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Polyolefin-Supported Recoverable/Reusable Cr(III)-Salen Catalysts

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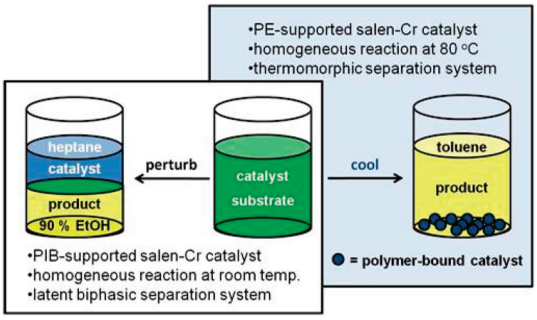

The design of functional soluble polyolefins for use as supports for salen ligands and metal complexes is described. Examples and applications that use both polyisobutylene (PIB)- and polyethylene (PE_{Olig})-bound recoverable/recyclable salen ligands/metal complexes are detailed. In the case of using PIB as a support, the polymer-bound complexes can be recovered through the use of latent biphasic or a thermomorphic mixed solvent systems. In the case of PE_{Olig}-supported complexes, the thermomorphic PE_{Olig}-bound salen species can be dissolved in "hot" solvents and quantitatively recovered as solids upon cooling to room temperature. Both the PIB- and PE_{Olig}-bound salen catalysts were shown to catalyze the ring-opening of epoxides with various nucleophiles. Both sorts of polyolefin-bound catalysts can be recycled and reused with no observed loss in activity. However, limitations of catalyst concentration make chiral versions of these complexes uncompetitive in comparison to conventional chiral salen catalysts that can be used in neat substrate at higher concentration to produce high enantioselectivity in the ring-opening products. The preparation of a PIB-bound "half-salen" catalyst was also briefly examined.

Introduction

Salen ligands and the transition metal complexes that they form are widely used in catalysis. They can be used in a variety of reactions to convert simple organic starting materials into useful products. Their use in ring-opening reactions of epoxides by nucleophiles is especially common,[1] and salen-catalyzed ring-openings are the basis of chemistry that has led to important new asymmetric syntheses. Similar epoxide opening chemistry is also the basis of new greener polymerization chemistry affording polycarbonates from carbon dioxide and epoxides.[2] The broad utility and effectiveness of salen ligands and chiral salen ligands is evidenced by their description in the literature as members of a class of "privileged" ligands.[3]

Because of the broad utility of salen transition metal complexes like **1** and **2** in catalysis, a variety of reactions and approaches for catalyst and ligand recovery have been explored.[4] Three general strategies to recover, reuse, or separate the catalyst and product have been used previously.

(1) (a) Gupta, K. C.; Sutar, A. K. *Coord. Chem. Rev.* **2008**, *252*, 1420–1450. (b) McGarrigle, E. M.; Gilheany, D. G. *Chem. Rev.* **2005**, *105*, 1563–1602. (c) Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Chem. Commun.* **2002**, 919–927.

(2) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410.

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(4) (a) Baleizao, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987–4043. (b) Holbach, M.; Weck, M. *J. Org. Chem.* **2005**, *71*, 1825–1836. (c) Angelino, M. D.; Laibinis, P. E. *Macromolecules* **1998**, *31*, 7581–7587. (d) Pozzi, G.; Shepperson, I. *Coord. Chem. Rev.* **2003**, *242*, 115–124. (e) Song, C. E.; Roh, E. J. *Chem. Commun.* **2000**, 837–838. (f) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345–3383. (g) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530–582. (h) Cavazzini, M.; Quici, S.; Pozzi, G. *Tetrahedron* **2002**, *58*, 3943–3949. (i) Yao, X.; Chen, H.; Lu, W.; Pan, G.; Hu, X.; Zheng, A. *Tetrahedron Lett.* **2000**, *41*, 10267–10271. (j) Dhal, P. K.; De, B. B.; Sivaram, S. *J. Mol. Catal. A: Chem.* **2001**, *177*, 71–87. (k) Madhavan, N.; Jones, C. W.; Weck, M. *Acc. Chem. Res.* **2008**, *41*, 1153–1165.

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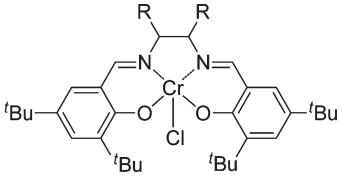
The first strategy uses a support that is insoluble before, during, and after the reaction.[4c] These approaches have typically used cross-linked polymer supports or inorganic solid supports. A second strategy is to use a biphasic system liquid/liquid system. Examples of this approach include the use of ionic liquid[4e] phase-immobilized catalysts and biphasic fluorous soluble supports.[4h] A third strategy has been to use soluble but phase-separable polymeric supports. This has involved polymers with pendant salen ligands or polymers that contain salen ligands that are repeating units in the polymer structure. The most successful examples of this strategy use salen complexes that are repeating units of the polymer backbone structure.[4k]



1: R = H, **2**: R = (*R*,*R*) -$CH_2(CH_2)_2CH_2$-

In the cases where achiral or chiral salen metal complexes are supported on soluble polymers, the salen ligands and catalysts are typically separated from products after a reaction as solids using solvent precipitation.[4] This is an effective way to separate a polymer from other materials but has the disadvantage that it requires relatively large amounts of solvent—a potential problem on any large-scale application of a supported catalyst. This paper describes the advantages and limitations of an alternative approach using polyolefin-bound salen ligands and salen metal complexes that phase separate from a single phase reaction either as a separable liquid phase or as solids. These soluble polymeric species enable the use of common organic solvents with either a thermomorphic or latent biphasic separation of a catalyst after a monophasic homogeneous reaction with minimal use of solvent. The results below show that this is an alternative and effective way to recover and reuse Cr-salen catalysts in epoxide ring-opening reactions. It is also a viable approach to immobilize catalysts for other salen metal complex mediated reactions. However, the use of these materials as effective asymmetric catalysts is frustrated by an inability to achieve sufficiently high catalyst concentrations.

Results and Discussion

Past work in our group has emphasized two general strategies for recycling catalysts that use soluble polymers as phase handles. The first of these strategies uses polymer supports that afford a monophasic mixture of solvents, substrate, and catalyst during a reaction with a subsequent polymer-facilitated liquid/liquid catalyst/ligand separation after the reaction is complete.[4f,g,5] The two general schemes that we have found most effective are shown in parts a and b of Figure 1a and either involve a thermomorphic phase separation where a polymer-bound catalyst and products separate into different density liquid phases after a change in temperature,[5a−d] or when a latent biphasic mixed solvent system is perturbed with small amounts of an additive to become a biphasic mixture.[5f,g] In either case, the catalyst and product are separable by a gravity-based separation.

The other general strategy we have developed is based on the thermomorphic solubility of polymers like polyethylene.[5h−k] In this case (Figure 1c), a terminally functionalized polyethylene oligomer or polymer is modified so that it can bind to a catalyst. Because polyethylene is completely insoluble in organic solvents at room temperature but soluble hot, such catalysts can be used in a heated solution as homogeneous catalysts but recovered on cooling by a solid/liquid separation. In this case, the product remains in solution while the catalyst self-separates as a solid.

To use the liquid/liquid separation strategies shown in Figure 1 in salen complex-catalyzed reactions requires an appropriate polymer-bound salen ligand. As described here, salen ligands **7** and **8** can be prepared by using a common intermediate **6** that was formed in a Friedel−Crafts alkylation, using the acid-catalyzed reaction of commercially available polyisobutylene oligomers containing terminal alkene groups[6] with 2-*tert*-butylphenol as shown in Scheme 1.[7] The product 4-polyisobutyl-2-*tert*-butylphenol was converted to a salicylaldehyde derivative by an acid-catalyzed alkylation and Cannizzaro reaction with use of paraformaldehyde. Subsequent imine formation then afforded both chiral and achiral salen ligands from suitable 1,2-diamines. These achiral and chiral ligands were then converted into metal complexes by using the same chemistry used in the syntheses of structurally similar low molecular weight salen metal complexes.[7,8]

Given the availability of the PIB-bound salicylaldehyde **6**, we briefly examined its use in the synthesis of other salen-like metal complexes. For example, the intermediate 3-*tert*-butyl-5-polyisobutylsalicylaldehyde formed in Scheme 1 was used to prepare a "half-salen" ligand **12** as shown in Scheme 2. This ligand, like the salen ligands **7** and **8**, could be metalated by using procedures like those used with low molecular weight analogues to form Cr complex **13**.[9]

Electrophilic substitution of phenol by vinyl-terminated polyisobutylene has the potential to be a general route to elaborated salen ligands too. This is shown by the chemistry in Scheme 3 where a 3-(piperindylmethyl)-5-polyisobutyl-salen ligand was prepared from 4-polyisobutylphenol via multiple acid-catalyzed formylations by using chemistry modeled after the chemistry reported by Kozlowski.[10]

(5) (a) Bergbreiter, D. E. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2351–2363. (b) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y.-S. *J. Am. Chem. Soc.* **1999**, *121*, 9531–9538. (c) Bergbreiter, D. E.; Osburn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058–9064. (d) Bergbreiter, D. E.; Osburn, P. L.; Frels, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 11105–11106. (e) Bergbreiter, D. E.; Osburn, P. L.; Smith, T. S.; Li, C.; Frels, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 6254–6260. (f) Bergbreiter, D. E.; Hughes, R.; Besinaiz, J.; Li, C.; Osburn, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 8244–8249. (g) Bergbreiter, D. E.; Blanton, J. R.; Chandran, R.; Hein, M. D.; Huang, K. J.; Treadwell, D. R.; Walker, S. A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4205–4206. (h) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1987**, *109*, 174–179. (i) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1985**, *107*, 4792–4793. (j) Bergbreiter, D. E.; Weatherford, D. A. *J. Org. Chem.* **1989**, *54*, 2726–2730. (k) Bergbreiter, D. E.; Walker, S. A. *J. Org. Chem.* **1989**, *54*, 5138–5141.

