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Modular Approach for the Development of Supported, Monofunctionalized, Salen Catalysts

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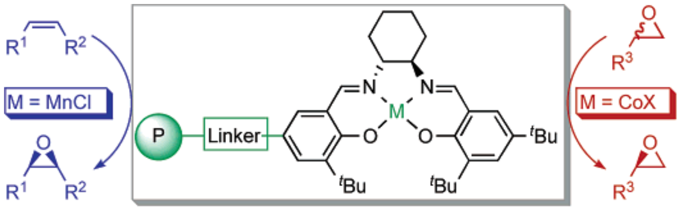

P = Poly(norbornene), X = OAc, I, OTs

We report a modular approach toward polymer-supported, metalated, salen catalysts. This strategy is based on the synthesis of monofunctionalized Mn− and Co−salen complexes attached to a norbornene monomer via a stable phenylene−acetylene linker. The resulting functionalized monomers can be polymerized in a controlled fashion using ring-opening metathesis polymerization. This polymerization method allows for the synthesis of copolymers, resulting in an unprecedented control over the catalyst density and catalytic-site isolation. The obtained polymeric manganese and cobalt complexes were successfully used as supported catalysts for the asymmetric epoxidation of olefins and the hydrolytic kinetic resolution of epoxides. All polymeric catalysts showed outstanding catalytic activities and selectivities comparable to the original catalysts reported by Jacobsen. Moreover, the copolymer-supported catalysts are more active and selective than their homopolymer analogues, providing further proof that catalyst density and site isolation are key toward highly active and selective supported salen catalysts.

Introduction

Metalated chiral salen ligands such as **1** are among the most successful and important asymmetric catalysts today.[1−3] These complexes were first introduced in the 1990s by Jacobsen and Katsuki as highly enantioselective catalysts for the asymmetric epoxidation (AE) of unfunctionalized olefins.[4,5] Over the past decade, metalated salen complexes have also been successfully employed as catalysts in a large variety of other asymmetric transformations[1−3] including ring-opening of epoxides,[6−10] hydrolytic kinetic resolution (HKR) of terminal epoxides,[11−13] hetero Diels−Alder reactions,[14,15] Pictet−Spengler reactions,[16] and hydrocyanations.[17−20] While a wide variety of different chiral salen ligands have been synthesized, metalated, and their catalytic properties studied in detail,[21,22] the original metal−salen complexes of the general structure **1** (Figure 1) developed by Jacobsen are still the most selective catalysts for a wide variety of catalytic reactions and a broad range of substrates.[2]

To utilize these catalysts in the pharmaceutical and fine chemical industries, the removal of the metal species and the reusability of the catalysts are key criteria. The most successful strategy to achieve this goal is the use of the supported analogues of these complexes.[3,23−28] However, immobilized versions of chiral salen complexes have been published only for a limited

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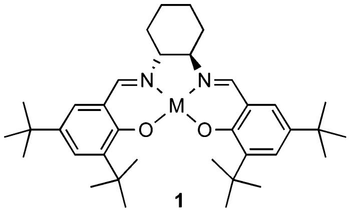

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FIGURE 1. Structure of the most widely active and selective metal−salen complex.

range of reactions such as AEs,[10,23,29−77] HKRs,[12,13,24,78−93] other ring-opening reactions,[9,10,94−98] hetero Diels−Alder reactions,[43,50] and others.[99−108] Despite the success of some of these strategies, no modular approach allowing a systematic and straightforward development of various different supported salen catalysts has been reported. In this article we describe our studies toward such a system for the development of polymer-supported salen catalysts by employing poly(norbornene)-immobilized salen complexes of manganese and cobalt.

The use of poly(norbornene) complexes as support has a number of advantages over other polymeric supports. As a result of the polymerization characteristics of ring-opening metathesis polymerization (ROMP),[109−116] the fully characterized monomeric complexes can be polymerized in a highly controlled fashion without the need for post-polymerization steps. Furthermore, the catalytic sites can be randomly dispersed within a copolymer, thereby allowing for controlled site isolation of the catalytic moieties. Our poly(norbornene) complexes are highly active and selective catalysts for the epoxidation of olefins and the HKRs of terminal epoxides. By comparing the catalytic performances of the polymeric complexes for these two reactions, which have very diverse requirements (vida infra), we set up general guidelines for the future development of supported salen catalysts.

Results and Discussion

Research Design. Among the main challenges in the development of immobilized, chiral, transition-metal catalysts is the problem of synthesizing uniform and well-defined

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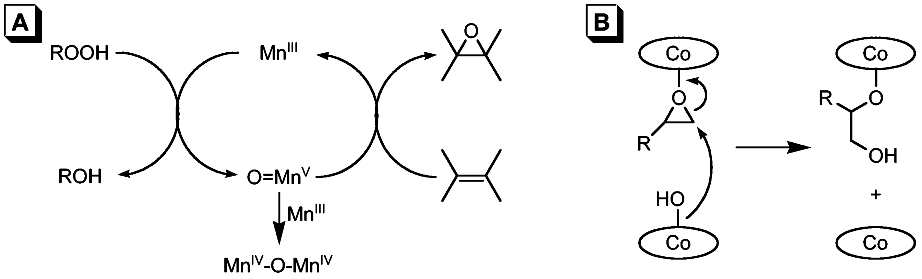
SCHEME 1. Proposed Mechanisms for (A) the AE of Olefins and (B) the HKR of Epoxides



supported complexes. Only these systems allow for a rational design and optimization of the catalysts. For polymeric supports, almost all studies report on the synthesis of a polymeric ligand and the subsequent complexation of a catalytically active metal in a post-polymerization process. When this strategy is used, a uniform system can only be obtained when the complexation step is quantitative and no side reactions occur, a prerequisite that most post-polymerization strategies do not fulfill, especially when using sterically congested polymeric ligands. The goal of this study is, thus, to overcome these shortcomings by first synthesizing well-characterized monomeric metal complexes that can be polymerized subsequently using a controlled polymerization method such as ROMP.[109−116]

The two polymer-supported salen catalysts that have been investigated in this study are active catalysts for the AE of olefins (manganese−salen) and the HKR of terminal epoxides (cobalt−salen). Besides their outstanding importance in industry, these two catalysts have several contradicting properties. They represent different methodologies for synthesizing chiral compounds (AE, asymmetric catalysis; HKR, resolution of enantiomers) and are suitable for the synthesis of different kinds of enantiomerically highly enriched epoxides (AE, highest enantioselectivities for synthesizing cis-disubstituted epoxides; HKR, highest selectivities for the resolution of terminal epoxides). Most importantly, both reactions differ dramatically in their reaction mechanisms (Scheme 1). In the case of AE, the Mn(III) complex is oxidized to Mn(V) by a single oxygen source, such as a peroxide, and the Mn(V) species is responsible for the epoxidation of the olefin, whereby the manganese is reduced back to Mn(III).[117,118] The most common deactivation pathway for this system is the dimerization of a Mn(III) and a Mn(V) complex, resulting in an oxo-bridged Mn(IV)−O−Mn(IV) species (Scheme 1A).[119] For this reason, it has been proposed that a highly active Mn−salen epoxidation catalyst can only be realized by immobilizing the complex in such a way that a perfect site isolation of all catalytic moieties is guaranteed.[27,51,52,74] The mechanism of the HKR, on the other hand, is believed to involve a cooperative bimetallic pathway, with one cobalt activating the epoxide while a second metal is activating the nucleophile (Scheme 1B).[12,13,88,120−122] In this case, a system allowing an easy interaction of the two metal centers is desired, whereas a system with site-isolated catalytic centers should be less selective. Because of the very different mechanistic properties of AE and HKR, we propose that, once a successful modular approach for the synthesis of catalysts for

