that the success of this polymerization can be attributed to the stabilization of the salen phenol moieties by the intramolecuar O–H···N hydrogen bonds, as evident by the downfield shifts of the phenolic protons in both **3** and **4** to $\delta = 13.6$–14.0 ppm in the ^{1}H NMR spectrum, and the relatively low tendency of the AIBN-based tertiary radicals for the extraction of hydrogen radi-



Scheme 1. Synthesis of styryl-substituted salen monomer **3**.

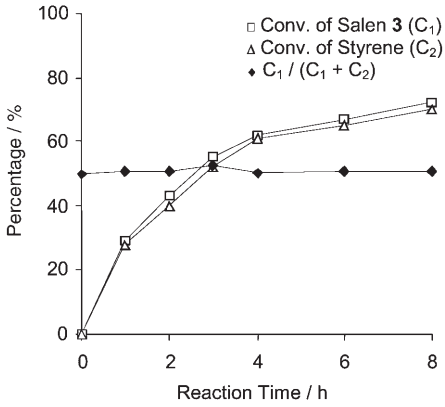
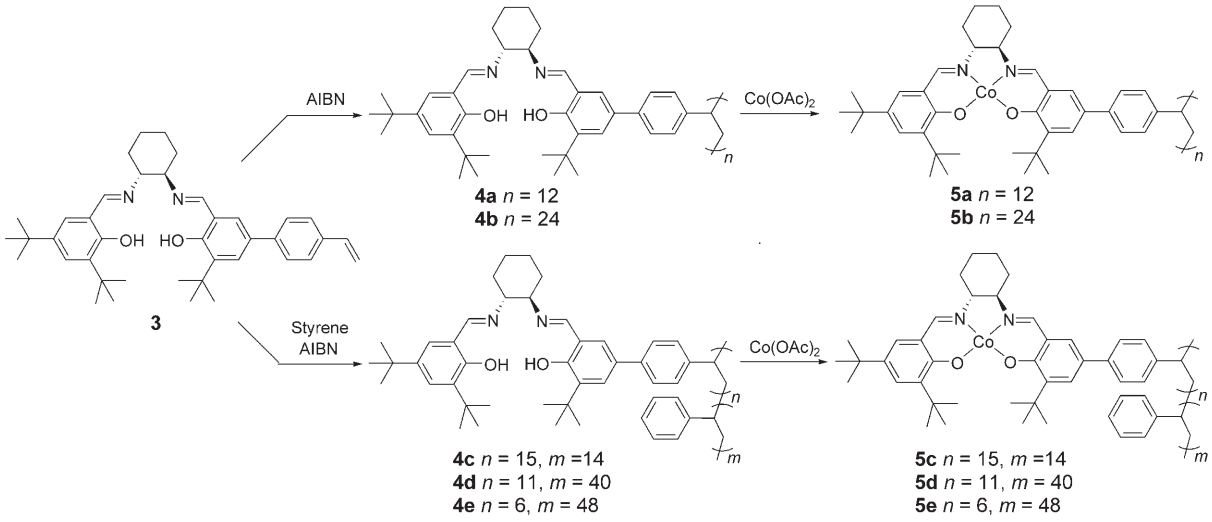


Figure 1. Kinetics of the copolymerization of **3** and styrene in 1:1 ratio.

cals. By varying the ratio of the initiator AIBN to the monomer, the number-average molecular weights (M_n) of the resulting polymers could readily be controlled. Gel-permeation chromatography (GPC) analyses showed that a polymer with on average 12 repeating units (**4a**) was obtained with an initiator loading of 10 mol%, whereas a polymer with approximately 24 repeating units (**4b**) was generated with a loading of 2.5 mol%.