(6) BASF: http://daile.com.cn/BASF/Glissopal%20550%201000%201300%202300.pdf (accessed Dec 2010).

(7) Hongfa, C.; Tian, J.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975–977.

(8) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897–5898.

(9) Dossetter, A. G.; Jamison, T. F.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2398–2400.

(10) Fennie, M. W.; DiMauro, E. F.; O'Brien, E. M.; Annamalai, V.; Kozlowski, M. C. *Tetrahedron* **2005**, *61*, 6249–6265.

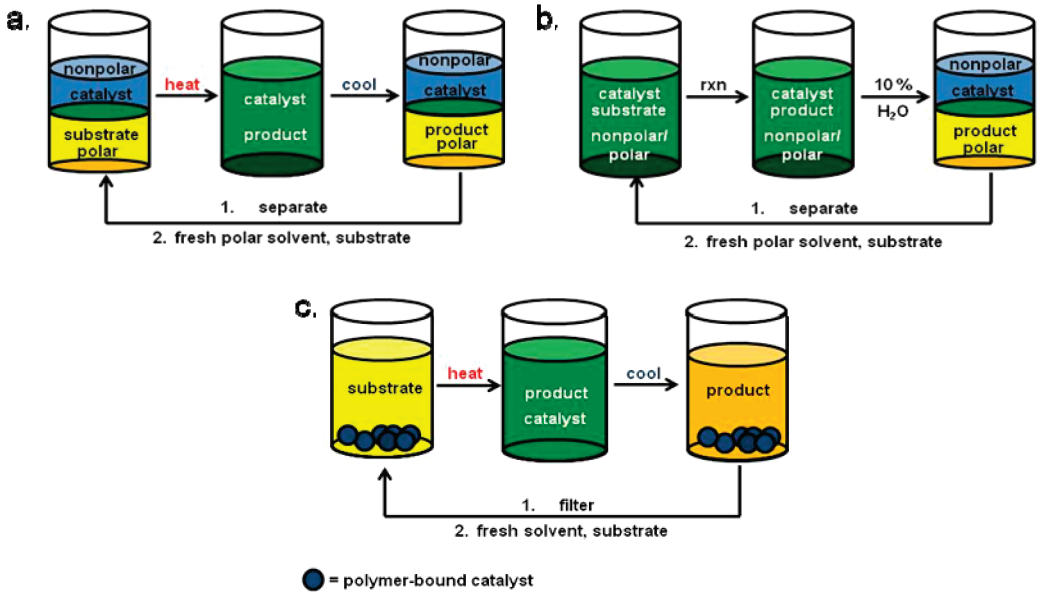
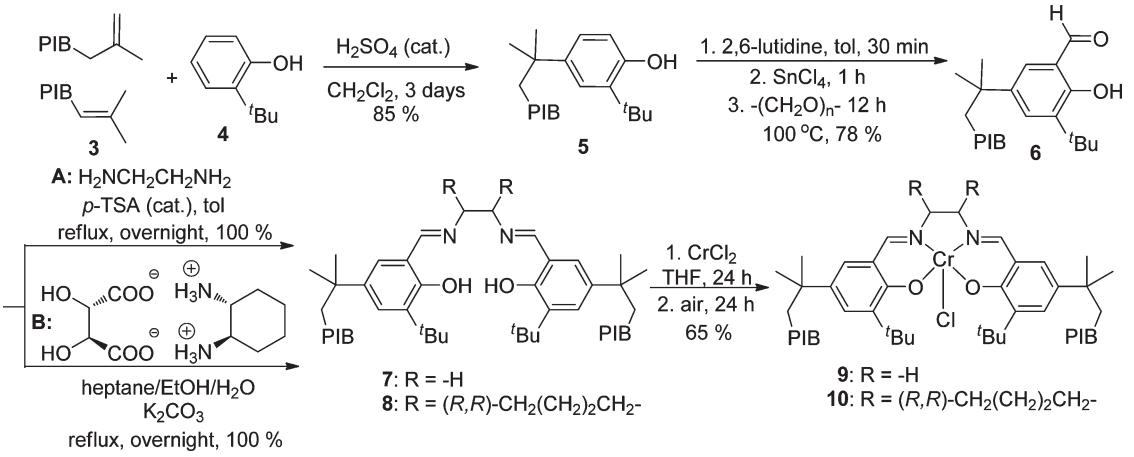
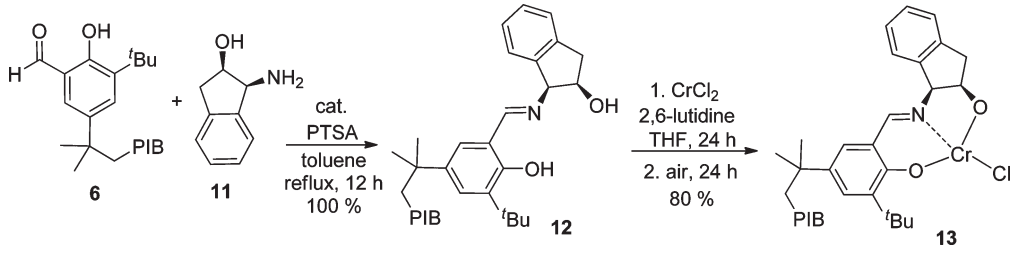


FIGURE 1. Strategies for separation of polyolefin-supported catalysts from products: (a) thermomorphic liquid/liquid separation, (b) latent biphasic liquid/liquid separation, and (c) thermomorphic solid/liquid separations.

SCHEME 1. Syntheses of PIB-Supported Salen Metal Complexes 9 and 10



SCHEME 2. Synthesis of a PIB-Supported Half-Salen Metal Complex 13

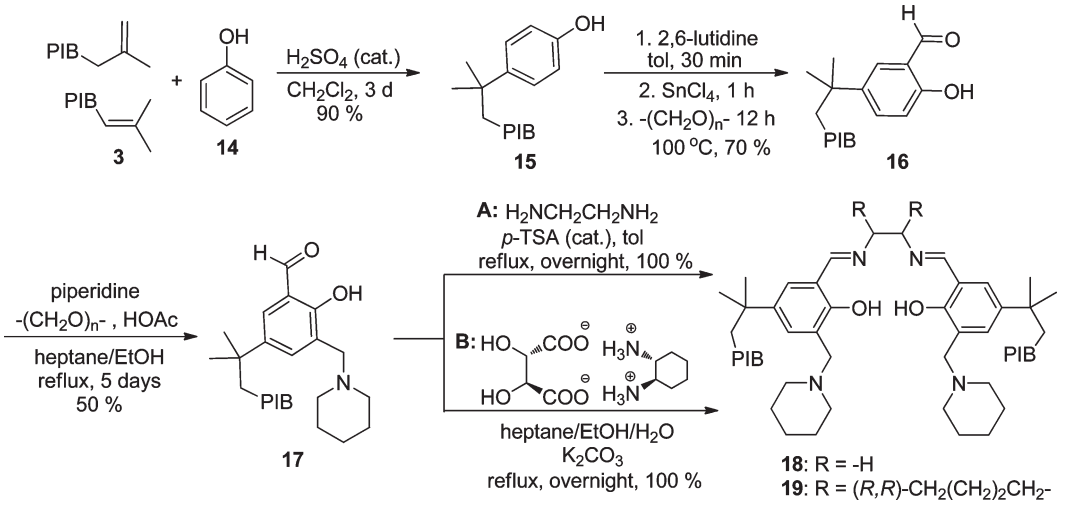


The second strategy for separation of polyolefin-bound catalysts and products is based on the thermomorphic properties of polymers like polyethylene that are soluble hot and insoluble cold. In this case, we prepared salen ligands and salen metal complexes using terminally functionalized thermomorphic polyethylene oligomers as supports. These studies stem from our prior successes with polyethylene oligomer (PE_{olig})-bound catalysts[5g−k] and were prompted by the success of a DuPont group that used commercially available terminally functionalized PE oligomers in the synthesis of PE_{Olig}-bound porphyrin and phthalocyanine metal complexes.[11]