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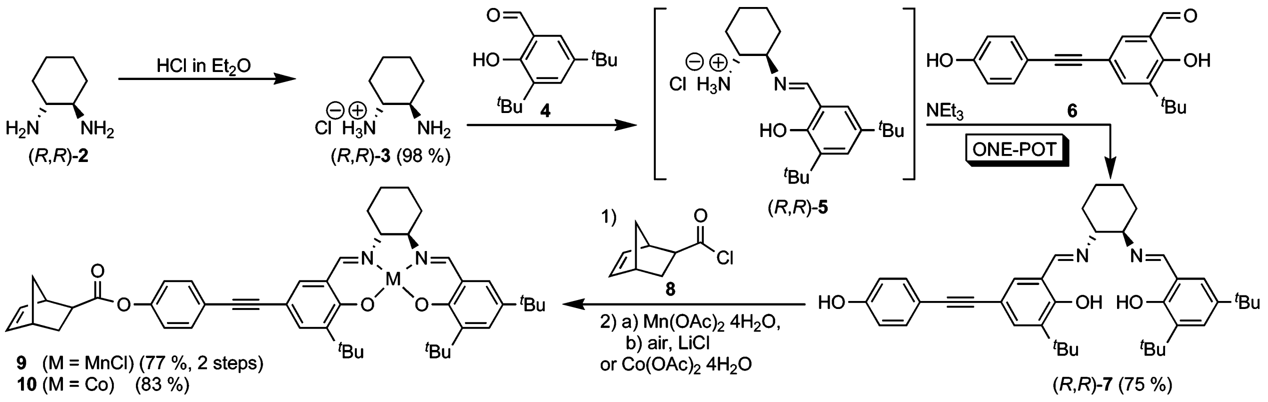
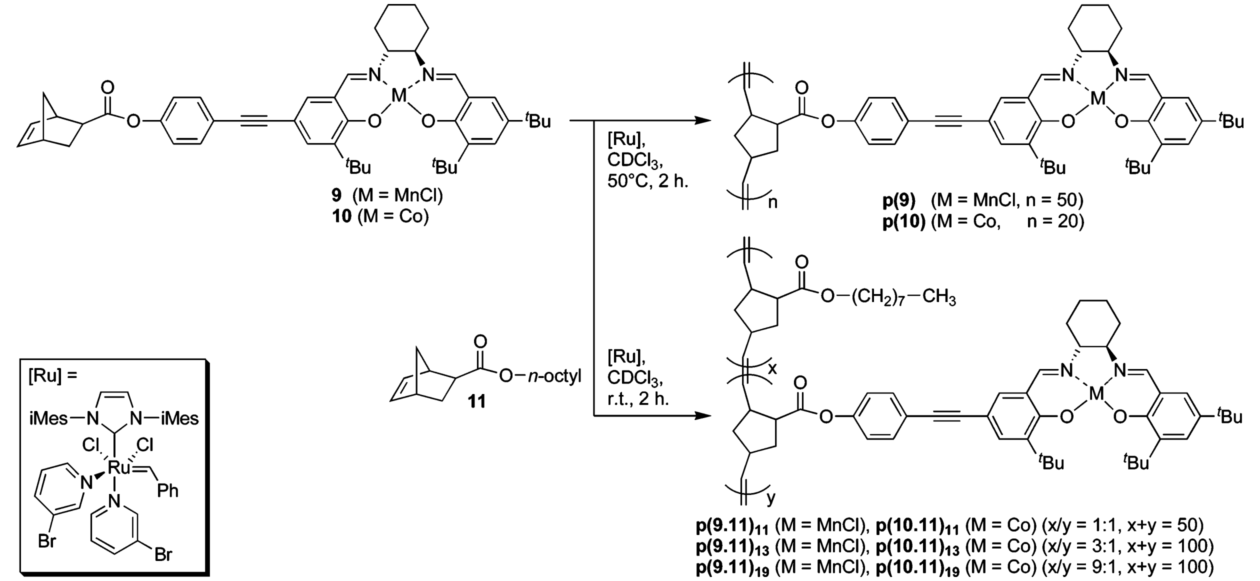
SCHEME 2. Synthesis of the Norbornene-Functionalized Manganese− and Cobalt−Salen Complexes 9 and 10



SCHEME 3. ROMP of the Norbornene-Functionalized Salen Complexes 9 and 10



these two reactions has been worked out, the development of supported salen catalysts for other reactions should be straightforward by adapting to the mechanistic properties of the studied reaction.

We rationalized that a modular salen support system can be developed for both systems by adapting criteria put forward by Sherrington et al.[52] These criteria include the following: (i) the supported catalyst should resemble the optimized salen ligand sphere **1** developed by Jacobsen et al.[21,22] as closely as possible; (ii) the salen ligand should be attached to the support via a single linker to minimize steric restrictions; (iii) for Mn−salen species, the catalyst loading should be sufficiently low to maximize site isolation of the catalytic centers and thus minimize the formation of catalytically inactive oxo-bridged dimers,[119,123] while for the Co species, catalyst density must be high enough to allow for the proposed simultaneous activation of the epoxide and the nucleophile via two different cobalt centers;[12,88,120,124] and (iv) the morphology of the supports should ensure free accessibility to all active sites.

To fulfill these requirements, we employed monofunctionalized salen cores attached via a single site to a soluble poly(norbornene) backbone. For the attachment, chemically inert C−C bond linkages via a phenylene−acetylene linker have been employed that have been proven to minimize catalyst degradation during the epoxidation reaction.[50] Variations of the catalyst density were realized by either homo- or copolymerizing the metalated salen monomers with a terminal alkyl group containing monomer, using ROMP as the highly controlled polymerization method.

Synthesis and Polymerization of the Mononorbornene Functionalized Salens. The monofunctionalized salens were obtained by the desymmetrization of 1,2-diaminocyclohexane **2** with HCl to yield the monoammonium salt **3**.[125] After the reaction of **3** with **4**, the resulting monoammonium imine **5** was deprotected with NEt$_3$ in a one-pot procedure and reacted with the functionalized aldehyde **6**. After an esterification of the resulting unsymmetrically substituted salen **7** with **8** and the subsequent metalation, the functionalized Mn− and Co−salen norbornenes **9** and **10** were obtained in good yield (Scheme 2). ROMP of the analytically pure and fully characterized monomers using the 3°-generation Grubbs catalyst,[109,110] yielded **p-(9)** and **p(10)** (Scheme 3). Furthermore, we prepared copolymers of **9** and **10** with the unfunctionalized norbornene **11**[126] (Scheme

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(125) Campbell, E. J.; Nguyen, S. T. *Tetrahedron Lett.* **2001**, *42*, 1221.

(126) Pollino, J. M.; Nair, K. P.; Stubbs, L. P.; Adams, J.; Weck, M. *Tetrahedron* **2004**, *60*, 7205.

TABLE 1. Elemental Analysis and ICP Data of the Polymers

		% found (% calcd)						
entry	polymer	C[a]	H[a]	N[a]	O[a]	Cl/S[b]	Me[c]	Me[d]
1	**p(9)**	68.67	7.02	3.27	9.09	n.d.[e]	11.95[f]	5.00
		(70.71)	(6.92)	(3.44)	(7.85)		(11.09)	(6.74)
2	**p(9.11)$_{11}$**	71.10	7.65	2.64	9.72	2.26	5.68	4.68
		(72.13)	(7.78)	(2.63)	(9.01)	(3.33)	(5.15)	(5.15)
3	**p(9.11)$_{13}$**	n.d.[e]	n.d.[e]	n.d.[e]	n.d.[e]	n.d.[e]	n.d.[e]	3.86
								(3.51)
4	**p(9.11)$_{19}$**	75.05	9.63	0.84	11.69	0.96	1.83	1.39
		(75.15)	(9.53)	(0.91)	(11.47)	(1.16)	(1.79)	(1.79)
5	**10**	73.33	7.21	3.49	8.33		7.64	8.00
		(73.54)	(7.20)	(3.57)	(8.16)		(7.52)	(7.52)
6	**p(10)**	71.06	7.06	3.57	8.95		9.36	6.96
		(73.54)	(7.20)	(3.57)	(8.16)		(7.52)	(7.52)
7	**p(10.11)$_{11}$**	72.88	7.89	2.76	9.89		6.58	5.96
		(74.32)	(7.99)	(2.71)	(9.28)		(5.70)	(5.70)
8	**p(10.11)$_{13}$**	74.25	8.73	1.95	11.15		3.92	3.95
		(75.11)	(8.80)	(1.82)	(10.42)		(3.84)	(3.84)
9	**p(10.11)$_{19}$**	75.50	9.50	0.90	11.96		2.14	2.02
		(75.92)	(9.62)	(0.92)	(11.59)		(1.94)	(1.94)
10	**p(10c)**	65.42	6.79	2.60	15.02	3.97	6.20	5.60
		(69.16)	(6.65)	(2.93)	(11.73)	(3.36)	(6.17)	(6.17)
11	**p(10c)_rec**	57.65	6.27	2.58	20.47	5.10	7.93	4.27
		(69.16)	(6.65)	(2.93)	(11.73)	(3.36)	(6.17)	(6.17)

[a] Determined by elemental analysis. [b] Determined by elemental analysis; S only for **p(10c.11)** and **p(10c.11)_rec** (entries 10 and 11). [c] Determined by 100 − (sum of percentages of other elements). [d] Determined by ICP. [e] Not determined as a result of lack of sample material. [f] Content of MnCl, determined by 100 − (sum of percentages of other elements).

3) to (i) site-isolate individual catalyst sites and (ii) probe the effect of catalyst loadings on the catalytic activity.

Characterization of the Polymers. Although the complexes **9** and **10** are paramagnetic, we were able to investigate the polymerization rates using ^{1}H NMR spectroscopy by solely focusing on the signals of the olefin protons. In all cases, monomer conversions (monomer-to-catalyst ratios up to 100:1) were quantitative after 1−2 h. Moreover, following the homopolymerizations of 10 equiv of **9**, **10**, or **11** by ^{1}H NMR, we found that the polymerization kinetics of all three monomers using the 3°-generation Grubbs catalyst are similar with complete monomer conversion after 2−5 min (see Supporting Information). These results suggest that the copolymerization of **9** and **11** and **10** and **11** yield statistical copolymers **p(9.11)** and **p(10.11)**, that is, the monomers containing the catalytic moiety are randomly interdispersed in the alkyl−norbornene matrix.

