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Kinetic Resolution of Chiral α-Olefins Using Optically Active *ansa*-Zirconocene Polymerization Catalysts

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Abstract: A series of enantiopure C_1-symmetric metallocenes, {$(SiMe_2)_2$[η^5-$C_5H(CHMe_2)_2$][η^5-C_5H_2((*S*)-CHMeCMe$_3$)]}$ZrCl_2$, (*S*)-**2**, {$(SiMe_2)_2$[η^5-$C_5H(CHEt_2)_2$][η^5-C_5H_2((*S*)-CHMeCMe$_3$)]}$ZrCl_2$, (*S*)-**6**, and {$(SiMe_2)_2$-[η^5-C_5HCy_2][η^5-C_5H_2((*S*)-CHMeCMe$_3$)]}$ZrCl_2$, (*S*)-**7** (Cy = cyclohexyl), zirconocene dichlorides that have an enantiopure methylneopentyl substituent on the "upper" cyclopentadienyl ligand, and diastereomerically pure precatalysts, {$(SiMe_2)_2$[η^5-C_5H((*S*)-CHMeCy)$(CHMe_2)$][η^5-C_5H_3]}$ZrCl_2$, (*S*)-**8a** and (*S*)-**8b**, which have an enantiopure, 1-cyclohexylethyl substituent on the "lower" cyclopentadienyl ligand, has been synthesized for use in the polymerization of chiral α-olefins. When activated with methylaluminoxane, these metallocenes show unprecedented activity for the polymerization of bulky racemic monomers bearing substitution at the 3- and/or 4-positions. Due to the optically pure nature of these single site catalysts, they effect kinetic resolution of racemic monomers: the polymeric product is enriched with the faster reacting enantiomer, while recovered monomer is enriched with the slower reacting enantiomer. The two components are easily separated. For most olefins surveyed, a partial kinetic resolution was achieved ($s = k_{faster}/k_{slower} \approx 2$), but, in one case, the polymerization of 3,4-dimethyl-1-pentene, high levels of separation were obtained ($s > 15$). ^{13}C NMR spectroscopy of poly(3-methyl-1-pentene) produced with (*S*)-**2** indicates that the polymers are highly isotactic materials. X-ray crystal structure determinations for (*S*)-**2**, {$(SiMe_2)_2$[η^5-$C_5H(CHMe_2)_2$]-[η^5-C_5H_2((*S*)-CHMeCMe$_3$)]}$Zr(SC_6H_5)_2$, (*S*)-**6**, and (*S*)-**7** have been used in combination with molecular mechanics calculations to examine the prevailing steric interactions expected in the diastereomeric transition states for propagation during polymerization. Precatalysts (*S*)-**8a** and (*S*)-**8b** are less selective polymerization catalysts for the kinetic resolution of 3-methyl-1-pentene than are (*S*)-**2**, (*S*)-**6**, and (*S*)-**7**.

Introduction

Simple nonracemic, chiral olefins represent a highly versatile substrate class for asymmetric synthesis and are potential monomers for the development of polymeric materials with previously inaccessible optical or physical properties. For these reasons, efficient routes to enantiopure alkenes are highly desirable. Kinetic resolution, especially catalytic kinetic resolution, is a particularly attractive approach because many racemic alkenes are readily available, while methods for the direct synthesis of enantiopure chiral alkenes are few.

Despite the growing number of both enzymatic and metal-mediated kinetic resolutions of a wide range of synthetically useful racemic substrates, the practical kinetic resolution of simple racemic alkenes (i.e., without heteroatom substituents) has not been realized.[1] This stems from the difficulty in producing diastereomeric transition states with sufficient energy differences due to the alkene's lack of functionality. Consequently, most successful attempts to kinetically resolve alkenes have focused on more or less functionalized substrates such as allylic alcohols,[2] allylic ethers,[3] and dienes,[4] which can participate in substrate-directed catalysis, primarily through chelation to the catalytically active metal center. There are a few examples where the antipodes of simple chiral alkenes can be separated by kinetic resolution. For example, the osmium tetraoxide-cinchona alkaloid system developed by Sharpless mediates the dihydroxylation of axially disymmetric internal olefins with modest efficiency.[5,6] In a related more recent report, asymmetric dihydroxylation was used to resolve 2,6-dimethylbenzylidenecyclohexane.[7] In contrast, reductive kinetic resolution strategies have not been reported for unfunctionalized olefins.[8] In addition to the limitations discussed above, reductive strategies for simple

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(2) (a) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. (b) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc*. **1981**, *103*, 6237. (c) Kitamura, M.; Kasahara, I.; Manbe, K.; Noyori, R.; Takaya, H. *J. Org. Chem.* **1988**, *53*, 708.

(3) (a) Adams, J. A.; Ford, J. G.; Stamatos, P. J.; Hoveyda, A. H. *J. Org. Chem.* **1999**, *64*, 9690. (b) Morken, J. P.; Didiuk, M. T.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1994**, *116*, 3123.

(4) (a) La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720.

(5) VanNieuwenhze, M. S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 7864.

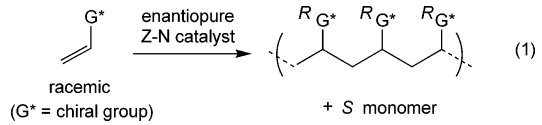
(6) (a) Hamon, D. P. G.; Tuck, K. L.; Christie, H. S. *Tetrahedron* **2001**, *57*, 9499. (b) Christie, H. S.; Hamon, D. O. G.; Tuck, K. L. *Chem. Commun.* **1999**, 1989.

(7) Gardiner, J. M.; Norret, M.; Sadler, I. H. *Chem. Commun.* **1996**, 2709.

10.1021/ja040021j CCC: $27.50

chiral alkenes suffer from the added difficulty of separating unreacted alkene from product alkane fractions. In an attempt to address limitations in the application of kinetic resolution to unfunctionalized olefins, we have explored olefin polymerization catalysis as a possible alternative.

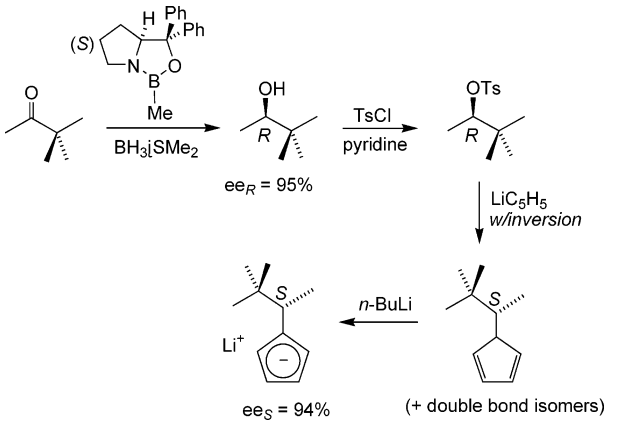
Ziegler−Natta and metallocene catalysts often exhibit very high levels of enantiofacial selectivity in the polymerization of prochiral olefins and can produce polymer with a well-defined microstructure or tacticity.[9] Moreover, these catalysts are extremely active, producing in many cases $>10^3$ kg of polymer/g of metal·h.[10] Hence, the prospects of using enantiopure Ziegler−Natta or metallocene catalysts as kinetic resolving agents to preferentially polymerize one enantiomer of a chiral alkene, leaving the less reactive enantiomer behind (eq 1), are particularly attractive. The enantio-enriched olefin should be recoverable by simple filtration. Moreover, a new class of polymer, one that is optically active by virtue of enantiopure substituents off the main chain, may likewise be isolated.

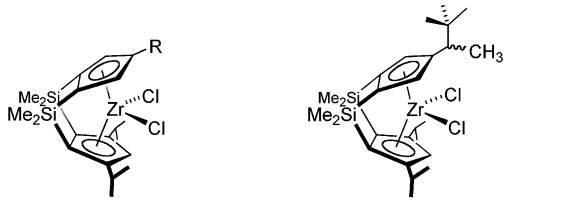


That enantiopure, chiral sites in heterogeneous Ziegler−Natta systems are sensitive to preexisting chirality in the olefin monomer has been established by a number of research groups.[11,12] However, due to the racemic nature of the active sites on a macroscopic level, resolution was not possible. A soluble enantiopure single site catalyst, (*S*)-ethylene-bis(4,5,6,7-tetrahydro-1-η^5-indenyl)Zr(O-acetyl-(*R*)-mandelate)$_2$/MAO (MAO = methylaluminoxane), has been used to effect a low efficiency resolution of 4-substituted chiral olefins such as 4-methyl-1-hexene ($s = k_{faster}/k_{slower} = 1.4$).[13,14] Unfortunately, poor catalyst activity prohibited the polymerization of chiral α-olefins with substituents in the 3-position. Although 3-methyl-1-pentene can be successfully polymerized with related metallocene catalysts, prior to the present work, only C_s- and racemic C_2-symmetric catalysts have been used, precluding any possible kinetic resolution.[15]

We recently reported that doubly bridged *ansa*-zirconocene catalysts (**1**) activated with MAO polymerize propylene with very high syndiospecificities and with extremely high activities.[16] Modification of this catalyst system with a racemic 3,3-dimethyl-2-butyl ("methylneopentyl") substituent has also been accomplished (**2**).[17]

Scheme 1





We now report that, with an enantiopure methylneopentyl substituent, partial kinetic resolution of simple racemic α-olefins can be carried out and that, for 3,4-dimethyl-1-pentene, synthetically useful degrees of separation can be achieved. This substrate represents one of the simplest organic molecules to be kinetically resolved to date.