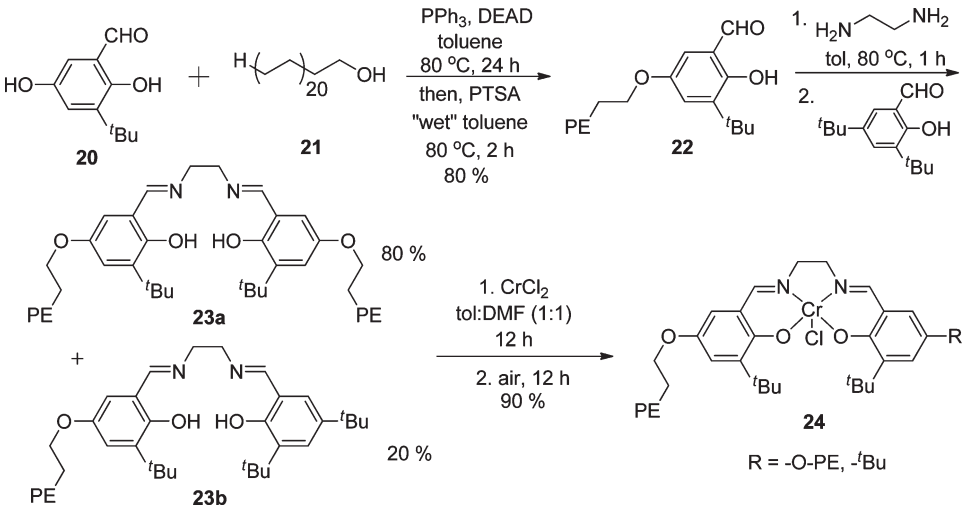
To prepare PE_{Olig}-bound salen ligands we used a regioselective Mitsunobu reaction of the less hindered hydroxyl group of 3-*tert*-butyl-5-hydroxysalicylaldehyde **20** with the

(11) Older, C. M.; Kristjansdottir, S.; Ritter, J. C.; Tam, W.; Grady, M. C. *Chem. Ind.* **2009**, *123*, 319–328.

SCHEME 3. Synthesis of 3-(Piperindylmethyl)-5-polyisobutyl-Salen Ligands



SCHEME 4. Synthesis of the PE_{Olig}-Bound Salen Metal Complex 24



terminal hydroxyl group of a commercially available hydroxyl-terminated polyethylene oligomer[12] to prepare the salen ligand precursor **22**. In these cases, the conditions for diimine formation that we used to form **7** from the PIB-substituted salicylaldehyde **6** led to formation of the diimine **23a** contaminated with 5−10% of the monoimine resulting from incomplete imine formation from the diamine. Quantitative formation of **23a** from a diamine was possible by using 10 mol % excess of the PE_{Olig}-bound salicylaldehyde. However, in this case, we could not easily separate the unreacted salicylaldehyde **22** from **23a**. Any mixtures of mono- and diimines occasionally seen in syntheses of a PIB-bound species could be separated by chromatography because of the high solubility of the PIB support. Chromatographic separation is not possible with polyethylene oligomeric ligands as the insolubility of the PE oligomers at room temperature makes chromatographic separation of these two products impractical. To obtain PE_{Olig}-bound product free of the salicylaldehyde or monoimine impurity we chose to use a slight excess of the diamine and to convert the 9:1 mixture of di- and monoimines that formed into a phase separable PE_{Olig}-bound salen ligand by reaction of the mixture of di- and monoimines with excess 3,5-di-*tert*-butylsalicylaldehyde. This in effect produces a more polydisperse but equally thermomorphic PE_{Olig}-bound salen ligand **23** as a mixture of **23a** and **23b**. Metalation of this product mixture in the DMF-toluene mixture used in metalation of PE_{Olig}-bound porphyrins and phthlalocyanines[11] then afforded a PE_{Olig}-bound salen-Cr complex **24** (Scheme 4), which was isolated as a dark brown solid.

The properties of polyolefins like polyisobutylene and polyethylene both have advantages and impose some limitations in these syntheses. First, PIB's solubility makes it feasible to separate PIB-containing intermediates from more polar low molecular weight starting materials or byproducts by a simple solvent extraction. This makes it possible to use excess reagents in ligand syntheses and to separate unreacted reagents from the PIB products by an extraction without a chromatographic separation. Likewise, PE_{Olig}-bound species separate from excess reagents as a solid. Second, both the

(12) Baker Hughes: http://www.bakerhughes.com/assets/media/technicaldatasheets/ 4c97b890fa7e1c37f100001b/file/28730_unilin-alcohol-sheet-2-5-10.pdf.pdf&fs=288204 (accessed Dec 2010).

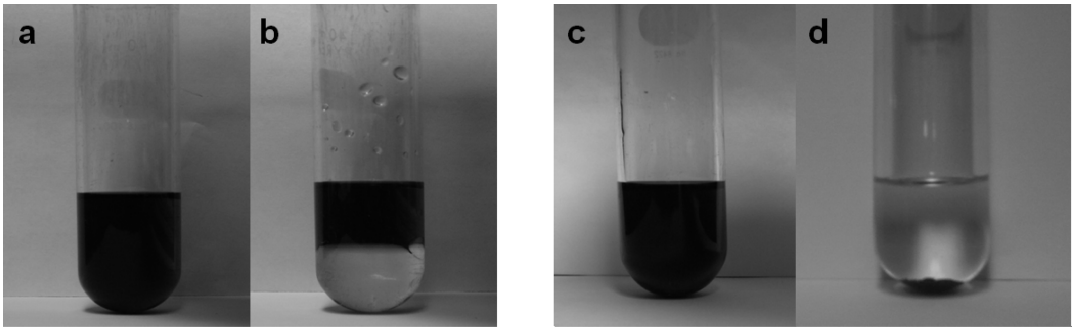


FIGURE 2. Thermomorphic phase separation of polyolefin-supported salen metal complexes: (a) complex **9** in a miscible mixture of heptane and ethanol, (b) complex **9** separated into the heptane-rich phase after the addition of 10 vol % water perturbed this miscible solvent mixture, (c) a monophasic solution of complex **24** in toluene at 80 °C, and (d) the biphasic mixture of toluene and of the PE_{Olig}-bound salen complex **24** formed after cooling to room temperature and centrifugation.

PIB- and PE_{Olig}-bound intermediates can be readily analyzed by solution-state NMR spectroscopy.[5g−k,7,11,13] However, there are also limitations associated with the use of polyolefin supports. For example, neither the PIB nor the PE supports can be used in a polar solvent like ethanol to form the salen ligands from a 1,2-diamine and the salicylaldehyde precursor because of their insolubility in ethanol. Instead, mixed solvent systems (e.g., heptane−ethanol) must be used. Finally, as was true in the synthesis of salen ligands from PE oligomers, it can be difficult to separate polymer-bound byproduct from the desired polymer product. This is not a problem in Schemes 1 or 2 where derivatives of the very soluble PIB support can often be separated from one another by column chromatography and methods to address this problem for thermomorphic PE oligomer supports can be devised as described above. Nonetheless, byproduct separation remains a possible limitation for syntheses of other polyolefin-bound ligands.

As noted above, polyolefin supports like PIB and PE have precedent in separation, recovery, and reuse of a variety of catalysts.[4f,g] Past work has shown that PIB is effective at making the Ru alkylidene complexes phase selectively soluble in the heptane phase of biphasic mixtures of heptane and polar organic solvents to facilitate recovery, separation, and reuse of ring-closing metathesis catalysts.[14] PIB was equally effective in effecting phase separation of salen complexes like **9** or **10**. This is visually apparent by comparison of the photographs in Figure 2a,b. In this example, a highly colored single phase mixture of absolute ethanol and heptane containing **9** (Figure 2a) is perturbed into a biphasic solvent mixture (Figure 2b) by the addition of 10 vol % water. Similar efficiency in phase separation of these PIB salen complexes was also achieved by using **9** in a thermomorphic mixture of heptane and *N*,*N*′-dimethylformamide (DMF). When a mixture of heptane and DMF was used, the PIB-bound salen complex **9** was soluble in a hot miscible mixture of these solvents at 80 °C. This solution was monophasic and deeply colored like that in Figure 2a. However, in the case of this DMF/heptane mixture, cooling this deeply colored monophasic solution produced a biphasic liquid/liquid mixture with the salen complex **9** separating into the less dense heptane-rich phase. The extent of phase separation was evaluated by UV−visible spectroscopy. On the basis of the absorbance of **9** at 350 nm, $<0.1\%$ of the salen complex remained in the polar DMF-rich phase after this thermomorphic liquid/liquid separation.