It is well-known that polyelectrolyte and metal-salt-containing polymers cannot be characterized by gel-permeation chromatography (GPC), most likely as a result of the interactions of the polymers with the packing material and the formation of aggregates during the process.[127] The same limitation holds true for our metal-containing polymers, and no GPC results of any polymer containing more than 10 repeating units could be obtained in either THF, chloroform, or methylene chloride. Therefore, no polydispersities (PDIs) or molecular weights for the high-molecular-weight polymers are reported. However, the values for the molecular weights and the PDIs of 10-mers of **p(9)** (M_w = 5,900; M_n = 4,400; PDI = 1.34) and **p(10)** (M_w = 55,400; M_n = 18,300; PDI = 3.03) confirmed a successful and quantitative ROMP of the monomeric complexes.

We used three different analysis methods to determine the metal content of all monomers and polymers. First, we carried out ICP analyses of all compounds. Second, we analyzed the C, H, N, and O contents by elemental analysis. Because the monomers contain only the elements C, H, N, and O, but for the metal and its ligands (such as chlorine, etc.), one can calculate the metal content by subtracting the C, H, N, and O (and in case of the Mn complexes, Cl) contents from 100 percent. The remaining contents must be the metal complex. The results of these two methods are shown in Table 1.

Finally, if possible, we determined the chlorine content of all polymers. The manganese-containing compounds contain one Cl ligand on all metals. Therefore, by analyzing the chlorine content, one can calculate the metal content.[128] Using this methodology, the manganese content of **p(9.11)$_{11}$** was calculated to be 3.50% (calcd, 5.15%), and that of **p(9.11)$_{19}$** was calculated to be 1.48% (calcd, 1.79%). While one should expect these three methods to agree in the metal contents, we found that all three methods slightly diverse from the theoretically expected metal-content values (some methods suggest a higher metal content, while others suggest a lower one), which we attribute to the error of the three analytical methods as a result of the small sample sizes and the low metal percentage of all polymers. With these limitations in mind, the values for the metal loadings of the polymers are within the error range (in most cases, ±0.5% for all three methods) and in good agreement with the theoretical values. These results suggest that the metalated salen complexes do not decompose during the ROMP (it is important to note that always fully characterized and purified, i.e., by column chromatography, metalated monomers were employed during the ROMP) and that the co-monomer ratios are approximately the same as the theoretical targeted ratios.

Asymmetric Epoxidation. For studying the properties of the polymeric Mn−salen complexes as AE catalysts, we chose styrene **12**, 1,2-dihydronaphthalene **14**, and *cis*-*β*-methylstyrene **16** as substrates, representing a terminal, a cyclic, and a cis-

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(127) Meier, M. A. R.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 852.

(128) % Mn = % Mn (calcd) × [% Cl/% Cl (calcd)].

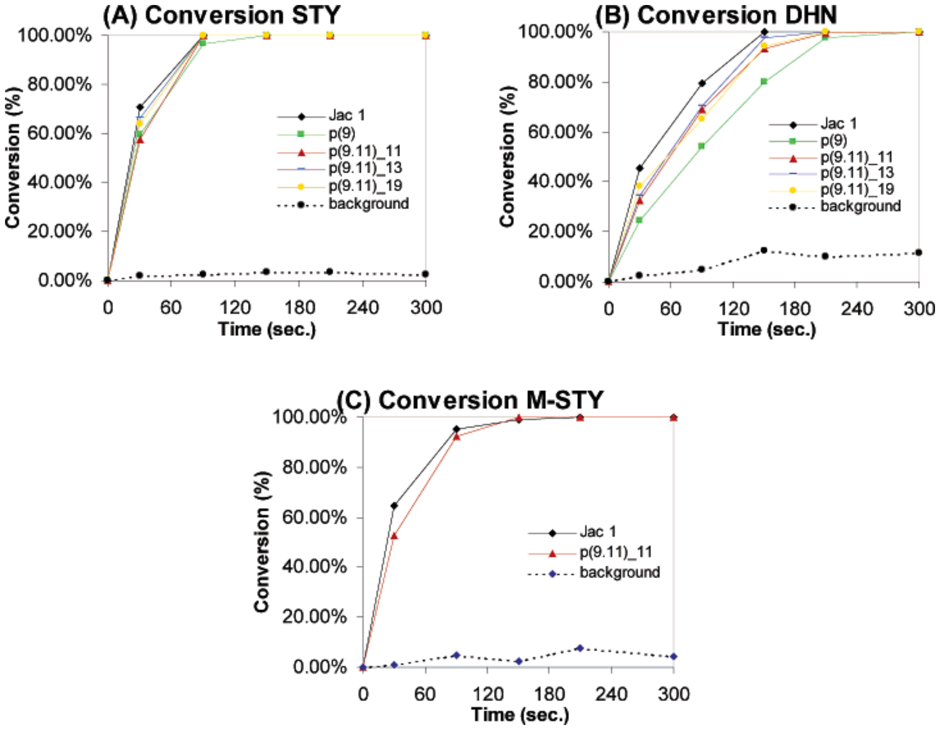
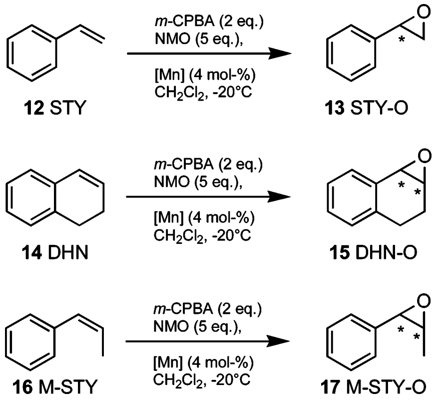


FIGURE 2. Kinetic study of the epoxidation of (A) styrene **12** (STY), (B) 1,2-dihydronaphthalene **14** (DHN), and (C) *cis*-β-methylstyrene **16** (M-STY) using the poly(norbornene)-based manganese catalysts via GC analysis of the reaction mixture (lines are just visual aids and not plots).

SCHEME 4. Epoxidations of Unfunctionalized Olefins



disubstituted, noncyclic olefin. Following published procedures,[10,51,52,129] we dissolved the polymeric catalysts, *N*-methylmorpholine-*N*-oxide (NMO), the olefin, and chlorobenzene or dodecane as an internal standard in methylene chloride, cooled the solutions to −20 °C, and added *meta*-chloroperoxybenzoic acid (*m*-CPBA) in three equal portions over a period of two minutes (Scheme 4).

Kinetic studies via the GC analysis of the reactions clearly showed the outstanding high activities of the polymer-supported salen systems with quantitative conversions using 4 mol % Mn after 150−300 s (Figure 2, Table 2). The epoxidations of styrene **12** and *cis*-β-methylstyrene **16** are as fast as the control experiments, using the original nonsupported Jacobsen complex (Figure 2A,C). Only in the case of 1,2-dihydronaphthalene **14** is the epoxidation rate with **p(9)** (Figure 2B, green) somewhat slower than the rate of the original Jacobsen catalyst (black line).

TABLE 2. Epoxidation of Unfunctionalized Olefins[a]

entry	olefin[b]	epoxide	catalyst	temp (°C)	conv.[c] (%)	ee (%)
1	**12**	**13**	Jacobsen	−20	100	34
2	**12**	**13**	**p(9)**	−20	100	32
3	**12**	**13**	**p(9.11)**$_{11}$	−20	100	33
4	**12**	**13**	**p(9.11)**$_{13}$	−20	100	32
5	**12**	**13**	**p(9.11)**$_{19}$	−20	100	33
6	**14**	**15**	Jacobsen	−20	100	88
7	**14**	**15**	**p(9)**	−20	100	76
8	**14**	**15**	**p(9.11)**$_{11}$	−20	100	81
9	**14**	**15**	**Cycle 2**	−20	100	47
10	**14**	**15**	**Cycle 3**	−20	85	6
11	**14**	**15**	**p(9.11)**$_{13}$	−20	100	81
12	**14**	**15**	**p(9.11)**$_{19}$	−20	100	82
13	**16**	**17**	**Jacobsen**	−20	100	93
14	**16**	**17**	**p(9.11)**$_{11}$	−20	100	92

[a] All epoxidations were carried out at −20 °C with *m*-CPBA (2 equiv), NMO (5 equiv), and a 4 mol % Mn catalyst in CH_2Cl_2. [b] Styrene **12**, *cis*-β-methylstyrene **16**, or 1,2-dihydronaphthalene **14**. [c] After a period of 5 min.

The copolymers, **p(9.11)**, have catalytic activities (Figure 2B) that are higher than their homopolymer analogue, **p(9)**. All reactions are quantitative after 5 min or less, suggesting a good accessibility to all catalyst sites.

Our supported catalysts have also outstanding selectivities (Figure 3, Table 2). For the epoxidation of styrene **12** and *cis*-β-methylstyrene **16**, the enantiomeric excesses (ee's) are on par with the unsupported Jacobsen catalyst (32−33 vs 34% ee for **13** and 92 vs 93% ee for **17**). For the epoxidation of 1,2-dihydronaphthalene **14**, the ee's with the polymeric catalysts are slightly lower than with the Jacobsen catalyst (76−82 vs 88% ee) but are among the highest ee's reported for any immobilized salen complexes (10−84% ee).[3,27,43,44,50] A possible reason for the somewhat lower selectivities of our supported systems is their slower reaction rate, which increases the amount

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(129) Palucki, M.; McCormick, G. J.; Jacobsen, E. N. *Tetrahedron Lett.* **1995**, *36*, 5457.