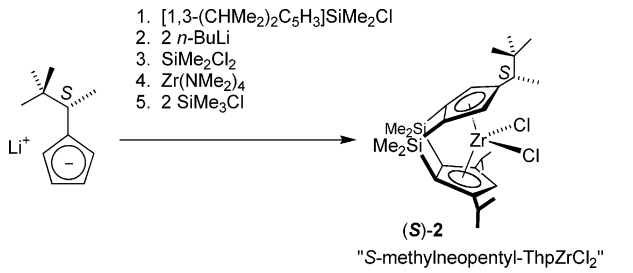
Results and Discussion

Synthesis of {(SiMe$_2$)$_2$[η^5-C$_5$H(CHMe$_2$)$_2$][η^5-C$_5$H$_2$((*S*)-CHMeCMe$_3$)]}ZrCl$_2$, (*S*)-2. Installation of a racemic methylneopentyl substituent in *rac*-**2** has been accomplished by methylation of 4-*tert*-butylfulvene.[16,17] As there are no precedents for highly asymmetric fulvene alkylation or reduction, a different route to the enantiopure metallocene was necessary (Scheme 1).

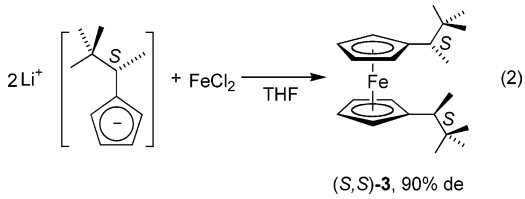
Access to metallocene (*S*)-**2** involves, as the first step, asymmetric borane reduction of pinacolone with an oxazaborolidine catalyst to give (*R*)-3,3-dimethylbutan-2-ol (ee_R > 95%).[18,19] The alcohol was converted to a tosylate, followed by nucleophilic attack with cyclopentadienide anion.[20] Remarkably, the reaction occurred with near perfect inversion of the

(8) Reductive strategies have been successfully employed for the resolution of allylic alcohols: Kitamura, M.; Kashara, I.; Manabe, K.; Noyori, R.; Takaya, H. *J. Org. Chem.* **1988**, *53*, 710.
(9) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Intl. Ed.* **1999**, *38*, 428. (c) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (d) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.
(10) Facts and Figures for the Chemical Industry. *Chem. Eng. News* **2001**, *79*, 42.
(11) Pino, P. *Adv. Polym. Sci.* **1965**, *4*, 393.
(12) (a) Carlini, C.; Altomare, A.; Menconi, F.; Ciardelli, F. *Macromolecules* **1987**, *20*, 464. (b) Vizzini, J.; Ciardelli, F.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 108. (c) Zambelli, A.; Proto, A.; Pasquale, L. *Zeigler Catalysis*; Springer-Verlag: New York, 1995; p 218. (d) Zambelli, A.; Ammendola, P.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1983**, *16*, 341.
(13) (a) Ciardelli, F.; Carlini, C.; Altomare, A. *Zeigler Catalysis*; Springer-Verlag: New York, 1995; p 455. (b) Chien, J. C. W.; Vizzini, J. C.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 479.
(14) s = (rate of fast reacting enantiomer)/(rate of slow reacting enantiomer). s may be determined using Kagan's equation, $s = \ln[(1 - c)(1 - ee)]/\ln[(1 - c)(1 + ee)]$, where ee is the enantiomeric excess of the recovered olefin and c is fraction conversion. Eliel, A. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley & Sons: New York, 1994.
(15) (a) Oliva, L.; Longo, P.; Zambelli, A. *Macromolecules* **1996**, *29*, 6383. (b) Sacchi, M. C.; Barsties, E.; Tritto, I.; Locatelli, P.; Brintzinger, H. H.; Stehling, U. *Macromolecules* **1997**, *30*, 1267.
(16) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988.
(17) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564.
(18) Corey, E. J.; Helal, C. J. *Chem. Rev.* **1998**, *37*, 1986.
(19) The enantiomeric excess of the alcohol was determined by chiral GC of the trifluoroacetyl derivative.
(20) Although the success of this synthetic strategy might be surprising, it has been shown that nucleophilic attack of cyclopentadienide anion on some hindered secondary tosylates can proceed with inversion of configuration: Giardello, M. A.; Conticello, V. P.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.

Scheme 2



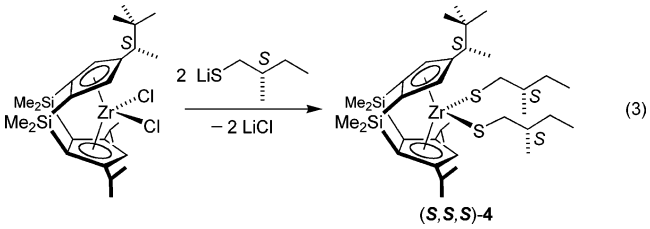
carbon stereocenter. The expected pathway, elimination, does not dominate, despite the highly hindered nature of the (*R*)-3,3-dimethylbutyl-2-*p*-toluenesulfonate substrate. The product forms as a mixture of double bond isomers, but deprotonation with *n*-BuLi yields a single species. The enantiomeric excess of the methylneopentyl substituent was determined by synthesis (eq 2) and NMR analysis of diastereomeric ferrocene derivatives.



(2)

In the reaction of $FeCl_2$ with Li[C_5H_4(*rac*-CHMeCMe$_3$)], essentially equimolar amounts of the *racemic* (*R*,*R*/*S*,*S*) and *meso* (*R*,*S*) products were obtained, while reaction with enantio-enriched Li[C_5H_4((*S*)-CHMeCMe$_3$)] gave only a small amount of the *meso* isomer (5.1% by ^{1}H NMR spectroscopy). This observed diastereomeric excess (de) corresponds to a 94% ee for Li[C_5H_4((*S*)-CHMeCMe$_3$)], approximating the ee of the starting alcohol.

Synthesis of the desired precatalyst (*S*)-**2** then follows the procedures already established for *rac*-methylneopentyl-ThpZrCl$_2$ (Scheme 2).[16,17] Following the isolation of enantio-enriched (*S*)-**2**, we found that a single recrystallization from toluene could be carried out to give optically pure material. The optical purity was assayed by reaction of (*S*)-**2** with 2 equiv of lithium (*S*)-3-methyl-1-butanethiolate (eq 3). The ^{1}H and ^{13}C NMR spectra



(3)

of (*S*,*S*,*S*)-{(SiMe$_2$)$_2$[η^5-C_5H(CHMe$_2$)$_2$][η^5-C_5H$_2$(CHMeCMe$_3$)]}-Zr(SCH$_2$CH(CH$_3$)CH$_2$CH$_3$)$_2$ ((*S*,*S*,*S*)-**4**) were compared to the NMR data obtained for a 1:1 mixture of diastereomers resulting from the reaction of *rac*-**2** with the (*S*)-thiolate. No resonances corresponding to the (*R*,*S*,*S*) diastereomer were observed, indicative of >98% optically pure material.

X-ray Crystal Structure Determinations for (*S*)-2 and {(SiMe$_2$)$_2$[η^5-C$_5$H(CHMe$_2$)$_2$][η^5-C$_5$H$_2$((*S*)-CHMeCMe$_3$)]}Zr(SC$_6$H$_5$)$_2$, (*S*)-5. Single crystals of (*S*)-**2** were grown from a saturated toluene solution. For comparison purposes, single crystals of {(SiMe$_2$)$_2$[η^5-C_5H(CHMe$_2$)$_2$][η^5-C_5H$_2$((*S*)-CHMeCMe$_3$)]}Zr(SC$_6$H$_5$)$_2$, (*S*)-**5**, prepared from the reaction of (*S*)-**2** with 2 equiv of Li(SC$_6$H$_5$), were grown from hexamethyldisiloxane. The molecular structures of (*S*)-**2** and (*S*)-**5** show that the large *tert*-butyl group of the methylneopentyl substituent is located above the upper cyclopentadienyl ligand of the metallocene (Figures 1 and 2). Newman projections (Figure 3) down the C15a−C4a bond of (*S*)-**2** and the C15−C4 bond of (*S*)-**5** indicate that the *tert*-butyl fragment is directed from the methine carbon C15 nearly perpendicular to the cyclopentadienyl plane

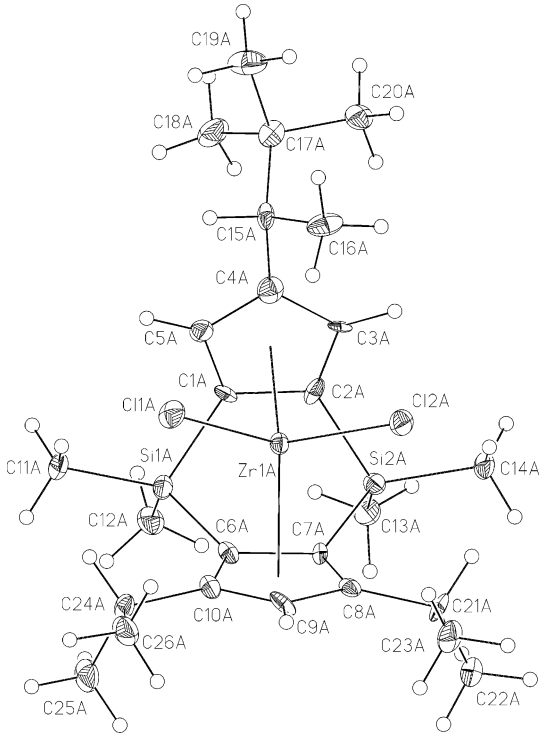


Figure 1. View of (*S*)-**2**.