To elucidate whether the dilution of the salen along the polymer backbone would have an effect on the catalytic properties of the supported complexes, we synthesized copolymers **4c–e** by the free-radical copolymerization of styrene and **3** in different molar ratios (**3**/styrene loading: **4c**= 50:50, **4d**=20:80, **4e**=10:90). A kinetic study on the 1:1 copolymerization of **3** and styrene was carried out to determine if the resulting copolymers are blocky, alternating, or statistical in nature (Figure 1). By means of ^{1}H NMR spectroscopy, we found that both monomers were consumed at almost identical rates from the initial stage to the end of the polymerization. Therefore, the ratios of monomer units in the copolymers remained almost constant and comparable to the loading ratios regardless of conversion levels (**3**/styrene loading: 50:50, found: 53:47–51:49). These results indicated that the copolymerization proceeded in a random fashion that excluded unambiguously the possibility of generating block or blocky copolymers.

Polymers **4a–e** were isolated in yields of 75–87% by repeated precipitation from methanol. All the polymers were characterized by ^{1}H and ^{13}C NMR, UV-visible, and FT-IR spectroscopy and GPC analysis. As shown in Figure 2, the signals in the ^{1}H NMR spectra of **4** showed characteristic broadening features associated with the polymers. No residual signals corresponding to the vinyl protons from monomer **3** were detectable, indicating all the remaining monomer was removed during the workup after polymerization. According to GPC determinations performed with poly(styrene)s as standards, polymers **4a–e** have number-average



Scheme 2. Synthesis of poly(styrene)-supported Co–salen complexes.

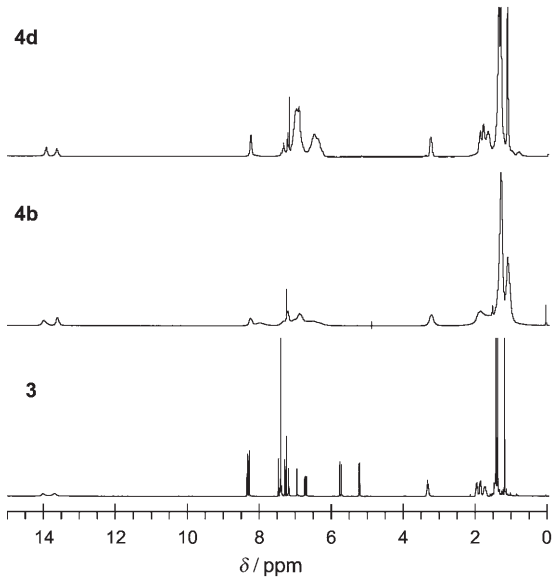


Figure 2. ^{1}H NMR spectra of salen monomer **3**, homopolymer **4b**, and copolymer **4d**.

molecular weights ranging from 7200 to 14600 with polydispersity indices (PDI) of 1.6 to 2.6 (Table 1). It is known that salen ligands can exchange the two salicylideneimine moieties especially in solution as a result of the disproportionation of the C=N bonds.[56,57] This imine metathesis reaction hardly plays any role with our polymers. A solution of **4a** in $CDCl_3$ can be stored at room temperature for a week without any detectable changes according to the ^{1}H NMR spectroscopy and GPC analysis.

Table 1. Free radical polymerization characterization of salen monomer **3**.

	Product	AIBN [mol%]	Yield [%]	*m*/*n* loading	*m*/*n*[a] exptl	*m*, *n*[b] exptl	M_n[c]	PDI[c]
1	**4a**	10	87	100:0	n.a.	12, n.a.	7200	1.6
2	**4b**	2.5	85	100:0	n.a.	24, n.a.	14600	1.9
3	**4c**	2.5	78	50:50	48:52	15, 14	10200	2.1
4	**4d**	2.5	75	20:80	22:78	11, 40	11000	2.6
5	**4e**	2.5	80	10:90	11:89	6, 48	8600	2.0

[a] Determined by ^{1}H NMR spectroscopy. [b] Calculated with data of *m*/*n* exptl and M_n. [c] Determined by GPC in THF using poly(styrene)s as standards.