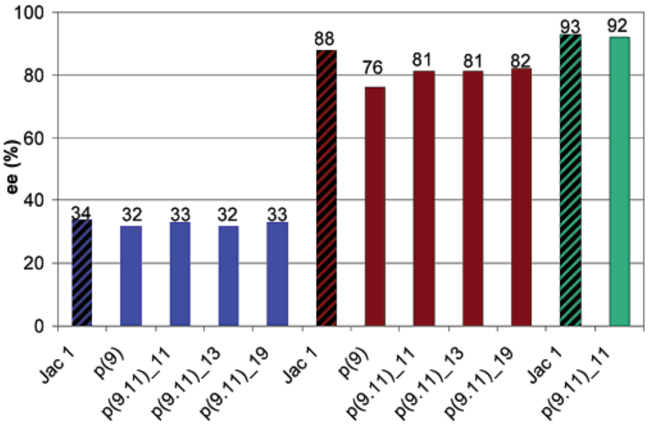
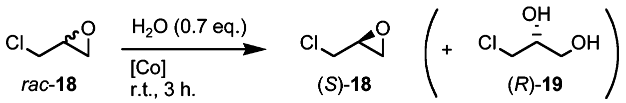


FIGURE 3. Enantiomeric excesses of the epoxidation of styrene **12** (blue bars), 1,2-dihydronaphthalene **14** (red bars), and *cis*-*β*-methylstyrene **16** (green bars) using the polymeric Mn−salen catalysts. **Jac 1** (original Jacobsen catalyst) is included as standard.

SCHEME 5. Reaction Conditions of the HKR of Epichlorohydrin 18



of racemic epoxide produced by a slow background reaction without the need of a catalyst (Figure 2B, dotted black line). As already seen for the epoxidation rates, the enantioselectivities of the copolymers **p(9.11)** are very similar (81−82% ee) and higher than the homopolymer **p**(**9**) (76% ee), suggesting a good site isolation of the manganese centers even for the 1:1 copolymer.

The polymeric Mn complexes could be separated easily from the reaction mixtures by the precipitation into Et$_2$O/MeOH and subsequent centrifugation. In all cases, the polymer was recovered quantitatively. For a first study of the reusability, we used **p(9.11)$_{11}$**, representing the copolymer system with the best catalytic performance and the highest manganese loading. Unfortunately, after separating the polymer by precipitation, the residue was not completely soluble in methylene chloride anymore. When the resulting suspension was used as a catalyst for the epoxidation of **14**, the epoxidation rate was slower than the one with the nonrecycled polymer (Figure 4A, red lines). This drop of activity after recycling is even more pronounced in the third cycle, where we could get only 85% conversion of **14** after 300 s (Figure 4A). Even more dramatic was the decline of the enantioselectivity from 81% ee to 47% ee (second cycle) to only 6% ee after the third cycle (Table 2, Figure 4B), showing that **p(9.11)$_{11}$** is not reusable. Whether the observed solubility problems and the subsequent drops in activity and selectivity are a result of the dimerization of Mn(III)− and Mn(V)═O centers (leading to cross-links between different polymer chains) or a degradation/chemical modification of the catalyst (i.e., the backbone olefins of the poly(norbornene) complexes could be cross-linked or epoxidized) is yet unclear. However, Janda and Reger reported similar problems for the solubility and recyclability of monofunctionalized, polymeric, Mn−salen catalysts with different linkers and different polymeric supports when using 1,2-dihydronaphthalene as starting material,[51] indicating that these difficulties may not be a shortcoming of our support, but a more general issue of monofunctionalized salen complexes attached to soluble supports.

Our results with the Mn−poly(norbornene) complexes as chiral epoxidation catalysts clearly reveal that, by following the above-described criteria, immobilized catalysts with outstanding activities and selectivities, that are on par with the catalytic activities and selectivities of the original Jacobsen catalyst, can be synthesized. Furthermore, the polymeric Mn−salen complexes can be easily removed by precipitation and subsequent centrifugation, allowing for the removal of the vast majority of the metal species after complete reactions.

Hydrolytic Kinetic Resolution. The catalytic performance of the polymeric cobalt complexes **p(10)** and **p(10.11)** were studied in the HKR of racemic epichlorohydrin **18** (Scheme 5). Because only the Co(III) complexes are catalytically active in this reaction, we oxidized the obtained Co(II) polymers, **p(10)** and **p(10.11)**, by stirring methylene chloride solutions of the polymers with acetic acid under an atmosphere of air (Scheme 6, X = OAc). After removal of the solvent and the excess AcOH in vacuo, the desired Co(III)−salen polymers **p(10a)** and **p(10a.11)**, with acetates as counterions, were obtained. For the HKR reactions, the Co(III) polymers were dissolved in a mixture of methylene chloride, **18**, and chlorobenzene as an internal standard, followed by the addition of 0.7 equiv of water to start the resolution. The addition of some methylene chloride as a solvent was necessary, because the copolymers were not fully soluble in **18**.

The reaction kinetics of the HKR were studied via chiral GC analysis. When either the homopolymer, **p(10a)**, or the two copolymers, **p(10a.11)$_{11}$** and **p(10a.11)$_{13}$**, are used, epoxide (*R*)-**18** is fully converted after 5 h to its corresponding diol, leaving pure (*S*)-**18** in the reaction mixture in above a 99% ee (Figure 5). After this time period, 55% of the racemic **18** is converted, that is, all of the unwanted (*R*)-enantiomer is converted to the

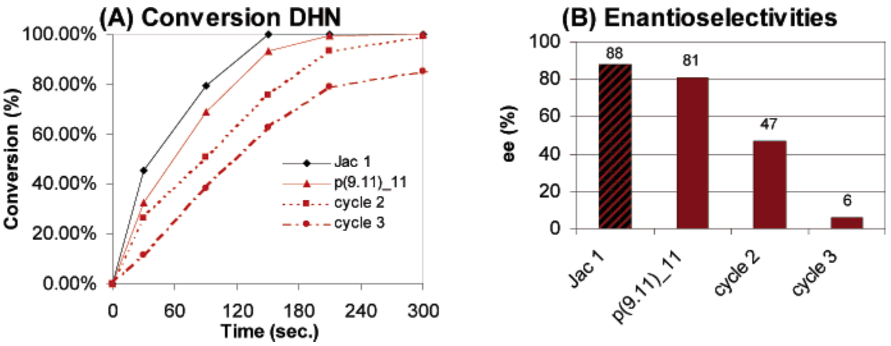


FIGURE 4. (A) Conversion vs time and (B) enantioselectivities of the epoxidation of 1,2-dihydronaphthalene **14** (DHN) with **p(9.11)$_{11}$** (lines are just visual aids and not plots).

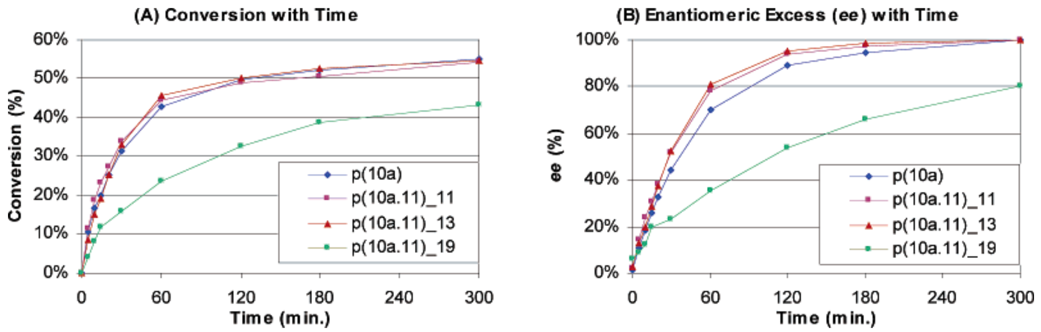


FIGURE 5. HKR of **18** with polymeric CoOAc−salen complexes (determined via chiral GC analysis of the reaction mixtures; lines are just visual aids and not plots).

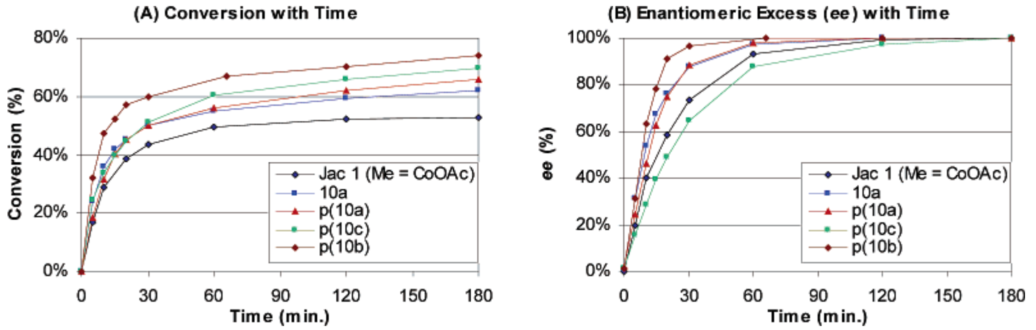
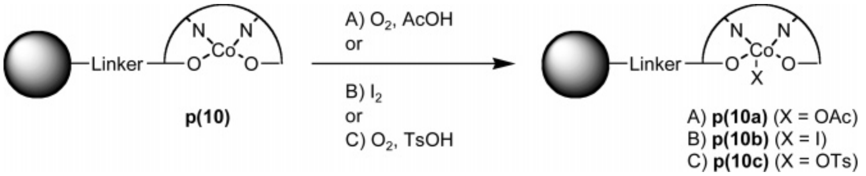


FIGURE 6. HKR of **18** with polymeric Co−salen complexes containing different counterions (determined via chiral GC analysis of the reaction mixtures; lines are just visual aids and not plots).