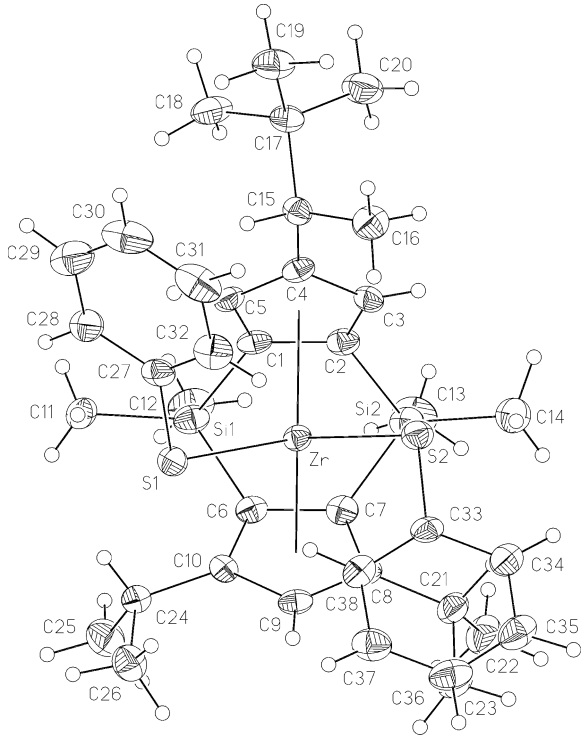


Figure 2. View (*S*)-**5**.

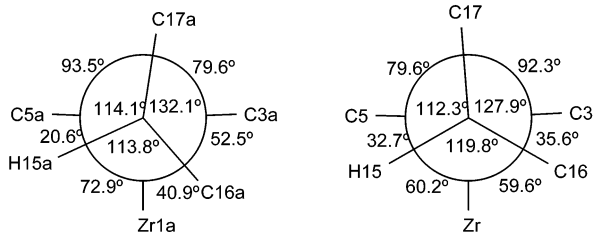


Figure 3. Newman projections showing the orientation of the methylneopentyl group in (*S*)-**2** and (*S*)-**5**.

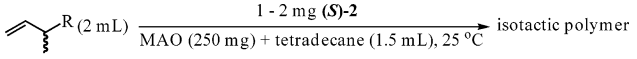
and that the methyl group is forced down into the wedge of the metallocene, effectively differentiating left from right in the molecule. The isopropyl substituents on the lower cyclopentadienyl assume a conformation in which the methine proton is directed back toward the bulky dimethylsilylene linker groups as has been observed for the structures of similarly substituted metallocenes.[16,17,21] In the case of (*S*)-**5**, the steric requirements of the thiophenoxy groups have rotated the C16 methyl group out of the wedge to some extent, but it is the relative position of each thiophenoxy ligand that is particularly noteworthy. The phenyl ligand attached to S1 occupies an open region of space in the upper left quadrant of the molecular structure, avoiding nonbonded contacts with C16 (Figure 2) and the left isopropyl group on the lower cyclopentadienyl ligand. As a consequence, the neighboring phenyl group attached to S2 is oriented down and toward the lower right quadrant. This anti arrangement clearly minimizes steric interactions between the thiophenoxy phenyls in the metallocene wedge. Deflection of the phenyl group into the lower half of the wedge may also prevent a direct steric interaction between the phenyl attached to S2 and C16. Finally, the plane defined by S1−Zr−S2 is 6.9° off the perpendicular to the ring centroid−Zr−ring centroid plane. For (*S*)-**2**, a smaller deviation of 3.1° of the Cl1a−Zr1a−Cl2a in the opposite direction is observed. For (*S*)-**2**, the distortion is in the direction expected to minimize interaction of the methylneopentyl methyl (C16a) with chlorine (Cl2a); for (*S*)-**5**, the distortion is in the opposite direction, probably because the phenyl ligand is forced down and experiences unfavorable steric interactions with the isopropyl substituent on the lower cyclopentadienyl ligand.

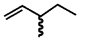
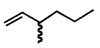
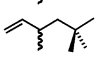
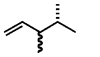
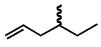
Polymerization of Chiral α-Olefins with {(SiMe$_2$)$_2$[η^5-C$_5$H(CHMe$_2$)$_2$][η^5-C$_5$H$_2$((*S*)-CHMeCMe$_3$)]}ZrCl$_2$, (*S*)-2. When activated with MAO, (*S*)-**2** catalyzes the polymerization of a variety of chiral α-olefins with moderate to good kinetic resolution. Polymerizations were carried out in tetradecane, which acts as both a solvent and an internal standard for GC analysis. The high boiling point of tetradecane also allows for facile recovery of volatile, unreacted monomer by vacuum transfer. When desired, the polymers were more conveniently isolated using toluene as solvent. All of the polymeric materials were isolated as white powders.

Olefin enantioassay required derivatization procedures to achieve useful separation by enantioselective GC. The recovered monomer is first converted to a carboxylic acid having one less carbon atom using Ru-catalyzed $NaIO_4$ oxidation. The acid is then treated with a BF_3/MeOH solution to give a methyl ester

(21) Veghini, D.; Day, M. W.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *280*, 226.

Table 1. Kinetic Resolutions of Chiral, 3- and 4-Methyl-Substituted α-Olefins Using (*S*)-**2**



olefin	t (hr)	TOF (hr^{-1})	% conv	% ee	$s = \frac{k_S}{k_R}$
	18 47	72 47	24 38.3	13.3 20.3	2.8 2.4
	13.5	551	75	40.0	1.8
	22.7 43	55.8 37	37.8 56.1	16.2 30.3	2.0 2.1
	40.5 69	45.6 34	32.5 42.4	40.6 58.6	17.6 15.9
	16.5 16.5	77.6 73.7	64.4 58.7	7.6 4.6	1.1 1.1

that is used for the enantiomeric excess (ee) assay. Because possible racemization during derivatization was a concern, a control experiment was carried out in which enantiopure (*S*)-3-methyl-1-pentene[22] was converted to the corresponding methyl ester with the same derivatization procedure. The resulting chiral GC trace showed a single peak with no evidence for racemization (ee_S > 98%), demonstrating that the enantioassay is valid for 3-methyl-1-pentene. The polymerization results obtained with the first-generation catalyst (*S*)-**2** are outlined in Table 1.[14,23]

The data show small but significant *s* values, even for the simplest possible chiral α-olefin, 3-methyl-1-pentene (3-MP1).

(22) (a) Fu, S. C. J.; Birnbaum, S. M.; Greenstein, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 6054. (b) Schurig, V.; Leyer, U.; Wistuba, D. *J. Org. Chem.* **1986**, *51*, 242. (c) Millar, J. G.; Underhill, E. W. *J. Org. Chem.* **1986**, *51*, 4726. (d) Wood, N. F.; Chang, F. C. *J. Org. Chem.* **1965**, *30*, 2054.

(23) For polymerizations with the (*S*)-**2**/MAO, the prevailing absolute configuration in the recovered monomers was determined by comparison of their optical rotations with literature reports. For 3,5,5-trimethyl-1-hexene, the rotation of enriched material has never been reported. The (*S*)-mandelic ester derivatives of enriched 3-methyl-1-pentene and 3,5,5-trimethyl-1-hexene were made as outlined in the Experimental Section. Both products show less intensity for the upfield signal of the diastereotopic methyl groups (α to the methyl mandelic ester moiety), arguing for a common absolute configuration in these olefins. The same is true for the ester derived from 3, 4-dimethyl-1-pentene. With these assignments in hand, the relative retention times for olefin derivatives as obtained from enantioselective GC were used to assign enantiomer selectivity with other catalyst systems. For literature reports on the optical rotation of olefins 3-methyl-1-pentene, 4-methyl-1-hexene, 3,5,5-trimethyl-1-hexene, and 3,4-dimethyl-1-pentene, see: (a) Schurig, V.; Leyrer, U.; Wistuba, D. *J. Org. Chem.* **1986**, *51*, 242. (b) Lazzaroni, R.; Salvadori, P.; Bertucci, C.; Veracini, C. A. *J. Organomet. Chem.* **1975**, *99*, 475. (c) Lardicci, L.; Caporusso, A. M.; Giacomelli, G. *J. Organomet. Chem.* **1974**, *70*, 333. (d) Lazzaroni, R.; Salvadori, P.; Pino, P. *Tetrahedron Lett.* **1968**, 2507. (e) Pino, P.; Lardicci, L.; Centoni, L. *Gazz. Chem. Ital.* **1961**, *91*, 428. During our analysis of the relevant literature, we found a discrepancy in the assignment of the absolute configuration and the optical rotation for enantiomers of 3,4-dimethyl-1-pentene. For the (+) specific rotation, one series of papers assigned the enantiomer (*S*)-3,4-DMP1 (ref 23d; Lardicci, L.; Menicagli, R.; Caporusso, A. M.; Giacomelli, G. *Chem. Ind.* **1973**, *4*, 184). However, another series of articles has correlated the (+) specific rotation to the enantiomer (*R*)-3,4-DMP1 (ref 23b,c; Caporusso, A. M.; Giacomelli, G. P.; Lardicci, L. *Atti Soc. Tosc. Sci. Nat., Mem.* **1973**, *80*, 40). Due to this conflict in the literature, it was necessary to unambiguously assign each enantiomer its proper optical rotation. The literature is in agreement regarding the absolute configuration of structurally related (−)(*R*)-2,3-dimethylbutyric acid (in this case, the absolute configuration has been established by comparison to well-established steroid natural products) (Sakai, K.; Tsuda, K. *Chem. Pharm. Bull.* **1963**, *11*, 650. Tarzia, G.; Tortorella, V.; Romeo, A. *Gazz. Chim. Ital.* **1967**, *97*, 102. di Maio, G.; Romeo, A. *Gazz. Chim. Ital.* **1959**, *89*, 1627). Because this acid is the product of 3,4-DMP1 oxidation with $NaIO_4$ and $RuCl_3$, and because the stereocenter is retained during the oxidation process (vide infra), determination of the absolute configuration of 3,4-DMP1 follows directly. Hence, the 3,4-DMP1 monomer recovered following polymerization with (*S*)-**2** was converted to 2,3-dimethylbutyric acid, and the optical rotation was measured: $\lambda = 598^{NaD}$ nm, $l = 50$ mm, $c = 0.9860$, $T = 25.9$ °C, specific rotation = −18.1156. The specific rotation is consistent with (−)(*R*)-2,3-dimethylbutyric acid, identifying the recovered olefin as (−)(*R*)-3,4-dimethyl-1-pentene. The *S* monomer then is preferentially polymerized.