PE is also effective at thermomorphic phase separation of the salen complex **24**. In this case, the PE_{Olig}-salen complex of Cr forms a dark brown solution on heating to 70 °C. Cooling this solution produces a water white supernatant and a dark brown PE solid, chemistry that is analogous to that reported by a DuPont group that used similar ligands to thermomorphically separate highly colored PE_{Olig}-bound Co complexes of porphyrins and phthalocyanines from solution on cooling.[11]

The penultimate test of the utility of these salen ligands is the ability of their metal complexes to effect reactions that their low molecular weight analogues promote. In preliminary experiments reported previously, we noted that the achiral catalyst **9** is as competent as its low molecular weight analogue in the polymerization of cyclohexene oxide and CO_2.[7] These studies showed that **9** is kinetically very similar to a low molecular weight Cr salen catalyst that had a *tert*-butyl group in the 5 position (versus the 5-polyisobutyl group in **9**) in CO_2−epoxide polymerization. The fact that this PIB-bound salen species was also readily separated from the catalyst and that the polycarbonate product was isolated with low Cr-contamination (so long as an acid workup that decomposes the Cr-salen complex was avoided) suggested that polyolefin-bound salen complexes **9**, **10**, **13**, and **24** should be similarly useful as recyclable separable catalysts in a variety of ring-opening reactions of low molecular weight epoxides or in other salen complex-mediated catalysis. This is indeed the case though catalyst concentration imposes some limitations on this chemistry as noted below.

Our initial studies focused on the utility of the achiral complex **9** as a recyclable catalyst for the ring-opening of epoxides with various thiolphenols (eqs 1 and 2).[15] These studies employed a heptane/ethanol solvent mixture and latent biphasic conditions for recovery and recycling of **9** in a liquid/liquid separation/recovery system. In this chemistry, we used a miscible mixture of heptane and ethanol which dissolved both catalyst **9** and the epoxide and thiophenol reactants. Ring-opening reactions of epoxides shown in eqs 1

(13) Li, J.; Sung, S.; Tian, J.; Bergbreiter, D. E. *Tetrahedron* **2005**, *61*, 12081–1209.

(14) (a) Hongfa, C. H.; Tian, J.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2007**, *9*, 3259–3261. (b) Hongfa, C. H.; Su, H.-L.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2009**, *11*, 665–667.

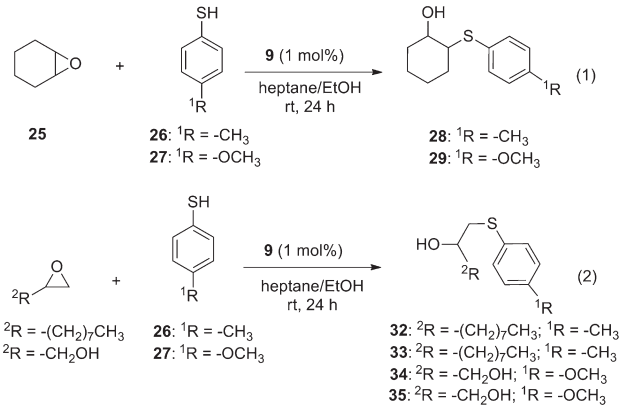
(15) Wu, M. H.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 5252–5254.

TABLE 1. Ring-Opening of Epoxides with Thiols Catalyzed by 9[a]

		yield (%)[b]				
entry	product	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5
1	**28**	76	84	84	95	96
2	**29**	94	90	99	99	
3	**32**	77	76	99	99	
4	**33**	34	42	81	93	99
5	**34**	58	55	88	78	99
6	**35**	73	70	84	98	99

[a]The reactions were conducted with 2 mmol of epoxide, 2 mmol of thiol, and 0.02 mmol of **9** in a mixture of 3 mL of heptane and 3 mL of absolute ethanol. The reaction mixture was stirred under N_2 at room temperature for 24 h. Recycling involved removal of the polar phase and addition of fresh ethanol and substrates to heptane phase. [b]The yield is based on mass of isolated product.

and 2 were carried out with three different epoxides and two different aromatic thiols. The results in Table 1 show that the PIB-bound catalyst **9** was as effective as an electronically analogous low molecular weight catalyst in this chemistry and that catalyst recycling and separation from product was feasible. In these recycling experiments, phase separation and catalyst recovery was achieved by the addition of 10 vol % water to the homogeneous reaction mixture after the reaction was complete. This added water produced a biphasic heptane/aqueous ethanol mixture. Gravity filtration of the less dense catalyst-containing nonpolar phase afforded a recyclable solution of the catalyst. The products of the reactions were isolated by removal of the solvent and characterized by ^1H and ^{13}C NMR spectroscopy and were >95% pure without the need for any chromatographic separation of catalyst residues.



Reuse of the catalyst **9** was affected by simply adding fresh ethanol and substrates to the recovered heptane-rich phase. The PIB-supported catalyst could be recycled through at least 4 cycles with no observed loss in catalytic activity. The extent of catalyst leaching was also tested using inductively coupled plasma mass spectroscopy (ICP-MS) analysis of the product phase. This analysis showed that products from the reaction between glycidol and 4-methylthiophenol showed only 0.26% chromium loss per cycle.

We briefly examined the rate of conversion of epoxide to product using this PIB-bound salen complex. These studies used similar concentrations of catalyst **1** and **9** and compared both **1** vs **9** and cycles 2 and 3 for the ring-opening of **31** by the thiol **26**. In these studies, the k_{obs} for reaction using the same

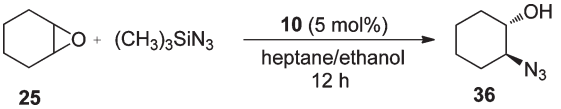
TABLE 2. ARO of Cyclohexene Oxide with Azidotrimethylsilane Catalyzed by 10[a]

entry	cycle	yield (%)[b]	ee (%)[c]
1	1	42	10
2	2	54	13
3	3	70	22
4	4	79	14
5	5	90	12
6	6	95	15

[a]Reaction conditions: 5 mol % of catalyst, 7.08 mmol of cyclohexene oxide, and 7.78 mmol of azidotrimethylsilane stirred under N_2 for 12 h in 5 mL of heptane and 5 mL of ethanol. Recycling involved removal of the polar phase and the addition of fresh ethanol and substrates to the heptane phase. [b]The yield is an isolated yield of pure product after removal of solvent under reduced pressure. [c]The % ee was determined by chiral HPLC analysis (ChiralCel OD column, hexanes/isopropanol (8:2)).

concentration of a low molecular weight catalyst was twice as large as the k_{obs} for either cycles 2 and 3 of the reaction using the PIB-supported catalyst **9**. There was no change in k_{obs} in cycles 2 and 3 for this ring-opening reaction using the PIB-supported catalyst **9** supporting the premise that this catalyst was recoverable and reusable.

After the discovery that **9** could be used as a recyclable catalyst for the ring-opening of epoxides with thiols, we examined the use of complex **10** (Scheme 1) as a catalyst for the asymmetric ring-opening (ARO) of epoxides.[8] We first tested the use of **10** as a catalyst for reaction of cyclohexene oxide and azidotrimethylsilane (eq 3). As expected based on the success of **9** in epoxide-thiol reactions (vide supra), complex **10** was able to catalyze the opening of epoxide **25** to afford azido alcohol **36**. The PIB-supported catalyst **10** was successfully recycled six times with use of latent biphasic conditions to recover the catalyst as shown in Table 2.

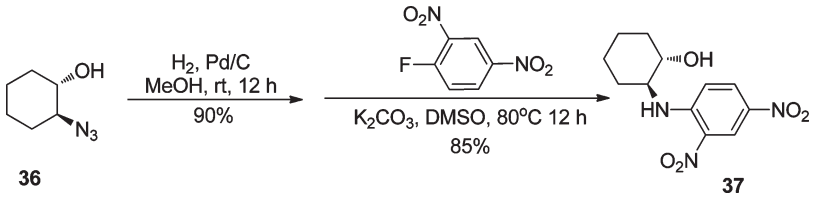


However, while **10** proved to be a recyclable catalyst, it was unfortunately not a very stereoselective catalyst, based on chiral HPLC analysis of a derivative of **37** formed as shown in Scheme 5.[16] In these cases, analyses of the reaction's enantioselectivity based on chiral HPLC analysis of products after reduction and arylation of **36** showed very low enantioselectivity as noted in Table 2.

The low enantioselectivity for reaction 3 can be explained by the low concentration of catalyst **10** in the reaction system. Jacobsen and co-workers have reported the best enantioselectivities for these Cr-salen catalyzed reactions are obtained under solvent-free conditions using neat substrate where catalyst concentrations are ca. 0.20 M.[8,16,17] In the case of the PIB-bound catalyst **10**, the insolubility of **10** in substrate required that a solvent be used. Thus, concentrations of **10** in these heptane−ethanol solutions were almost a factor of 10 lower (0.03 M). Control experiments suggest that the lower enantioselectivity seen with **10** is mainly due to this

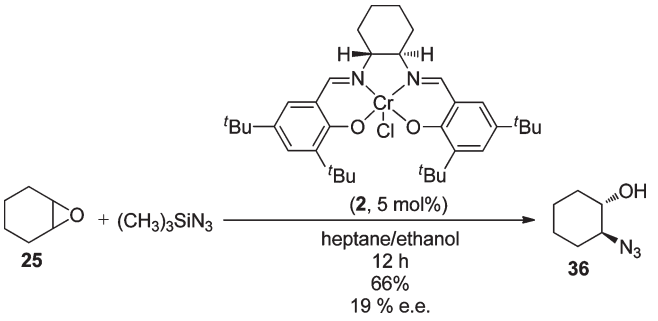
(16) Shaus, S. E.; Larrow, J. F.; Jacobsen, E. N. *J. Org. Chem.* **1997**, *62*, 4197–4199.
(17) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 10924–10925.