Metallation of salen polymers with cobalt(II) acetate: The salen polymers **4a–e** were converted to the corresponding Co^{II} complexes **5a–e** by refluxing them in the presence of cobalt(II) acetate tetrahydrate under the protection of an atmosphere of argon. The color of the polymers changed from yellow to deep red, a characteristic of Co^{II}–salen species, after the transformation. UV-visible spectra indicated that, in addition to the appearance of two new metal d–d migration bands at 370 and 422 nm, a blue shift of the band at 254 nm (**4b**) to 265 nm (**5b**) was observed upon complexation (Figure 3). The loading of cobalt in the polymers was characterized by elemental analyses. The final metal contents ranged from 0.59 to 1.37 mmol g^{-1}, indicating that 84–89% of the salen centers were loaded with cobalt. The obtained Co–salen polymers are soluble in THF and halogenated solvents, such as dichloromethane, but insoluble in methanol and hexane.

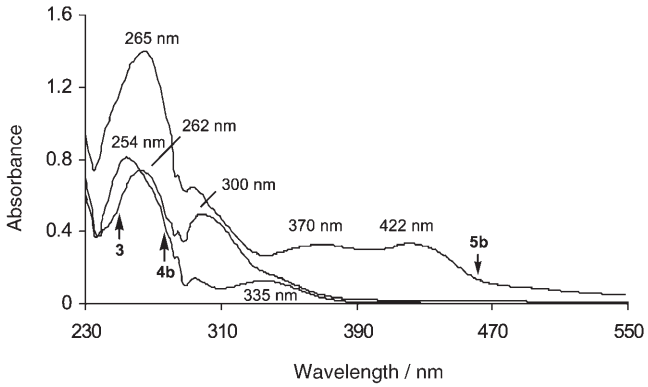
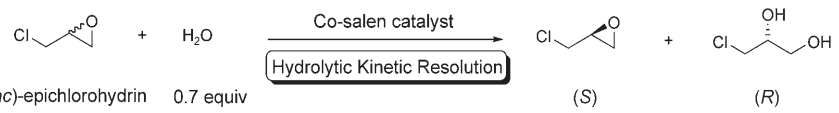


Figure 3. UV-visible spectra of salen monomer **3**, polymer **4b**, and metallated polymer **5b**.

Hydrolytic kinetic resolution of epichlorohydrin: The poly(styrene)-supported Co–salen complexes **5a–e** were examined for their catalytic efficiency in the HKR of racemic epichlorohydrin (Scheme 3). With multiple functional groups in the structure, enantiopure epichlorohydrin represents an extremely useful intermediate for asymmetric syntheses.[58] This substrate was suspected to undergo chlorine-catalyzed racemization that can be promoted in the presence of Co^{III}–salen species.[59–61] Therefore, supported Co–salen catalysts are advantageous, because the catalysts can readily be removed from the reaction mixture after the HKR.[42]

Prior to the catalytic reaction, Co^{II} precatalysts **5a–e** were oxidized to the corresponding Co^{III} active species in the open air with the help of excessive acetic acid. The oxidation process was evidenced by a dramatic color change from deep red to dark brown, which is well documented in the literature.[9] The HKR's were carried out at ambient temperatures in the presence of 0.5 mol% catalyst calculated on the basis of cobalt. The conversions and enantiomeric excesses (*ee*) of the substrate were monitored by GC analysis. The catalytic data are compiled in Table 2 and a kinetic plot of *ee* versus the reaction time is presented in Figure 4. All the



Scheme 3. Hydrolytic kinetic resolution of epichlorohydrin.

Table 2. Hydrolytic kinetic resolution of epichlorohydrin.

	Catalyst	*t* [h]	Conv.[a] [%]	*ee*[a] [%]
1	**2a**	1.0	49	93
	2a	1.5	52	>99
2	**5a**	1.0	47	81
	5a	2.0	55	>99
3	**5b**	1.0	48	83
	5b	2.0	55	>99
4	**5c**	1.0	50	90
	5c	1.5	54	>99
5	**5d**	1.0	54	>99
6	**5e**	1.0	54	>99

[a] Determined by GC analyses using a Chiraldex G-TA column. The *ee* refers to the enatiomeric excess of the remaining epichlorohydrin.