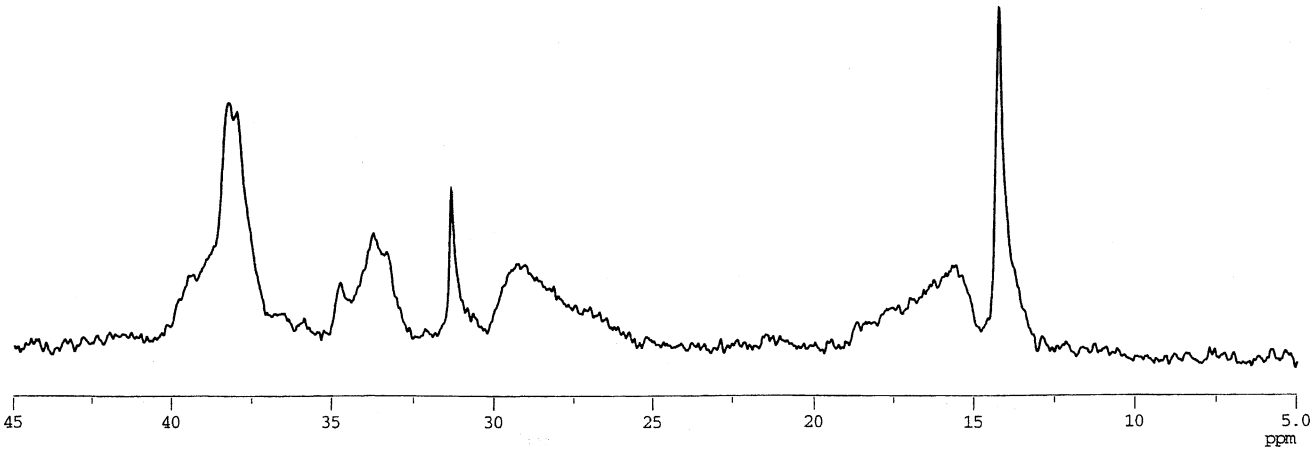
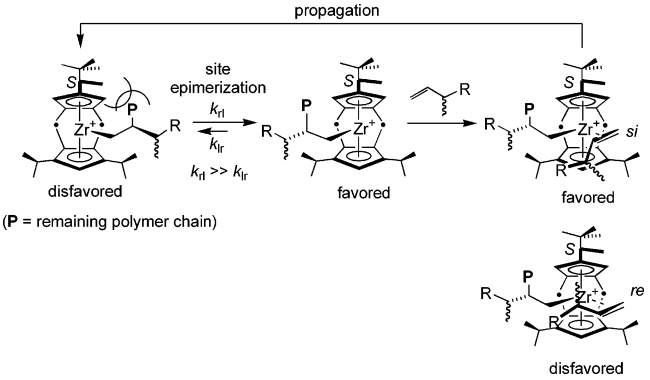
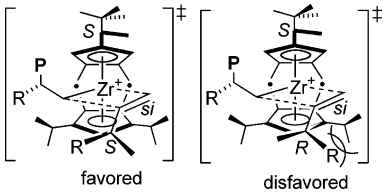


Figure 4. ^{13}C NMR spectrum (125.72 MHz) of poly(3-methyl-1-pentene) made with catalyst (*S*)-**2**/MAO.

Scheme 3



Scheme 4



Most interestingly, a synthetically useful *s* value is obtained for an olefin bearing substitution at both the 3- and the 4-positions; 3,4-dimethyl-1-pentene (3,4-DMP1) was resolved with $s > 15$. Increasing the substitution at the 5-position, as in 3,5,5-trimethyl-1-hexene (3,5,5-TMH1), has a less dramatic effect. Very poor resolution was observed for 4-methyl-1-hexene (4-MH1) in which the stereogenic center is separated from the olefin moiety by a methylene unit. In all cases, (*S*)-**2** preferentially incorporates the *S* antipode of the racemic olefin into the polymer. Although we have measured some selectivity for 3-phenyl-1-hexene polymerization ($s = 1.3$), the antipode selectivity remains uncertain at this time.

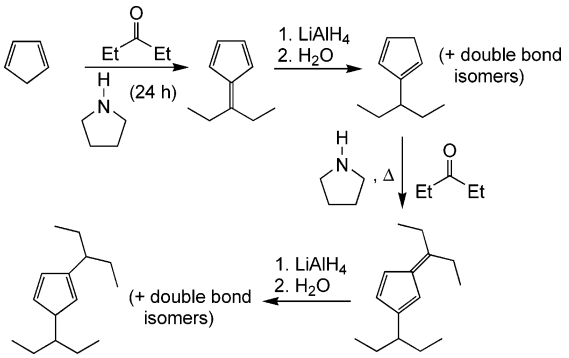
Significantly, the ^{13}C NMR spectrum of poly(3-methyl-1-pentene) made with (*S*)-**2** was consistent with a predominantly isotactic microstructure (Figure 4).[12c,15a] Analysis of the prevailing steric interactions in the active site of the catalyst suggests that isotactic polymer results from a rapid site epimerization process (polymer chain swinging to the opposite side of metallocene wedge after each migratory insertion of monomer), as has been established for *rac*-**2**/MAO-catalyzed propylene polymerization under dilute monomer conditions.[17] Hence, to minimize steric interactions, the growing polymer chain swings to the more open (left) side of the wedge, avoiding contact with the methyl group of the chiral substituent (Scheme 3). Because the chiral olefins polymerized with enantiopure **2** are bulkier than propylene, and are therefore enchained more slowly, it is likely that the rate of site epimerization greatly exceeds the rate of propagation. With a high rate of site epimerization (relative to olefin uptake and insertion), the olefin encounters the same steric environment (the chiral pocket on the right side of the metallocene wedge) during each enchainment event, consistent with the highly isotactic poly-(3-methyl-1-pentene).

Although the differences in transition state energies are clearly small, one can rationalize the enantiomeric preferences on the basis of relative steric interactions. For these 3-methyl-substituted α-olefins, uptake of the *S* enantiomer on the right side of the wedge is favored. If one assumes conformational freedom for the incoming olefin, then for the olefin adduct (a first-order model of the insertion transition state) *S*-monomer binding places the larger 3-position substituent (R = Et, isopropyl, neopentyl vs Me) in the more open region between the lower cyclopentadienyl ligand isopropyl groups. For the *R*-monomer, the olefin R substituent is directed more toward the lower right [$CHMe_2$] cyclopentadienyl substituent (Scheme 4). Hence, the antipode selectivity of this system is the result of an indirect mechanism. An interaction between the chiral methylneopentyl substituent of the "upper" cyclopentadienyl dictates the preferred side of the wedge for the growing polymer chain, which in turn allows the incoming olefin access to only one side of the metallocene wedge. The steric interactions of the side chain of the monomer with the chiral pocket provided by the "lower" cyclopentadienyl ligand, not the cyclopentadienyl directly bearing the enantiopure methylneopentyl substituent, lead to selectivity!

To support these conclusions, molecular mechanics calculations (CAChe) were carried out for olefin binding into the right side of the wedge using [{$(SiMe_2)_2$[η^5-$C_5H(CHMe_2)_2$][η^5-C_5H_2-((*S*)-$CHMeCMe_3$)]}$ZrCH_3$]$^+$ as a model for the active catalyst.[24] Consistent with the experimental results, for 3-MP1, *S* antiopode binding is slightly favored ($\Delta E = 0.8$ kcal mol^{-1}). On the other hand, care should be exercised when using these computational

(24) Molecular mechanics calculations were carried out using the CAChe software package (v. 4.9). A model complex {$(SiMe_2)_2$[η^5-$C_5H(CHMe_2)_2$]-[η^5-C_5H_2((*S*)-$CHMeCMe_3$)]}$ZrMe$(η^2-olefin)$\}^+$ was used for the active site. The Zr atom, the methyl group, and the olefinic carbons were forced to be coplanar. The α-substituent was fixed at 90° to the plane containing the Zr atom and the olefin carbons.