SCHEME 5. Reaction of 36 and 1-Fluoro-2,4-dinitrobenzene To Form 37



36 37

SCHEME 6. ARO of 25 with Azidotrimethylsilane Using Catalyst 2



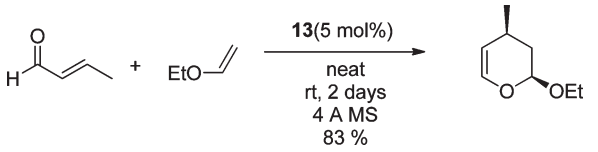
25 36

lowered catalyst concentration as opposed to the presence of the PIB oligomer. Two control experiments with Jacobsen's catalyst **2** were performed. First, when the low molecular weight catalyst **2** was used in place of **10** in reaction 3 at 0.032 M, the enantioselectivity of the reaction was 19%. The 19% ee seen in Scheme 6 with 0.032 M **2** as a catalyst is very close to the average 14% ee reported in Table 2. A second experiment examined the reaction of cyclohexene oxide with azidotrimethylsilane catalyzed by 5 mol % of **2** in methylene chloride. When **2** was present at 0.035 M, ring-opened product was obtained with 33% ee. While these results suggest a slight solvent effect, these control experiments suggest that the diminished enantioselectivity seen with **10** is in large part due to the lower catalyst concentration. Catalyst concentration affects selectivity because of the importance of the bimolecular reaction mechanism proposed by Jacobsen.[17]

Given the success of the polyolefin-bound salen complexes in epoxide ring-opening reactions, we also briefly studied the use of a PIB-bound "half-salen"[9] Cr complex as a catalyst for other reactions. Low molecular weight analogues of **13** have previously been used as catalysts for carbonyl-ene reactions,[18] Diels–Alder reactions,[19] inverse electron demand Diels–Alder reactions,[20] and hetero-Diels–Alder reactions.[9] We set out to investigate the activity of **13** by attempting to catalyze the reaction of crotonaldehyde and ethyl vinyl ether (Scheme 7).

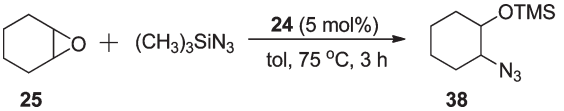
In this study, the PIB-bound catalyst **13** was dissolved in ethyl vinyl ether and crotonaldehyde was added to the solution and the reaction mixture was allowed to stir for 2 days. Separation was effected by the removal of solvent and the addition of heptane and acetonitrile to the reaction flask. This produced a biphasic mixture with the polymer-bound

SCHEME 7. Hetero-Diels–Alder Reaction of Crotonaldehyde and Ethyl Vinyl Ether Catalyzed by 13



catalyst in the heptane-rich phase and the product in the polar acetonitrile-rich phase. Even though preliminary trials of this catalytic system seemed promising (83% yield), recycling of the polymer-bound catalyst was not feasible. Diminished yields of the product (ca. 25%) were seen in cycle 2. In this case, ^{1}H NMR analysis showed that the reason for these diminished yields was decomposition of the catalyst due to the 4 Å MS present in the reaction mixture. Because of this, further investigations of this system were not continued.

We also explored the use of the thermomorphic polyethylene-supported Cr-salen complex **24** as a recyclable catalyst for the ring-opening of cyclohexene oxide with azidotrimethylsilane (eq 4). This chemistry involved the use of thermomorphic solubility of polyethylene and a solid/liquid separation (Figure 1c) to separate the PE_{Olig}-bound catalyst **24** from product. In the event, we first dissolved 5 mol % of **24** in 3 mL of toluene at 75 °C under N_2. After a homogeneous solution was obtained, cyclohexene oxide and azidotrimethylsilane were sequentially added to the reaction flask with a syringe. The reaction mixture was then stirred 3 h under N_2 at 75 °C. Workup and catalyst separation and recovery was then accomplished by simply cooling the reaction mixture to room temperature. Phase separation of solvent containing the product and polymer-bound catalyst was visually apparent. At this point an additional 5 mL of toluene was added and the supernatant solution containing the product was separated from the PE_{Olig}-bound **24**. To ensure quantitative recovery of the product, this isolation procedure was repeated twice. Recycling of the solid catalyst was achieved by then dissolving the recovered solid **24** in 3 mL of fresh toluene at 75 °C and treating this solution with fresh substrate.



(4)

25 38

As can be seen in Table 3, complex **24** was very successful as a recyclable separable catalyst in this ring-opening reaction. The efficiency of catalyst **24** is shown by the recycling data in Table 3. PE_{Olig}-supported catalyst **24** could be recycled six times with no loss in catalytic activity. The effectiveness of this process in minimizing catalyst leaching was also tested by using inductively coupled plasma mass spectroscopy (ICP-MS) analysis.

(18) Grachan, M. L.; Tudge, M. T.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2008**, *47*, 1469–1472.
(19) Jarvo, E. R.; Lawrence, B. M.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 6043–6046.
(20) Gademan, K.; Chavez, D. E.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3059–3061.

TABLE 3. Ring-Opening of Cyclohexene Oxide with Azidotrimethylsilane Catalyzed by 24[a]

entry	cycle	yield (%)[b]
1	1	88
2	2	90
3	3	100
4	4	100
5	5	100
6	6	100

[a]Reaction conditions: 5 mol % of catalyst, 0.95 mmol of cyclohexene oxide, and 1 mmol of azidotrimethylsilane were stirred under N_2 for 3 h in 3 mL of toluene at 75 °C. Recycling involved cooling the reaction mixture to room temperature and separating the solid **24** from the toluene solution of the product by centrifugation. [b]These yields are isolated yields of spectroscopically pure products obtained after removal of the toluene solvent under reduced pressure.

The analysis showed that for the reaction in Table 3, metal leaching was found to be ca. 0.3%.

Conclusion

We have shown that recovery and recycling of salen ligands and their metal complexes can be facilitated with the use of soluble polyolefin oligomers as phase anchors for such ligands/catalysts. Using PIB-bound salen-Cr complexes, we have shown that ring-opening of various epoxides with thiols and an azide source can be facilitated and the catalyst can be recycled with minimal metal leaching. However, applications of this chemistry to asymmetric catalysis are limited by the low enantioselectivity achieved because of the polyolefin catalyst's concentration. Other PIB-bound salen ligands as well as a "half-salen" catalyst were also prepared. The latter "half-salen" catalyst effectively catalyzed a hetero-Diels−Alder reaction but could not be recycled because of the instability of the ligand to the reaction conditions. The preparation of a PE_{Olig}-bound salen ligand was also achieved by using a regioselective Mitsunobu reaction and the products were converted into a PE_{Olig}-bound salen-Cr(III) complex. This complex was used as a soluble thermomorphic catalyst in the ring-opening of cyclohexene oxide with azidotrimethylsilane at 75 °C and was recycled six times with no loss in catalytic activity.

Experimental Section

Vinyl-terminated PIB oligomers (Glissopal 1000 and 1300) with M_n values of 1000 or 1300 Da and hydroxyl-terminated PE oligomers (Unilin 550) with a nominal M_n of 550 are commercial products and were obtained from BASF and Baker-Hughes, respectively.[6,12] All other reagents were purchased from commercial sources and used without further purification unless otherwise stated. ^{1}H NMR spectra were recorded on an 500 MHz spectrometer operating at 499.95 MHz or on a 300 MHz spectrometer operating at 299.91 MHz. ^{13}C NMR spectra were recorded on an 500 MHz spectrometer operating at 125.72 MHz or on a 300 MHz spectrometer operating at 75.41 MHz. NMR spectra in the case of PE_{Olig}-bound substrates were obtained at 70 °C. ^{13}C NMR spectra for PE_{Olig}-bound substrates were obtained at concentrations of 10 mg/mL. Concentrations higher than this resulted in poorer S/N ratios. Chemical shifts were reported in parts per million (δ) relative to residual proton resonances in deuterated chloroform ($CDCl_3$), deuterated benzene (C_6D_6), or deuterated methanol (CD_3OH). Coupling constants (J values) were reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), and m (multiplet). High-resolution MS data were collected from a MALDI/TOF mass spectrometer with 2,4,6-trihydroxyacetophenone (THAP) as matrix.

Analysis of Cr(III) Loading on Polymer-Bound Catalysts. Cr(III) loading of the polymer-bound species was determined by UV−visible analysis of solutions of the polymer-bound complexes. First, a UV−visible spectrum was obtained for a low molecular weight catalyst at varying concentrations. These data were used in a Beer's law plot to obtain a value for an extinction coefficient for the low molecular weight complex. The UV−visible spectrum of the polymer-bound complex was then measured and this extinction coefficient was used to determine Cr(III)-salen loading.