SCHEME 6. Oxidation of the Polymer-Supported Cobalt−Salen Catalysts



diol, while only 5% of the desired epoxide has been converted, indicating selectivities similar to the original Jacobsen CoOAc catalyst (53% conversion, >99% ee under solvent-free conditions). The epoxidation rates with **p(10a.11)$_{11}$** and **p(10a.11)$_{13}$** are slightly higher than the rates using **p(10a)** (Figure 5). This finding, which on first sight contradicts the assumption of a bimetallic mechanism for the HKR (see Scheme 1), may be the result of a higher backbone flexibility of the copolymers in comparison to the sterically more congested homopolymers. However, further dilution of the salen moieties along the polymer backbone (polymers **p(10a.11)$_{19}$**) resulted in a dramatic drop of the activity (Figure 5C, only 43% conversion and 80% ee after 5 h), while the selectivities stay the same (e.g., **p(10a.11)$_{11}$**, 44.5% conversion, 78.4% ee and **p(10a.11)$_{13}$**, 45.5% conversion, 81.0% ee after 1 h). This result clearly suggests that the extreme dilution of the catalytic moieties along the polymer backbone results in the deactivation of the catalysts as a result of the unlikelihood of two catalytic moieties being in close proximity to each other, a prerequisite for the bimetallic catalytic pathway.

When **p(10a)** is used, the HKR of **18** can also be carried out under solvent-free conditions (Figure 6, red line). In this case, the reaction rates are faster than the rate with **p(10a)**, using CH_2Cl_2 as the solvent, as well as the rate of the original Jacobsen complex, resulting in (*S*)-**18** with >99% ee after less than 2 h. However, an increase in conversion (62%) suggests that the polymeric catalyst is less selective under these reaction conditions. When comparing the kinetics of the original Jacobsen CoOAc−salen catalyst **1** (Me = CoOAc) with the monomeric catalysts **10a** (Figure 6, black and blue lines), we found that **10a** is slightly less selective than the original Jacobsen catalyst, indicating that the lower selectivities of the polymers are primarily a result of the different catalyst structure (a phenylene−acetylene linker instead of a *tert*-butyl group in the 5 position of one of the aromatic rings) and not based on the polymeric support. This result suggests that even small changes in the structure of the salen core can have a significant effect on the catalytic properties of the resulting complexes.

Another important variable that has been studied with Co−salen catalysts is the choice of the counterion on the metal center.[83,88,122] It has been reported that very nucleophilic counterions such as Cl can attack the epoxide very fast, resulting in small amounts of byproduct, while catalyst activity can be increased dramatically with more electronegative counterions such as OTs.[80,122] Finally, noncoordinating counterions such as PF_6^- or BF_4^- can suppress the undesired reduction of Co(III) to Co(II).[83] To investigate if this counterion effect holds true in our polymeric system and if we can tailor the activities and selectivities of our polymeric catalysts through changes of the counterion, we synthesized **p(10b)** and **p(10c)** with an iodide and a tosylate as counterions, respectively. Polymer **p(10b)** was obtained by oxidizing **10** with iodine and a subsequent ROMP

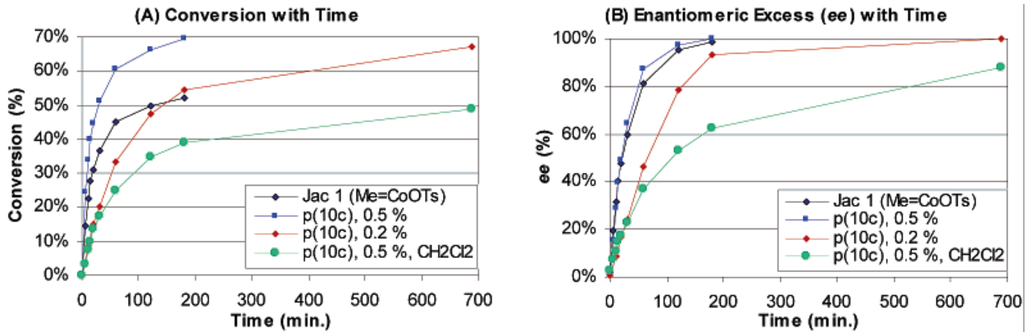


FIGURE 7. HKR of **18** with polymeric CoOTs−salen complexes (determined via chiral GC analysis of the reaction mixtures; lines are just visual aids and not plots).

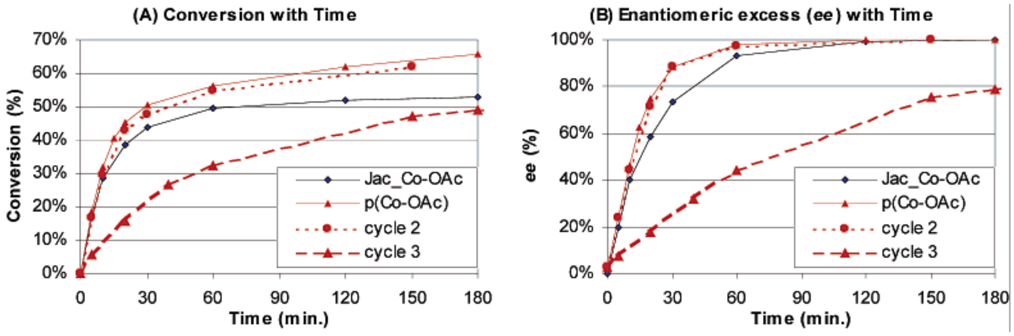


FIGURE 8. HKR of **18** with polymeric CoOAc−salen complexes (determined via chiral GC analysis of the reaction mixtures; lines are just visual aids and not plots).

of **10·I**. In contrast, **p(10c)** was obtained by oxidizing the polymer **p(10)** with O_2/*p*-toluenesulfonic acid (Scheme 6). Interestingly, when either **p(10b)** or **p(10c)** was employed as a catalyst in the HKR of **18** under solvent-free conditions, both catalysts showed higher activities than **p(10a)** (Figure 6). In particular, **p(10b)** was highly active, with (*S*)-**18** being obtained in >99% ee after less than 1 h (Figure 6, purple line). However, the selectivities of **p(10b)** and **p(10c)** are somewhat lower than that of **p(10a)** (conversions for obtaining (*S*)-**18** with >99% ee, 66.7% using **p(10b)**, 69.7% using **p(10c),** and 62.0% using **p(10a)**). These results prove that a counterion effect exists also in our polymer-supported Co−salen catalysts.

As a result of the outstanding activities of **p(10c)**, we used this polymeric catalyst to optimize our reaction conditions.[12,122] We first tried to improve the selectivity by adding CH_2Cl_2 as a solvent to the reaction (Figure 7, green line). Unfortunately, the reaction was significantly slower, with only 49.0% of **18** converted after 11.5 h (87.9% ee of (*S*)-**18**). Nevertheless, higher ee's of (*S*)-**18** at 50% conversion were observed under these reaction conditions, which indicate an increase in selectivity of **p(10c)** when adding a solvent. We also investigated the effect of decreasing the catalyst loading on the activities and the selectivities. When decreasing the catalyst loading of the polymeric CoOTs catalyst to 0.2 mol % Co for the HKR of **18**, we observed a decrease in activity (the reaction takes 11 h for a complete conversion of (*R*)-**18**) as well as a decrease in selectivity (after 11 h, 67.2% of the racemic epoxide is converted). Moreover, a comparison of the ee of the remaining (*S*)-**18** at similar conversions suggests an increased selectivity with a decrease of the CoOTs amount (0.2 mol % **p(10c)**, 47.4% conversion, 78.2% ee; 0.5 mol %, 51.4% conversion, 64.4% ee). These results demonstrate that, for the CoOTs−poly (norbornene) catalyst, the use of less catalyst loading might be advantageous.