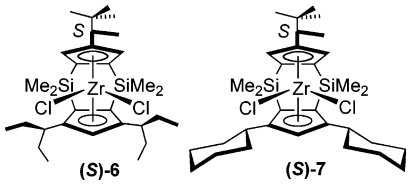
Scheme 5



predictions with such a simple model (e.g., for 3,4-DMP1, the *R* antipode is favored by more than 1.5 kcal mol^{-1}, contrary to experiment!), especially when the transition state energy differences are so very small, as indicated by the relatively small *s* values. Moreover, it is likely that the ΔE of the diastereomeric transition states for an alkyl migration process, rather than the ΔE for a discrete olefin intermediate, as in these approximations, determines the relative rates of enantiomer polymerization in the current system. Finally, several recent lines of evidence (vide infra) suggest that additional interactions arising from the chiral monomer and asymmetric zirconocene fragment with the asymmetric β and γ centers of the migrating polymeryl chain are also important and should therefore be included in the transition state computations.

Synthesis and Kinetic Resolution Trials with {(SiMe$_2$)$_2$-[η^5-C$_5$H(CHEt$_2$)$_2$][η^5-C$_5$H$_2$((*S*)-CHMeCMe$_3$)]}ZrCl$_2$, (*S*)-6, and {(SiMe$_2$)$_2$[η^5-C$_5$HCy$_2$][η^5-C$_5$H$_2$((*S*)-CHMeCMe$_3$)]}ZrCl$_2$, (*S*)-7. Because the steric interactions between substituents on the 3 carbon of the incoming chiral olefin and the isopropyl substituents on the "lower" cyclopentadienyl ligand for (*S*)-**2** appear to be key factors in differentiating the diastereotopic transition states for propagation, we next sought to examine the effect of changing the nature of the 3,5-substituents on the lower ligand of the zirconocene catalyst. For (*S*)-**2**, the incorporation of two isopropyl groups involves successive condensation reactions of cyclopentadiene with acetone to give as a primary ligand fragment, 1,3-(CHMe$_2$)$_2$C$_5$H$_4$.[16,25] A similar synthetic route was taken here for the incorporation of 3-pentyl substituents (Scheme 5). The preparation of 1,3-Cy$_2$C$_5$H$_4$ was carried out according to the literature procedure.[25b]

Starting from the appropriately substituted cyclopentadiene and using a procedure analogous to that used in the preparation of (*S*)-**2**, 3-pentyl or cyclohexyl substitution was introduced at the 3,5-positions to give enantiopure precatalysts (*S*)-**6** and (*S*)-**7**, respectively.[16,17]



The molecular structure of (*S*)-**6** is shown in Figure 5, and that for (*S*)-**7** is shown in Figure 6. As expected on the basis of

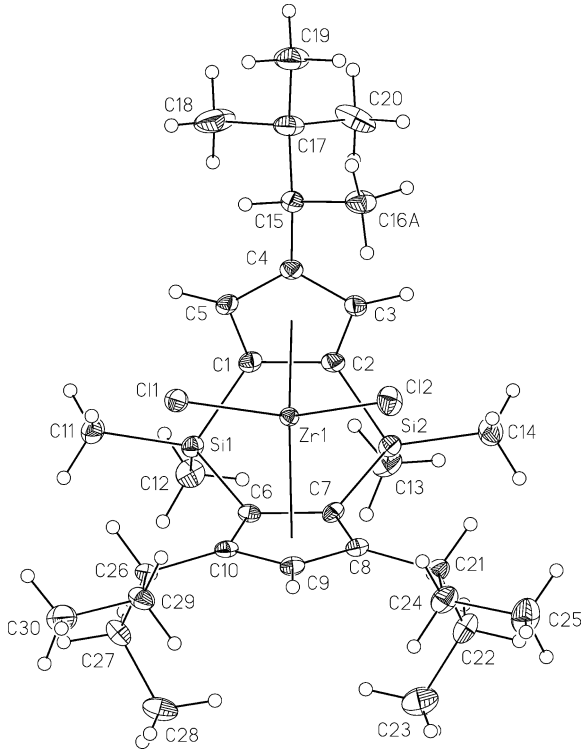


Figure 5. View of (*S*)-**6**.

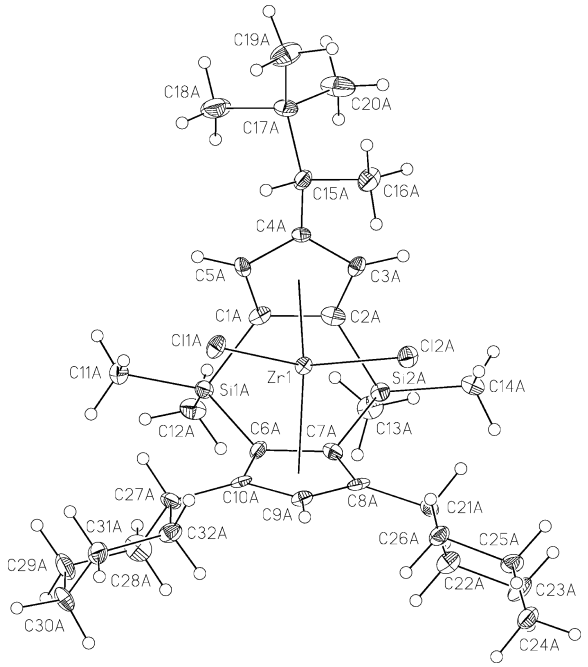


Figure 6. View of (*S*)-**7**.

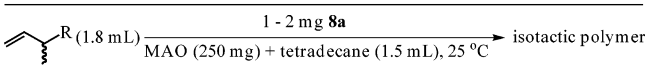
the X-ray data for complexes (*S*)-**2** and (*S*)-**5** (Table 4), the methylneopentyl groups adopt a conformation that orients the methyl group toward one side of the metallocene wedge. Figure 5 also shows that the 3-pentyl substituents at the 3,5-positions of the "lower" cyclopentadienyl ligand adopt a staggered conformation and are rotated so that the methine proton is directed back toward the SiMe$_2$ groups, much like the isopropyl substituents of (*S*)-**2**. When comparing the molecular structures of (*S*)-**2** (Figure 1) and (*S*)-**6** (Figure 5), it is evident that for each catalyst the open areas between the 3,5-substituents on the "lower" cyclopentadienyl ligand are not greatly different.

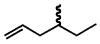
(25) (a) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849. (b) Clark, T. J.; Killian, C. M.; Luthra, S.; Nile, T. A. *J. Organomet. Chem.* **1993**, *462*, 247.

Table 2. Comparisons of the Kinetic Resolutions of Chiral, 3- and 4-Methyl-Substituted α-Olefins Using (*S*)-**2**, (*S*)-**6**, and (*S*)-**7**

olefin	(*S*)-2 TOF (hr^{-1})	(*S*)-2 $s = \frac{k_S}{k_R}$	(*S*)-6 TOF (hr^{-1})	(*S*)-6 $s = \frac{k_S}{k_R}$	(*S*)-7 TOF (hr^{-1})	(*S*)-7 $s = \frac{k_S}{k_R}$
	60 (12)	2.6 (2)	266	2.3 (2)	374	2.5 (1)
	551 (50)	1.8 (2)	299	1.8 (1)	706	1.9 (1)
	46 (10)	2.1 (1)	49	6.4 (7)	111	1.6 (3)
	40 (11)	16.8 (8)	109	12.5 (4)	450	14.0 (2.8)
	75 (2)	1.1 (1)	111	1.2 (1)	633	1.2 (1)

Table 3. Kinetic Resolutions of Chiral, 3- and 4-Methyl-Substituted α-Olefins Using Diastereomer **8a**



olefin	TOF (hr^{-1})	$s = \frac{k_B}{k_S}$
	396	1.1
	26	1.1
	55	1.2
	30	2.6
	47	1.0

The cyclohexyl groups of precatalyst (*S*)-**7** take eclipsed, chair conformations, leading to an even smaller change in steric bulk relative to (*S*)-**2** (Figure 6). Overall then, the prevailing steric interactions presented by complexes (*S*)-**2**, (*S*)-**6**, and (*S*)-**7** are rather similar.

Activation of (*S*)-**6** or (*S*)-**7** with MAO affords highly active catalysts suitable for the polymerization of 3-substituted olefins. The results of the kinetic resolution are given in Table 2 together with the average *s* values for (*S*)-**2**.[23] Readily apparent is that, relative to (*S*)-**2**, only minor changes in *s* are obtained for most of the olefins surveyed. In the few deviations of note, precatalyst (*S*)-**6** showed a small increase in *s* for the polymerization of 4-methyl-1-pentene and more significantly a 3-fold increase for 3,5,5-trimethyl-1-hexene ($s = 6$) relative to (*S*)-**2** and (*S*)-**7** ($s = 2$). This increase in selectivity is consistent with a "fine-tuning" of the catalyst chiral pocket for interaction with 4-MH1 and 3,5,5-TMH1. For 3,4-DMP1, there is a slight decrease in *s* relative to that for (*S*)-**2**. The variation in turnover numbers is not readily understood, but may reflect different percentages of active zirconium centers and/or differing catalyst stabilities. Overall, the general trends in the observed *s* values for (*S*)-**2**, (*S*)-**6**, and (*S*)-**7** track well with expectations based on the molecular structures of (*S*)-**2** and (*S*)-**6** (see above).