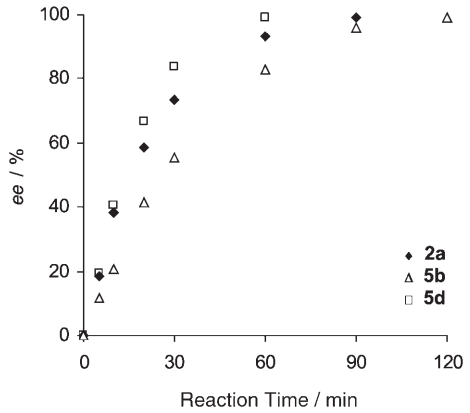


Figure 4. Plot of *ee* vs. reaction time in the HKR of epichlorohydrin.

poly(styrene)-supported catalysts are highly reactive and enantioselective for the HKR of epichlorohydrin. As shown in Table 2, the copolymer-supported catalysts **5d** (entry 5) and **5e** (entry 6) showed the most desired catalytic performances. The remaining epichlorohydrin was determined to have enantiomeric excesses higher than 99% within one hour with a conversion of 54%. In comparison, the Jacobsen's catalyst **2a** (entry 1) gave 93% *ee* in 49% conversion under the same reaction conditions and it took 1.5 h for it to reach >99% *ee*.

It is worth noting that the copolymer-supported catalysts **5c** and **d** in general exhibited improved reactivity and enantioselectivity compared with their homopolymer analogues **5a** and **5b**. For example, for the homopolymer catalyst **5a**, the reaction time had to be prolonged to two hours (entry 2) to obtain >99% *ee* with a conversion of 55%. We attributed this observation to the greater complex mobility in the copolymer-bound salen catalysts. Dilution of the salen moieties in the poly(styrene) main chain might make the catalytic sites more accessible to the substrate. In addition, the copolymers might have more flexible polymer backbones that would increase the possibility of intramolecular cooperation between cobalt catalytic sites.

A key motivation to develop immobilized metal complexes lies in their potential for facile recovery and reuse in subsequent reactions. The recycling of the copolymer-bound Co–salen complex **5d** (Table 3) was studied by precipitation of the catalyst after the HKR of epichlorohydrin by the addition of diethyl ether. The precipitated catalyst was reactivated with acetic acid and then reused under strictly identical conditions to the first run. Whereas the enantioselectivity of the reused catalyst remained almost unchanged after four cycles, the catalytic reactivity fell gradually. The reaction time had to be extended to two hours in the fourth cycle to obtain an *ee* of 98%. The same phenomenon of longer reaction times has been observed before when isolating supported Co–salen catalysts in main-chain polymers through precipitation methods.[38] To evaluate whether the deactivation was due to leaching of catalyst, more racemic epichlorohydrin and water were charged into the pale yellowish organic phase from the workup of the first catalytic run of precatalyst **5d**. About 4% additional epichlorohydrin was consumed in an hour. Control experiments showed that no background reaction was detected in the absence of the catalyst or in the presence of the unmetallated salen polymer. These results indicated that, at least in part, the loss of catalysts during workup was responsible for the observed deactivation on recycle, which is quite a common phenomenon for soluble polymer-supported catalysts.[62] It is not clear what the role of other factors such as potential morphological changes of the polymers have on the long-term performance characteristics of the catalysts.

Table 3. Recycling of catalyst **5d** in the HKR of epichlorohydrin.

Cycle	*t* [h]	Conv.[a] [%]	*ee*[a] [%]
1	1.0	54	>99
2	1.5	55	>99
3	2.0	55	>99
4	2.0	53	98

[a] Determined by GC analyses using a Chiraldex G-TA column; The *ee* refers to the enatiomeric excess of the remaining epichlorohydrin.