All polymeric Co complexes could be separated easily from the reaction mixtures by precipitation into Et_2O and subsequent centrifugation. By simply washing the obtained Et_2O solution with water, (*R*)-3-chloro-1,2-propandiol **19** can be removed nearly quantitatively, resulting in pure (*S*)-**18**. This protocol is considered to be an important advantage to the normally used methodology of distilling off **18** from the crude reaction mixture, because remaining Co(III)−salen complexes are reported to catalyze the decomposition and the racemization of the epoxide during the purification process.[13,130,131] Because the polymeric CoOAc complex **p(10a)** gave the best selectivities, we chose this catalyst to study the reusability of our polymeric Co−salen catalysts. After reoxidation with O_2 in the presence of acetic acid, recycled **p(10c)** showed the same resolution rate and selectivity as the original polymeric catalyst **p(10c)** (Figure 8, 61.8% conversion, > 99% ee of (*S*)-**18** after 150 min). However, the need for ultrasonication to dissolve **p(10a)** fully in a solution of **18** and chlorobenzene before the catalysis already pointed toward a reduced solubility. The solubility of the polymeric catalyst worsened for the third catalytic cycle. We were not able to dissolve the twice-recycled **p(10a)** fully in the reaction mixture, even after the addition of CH_2Cl_2 as a solvent and ultrasonicating the mixture. As a result of the lower solubility, the reaction rate dropped by a third, with only 78.8% ee after 3 h (49.6% conversion). However, after 11 h, 61.0% of the racemic epoxide is converted and (*S*)-**18** is obtained with 97.8% ee, indicating that the polymeric catalyst is still active and very

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(130) Aouni, L.; Hemberger, K. E.; Jasmin, S.; Kabir, H.; Larrow, J. F.; Le-Fur, I.; Morel, P.; Schlama, T. *Asymmetric Catal. Ind. Scale* **2004**, 165.

(131) Larrow, J. F.; Hemberger, K. E.; Jasmin, S.; Kabir, H.; Morel, P. *Tetrahedron: Asymmetry* **2003**, *14*, 3589.

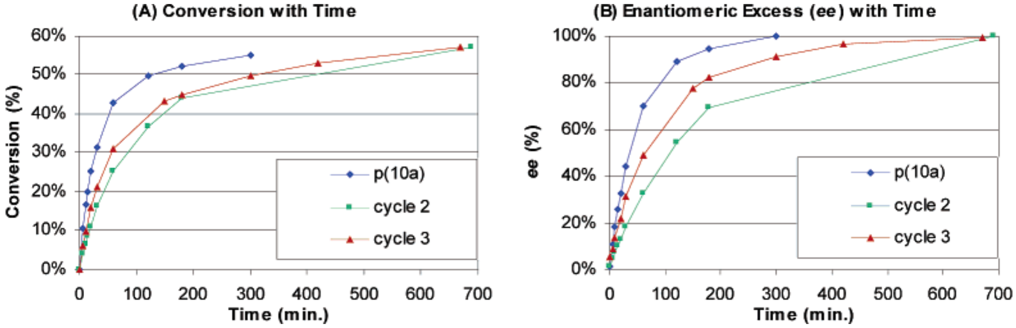

FIGURE 9. HKR of **18** with polymeric CoOAc−salen complexes (determined via chiral GC analysis of the reaction mixtures; lines are just visual aids and not plots).

selective and that after an appropriate reaction time enantiomerically pure (*S*)-**18** can be isolated in good yields.

Similar results for the reusability (i.e., the solubility problems and subsequent low resolution rates) were obtained with the polymeric CoOTs−salen **p(10c)** (see Supporting Information for kinetic data). Analysis of **p(10c)** by ICP before starting the recycling experiments and after the third catalysis cycle showed that the metal content of the polymer decreased from 5.60 to 4.27%. This decrease in metal content cannot be explained with the error range of the elemental analysis. Because a leaching of metallic cobalt is not reported in the literature, we suggest that this slight decrease in metal content may be a result of a cleavage of the ester bonds resulting in a loss of a complete salen moiety from the polymer. Nevertheless, while we recently reported on the stability of the norbornene ester linkages under a variety of reaction conditions,[132] we cannot exclude (also unlikely) some metal leaching of the cobalt from the polymer at this point. Additionally, the percentages of carbon, oxygen, and sulfur are increasing (Table 1, entries 10 and 11), indicating that either *para*-toluenesulfonic acid is not completely separated during the precipitation or that the acid is reacting with the double bond along the polymer backbone.

A second recycling method that has been reported in the literature is the removal of the substrates by fractionated distillation followed by the addition of more starting material to the metal-containing residue.[133] While this method suggests repeated usability of the Co catalysts, it has several disadvantages including the potential for the undetected decomposition of the catalyst (i.e., leaching of cobalt) and that epoxides such as (*S*)-**18** may racemize during this process.[13,130,131] However, because of the solubility issues we encountered during the separation of the catalyst by precipitation, we also studied this recycling method, whereby we also used CH_2Cl_2 as a solvent. Starting with 11 mg of **p(10a)** in the first cycle, we obtained 56 mg of a red-brown solid after distilling off CH_2Cl_2, (*S*)-**18**, and **19**. Subsequently, the residue was dried in vacuo, and the Co(II) complex was reoxidized with O_2/AcOH. The increased mass indicates an incomplete removal of the substrates, in particular, 3-chloropropane-1,2-diol (boiling point 213 °C). The recycled polymeric catalyst showed a somewhat lower activity in the second cycle. It took 11 h instead of 5 h to obtain (*S*)-**18** with >99% ee (57% convervision; Figure 9). After recycling and reoxidation, we isolated 99 mg of a brown residue after the second catalysis cycle. In the third cycle, this residue showed a catalytic performance that is comparable to the one described for the second cycle (Figure 9). Interestingly, we did not observe any solubility problems using this methodology, contrasting our results with the precipitation method. While the reason for this is still unclear and a matter of current investigations, it shows that the method of recycling may be an important factor in determining the properties and performance of a recycled catalyst.

The polymeric cobalt−salen results clearly demonstrate that we successfully synthesized a highly active and selective supported version of the Jacobsen's cobalt−salen catalyst. Furthermore, we have shown that the copolymers are slightly more active than their homopolymer analogues. Finally, we have also observed the often-described counterion effect in our supported catalyst system, allowing for the tailoring of activities and selectivities. While the catalysts can be removed from the reaction mixture allowing for the easy removal of metal species from the product, using the precipitation method, our supported catalysts can only be recycled once as a result of their decreased solubility after the reoxidation step.

Conclusion

In this contribution, we describe the synthesis of monofunctionalized Mn− and Co−salen complexes **9** and **10** attached to a norbornene monomer via a stable phenylene−acetylene linker. The analytically pure and fully characterized monomeric complexes were homo- and copolymerized using the controlled polymerization method, ROMP, thus circumventing the usually applied post-polymerization complexation step, allowing for the synthesis of fully functionalized immobilized metal−salen catalysts. The obtained polymeric manganese and cobalt complexes were successfully used as supported catalysts for AEs of different olefins and for the HKR of epoxides. All polymeric catalysts showed outstanding catalytic activities and selectivities that are comparable to the original catalysts reported by Jacobsen, thus proving the effectiveness of our design criteria. Interestingly, we found a dependence of the activity and selectivity of the catalyst on the density of the catalytic moieties along the polymer backbones. In general, we found that the copolymers are slightly more active and selective catalysts than their homopolymer analogues. This holds true for both the manganese as well as the cobalt-based systems. Only when diluting the cobalt−salen moieties to less than 15% along the polymer backbone was a drop in catalytic activity observed. Our polymeric catalysts can be easily removed from the reaction mixtures, demonstrating the possibility of easy metal removal

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from the products. The polymeric cobalt−salen catalysts can be recycled at least once with retention of their outstanding activities and selectivities. Currently, we are investigating the use of other insoluble supports. Moreover, investigations into the effect of the linker as well as polymer backbone flexibility on the activity and selectivity of immobilized metal−salen catalysts is being studied in our laboratory.

Experimental Section.

5-(4-Hydroxyphenylethinyl)-3-*tert*-butyl-2-hydroxybenzaldehyde, 6. An in vacuo flame-dried, 100-mL Schlenk flask under argon, equipped with a magnetic stir bar and a septum was charged with 1.714 g of 4-iodophenol (7.79 mmol, 1.0 equiv), 278 mg of [$PdCl_2(PPh_3)_2$] (0.397 mmol, 5 mol %), and 51 mg of triphenylphosphane (0.195 mmol, 2.5 mol %). The flask was evacuated and subsequently flushed with Ar. After the evacuating−flushing procedure had been repeated twice, 10 mL of anhydrous THF, a solution of 1.576 g of 5-ethinyl-3-*tert*-butyl-2-hydroxybenzaldehyde[50] (7.79 mmol, 1.0 equiv) in 15 mL of anhydrous THF, and 2.2 mL of NEt_3 (1.58 g, 15.54 mmol, 2.0 equiv) were added via a syringe, respectively, and the slurry was stirred at room temperature for 20 min. CuI, in the amount of 28 mg (0.117 mmol, 1.5 mol %), was added, and the dark red solution was stirred at room temperature for 27 h. The mixture was diluted with 100 mL of H_2O and 50 mL of Et_2O, and the phases were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with brine (40 mL) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, 4.16 g of the crude product was obtained as a red oil. Purification by column chromatography (SiO_2, 4 × 58 cm^2, ethyl acetate/hexanes = 1:7) yielded 1.224 g of product (51%) as a yellow powder. ^1H NMR (500 MHz, $CDCl_3/CD_2Cl_2$): δ 1.41 (s), 5.19 (br s), 6.80 (d), 7.40 (d), 7.57 (d), 7.63 (dd), 9.84 (br s), 11.88 (dd). ^{13}C NMR (125 MHz, $CDCl_3/CD_2Cl_2$): δ 29.0, 35.0, 86.9, 88.1, 114.6, 115.4, 115.6, 120.5, 133.2, 134.9, 137.0, 138.8, 155.9, 161.0, 196.9. HRMS (ESI): calcd for $C_{19}H_{18}O_3$, 294.1256; obsd, 295.1341 $[M + 1]^+$. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; O, 16.31. Found: C, 77.20; H, 6.37; O, 16.27.