{(SiMe$_2$)$_2$[η^5-C$_5$H((*S*)-CHMeCy)(CHMe$_2$)][η^5-C$_5$H$_3$]}ZrCl$_2$ (8a), a Precatalyst with an Enantiopure Substituent on the "Lower" Cyclopentadienyl Ligand. In addition to relatively simple extensions that involve (minor) variances in the steric interactions at the 3,5-substituents of the lower cyclopentadienyl ligand, a rather different strategy was explored: introduction of an enantiopure chiral group at one of these positions. Catalysts based on (*S*)-**2**, for which the enantiopure group dictates the orientation of the polymer chain, relay the chiral information of the C_1-symmetric metallocene framework to the olefin, repeatedly approaching from the same side of the metallocene wedge. For this second-generation catalyst, a more direct interaction was anticipated between the incoming chiral monomer and the chiral substituent in the ligand framework. The choice of enantiopure 1-cyclohexylethyl as the chiral substituent requires as a key component 1-((*S*)-1-cyclohexylethyl)-3-(isopropyl)cyclopentadienide. The successful strategy follows the sequence shown in Scheme 6. As before with the methylneopentyl substituent, access to enantiopure metallocene begins with an optically pure alcohol. A known, enzymatically catalyzed kinetic resolution of 1-cyclohexylethanol was amenable to scale-up and could be used to give both (*R*)- and (*S*)-1-cyclohexylethanol in high enantiopurity (ee > 96%).[19,26] Conversion of the alcohol to mesylate and nucleophilic attack by cyclopentadienide anion affords (*S*)-1-cyclohexylethylcyclopentadiene. Pyrrolidine-catalyzed condensation with acetone gives 6,6-dimethyl-(*S*)-1-cyclohexylethylfulvene as a single regioisomer.[25] Reduction with $LiAlH_4$ gives the desired cyclopentadiene as a mixture of double bond isomers, and subsequent deprotonation with *n*-butyllithium gives a single product. At this stage, synthesis of ferrocene derivatives was again used to establish that (near) perfect inversion of the carbon stereocenter had once again occurred during the S_N2 reaction (ee_S > 96%): although ^{1}H NMR was not very informative due to strong overlap of reasonances for *rac* and *meso* isomers in all regions of the spectrum, examination of the ^{13}C NMR spectrum showed the presence of only the *S*,*S* diastereomer (de > 99%) in the reaction of $FeCl_2$ with Li[C_5H_4((*S*)-1-cyclohexylethyl)].

From this point on, a modified version of the procedures used for preparing the ligand for (*S*)-**2** was employed; however, due to the nonequivalence of the 1,3-substituents, two products are possible on reaction with $SiCl_2Me_2$, and both are observed (Scheme 6). As expected, a complicated ^{1}H NMR spectrum was obtained due the presence of double bond isomers, but deprotonation gave a more easily interpreted spectrum, and the presence of two regioisomers in an approximate 1:1 ratio could be identified. Reaction with Li(C_5H_5) followed by deprotonation gives a 1:1 mixture of the singly bridged linkage isomers. Addition of $SiCl_2Me_2$ to the doubly deprotonated mixture of regioisomers then yields a single species through formation of what appears to be the stable tricyclic ligand arrangement. A final deprotonation with 2 equiv of *n*-butyllithium gives the dilithio salt, "(*S*)-1-cyclohexylethyl-ThpLi$_2$", in high yield.

Metalation of the above ligand was not straightforward. The lack of symmetry of the ligand allows for two possible diastereomers on metalation. Although some diastereoselectivity was expected, to our surprise, reaction of (*S*)-1-cyclohexylethyl-ThpLi$_2$ with $ZrCl_4$ gave an essentially 1:1 ratio of diastereomers (Scheme 7). It is likely that the diastereotopic faces of the less substituted "upper" cyclopentadienyl ligand encounter the zirconium metal first in a nonselective coordination event, followed by a rapid coordination of the bulky "lower" cyclopentadienyl ligand, giving roughly equal amounts of each diastereomer. Although the salt metathesis route is nonselective, a single diastereomer could be isolated by washing the mixture with cold petroleum ether to remove the much more soluble

(26) (a) Frykman, H.; Öhrner, N.; Norin, T.; Hult, K. *Tetrahedron Lett.* **1993**, *34*, 1367. (b) Öhrner, N.; Martinelle, M.; Mattson, A.; Norin, T.; Hult, K. *Biotechnol. Lett.* **1992**, *14*, 263.

Table 4. X-ray Experimental Data[a]

compound	(*S*)-**2**	(*S*)-**5**	(*S*)-**6**·toluene	(*S*)-**7**·dichloromethane
formula	$C_{26}H_{42}Cl_2Si_2Zr$	$C_{38}H_{52}S_2Si_2Zr$	$C_{33.50}H_{54}Cl_2Si_2Zr$ [$C_{30}H_{50}Cl_2Si_2Zr \cdot {}^1/_2(C_7H_8)$]	$C_{33.32}H_{52.64}Cl_{4.64}Si_2Zr$ [$C_{32}H_{50}Cl_2Si_2Zr \cdot 1.32(CH_2Cl_2)$]
formula weight	572.90	720.32	675.09 [629.02·${}^1/_2$(92.14)]	765.15 [653.04·1.32(84.93)]
crystal system	monoclinic	tetragonal	triclinic	monoclinic
space group	$P2_1$ (No. 4)	$P4_32_12$ (No. 96)	$P1$ (No. 1)	$P2_1$ (No. 4)
a, Å	8.8568(8)	12.6459(8)	10.3602(5)	13.2833(7)
b, Å	19.7932(18)	12.6459(8)	13.1543(7)	19.3805(10)
c, Å	16.5826(15)	47.844(4)	14.0843(7)	14.7651(8)
α, deg	90	90	97.199(1)	90
β, deg	105.522(1)	90	104.068(1)	107.195(1)
γ, deg	90	90	106.275(1)	90
volume, Å^3	2801.0(4)	7651.1(10)	1748.26(15)	3631.2(3)
Z	4	8	2	4
ρ_{calc}, g/cm^3	1.359	1.251	1.282	1.400
μ, mm^{-1}	0.68	0.48	0.56	0.73
F_{000}	1200	3040	714	1598
crystal shape	blade	irregular block	plate	plate
crystal color	colorless	pale yellow	colorless	colorless
crystal size, mm	0.16 × 0.23 × 0.27	0.17 × 0.22 × 0.26	0.15 × 0.22 × 0.24	0.09 × 0.20 × 0.26
T, K	98	98	100	100
θ range, deg	1.6, 28.3	1.7, 28.6	1.6, 28.2	1.4, 28.4
h,*k*,*l* limits	−11, 11; −26, 25; 21,21	−16, 16; −16, 16; −64, 63	−13, 13; −17, 17; −17, 18	−17, 16; −25, 25; −19, 19
data measured	48 755	75 962	39 577	54 234
unique data	12 773	9368	15 367	16 726
R_{int}	0.066	0.082	0.041	0.064
data, $F_o > 4\sigma(F_o)$	11 952	7859	13 420	12 842
parameters/restraints	583/1	544/0	716/3	765/1
R1,[b] wR2;[c] all data	0.038, 0.058	0.057, 0.060	0.036, 0.063	0.059, 0.064
R1,[b] wR2;[c] $F_o > 4\sigma(F_o)$	0.034, 0.058	0.043, 0.059	0.030, 0.062	0.037, 0.060
GOF[d] on F^2	1.21	1.55	1.45	1.13
$\Delta\rho_{max,min}$, e Å^{-3}	1.26, −0.48	0.98, −0.72	0.60, −0.31	1.17, −0.76

[a] All data were collected on a Bruker SMART 1000 ccd with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [d] $GOF = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

diastereomer **8b**. The identity of the less soluble diastereomer as **8a** was established by ^{1}H and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectrum of **8a** shows two resonances at higher field corresponding to "axial" methyl groups of the isopropyl and cyclohexylethyl substituents, respectively (see below), those lying almost perpendicular to and below the plane of the "lower" Cp ligand. A single resonance appearing at lower field corresponds to an equatorial methyl group (also part of the isopropyl substituent) which is approximately coplanar with the "lower" cyclopentadienyl ligand. The chemical shift assignments are consistent with a greater ring current effect on the axial methyl hydrogens[27] and have been corroborated by comparison to ^{1}H NMR data obtained for a related, X-ray structurally characterized zirconocene dichloride also bearing isopropyl and cyclohexylethyl substituents at the 3,5-positions.[28] As a consequence, the large cyclohexyl group points forward and out of the metallocene wedge in the prevailing conformation, while the methine proton is directed back toward the dimethylsilylene group, consistent with the molecular structures of (*S*)-**2** and (*S*)-**6** and (*S*)-**7** (Figures 1, 5, and 6). Molecular mechanics calculations were carried out for **8a**, and the minimized structure is fully consistent with the cyclohexylethyl group favoring the conformation shown in Scheme 7.