2-*tert*-Butyl-4-polyisobutylphenol (5). To a 500-mL round-bottomed flask equipped with a stir bar and rubber septum were added **3** (15 g, 100 mmol), **4** (8.9 g, 8.9 mmol) in CH_2Cl_2 (200 mL), and concd H_2SO_4 (1.05 g, 10.7 mmol). The mixture was then stirred under N_2 for 3 days at room temperature. At this point, the solvent was removed under reduced pressure and 250 mL of hexanes was added to the viscous oil. The hexanes solution was washed with 3 150-mL portions of *N*,*N*-dimethylformamide and 3 150-mL portions of 90% ethanol/water. The organic phase was dried over Na_2SO_4 and filtered and solvent was removed under reduced pressure to give 8.27 g of **5** as a viscous, light yellow oil, in 85% yield. Spectroscopic analyses were identical with those previously reported.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (s, 1H), 7.05 (m, 1H), 6.6 (d, J = 7.75 Hz, 1H), 1.8 (s, 2H), and 0.8−1.6 (m, 140H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 142.1, 135.0, 125.4, 124.5, 115.9, multiple poorly resolved peaks between 58−60 and 22−39.

3-*tert*-Butyl-5-polyisobutylsalicylaldehyde (6). To a 100-mL round-bottomed flask equipped with a stir bar, rubber septum, and a water-jacketed reflux condenser were added **5** (3.42 g, 3.13 mmol) and 2,6-lutidine (0.58 g, 5 mmol) in 40 mL of toluene. The mixture was stirred at room temperature for 30 min. At this time, $SnCl_4$ (0.15 mL, 1.25 mmol), in 10 mL of toluene, was added dropwise with a syringe. The reaction mixture was then stirred at room temperature for 1 h. At this point, paraformaldehyde (0.56 g, 18.78 mmol) was added to the flask. The reaction mixture was then placed on an oil bath at 100 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature and acidified to pH 2 with 2 M HCl. The organic phase was isolated and solvent was removed under reduced pressure. Addition of 250 mL of hexanes to the viscous oil, washing successively with 3 150-mL portions of *N*,*N*-dimethylformamide and 3 150-mL portions of 90% ethanol/water produced a hexanes phase containing the product **6** that was then dried over Na_2SO_4 and filtered then the solvent was removed under reduced pressure to yield 2.8 g of **6** as a viscous, yellow oil in 76% yield. Spectroscopic analyses were identical with those previously reported.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.62 (s, 1H), 9.9 (s, 1H), 7.57 (s, 1H), 7.32 (s, 1H), 1.8 (s, 2H), and 0.8−1.6 (m, 140H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 159.3, 140. 9, 137.4, 133.2, 128.7, 120.2, multiple poorly resolved peaks between 58 and 60 and 22−39.

***N*,*N*′-Bis(3-*tert*-butyl-5-polyisobutylsalicylidene)-1,2-ethylenediimine (7).** To a 50-mL round-bottomed flask was added **6** (3.0 g, 2.6 mmol), ethylenediamine (0.08 g, 1.3 mmol), and a catalytic amount of PTSA in 30 mL of toluene. The reaction mixture was stirred at reflux overnight with a Dean−Stark trap. The solvent was removed under reduced pressure and then 150 mL of hexanes was added to the viscous residue. The hexane solution was washed with 3 100-mL portions of *N*,*N*-dimethylformamide, then 3 100-mL portions of 90% ethanol/water, dried over Na_2SO_4, and filtered, then the hexane was removed under reduced pressure to give a quantitative yield of 6.1 g of **7** as a viscous yellow oil . Spectroscopic analyses were identical with those previously reported.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 2H), 7.40 (s, 1H), 7.05 (s, 1H), 3.95 (s, 4H), 1.8 (s, 4H), and 0.8−1.6 (m, 280H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 158.2, 139.8, 136.5, 128.4, 127.7, 118.2, multiple poorly resolved peaks between 58 and 60 and 22−39.

(*R*,*R*)-*N*,*N*′-Bis(3-*tert*-butyl-5-polyisobutylsalicylidene)-1,2-cyclohexanediimine (8). To a 50-mL round-bottomed flask equipped with a water-jacketed reflux condenser and a 10-mL addition funnel was added the L-tartrate salt of cyclohexenediamine (0.265 g, 1 mmol), K_2CO_3 (1.66 g, 2 mmol), and 3 mL of water. Then 11 mL of absolute ethanol was added and the suspension was heated to reflux and became homogeneous. Then **6** (2.965 g, 2 mmol) in 5.5 mL of heptane was added dropwise with an addition funnel. The yellow reaction mixture was allowed to stir at reflux for 12 h under N_2. At this point, the reaction mixture was cooled to room temperature and 100 mL of hexanes was added. The organic phase was washed with 3 50-mL portions of 90% ethanol/water, dried over Na_2SO_4, and filtered, then the solvent was removed under reduced pressure to afford a quantitative yield (2.73 g) of **8** as a viscous yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.29 (s, 2H), 6.94 (s, 2H), 3.37−3.30 (m, 2H), 1.8−0.8 (m, 380H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 156.9, 137.8, 134.9, 126.9, 125.7, 116.8, multiple poorly resolved peaks were present between 57 and 60 and 20−40.

***N*,*N*′-Bis(3-*tert*-butyl-5-polyisobutylsalicylidene)-1,2-ethylenediimino-Cr(III) Chloride (9).** To a 50-mL round-bottomed flask equipped with a stir bar and rubber septum were added **7** (6.62 g, 2.78 mmol) and $CrCl_2$ (0.374 g, 3.05 mmol) in 30 mL of THF. The mixture was then stirred under N_2 at room temperature for 24 h then stirred under air for 24 h. The solvent was removed under reduced pressure and then a 150-mL portion of hexanes was added to the viscous residue. The hexane solution was washed with a solution of 3 100-mL portions of a saturated aqueous solution of NH_4Cl and with 3 100-mL portions of a saturated aqueous solution of NaCl, dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure to give 4.30 g of **7** as a dark-brown, viscous residue in 65% yield. IR (neat, cm^{-1}) 1625, 1535, 1467, 1394, 1364, and 1235. UV−visible spectroscopy (THF, λ_{max} = 350 nm). Separate experiments with **1** in THF showed it had a λ_{max} of 350 nm with ε = 4514 M^{-1} cm^{-1}) and this extinction coefficient was used to calculate the Cr(III) loading of **9**.

(*R*,*R*)-*N*,*N*′-Bis(3-*tert*-butyl-5-polyisobutylsalicylidene)-1,2-cyclohexanediimine-Cr(III) Chloride (10). Complex **10** was prepared by using the same procedure used to prepare **9**.

General Procedure for Epoxide Ring-Opening Reactions with Thiols. To a 25-mL, round-bottomed flask equipped with a magnetic stirbar and rubber septum were added epoxide (2 mmol), thiol (2 mmol), **9** (0.05 g, 0.02 mmol), heptane (3 mL), and EtOH (3 mL). The reaction mixture was placed under N_2 and allowed to stir for 24 h. At this point, approximately 0.3 mL of water was added to the reaction mixture to induce phase separation to form a biphasic mixture. The phases were allowed to separate and the polar phase was removed, dried over Na_2SO_4, and filtered, then the solvent was removed under reduced pressure.

28:[21a] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (d, J = 7.83 Hz, 2H), 7.1 (d, J = 7.83 Hz, 2H), 3.3 (m, 1H), 2.7 (m, 1H), 2.37 (s, 3H), 2.1 (m, 2H), 1.7 (m, 2H), and 1.3 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 134.8, 13.00, 128.0, 72.0, 56.8, 34.0, 32.7, 26.4, 24.5, and 21.4.

29:[21b] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.82 Hz, 2H), 6.85 (d, J = 8.82 Hz, 2H), 3.8 (s, 3H), 3.23 (m, 1H), 2.6 (m, 1H), 2.1 (m, 2H), 1.75 (m, 2H), and 1.25 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 137.3, 122.0, 114.7, 71.6, 57, 55.6, 33.9, 32.5, 26.4, and 24.5.

32:[21c] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (d, J = 8.60 Hz, 2H), 7.1 (d, J = 8.60 Hz, 2H), 3.6 (m, 1H), 3.1 (m, 1H), 2.8 (m, 1H), 2.35 (s, 3H), 1.2−1.6 (m, 14H), and 0.9 (t, J = 6.91 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 13.01, 130.0, 128.0, 69.0, 4.03, 36.0, 29.4, 29.2, 17.5, 23.0, 21.0, and 14.0.

33: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (d, J = 8.47 Hz, 2H), 6.83 (d, J = 8.47 Hz, 2H), 3.8 (s, 3H), 3.05 (m, 1H), 2.78 (mm, 1H), 1.2−1.6 (m, 14H), and 0.9 (t, J = 7.04 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 134.0, 125.5, 115.0, 69.2, 55.8, 45.0, 36.5, 32.0, 29.6, 29.3, 27.5, 26.0, 23.0, and 14.3. HRMS calcd for $[C_{17}H_{28}SO_2]^+$ 297.1888, found 297.1782.