Salen Linker, 7. Under an argon atmosphere in a flame-dried, 25-mL, three-necked flask, equipped with a magnetic stir bar, a septum, and a gas inlet, 301 mg of (*R*,*R*)-1,2-diaminocyclohexane-*mono*-aminochloride **3** (2 mmol, 1.0 equiv) and some 4 Å molecular sieves were slurried in 7 mL of anhydrous ethanol and 7 mL of anhydrous methanol. To this slurry was added 487 mg of 5-(4-hydroxyphenylethinyl)-3-*tert*-butyl-2-hydroxybenzaldehyde, **6** (2 mmol, 1.0 equiv). The bright yellow solution was stirred at room temperature. After 4 h, a solution of 589 mg of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, **4** (2 mmol, 1.0 equiv), in 15 mL of anhydrous CH_2Cl_2, and 0.56 mL of anhydrous NEt_3 (4 mmol, 2.0 equiv) was added. The red solution was stirred at room temperature for an additional 4 h. The mixture was filtered, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (dry SiO_2, 2.5 × 40 cm^2, ethyl acetate/hexanes = 1:5). Product, in the amount of 910 mg (64%), could be isolated as a yellow-orange powder. ^1H NMR (500 MHz, $CDCl_3/CD_2Cl_2$): δ 1.26 (s), 1.44 (s), 1.46 (s), 1.40−1.53 (m), 1.82−1.93 (m), 1.66−1.81 (m), 1.93−2.05 (m), 3.25−3.77 (m), 6.81 (d), 7.00 (d), 7.19 (d), 7.35 (d), 7.40 (d), 7.41 (d), 8.22 (s), 8.28 (s). ^{13}C NMR (125 MHz, $CDCl_3/CD_2Cl_2$): δ 24.4, 29.4, 29.6, 31.5, 33.1, 33.2, 35.0, 34.2, 35.1, 72.0, 72.2, 87.2, 88.3, 112.5, 115.7, 115.7, 117.7, 118.4, 126.1, 127.3, 132.7, 133.2, 133.2, 136.7, 137.9, 140.1, 155.7, 158.4, 161.5, 165.2, 166.2. MS (ESI, %) *m*/*z*: 607.3888 (±0.025; 56, $[M + 1]^+$), 391.2 ($C_{25}H_{31}N_2O_2$, 100), 331.3 ($C_{21}H_{35}N_2O$, 72). Anal. Calcd for $C_{40}H_{50}N_2O_3$: C, 79.17; H, 8.30; N, 4.62; O, 7.91. Found: C, 78.61; H, 8.26; N, 4.63; O, 8.06.

Salen−Norbornene. Under an argon atmosphere, 720 mg of **7** (1.186 mmol, 1.0 equiv) was dissolved in 20 mL of anhydrous CH_2Cl_2 in a dry, 50-mL, Schlenk flask, equipped with a magnetic stir bar and a septum. The red solution was cooled to 0 °C. A solution of 204 mg of norbornene carbonyl chloride, **8** (1.31 mmol, 1.1 equiv), in 8 mL of anhydrous CH_2Cl_2 and 0.18 mL of anhydrous NEt_3 (1.31 mmol, 1.1 equiv) was added dropwise via a syringe, respectively. The yellow solution was stirred at 0 °C for 30 min and was then allowed to warm to room temperature over a period of 30 min. The reaction mixture was filtered through a pad of dry silica, and the silica was flushed with CH_2Cl_2. After the removal of the solvent under reduced pressure, 913 mg of product (96%) was obtained as a yellow solid. Usually, the crude product was used in the following steps. For characterization purposes, a part of the norbornene was purified by column chromatography (dry SiO_2, Et_2O/hexanes = 1:10). ^1H NMR (500 MHz, $CDCl_3/CD_2Cl_2$): δ 1.24 (s), 1.42 (s), 1.43 (s), 1.35−1.39 (m), 1.45−1.50 (m), 1.83−1.94 (m), 1.50−1.64 (m), 1.68−1.82 (m), 1.94−2.01 (m), 2.01−2.10 (m), 2.97−3.02 (m), 3.19−3.25 (m), 3.22−3.37 (m), 3.37−3.41 (m), 6.09 (dd), 6.28 (dd), 6.18 (dd), 6.21 (dd), 6.96 (d), 7.01 (d), 7.08 (d), 7.19 (d), 7.32 (d), 7.39 (d), 7.47 (d), 7.80 (d), 8.25 (s), 8.28 (s), 13.62 (br s), 14.28 (br s). ^{13}C NMR (125 MHz, $CDCl_3/CD_2Cl_2$): δ 24.4, 29.3, 29.6, 29.5, 30.7, 31.6, 33.1, 33.3, 34.2, 35.0, 35.1, 41.9, 42.8, 43.5, 43.8, 46.1, 46.5, 46.9, 49.9, 72.4, 72.5, 86.7, 89.7, 112.2, 117.8, 118.6, 121.2, 121.7, 126.0, 127.1, 132.3, 132.6, 132.7, 133.4, 135.8, 136.6, 137.9, 138.4, 140.2, 150.5, 158.0, 161.3, 165.1, 166.2, 173.2. MS (ESI, %) *m*/*z*: 727.5 (100, $[M + 1]^+$), 525.4 (19). Anal. Calcd for $C_{40}H_{58}N_2O_4$: C, 79.30; H, 8.04; N, 3.85; O, 8.80. Found: C, 79.07; H, 8.06; N, 3.79; O, 8.86.

Mn−Salen−Norbornene, 9. Under an argon atmosphere, an in vacuo flame-dried, 100-mL, three-necked flask, equipped with a magnetic stir bar, a septum, an addition funnel, and a reflux condenser with gas inlet, was charged with 923 mg of $Mn(OAc)_2 \cdot 4H_2O$ (3.77 mmol, 3.0 equiv) and 15 mL of anhydrous ethanol. The white slurry was heated to reflux (90 °C, oil-bath temperature), and a solution of 913 mg of salen−norbornene (1.26 mmol, 1.0 equiv) in 15 mL of anhydrous toluene was filled into the addition funnel. The ligand solution was added dropwise to the manganese solution, and the addition funnel was washed with anhydrous ethanol (2 × 5 mL). The reaction mixture was heated under reflux for 2 h. Then a needle connected to an air cylinder was placed in the solution through the septum, air was slowly bubbled through the refluxing mixture, and the conversion of the ligand was monitored by the TLC analysis of the red solution. After 1 h, TLC analysis indicated a complete conversion of the free ligand. Then 160 mg of lithium chloride (3.77 mmol, 3.0 equiv) was added, and the mixture was allowed to cool to room temperature over a period of 1 h. The mixture was transferred into a separatory funnel, and the toluene layer was washed with H_2O (3 × 50 mL) and brine (50 mL) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, 1.93 g of crude product was obtained as a dark red oil. Purification by column chromatography (dry SiO_2, 4 × 30 cm^2, $CH_2Cl_2 \rightarrow CH_2Cl_2$/ethyl acetate = 5:1) yielded 813 mg of product (79%) as a dark red solid. MS (ESI, %) *m*/*z*: 779.35 (100, $[M - Cl]^+$). Anal. Calcd for $C_{40}H_{56}ClMnN_2O_3$: C, 70.71; H, 6.92; N, 3.44. Found: C, 70.34; H, 7.11; N, 3.37.

Poly(Mn−salen−norbornene), p(9) (Synthesis of a 50-mer). In an in vacuo flame-dried, 50-mL, three-necked flask equipped with a magnetic stir bar, a septum, and a reflux condenser with a gas inlet, 122 mg of Mn−salen−norbornene, **9** (150 μmol, 50 equiv), was dissolved in 3 mL of anhydrous $CDCl_3$, and the solution was heated to 40 °C. Grubbs catalyst (3°-generation) in the amount of 2.7 mg (3 μmol, 1 equiv) was added as a solid, and the mixture was stirred for 2.5 h at 40 °C. The polymerization was quenched by adding 3 drops of ethyl vinyl ether, and the polymer was precipitated by adding 30 mL of Et_2O. The polymer was separated by centrifugation and washed with Et_2O three times (the polymer was suspended in Et_2O and subsequently separated by centrifugation). After drying the residue in vacuo, 96 mg (79%) of an ether-insoluble polymer fraction was obtained as a dark red-brown powder. Anal. Calcd for $C_{40}H_{56}ClMnN_2O_3$: C, 70.71; H, 6.92; N, 3.44; O, 7.85. Found: C, 68.67; H, 7.02; N, 3.27; O, 9.09. ICP calcd: Mn, 6.74. Found: Mn, 5.00.