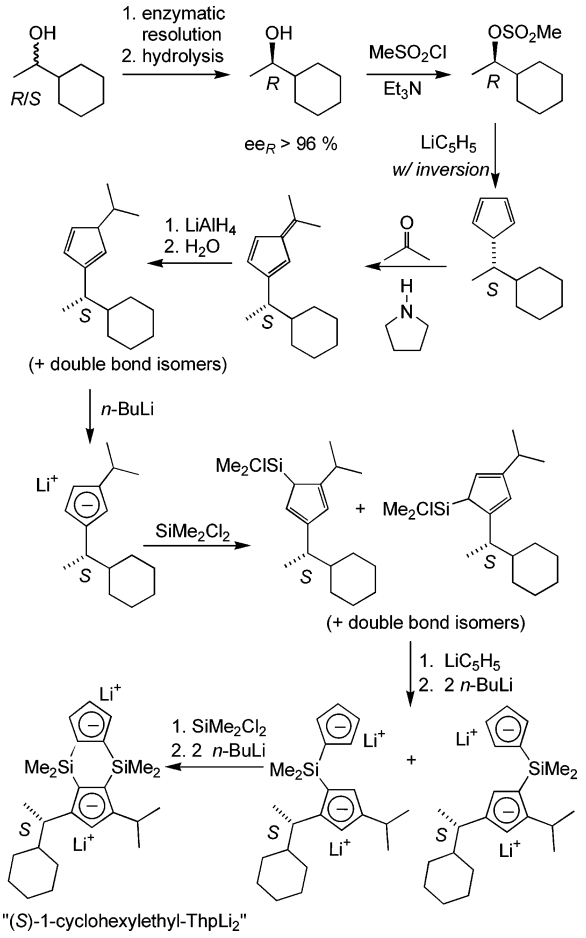
Molecular mechanics calculations also predict that diastereomers **8a** and **8b** are of substantially different energy with **8b** favored by 1.7 kcal mol^{-1}. Salt metathesis, then, appears to give a kinetic mixture of products rather than a thermodynamically established one. Isolation of **8b** was accomplished using the fully reversible amine elimination procedure recently developed for the improved synthesis of *rac*-(EBTHI)$ZrCl_2$ complexes (EBTHI = ethylene-bis(4,5,6,7-tetrahydro-1-η^5-indenyl)).[29] For the present system, reaction of the diprotio form of the ligand with $Zr(NMe_2)_4$ gives a ≤1:10 ratio of **9a**:**9b** at equilibrium (Scheme 8).

Reaction of the diastereomeric mixture of diamides with Me_3SiCl gives the desired precatalyst **8b** as the main species (>90%). The ^{1}H NMR spectrum of **8b** showed the presence of two downfield resonances at δ 1.26 and δ 1.34 for methyl groups that are approximately coplanar with the "lower" Cp. A single upfield resonance for an axial methyl group is present at δ 0.90. These ^{1}H NMR parameters are in contrast to those observed for **8a** and indicate that the large cyclohexyl group is rotated out of plane in diastereomer **8b**. The minimized structure obtained from molecular mechanics calculations is consistent with this conclusion. Unfortunately, despite repeated efforts, the extreme solubility of **8b** prevented successful crystallization, and **8b** could not be isolated in analytically pure form (impurities <10% by ^{1}H NMR spectroscopy). Despite this difficulty, we considered the complex to be of sufficient purity for use in kinetic resolution procedures, and some data were acquired (vide infra).

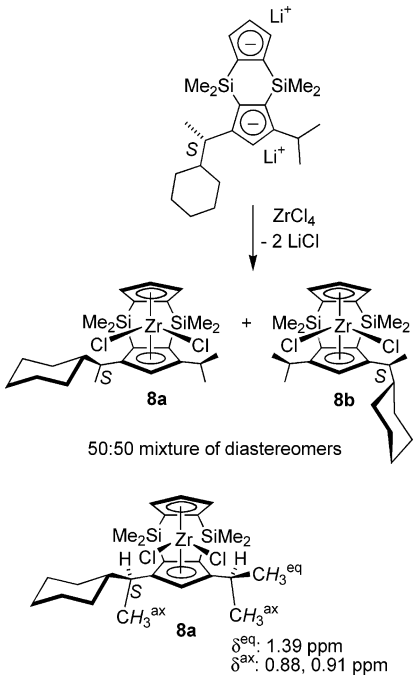
The kinetic resolution results for **8a** are given in Table 3.[23] The data show that the *s* values are markedly diminished relative to those with (*S*)-**2**, (*S*)-**6**, and (*S*)-**7**. Indeed, the only olefin to show even a small degree of selectivity was 3,4-DMP1 (s = 2.6). Significantly, in all cases, the *R*-monomer was polymerized

(27) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 3rd ed.; Wiley-VCH: New York, 1998.
(28) Baar, C. R.; Day, M. W.; Bercaw, J. E., manuscript in preparation.
(29) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5.

Scheme 6



Scheme 7



at a higher rate than the *S*-monomer, opposite to that observed for (*S*)-**2**, (*S*)-**6**, and (*S*)-**7**. With diastereomer **8b**, 3,4-DMP1 was polymerized with very low selectivity, $s = 1.4$, again with a preference for the *R* antipode. This diminished selectivity is almost certainly a consequence of the cyclohexyl group's axial orientation, and hence its minimal role in steric interactions with the bound olefin or with the growing polymer chain. Diastereomer **8b** then behaves much like an achiral, C_s-symmetric system, precluding selectivity for kinetic resolutions. For this reason, other, less bulky, olefins were not examined.

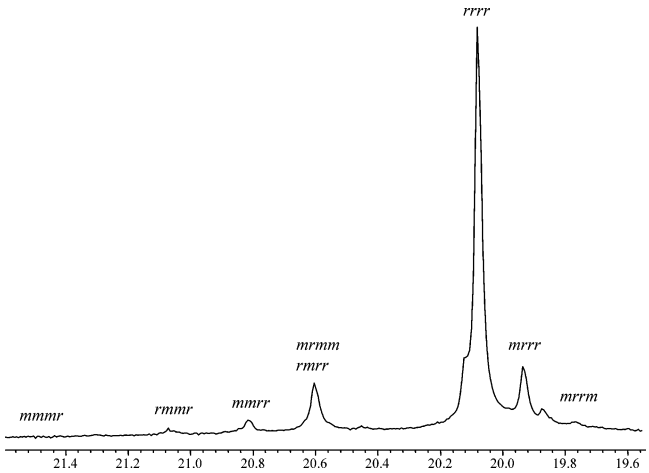
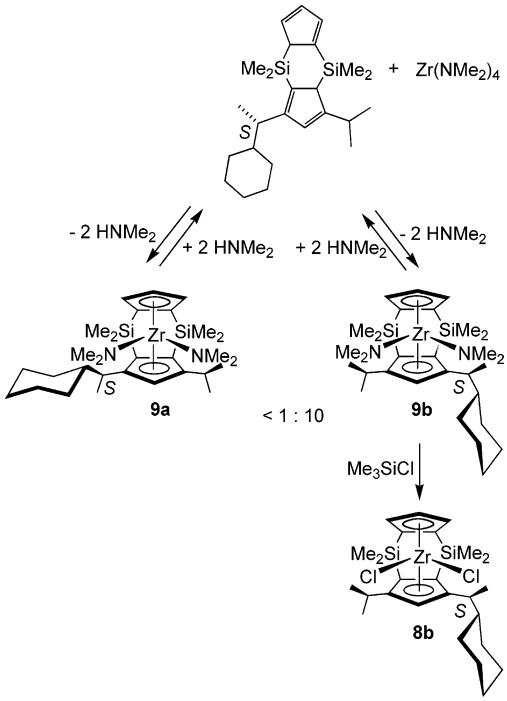


Figure 7. ^{13}C NMR spectrum (125.72 MHz) of polypropylene made with catalyst **8a**/MAO.

Scheme 8



On the basis of our steric model, a predominantly syndiotactic enchainment is perhaps expected with catalysts derived from **8a** and **8b**, because, in the absence of an "upper" methyl-neopentyl substituent, the polymeryl chain can access open regions of space on either side of the metallocene wedge.[30] This expectation is borne out for polymerization of (liquid) propylene with **8a**, which gives rise to a mainly syndiotactic polymer, [*r*] = 91.5% (Figure 7).[30a] In contrast, the ^{13}C NMR spectrum obtained for poly(3-methyl-1-pentene) was consistent with a prevailingly isotactic polymer (Figure 8).[12c,15]

(30) In a C_S-symmetric catalyst, syndiotactic polymer microstructure arises from propylene insertion from regularly alternating sides of the metallocene wedge: (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1223. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1253.