By means of enforcing the intramolecular bimetallic cooperation for the ring-opening step, the Jacobsen's cyclic oligomeric salen complexes displayed superior reactivity in the epoxide ring-opening reactions.[34–36] However, the possibility of easy recycling of these oligomeric systems by using precipitation methods is limited due to the low molecular weight of these catalysts. Normally, these low-molecular-weight catalysts have been recycled by removing the volatile reactants followed by the addition of more starting material to the reaction vessel without the isolation of the catalytic species.[8] In contrast, our polymeric Co–salen complexes, besides having the desirable catalytic performance in the HKR, hold advantages of facile product separation and catalyst recycling. Hence, these supported catalysts are particularly suitable for the kinetic resolution of epoxides (e.g., epichlorohydrin) that are prone to racemization in the presence of the catalysts.

Concluding Remarks

In this contribution, we have demonstrated that a novel family of polymer-supported salen catalysts can readily be formed by means of the free radical homo- and copolymerizations of an unsymmetrical monostyryl-substituted salen monomer. The advantage of this methodology lies in the fact that the salen moieties are immobilized onto the polymers in a pendant fashion and hence possess a higher degree of flexibility and accessibility. The corresponding cobalt-loaded salen catalysts are highly active and selective in the HKR of racemic epichlorohydrin. We were able to prove that diluting the Co–salen catalysts along the polymer backbone through copolymerizations with unfunctionalized comonomers resulted in increased activity and selectivity in comparison to the homopolymer analogues. This difference might be due to dilution effects or better catalyst accessibility as a result of more flexible polymer backbones. Ongoing research in this laboratory has been directed to the design and immobilization of chiral salen complexes on polymers with relatively flexible linkers and/or main chains.

Experimental Section

General: Reagents were purchased from Aldrich, Acros, or Alfa, and used as received unless noted below. Dichloromethane and THF were dried by passing through columns of activated copper and alumina successively. Chlorobenzene was distilled under an atmosphere of argon prior to use. (1*R*,2*R*)-1,2-Diaminocyclohexane monohydrochloride salt,[50] 3-bromo-5-*tert*-butyl-2-hydroxybenzaldehyde,[63] and 3-*tert*-butyl-2-hydroxy-5-(4′-vinylphenyl)benzaldehyde[30] were prepared according to published procedures. NMR spectra were acquired with a Varian Mercury 400 (^{1}H, 400.0 MHz; ^{13}C, 100.6 MHz) spectrometer. Chemical shifts are reported in ppm and referenced to the corresponding residual nuclei in deuterated solvents. IR and UV-visible spectra were recorded with a Shimadzu FTIR-8400S and a Shimadzu UV-2401PC spectrometer, respectively. Mass spectra were recorded with a VG 7070 EQ-HF hydrid tandem mass spectrometer. Gel-permeation chromatography (GPC) analyses were performed with American Polymer Standards columns equipped with a Waters 510 pump and a UV detector, using poly(styrene)s as standards for calibration and THF at a flow rate of 1.0 mL min^{-1} as a mobile phase. Enantiomeric excesses were determined by capillary gas-phase chromatography (GC) analysis on a Shimadzu GC 14 A instrument equipped with a FID detector and a Chiraldex G-TA column (30 m × 0.25 mm) with helium as a carrier gas. Melting points were determined with a Laboratory Devices MEL-TEMP II apparatus and are uncorrected.