34:[21d] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (d, J = 8.29 Hz, 2H), 7.1 (d, J = 8.29 Hz, 2H), 3.77 (m, 1H), 3.58 (m, 1H), 3.03 (m, 1H), 2.95 (m, 1H), and 2.3 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 135.2, 131.3, 130.2, 69.8, 65.4, 38.9, and 21.3.

35:[21e] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (d, J = 8.51 Hz, 2H), 6.9 (d, J = 8.51 Hz, 2H), 3.82 (s, 3H), 3.77 (m, 1H), 3.6 (m, 1H), 3.03 (m, 1H), and 2.9 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 132.9, 115.1, 114.8, 69.7, 65.4, 55.6, and 40.2.

ARO of Cyclohexene Oxide with TMS-N_3 Catalyzed by 10. To a 50-mL Schlenk tube equipped with a stir bar and rubber septum was added **10** (1 g, 0.35 mmol) in a mixture of 5 mL of heptane and 5 mL of ethanol. To this solution was added cyclohexene oxide (0.7 mL, 7.08 mmol) and TMS-N_3 (1 mL, 7.78 mmol). The dark reaction mixture was allowed to stir for 12 h under N_2, at which time stirring was stopped and 0.5 mL of water was added to the reaction mixture to induce phase separation. The aqueous layer was removed and dried over Na_2SO_4 and solvent was removed from this polar phase under reduced pressure to yield **36** as a yellow oil. Spectroscopic analyses were identical with those previously reported.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28−3.16 (m, 1H), 3.06−2.97 (m, 1H), 1.94−1.79 (m, 3H), 1.66−1.46 (m, 2H), 1.3−0.97 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.0, 67.0, 30.0, 29.5, 24.1, 23.5. FT-IR (neat, cm^{-1}) 3350, 2940, 2860, and 2098. Recycling of the catalyst was achieved by simply adding fresh ethanol and substrates to the organic phase.

Reduction and Derivatization of 36. The azido alcohol product **36** (0.63 g, 2.96 mmol) was placed in a vial equipped with a stir bar. To this vial was added 5 mL of methanol and 0.05 g of 10% Pd/C. The reaction mixture was equipped with a hydrogen balloon. The mixture was monitored by IR spectroscopy and stirred for 12 h, at which time it was diluted with 10 mL of methanol and passed through a pad of Celite. The solvent was removed under reduced pressure to yield the 2-aminocyclohexanol as a colorless oil. ^{1}H NMR (300 MHz, CD_3-OD) δ 3.36−3.41 (m, 1H), 2.79−2.85 (m, 1H), 2.01−2.04 (m, 2H), 1.76−1.78 (m, 2H), 1.30−1.40 (m, 4H). Derivatization of this product was carried out by using a method similar to that described previously.[22] The amino alcohol (0.211 g, 1.83 mmol) was dissolved in 2 mL of DMSO and placed in a 10-mL round-bottomed flask equipped with a stir bar and rubber septum. To the flask was then added K_2CO_3 (0.28 g, 2.03 mmol) and 1-fluoro-2,4-dinitrobenzene (0.25 mL, 1.83 mmol). The reaction turned red and was allowed to stir under N_2 for 10 h at 80 °C. At this point, the reaction mixture was cooled to room temperature and 5 mL of water was added. The yellow solid product that formed (**37**) was isolated by filtration, washed with water, and dried under vacuum and directly used without further purification. The yield was 85%. Enantioselectivities were determined by chiral HPLC [Chiralcel OD (0.40 cm ×5 cm), Chiral Technologies, Inc., 0.5 mL/min, 80/20 (hexanes/IPA)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (d, J = 2.69 Hz, 1H), 8.68 (bs, 1H), 8.23 (dd, J = 2.72, 6.80 Hz, 1 H), 7.16 (d, J = 9.65 Hz, 1 H), 4.86−3.67 (m, 1H), 3.77−3.51(m, 1H), 2.4−2.26 (m, 2H), 2.26−2.08 (m, 2H), 1.94−1.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$)

(21) (a) Yang, M.-H.; Yan, G.-B.; Zheng, Y.-F. *Tetrahedron Lett.* **2008**, *49*, 6471–6474. (b) Reddy, M. S.; Srinivas, B.; Sridhar, R.; Narender, M.; Rao, K. R. *J. Mol. Catal.* **2006**, *255*, 180–183. (c) Solladié, G.; Demailly, G.; Greck, C. *Tetrahedron Lett.* **1985**, *26*, 435–438. (d) Culvenor, C. C. J.; Davies, W.; Savige, W. E. *J. Chem. Soc.* **1949**, 2198–2206. (e) Owen, L. N.; Muhammad, S. *J. Chem. Soc. C* **1971**, 1442–1447.

(22) Buckingham, J.; Guthrie, R. D. *J. Chem. Soc. C* **1970**, 106–108.

δ 148.7, 135.9, 130.3, 130.0, 124.4, 115.1, 75.9, 74.5, 58.7, 52.8, 34.2, 33.7, 31.4, 30.8, 30.5, 24.6, 24.4, 23.9, 23.4. Mp 184 −187 °C.

ARO of Cyclohexene Oxide with TMS-N_3 Catalyzed by 2. To a 50-mL Schlenk tube equipped with a stir bar and rubber septum was added Jacobsen's catalyst **2** (0.116 g, 0.184 mmol), cyclohexene oxide (0.37 mL, 3.68 mmol), and azidotrimethylsilane (0.537 mL, 4.05 mmol) in a mixture of 5 mL of heptane and 5 mL of absolute ethanol. The reaction mixture was stirred under N_2 for 12 h at room temperature. At this time, the solvent was removed and the viscous oil was worked up by dissolving it in 20 mL of hexanes and passing the resulting solution through a plug of Celite. The solvent was removed under reduced pressure to give 0.514 g of **36** in 66% yield. Spectroscopic analyses showed that this product was identical with that formed in reactions catalyzed by **10**.

3-*tert*-Butyl-5-polyisobutylsalicylidene-(1*R*,2*S*)-(1-amino-2-indanol)imine (12). To a two-necked, 50-mL round-bottomed flask equipped with a stir bar, water-jacketed reflux condenser, and a Dean−Stark trap were added **6** (2.94 g, 2.028 mmol) in 21 mL of toluene, **11** (0.333 g, 2.230 mmol), and a catalytic amount of PTSA. The reaction mixture was stirred with azeotropic removal of water for 12 h and then cooled to room temperature. The solvent was then removed under reduced pressure and to the viscous oil was added 150 mL of hexanes. The solution was washed with 3 100-mL portions of DMF and 3 100-mL portions of 90% ethanol/water. The organic phase was dried over Na_2SO_4 and filtered and the solvent was removed under reduced pressure to yield 3.19 g of **12** as a viscous yellow oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.40 (s, 1H), 7.35−7.17 (m, 4H), 7.12 (s, 1H), 4.80 (d, J = 5.32 Hz, 1H), 4.73 (bs, 1H), 3.25 (m, 2H), 1.80−0.80 (m, 160H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 158.0, 141.0, 140.8, 139.5, 136.5, 128.6, 128.5, 127.2, 127.0, 125.5, 125.0, 117.7, 75.8, 75.3, multiple poorly resolved peaks were present between 57 and 60 and 20−40.

PIB-Supported Half-Salen-Cr Complex (13). To a 50-mL round-bottomed flask equipped with a stir bar and rubber septum was added **12** (2.74 g, 1.73 mmol) and $CrCl_2$ (0.233 g, 1.90 mmol) in 21 mL of THF. The dark reaction mixture was allowed to stir under N_2 for 24 h at room temperature, at which point the reaction system was exposed to air and stirred for 24 h. The solvent was removed under reduced pressure and 150 mL of hexanes was added to the dark, viscous oil. The hexanes solution was then washed with 3 50-mL portions of a saturated aqueous solution of NH_4Cl and 3 50-mL portions of a saturated aqueous solution of NaCl. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield 2.82 g of **13** as a dark viscous oil in quantitative yield. UV−visible spectroscopy (THF, λ_{max} = 348 nm).

4-(Polyisobutyl)phenol (15). This compound was prepared by using the procedure described above leading to **5**. Spectroscopic analyses were identical with those previously reported.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.79 Hz, 2H), 6.75 (d, J = 8.79 Hz, 2H), 1.8 (s, 2H), and 0.8−1.6 (m, 140H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 142.9, 127.5, 114.7, multiple poorly resolved peaks between 58 and 60, 38−39, and 30−33.

5-Polyisobutylsalicylaldehyde (16). This compound was prepared analogously to **6**. Spectroscopic analyses were identical with those previously reported.[14a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.88 (s, 1H), 9.9 (s, 1H), 7.57 (dd, J = 2.44, 8.54 Hz, 1H), 7.48 (m, 1H), 6.94 (d, J = 8.54 Hz, 1H), 1.8 (s, 2H), and 0.8−1.6 (m, 140H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 159.6, 142.4, 135.7, 130.7, 120.2, 117.2, multiple poorly resolved peaks between 58 and 60, 38−39, and 30−33.