Poly(Mn−salen−norbornene-*co*-*n*-octylnorbornenecarbonyl Ester), p(9.11) (x/y = 1:1, x + y = 50). In an in vacuo flame-dried, 25-mL, three-necked flask under Ar, equipped with a magnetic stir bar, a septum, and a reflux condenser with a gas inlet, were dissolved 79 mg of Mn−salen−norbornene, **9** (94 μmol, 25 equiv), and 24 mg of *n*-octylnorbornenecarbonyl ester, **11** (94 μmol, 25 equiv), in 4 mL of anhydrous $CDCl_3$. Then 3.3 mg of Grubbs catalyst (3°-generation; 3.75 μmol, 1 equiv) was added as a solid, and the mixture was stirred at room temperature. After 20 min, TLC analysis as well as analysis of an aliquot by ^{1}H NMR spectroscopy indicated complete conversion of both monomers. The polymerization was quenched by adding 2 drops of ethyl vinyl ether, and the polymer was precipitated by adding 20 mL of Et_2O. After the separation of the solid by centrifugation and drying in vacuo, 82 mg (82%) of an ether-insoluble polymer fraction was obtained as a dark red-brown powder. Anal. Calcd for $[C_{40}H_{56}ClMnN_2O_3]_1[C_{16}H_{26}O_2]_9$: C, 72.13; H, 7.78; N, 2.63; O, 9.01; Cl, 3.33. Found: C, 71.10; H, 7.65; N, 2.64; O, 9.72; Cl, 2.26. ICP calcd: Mn, 5.15. Found: Mn, 4.68.

Typical Procedure for the Epoxidation of 1,2-Dihydronaphthalene, 14, with Poly(Mn−salen−norbornene), p(9). Under an argon atmosphere in a dry, 10-mL, Schlenk flask, 13 mg of poly(Mn−salen−norbornene), **p(9)** (16 μmol, 4 mol %), and 234 mg of NMO (2 mmol, 5.0 equiv) were dissolved in 2 mL of anhydrous CH_2Cl_2. Then 52 μL of 1,2-dihydronaphthalene, **14** (52 mg, 0.4 mmol, 1.0 equiv), and about 0.04 mL of chlorobenzene as an internal standard were added via a microsyringe, and the solution was cooled to −20 °C. *m*-CPBA in the amount of 138 mg (0.8 mmol, 2.0 equiv) was added in 3 equal portions at $t = 0$, 60, and 120 s. Aliquots (ca. 0.2 mL) were taken after 0, 30, 90, 150, 210, and 300 s. All aliquots were filtered through a pipet with cotton and some Al_2O_3, and the Al_2O_3 was flushed with about 1.5 mL of CH_2Cl_2. The resulting solutions were analyzed via GC-FID (HP-5). The aliquots at $t = 210$ s and $t = 300$ s were also analyzed by chiral GC-MS (β-CD).

Co−Salen−Norbornene, 10. In an in vacuo flame-dried, 10-mL, Schlenk flask under Ar, equipped with a magnetic stir bar and a septum, 146 mg of salen−norbornene (0.20 mmol, 1.0 equiv) was dissolved in 1.5 mL of anhydrous CH_2Cl_2. A solution of 60 mg of $Co(OAc)_2 \cdot 4H_2O$ (0.24 mmol, 1.1 equiv) in 2 mL of anhydrous MeOH was added dropwise via a syringe. The resulting red suspension was stirred for 30 min at room temperature, cooled in a ice bath, and stirred for another 30 min at 0 °C. The orange-red precipitate was separated by vacuum filtration, washed with cold MeOH, and dried in vacuo to yield 121 mg (77%) of **10** as an orange-red powder. MS (ESI, %) *m*/*z*: obsd, 783.3517 (±0.01; 100, $[M]^+$); calcd, 783.3572. Anal. Calcd for $C_{48}H_{56}CoN_2O_4$: C, 73.54; H, 7.20; N, 3.57; O, 7.52. Found: C, 73.33; H, 7.21; N, 3.49; O, 7.64. ICP calcd: Co, 7.52. Found: Co, 8.00.

Poly(Co(II)−salen−norbornene) p(10)′ (Synthesis of a 20-mer). In an in vacuo flame-dried, 25-mL, three-necked flask under Ar, equipped with a magnetic stir bar, a septum, and a gas inlet, 111 mg of Co(II)−salen−norbornene, **10** (151 μmol, 20 equiv), was dissolved in 10 mL of anhydrous $CDCl_3$. Then 6.7 mg of Grubbs catalyst (3° generation; 7.5 μmol, 1 equiv) was added as a solid, and the mixture was stirred at room temperature. After 2 h, analysis of an aliquot by ^{1}H NMR spectroscopy showed complete conversion of the monomer (absence of monomeric olefin peaks). The polymerization was quenched by adding 3 drops of ethyl vinyl ether, and the mixture was poured into 50 mL of cold Et_2O. The precipitated polymer was separated by centrifugation and washed with Et_2O (the polymer was suspended in Et_2O and subsequently separated by centrifugation). After drying the residue in vacuo, 105 mg (94%) of an ether-insoluble polymer fraction was obtained as a dark red powder. Anal. Calcd for $C_{48}H_{56}CoN_2O_4$: C, 73.54; H, 7.20; N, 3.57; O, 7.52. Found: C, 71.06; H, 7.06; N, 3.57; O, 8.16. ICP calcd: Co, 7.52. Found: Co, 6.96.

Poly(Co−salen−norbornene-*co*-*n*-octyl-norbornenecarbonyl Ester) p(10.11) (x/y = 1:1, x + y = 50). In an in vacuo flame-dried, 10-mL, Schlenk flask under Ar, equipped with a magnetic stir bar and a septum, 78 mg of Co−salen−norbornene, **10** (100 μmol, 25 equiv), and 25 mg of *n*-octylnorbornenecarbonyl ester, **11** (100 μmol, 25 equiv), were dissolved in 5 mL of anhydrous $CDCl_3$. Then 3.5 mg of Grubbs catalyst (3° generation; 4 μmol, 1 equiv) was added as a solid, and the mixture was stirred at room temperature. After 40 min, TLC analysis as well as an analysis of an aliquot by ^{1}H NMR spectroscopy indicated complete conversion of both monomers. The polymerization was quenched by adding 2 drops of ethyl vinyl ether. The solvent was removed under reduced pressure, the residue was redissolved in some CH_2Cl_2, and the polymer was precipitated by adding 40 mL of cold Et_2O. After the separation of the solid by centrifugation and drying in vacuo, 94 mg (91 mol %) of an ether-insoluble polymer fraction was obtained as a dark brown powder. Anal. Calcd for $[C_{48}H_{56}CoN_2O_4]_1[C_{16}H_{26}O_2]_1$: C, 75.11; H, 8.80; N, 7.82; O, 10.42. Found: C, 74.25; H, 8.73; N, 1.95; O, 11.15. ICP calcd: Co, 3.84. Found: Co, 3.95.

Typical Procedure for the HKR of Racemic Epichlorohydrin *rac*-18 with Poly(Co(III)(OTs)−salen−norbornene) p(10c). In a vial with a magnetic stir bar, 48.7 mg of poly(Co(III)(OTs)−salen−norbornene), **p(10c)** (50 μmol, 0.5 mol %) was dissolved in 100 μL of chlorobenzene (as an internal standard) and 784 μL of epichlorhydrin (10 mmol, 1.0 equiv). After taking an aliquot (2 μL), 126 μL of water (7 mmol, 0.7 equiv) was added. Aliquots (2 μL) were taken after 5, 10, 15, 20, 30, 60, 120, and 180 min. All aliquots were filtered through a pipet with cotton and some silica, and the silica was flushed with 1.5−2 mL Et_2O. The resulting solutions were analyzed via chiral GC-FID (γ-TA). After 3 h, the dark mixture was diluted with 2 mL of CH_2Cl_2 and added dropwise to cold Et_2O (ca. 40 mL). The resulting precipitate was separated by centrifugation, “washed” with cold Et_2O (the polymer was suspended in Et_2O and subsequently separated by centrifugation), and subsequently dried in vacuo.

Recycling and Reoxidation of the Cobalt Polymers. All polymeric Co complexes were separated from the reaction mixtures by precipitation into Et_2O and by subsequent centrifugation. The residue obtained after centrifugation was dissolved in CH_2Cl_2; 9.5 mg of *para*-toluenesulfonic acid monohydrate (50 μmol, 1.0 equiv according to Co) was added, and the mixture was stirred under an atmosphere of air for 1 h. The CH_2Cl_2 solution was added dropwise to cold Et_2O (ca. 40 mL), and the precipitate was separated by centrifugation and “washed” with cold Et_2O. The obtained residue was dried in vacuo to yield 45 mg (93%) of reoxidized **p(10c)_rec** as a dark green powder.

The polymeric catalysts could be recovered quantitatively. For example, for CoOAc−salen complex **p(10a)**, we started with 23 mg for the first catalytic cycle and obtained 24 mg after recycling and reoxidation in the second cycle and 24 mg for the third cycle. These data clearly prove that the polymer was recycled quantitatively.

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Supporting Information Available: Detailed experimental procedures and characterization data are described. This information is available free of charge via the Internet at http://pubs.acs.org.

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