(*R*,*R*)-*N*-(3,5-Di-*tert*-butylsalicylidene)-*N*′-(3-(4′-vinylbenzene)-5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (3): A 250 mL flask was charged with (1*R*,2*R*)-1,2-diaminocyclohexane monohydrochloride salt (1.51 g, 10 mmol), activated 4 Å molecular sieves (4.0 g), anhydrous methanol (40 mL), and anhydrous ethanol (40 mL). 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) was added in one portion and the reaction mixture was stirred at RT for four hours. After complete consumption of the aldehyde as monitored by TLC, a solution of 3-*tert*-butyl-2-hydroxy-5-(4′-vinylphenyl)benzaldehyde (2.74 g, 10 mmol) in dichloromethane (80 mL) was added to the reaction system, followed by the slow addition of triethylamine (2.8 mL, 20 mmol). The reaction mixture was stirred at RT for additional four hours followed by the removal of the solvents. The residue was dissolved in dichloromethane (100 mL), washed with aqueous hydrochloric acid (1 M, 50 mL) and water (2 × 50 mL), and dried with magnesium sulfate. Flash chromatography of the crude product with ether/hexanes (1/50) afforded the target compound **3** as a yellow solid (5.05 g, 85.2 %). M.p.: 177–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$ (s, 9H; CMe_3), 1.42 (s, 9H; CMe_3), 1.44–1.51 (m, 2H; CH_2), 1.46 (s, 9H; CMe_3), 1.70–1.84 (m, 2H; CH_2), 1.88–1.91 (m, 2H; CH_2), 1.97–2.02 (m, 2H; CH_2), 3.30–3.78 (m, 2H; 2NC*H*CH_2), 5.25 (d, $J = 11.0$ Hz, 1H; CH=CH_2), 5.77 (d, $J = 17.6$ Hz, 1H; CH=CH_2), 6.74 (dd, $J = 11.0$, 17.6 Hz, 1H; CH=CH_2), 6.97 (d, $J = 2.5$ Hz, 1H; ArH), 7.21 (d, $J = 2.5$ Hz, 1H; ArH), 7.31 (d, $J = 2.5$ Hz, 1H; ArH), 7.40–7.45 (m, 4H; ArH), 7.49 (d, $J = 2.5$ Hz, 1H; ArH), 8.30 (s, 1H; N=CH), 8.35 (s, 1H; N=CH), 13.69 (brs, 1H; OH), 14.01 ppm (brs, 1H; OH); ^{13}C,^{1}H NMR (100.6 MHz, $CDCl_3$): $\delta = 24.53$, 24.54, 29.59, 29.62, 31.60, 33.32, 33.37, 34.23, 35.15, 35.17, 72.58 (2 overlapping lines, 2CHN), 113.64, 117.98, 118.94, 126.22, 126.74, 126.88, 127.11, 128.23, 128.33, 130.51, 135.99, 136.59, 136.68, 137.76, 140.21, 140.70, 158.15, 160.26, 165.81, 166.24 ppm; IR (KBr): $\tilde{\nu} = 3082$, 2999, 2952, 2933, 2860, 1628, 1467, 1440, 1390, 1360, 1271, 1252, 1171, 840 cm^{-1}; UV/Vis (THF): $\lambda_{max} = 262$, 300, 340 nm; MS (70 eV, FAB+): *m*/*z* (%): 592 (100) [M^+]; elemental analysis calcd (%) for $C_{40}H_{52}N_2O_2$ (592.85): C 81.04, H 8.84, N 4.73; Found: C 81.06, H 8.95, N 4.72.

Synthesis of homopolymers 4a,b: A Schlenk tube was charged with monomer **3** (237 mg, 0.40 mmol) and 10 mol % of AIBN (6.6 mg, 0.040 mmol). The system was purged several times with argon and degassed chlorobenzene (2 mL) was added. The reaction mixture was stirred at 80 °C for 48 h and then cooled to RT. The mixture was slowly poured into methanol (20 mL) to precipitate the crude product as a yellow power and the suspension was stirred at RT for 30 min. The powder was collected by filtration and washed with 1:20 dichloromethane/methanol (3 × 10 mL). The crude product was dissolved in dichloromethane (2 mL) and reprecipitated with methanol (20 mL). The solid was collected on a frit, washed with methanol (10 mL), and dried under high vacuum to afford polymer **4a** as a yellow powder (206 mg, 87 %). Following the aforementioned procedure, polymerization of **3** (237 mg, 0.40 mmol) in chlorobenzene (2 mL) using 2.5 mol % of AIBN (1.7 mg, 0.010 mmol) as an initiator afforded polymer **4b** as a yellow powder (201 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.14$ (s, 9H; CMe_3), 1.33 (br, 18H; 2 CMe_3), 1.40–1.80 (brm, 11H), 3.25 (brm, 2H; 2 NC*H*CH_2), 6.20–7.45 (brm, 8H; ArH), 8.01 (brs, 1H; N=CH), 8.27 (brs, 1H; N=CH), 13.62 (brs, 1H; OH), 13.99 ppm (brs, 1H; OH); ^{13}C,^{1}H NMR (100.6 MHz, $CDCl_3$): $\delta = 24.46$ (br), 29.66, 31.60, 33.10 (br), 34.14, 35.00, 35.10, 40.87 (br), 71.47, 72.62, 117.91, 118.82, 126.16 (br), 127.01, 128.41 (br), 131.06, 136.45, 137.36, 138.50 (br), 140.00, 143.23 (br), 158.08, 159.71, 165.76, 166.19 ppm; IR (KBr): $\tilde{\nu} = 3045$, 3020, 2997, 2952, 2862, 1628, 1470, 1441, 1393, 1362, 1271, 1252, 1171, 827 cm^{-1}; UV/Vis (THF): $\lambda_{max} = 254$, 294, 335 nm.