3-(Piperindylmethyl)-5-polyisobutylsalicyladehyde(17). To a 50-mL round-bottomed flask equipped with a stir bar, rubber septum, and a water-jacketed reflux condenser was added piperidine (0.44 mL, 4.46 mmol) and paraformaldehyde (0.15 g, 4.90 mmol) in glacial acetic acid (3.19 mL). The mixture was stirred at room temperature for 3 h. At this point, **16** (5 g, 4.46 mmol) in a mixture of heptane and ethanol (1:1, 13 mL) was added to the reaction flask and placed on an oil bath regulated at 90 °C and allowed to stir for 5 days. At this point, the reaction was cooled to room temperature and hexanes (50 mL) was added. The mixture was washed with 1 25-mL portion of saturated $NaHCO_3$(aq) and 3 25-mL portions of 90% ethanol/water. The organic phase was dried over Na_2SO_4 and filtered and solvent was removed under reduced pressure to give a viscous yellow oil that was then subjected to column chromatography (silica, hexanes:ethylacetate (9:1)) to give 2.6 g of **17**, 50%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.65 (d, J = 2.5 Hz, 2H), 7.22 (d, J = 2.4 Hz, 2 Hz), 3.70 (s, 2H), 2.55 (m, 4H), 1.8 (s, 2H), and 0.8−1.6 (m, 140H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 159.7, 140.9, 133.8, 125.4, 122.2, multiple poorly resolved peaks between 58 and 60, 38−39, and 30−33.

***N*,*N*′-Bis((3-piperidylmethyl)-5-polyisobutylsalicylidene)-1,2-ethylenediimine (18).** This compound was prepared by using the same procedure used to prepare **7**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 2H), 7.31 (s, 2H), 7.19 (s, 2H), 3.70 (s, 2H), 2.60 (m, 8H), 1.8 (s, 4H), and 0.8−1.6 (m, 300H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 157.1, 139.9, 132.0, 127.2, 124.1, 117.8, multiple poorly resolved peaks between 58 and 60.0, 38−39, and 30−33.

(*R*,*R*)-*N*,*N*′-Bis((3-piperidylmethyl)-5-polyisobutyl)salicylidene-1,2-cyclohexanediimine (19). This compound was prepared by using the same procedure used to prepare **8**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.36 (s, 2H), 7.03 (s, 2H), 3.60 (d, J = 12.7 Hz, 2H), 3.47 (d, J = 12.71 Hz, 2H), 3.3 (m, 2H), 2.60 (m, 8H), 1.8 (s, 4H), and 0.8−1.6 (m, 300H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 156.1, 138.7, 130.8, 127.4, 126.5, 116.7, multiple poorly resolved peaks between 58 and 60, 38−39, and 30−33.

3-*tert*-Butyl-5-hydroxysalicylaldehyde (20). This compound was prepared according to a literature procedure.[23]

PE_{Olig}-Bound Salicylaldehyde Derivative (22). To a 150-mL, round-bottomed flask equipped with a stir bar, pressure-equalized addition funnel, and a rubber septum was added **20** (1.88 g), **21** (1.33 g, 6.84 mmol), and triphenylphosphine (3.47 g, 17.09 mmol) in toluene (34 mL). The mixture was placed in an oil bath regulated at 80 °C and the contents were allowed to dissolve. At this point, a solution of DEAD (2.69 mL, 17.09 mmol) in toluene (10 mL) was added dropwise with the addition funnel. The dark reaction mixture was allowed to stir at 80 °C for 24 h. Then the reaction mixture was cooled to room temperature whereupon the PE_{Olig}-bound product precipitated. This product was collected by vacuum filtration and washed with toluene (50 mL) and THF (50 mL). This product was then placed in a 25-mL round-bottomed flask equipped with a stir bar and rubber septum and 10 mL of toluene containing 0.5 mL of water was added to this flask along with 0.45 g of PTSA. The flask was placed on an oil bath at 80 °C for 2 h. This procedure converted any imine derivative of the aldehyde group of **22** back into an aldehyde group. The PE_{Olig}-bound product **22** that precipitated on cooling of the reaction mixture at this point was collected by vacuum filtration and washed with toluene (50 mL) and THF (50 mL) to yield 1.1 g of **22** as an light orange solid (80% yield). ^{1}H NMR (500 MHz, benzene-d_6, 70 °C) δ 11.87 (s, 1H), 9.38 (s, 1H), 7.26 (d, J = 3.06 Hz, 1H), 6.43 (d, J = 1.9 Hz, 1H), 3.71 (t, J = 6.26 Hz, 2H), 1.71 (m, 1H), 1.49−1.30 (bs, 230H), 0.91 (t, J = 6.58 Hz, 5H). ^{13}C NMR (125 MHz, benzene-d_6, 70 °C) δ 196.0, 155.9, 151.7, 139.9, 123.9, 120.1, 113.1, 68.6, 34.8, 31.9, 29.7, 29.3, 29.2, 28.9, 26.1, 22.5, 13.9.

PE_{Olig}-Bound Salen Derivative (23). To a 25-mL, round-bottomed flask equipped with a stir bar and a rubber septum was added **22** (0.80 g) in toluene (6 mL). The mixture was placed under N_2 and the reaction flask was placed on an oil bath regulated at 80 °C. To the reaction mixture was added ethylenediamine

(23) Anyanwu, U. K.; Venkataraman, D. *Green Chem.* **2005**, *7*, 424–425.

(0.011 mL, 0.163 mmol). Upon addition of ethylenediamine, the reaction became bright yellow. The reaction was allowed to stir for 1 h, at which point 3,5-di-*tert*-butylsalicylaldehyde (0.25 g, 1.30 mmol) was added to the reaction mixture, which was allowed to stir for an additional hour. At this point, the reaction was cooled to room temperature and the product was collected by vacuum filtration, then washed with toluene (20 mL) and THF (20 mL) to give 0.7 g of **23** as a yellow solid (as a mixture of the bis-PE_{Olig} and mono-PE_{Olig}-bound species), 90%. ^{1}H NMR (500 MHz, benzene-d_6, 70 °C) δ 7.86 (s, 2H), 7.54 (s, 1H), 6.51 (m, 2 H), 3.83 (t, J = 6.42 Hz, 4 H), 3.35 (s, 4 H), 1.49−1.30 (bs, 420H), 0.91 (t, J = 6.58 Hz, 5H)). ^{13}C NMR (125 MHz, benzene-d_6, 70 °C) δ 167.5, 166.9, 155.1, 151.3, 143.6, 139.9, 138.9, 119.0, 118.2, 113.1, 68.6, 59.1, 34.9, 31.8, 31.2, 30.8, 29.6, 29.4, 29.2, 26.1, 22.5, 13.6.

PE_{Olig}-Bound Salen-Cr Complex (24). To a 10-mL, round-bottomed flask equipped with a stir bar, a rubber septum, and a water-jacketed reflux condenser were added **23** (0.7 g), $CrCl_2$ (0.086 g, 0.7 mmol), toluene (2 mL), and DMF (2 mL) and the flask was placed under N_2. The mixture was placed on an oil bath regulated at 100 °C and allowed to stir for 12 h. At this point, the flask was exposed to air and the reaction allowed to stir for 12 h. The reaction was then allowed to cool to room temperature and the product was collected by vacuum filtration and washed with THF (100 mL) to give 0.63 g of **24** as a brownish/yellow solid, 90%. UV−visible spectroscopy (toluene, 70 °C, λ_{max} = 366 nm). Separate UV−visible analysis of **1** in toluene showed it had a λ_{max} of 366 nm with ε = 7566 M^{-1} cm^{-1}, and this extinction coefficient was used to calculate the Cr(III) loading of **24**.

Ring-Opening of Cyclohexene Oxide with TMS-N_3 Catalyzed by 24. To a 50-mL round-bottomed Schlenk tube equipped with a stir bar and rubber septum were added complex **24** and toluene (3 mL). The reaction vessel was then placed under N_2 and placed on an oil bath regulated at 75 °C. Once dissolution of the solid was achieved, cyclohexene oxide (0.097 mL, 0.95 mmol) was added by syringe followed by azidotrimethylsilane (0.126 mL, 0.95 mmol). The reaction mixture was allowed to stir at 75 °C for 3 h. At this point, the reaction vessel was removed from the oil bath and allowed to cool to room temperature, inducing precipitation of the catalyst. The reaction vessel was then exposed to air and 5 mL of toluene was added. The system was then subjected to centrifugation for 10 min at 1100 rpm. The solvent was decanted and the process was repeated. The toluene layers were combined and the solvent was removed under reduced pressure to yield the product as a light yellow oil. Spectra were identical with those found in the literature.[7] To facilitate recycling of the catalyst, toluene (3 mL) was added to the recovered catalyst and the entire process was repeated.

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Supporting Information Available: NMR spectra and structures for selected compounds, phase-selectivity, and ICP-MS digestion procedures for metal analysis. This material is available free of charge via the Internet at http://pubs.acs.org.