Synthesis of copolymers 4a–c: A Schlenk tube was charged with monomer **3** (119 mg, 0.20 mmol) and AIBN (1.7 mg, 0.010 mmol). The system was purged several times with argon. Freshly distilled styrene (23 μl, 10.8 mg, 0.20 mmol) and degassed chlorobenzene (1 mL) were added. The reaction mixture was stirred at 80 °C for 48 h, cooled to RT, and slowly poured into methanol (20 mL) to precipitate the crude product as a yellow powder. After the suspension was stirred at RT for 30 min, the power was collected by filtration and washed with 1:20 dichloromethane/methanol (3 × 10 mL). The crude product was dissolved in dichloromethane (2 mL) and reprecipitated with methanol (20 mL). The solid was collected on a frit, washed with methanol (10 mL), and dried under high vacuum to afford the target copolymer **4c** as a yellow powder (109 mg, 78 %). Following the aforementioned procedure, copolymerization of **3** (119 mg, 0.20 mmol) and styrene (92 μL, 83 mg, 0.80 mmol) in chlorobenzene (1 mL) using AIBN (4.1 mg, 0.025 mmol) as an initiator afforded the copolymer **4d** as a yellow powder (152 mg, 75 %). Copolymerization of **3** (119 mg, 0.20 mmol) and styrene (206 μL, 188 mg, 1.8 mmol) in chlorobenzene (2 mL) using AIBN (3.3 mg, 0.02 mmol) as an initiator afforded the copolymer **4e** as a yellow powder (246 mg, 80 %). Copolymers **4c**–**e** have very similar spectroscopic properties and, hence, only the data for **4d** is listed in the following. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.82$–2.18 (m), 1.21 (s, CMe_3), 1.40 (s, CMe_3), 1.45 (s, CMe_3), 3.34 (br, 2NC*H*CH_2), 6.22–7.45 (br, ArH), 8.32 (br, 2 N=CH), 13.68 (brs, OH), 13.97 ppm (brs, OH); ^{13}C,^{1}H NMR (100.6 MHz, $CDCl_3$): $\delta = 24.54$, 29.68, 31.63, 33.54, 34.23, 35.1, 40.36 (br), 72.72 (br), 118.01, 118.91, 125.87, 126.23, 127.05, 128.17 (br), 131.17 (br), 136.55, 137.51, 138.44 (br), 140.15,

145.40 (br), 158.18, 159.85, 165.78, 166.20 ppm; IR (KBr): $\tilde{\nu}$ = 3082, 2059, 3024, 2951, 1930, 2860, 1628, 1601, 1470, 1441, 1391, 1362, 1273, 1264, 1173, 829, 750, 698 cm^{-1}; UV/Vis (THF): λ_{max} = 254, 293, 335 nm.

Kinetic study of the copolymerization of 3 and styrene: Salen monomer **3** (237 mg, 0.40 mmol) and AIBN (3.3 mg, 0.020 mmol) were charged to a Schlenk tube and the system was purged with argon several times. Freshly distilled styrene (46 μL, 41.7 mg, 0.40 mmol) and degassed chlorobenzene (2 mL) were added under the protection of argon. The system was immersed into an oil bath preheated at 80 °C. At each designed time, 0.1 mL of the reaction mixture was withdrawn from the system under the protection of argon. The sample was diluted with $CDCl_3$ and a ^1H NMR spectrum was acquired. The total conversion of **3** and styrene was calculated by comparing the integrals of the signals at δ = 3.34 ppm (2H, NC*H*CH_2 from **3**) and 5.77 ppm (1 + 1H, CH=CH_2 from overlapping signals of **3** and styrene). The volatile including remaining styrene and solvents was completely removed from the sample under high vacuum. The ^1H NMR spectrum of the residue was acquired to give the conversion of **3**. The conversion of styrene was calculated based on the total conversion and the conversion of **3**.

Synthesis of Co^{II}–salen-immobilized polymers 5a–e: Polymer **4a** (95 mg, 0.16 mmol) was charged into a 50 mL flask equipped with a condenser. After the system was thoroughly purged with argon, degassed CH_2Cl_2 (2 mL) was added to dissolve the polymer. A solution of cobalt(II) acetate tetrahydrate (50 mg, 0.20 mmol) in degassed methanol (2 mL) was transferred into the flask by means of a cannula with careful exclusion of air. A red powder formed immediately in the reaction mixture. After the suspension was heated at reflux under an atmosphere of argon for 24 h, additional degassed methanol (2 mL) was added and the reaction mixture was stirred at RT for twelve hours. The solid was collected by filtration under the protection of argon, washed with 1:10 degassed dichloromethane/methanol (2 × 10 mL) and methanol (10 mL), and dried in vacuo to give **5a** as a dark red solid (99 mg, 95 %). Elemental analysis (ICP) indicated that **5a** contains 7.85 % of elemental cobalt, corresponding to a loading of 1.33 mmol g^{-1}. Using a similar procedure, metallation of **4b**,**c** with cobalt(II) acetate tetrahydrate afforded **5b**,**c**.

Complex 5b: 96 % yield; Co loading: 1.37 mmol g^{-1}; IR (KBr): $\tilde{\nu}$ = 3078, 3018, 2951, 2866, 1597, 1526, 1461, 1421, 1387, 1360, 1338, 1321, 1254, 1175, 829, 787 cm^{-1}; UV/Vis (THF): λ_{max} = 265, 294, 370, 422 nm.

Complex 5c: 93 % yield; Co loading: 1.20 mmol g^{-1}.

Complex 5d: 95 % yield; Co loading: 0.82 mmol g^{-1}; IR (KBr): $\tilde{\nu}$ = 3082, 2059, 3024, 2949, 2864, 1599, 1526, 1492, 1452, 1421, 1392, 1360, 1338, 1321, 1256, 1175, 831, 786, 758, 698 cm^{-1}; UV/Vis (THF): λ_{max} = 267, 294, 372, 421 nm.

Complex 5e: 91 % yield; Co loading: 0.59 mmol g^{-1}.

General procedure for the hydrolytic kinetic resolution of (*rac*)-epichlorohydrin: The precatalyst **5** (0.025 mmol on the basis of cobalt) was dissolved in dichloromethane (1 mL) in a 10 mL flask. Glacial acetic acid (0.10 mL) was added and the reaction mixture was stirred in the open air for 30 min. The solvent and the excess acetic acid were roughly removed in vacuo. The brown-black residue was pumped under vacuum (10 mbar) for 5 min to give **5** (OAc). Racemic epichlorohydrin (391 μL, 5.0 mmol) and chlorobenzene (50 μL, internal reference) were added to dissolve the activated catalyst and the flask was immersed into a water bath at RT. Deionized water (0.70 equiv, 63 μL, 3.5 mmol) was injected into the system to start the reaction. Samples (2 μL) were taken from the reaction mixture with a micro-syringe at each designed time, diluted with anhydrous diethyl ether (2 mL), and passed through a plug of silica gel in a Pasteur pipet to remove the polymeric catalyst and water. The conversions and enantiomeric excesses of epichlorohydrin were measured by GC.

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