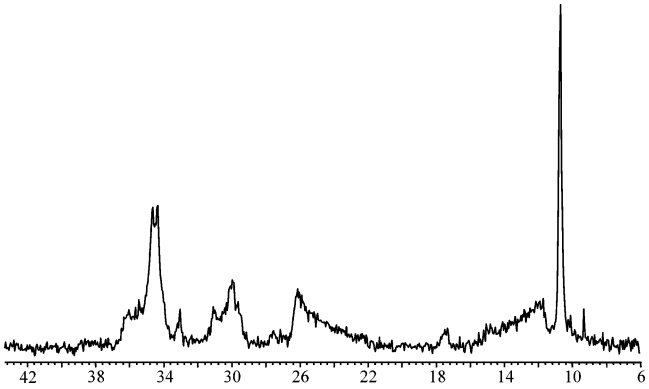
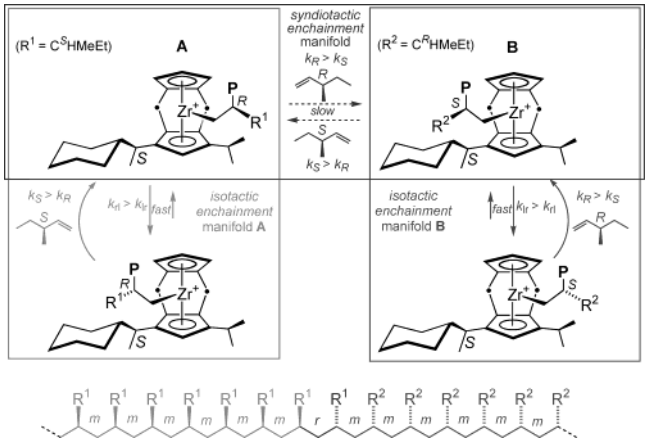


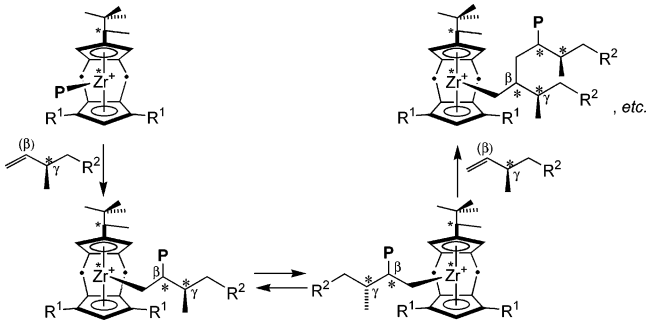
Figure 8. ^{13}C NMR spectrum (125.72 MHz) of poly(3-methyl-1-pentene) made with catalyst **8a**/MAO.

Scheme 9



Initially, it seemed difficult to rationalize a highly isotactic polymer in combination with low resolving power for **8a** (Table 3): if isotacticity was the result of the polymer chain lying predominantly on one side of the metallocene wedge (as is the case for (*S*)-**2**), then one would expect at least a similar degree of resolution, because the sterics of the 3,5-substituents of the "lower" cyclopentadienyl ligand are at least as large in the present catalyst as in the original system. Instead, we propose that the polymer chain does have access to both sides of the metallocene wedge through the mechanism shown in Scheme 9. A similar mechanism was proposed by Zambelli to explain the formation of isotactic blocks during the polymerization of bulky 3-substituted olefins (e.g., 3-methyl-1-butene) using an achiral C_s-symmetric metallocene catalyst.[31] In this mechanism, a chain-end-mediated site epimerization controls which diastereomeric active site is favored for a β-*R* or β-*S* chain end, respectively (equilibrium **A** ⇔ **B** in Scheme 9). If the energy difference between diastereomeric transition states using either **A** or **B** is large, then one expects site epimerization to be fast relative to olefin uptake and insertion. As a result, enchainment occurs mainly from one side of the metallocene wedge, producing an isotactic block until a syndiotactic enchainment error occurs (by olefin insertion prior to site epimerization). A syndiotactic insertion error, followed by rapid site epimerization, switches olefin uptake from one side of the wedge to the other. Once again, isotactic enchainment occurs (but with opposite enantiofacial selectivity) until another syndiotactic insertion error switches the side of olefin uptake yet again. In this way, a polymer that is predominantly isotactic (with isolated *r* diads) will be formed, but it will contain stereoblocks of opposite absolute configuration at the carbons within the polymer backbone (−*RRRRR*− and −*SSSSS*−).

Scheme 10



Although in Scheme 9 we have indicated that the stereoselectivities for a single antipode of racemic 3MP1 are very high for each of the three manifolds, this need not be the case. The observed *s* value of 1.1 indicates that if stereoselectivities are high, then there are nearly equal rates for isotactic enchainment manifolds **A** and **B**. Alternatively (and more likely), the stereoselectivities for both manifolds are low.

Conclusions

We have developed a series of enantiopure C_1-symmetric metallocene catalysts that polymerize relatively bulky, racemic 3-methyl-substituted α-olefins with unprecedented activities. In addition, the enantiomers react at different rates, allowing for the partial kinetic resolution of simple racemic alkenes. For 3,4-dimethyl-1-pentene, $s > 15$ has been achieved, marking the first practically useful kinetic resolution of such a simple unfunctionalized monomer. We have proposed a general mechanism to explain both the isotacticity of the resulting polymers as well as the preferred antipodal selectivity for catalysts (*S*)-**2**, (*S*)-**6**, and (*S*)-**7**. We note, however, that the situation is significantly more complicated, considering the number of stereocenters in the vicinity of the active site (Scheme 10).

That chain-end chirality at the γ stereocenter may be important in determining the relative rates of enantiomer polymerization was recently demonstrated using *rac*-C_2-symmetric and C_s-symmetric metallocene catalysts.[15] Similarly, polymerization of 3-methyl-1-pentene with **8a** gives isotactic polymer due to a chain-end-mediated site epimerization process. This process is thought to be controlled by chirality at the β-stereocenter.[31,32] The extent to which the chiral polymer chain end influences site epimerization in catalysts (*S*)-**2**, (*S*)-**6**, and (*S*)-**7** remains unknown. Considering catalyst (*S*)-**2**, for example, the influence of the methylneopentyl group on the preferred orientation of the polymer chain, that is, right or left in the zirconocene wedge, could work in concert with or against any preference for the chain to be right or left due to influences from the chiral polymer chain end itself. Similarly, during enchainment, the antipodal preference for chiral monomer will be a function of both the enantiomorphic catalyst site and the polymer chain-end chirality (largely at β and γ positions).

Future directions for the project will focus on copolymerization experiments with mixtures of chiral and achiral olefins

(31) Grisi, F.; Longo, P.; Zambelli, A.; Ewen, J. A. *J. Mol. Catal. A* **1999**, 225.

(32) Borriello, A.; Busico, V.; Cipullo, R.; Chadwick, J. C.; Sudmeijer, O. *Macromol. Chem., Rapid Commun.* **1996**, 589.

that are intended to indirectly probe the role that the stereogenic centers of the polymer chain end play in the resolution process. We are also developing new C_1-symmetric catalysts that contain multiple enantiopure substituents, nonracemic C_2-symmetric metallocenes, and we are exploring nonmetallocene strategies in an effort to design more general and selective kinetic resolution catalysts.

Experimental Section

General Considerations. All air- and/or moisture-sensitive compounds were manipulated using standard high-vacuum line, swivel frit assembly, Schlenk and cannula techniques, or in a glovebox under a nitrogen atmosphere as described previously.[33] Argon was purified and dried by passage through columns of MnO on vermiculite and activated 4 Å molecular sieves. All solvents were stored under vacuum over sodium benzophenone ketyl, titanocene, or calcium hydride prior to use. Pinacolone was dried over anhydrous $CaSO_4$ and distilled prior to use. Methylaluminoxane (MAO) was purchased from Albemarle, and all volatiles were removed in vacuo to give a white powder. The CBS catalyst (*S*)-tetrahydro-1-methyl-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-*c*]-[1,3,2]oxazaborole-borane and the Novozyme-435 enzyme were purchase from Aldrich. Olefins were purchased from Chemsampco and stored under vacuum over lithium aluminum hydride. (*S*)-2-Methylbutane-1-thiol[34] and Li[(*rac*)-MNCp][16] (MN = methylneopentyl) were synthesized according to literature methods. (*S*)-**2** was synthesized by the route previously reported for the racemic counterpart, except that [((*S*)-CHMeCMe$_3$)C$_5$H$_4$]Li was used in place of the racemate.[17] Mandelic esters of alcohols and carboxylic acids were synthesized on the basis of literature procedures.[35] (*S*)-Ethylthiooctanoate was made according to the literature procedure.[26a]

NMR spectra were recorded on a General Electric QE300 (300 MHz for ^{1}H), Bruker AMX (500 MHz for ^{1}H), JEOL Delta (400 MHz for ^{1}H), or Varian Mercury (300 MHz for ^{1}H) spectrometer. Gas chromatographs were obtained on an Agilent 6890 Series gas chromatograph using a 30 m × 0.25 mm, γ-cyclodextrin trifluoroacetyl "Chiraldex-TA" column from Advanced Separations Technology. Optical rotations were measured on a Jasco P1030 polarimeter at ambient temperature. A 1 mL cell with a 1 dm path length was used.

(*R*)-3,3-Dimethyl-2-butanol. The borane adduct of the (*S*)-CBS catalyst (14.6 g, 50 mmol) was placed in a 500 mL two-neck flask along with a magnetic stir bar, under a nitrogen atmosphere in a glovebox. Dry methylene chloride (50 mL) and borane−dimethyl sulfide complex (100 mL, 1.00 mol) were added to the argon-flushed flask, and the mixture was cooled to −20 °C with an ethylene glycol/water slush bath. Pinacolone (125.0 mL, 1.00 mol) was added over a 4 h period via a syringe pump. Stirring at −20 °C was continued for 4 h after the addition was complete. The reaction was quenched by dropwise addition of methanol in a 1 L beaker cooled in an ice bath. After addition of the reaction mixture, the solution was allowed to warm to room temperature and was stirred for 1 h, after which time no further hydrogen evolution was evident. The solution was concentrated to 150 mL by distillation, 250 mL of methanol was added, and the process was repeated to remove the volatile boron compounds from the reaction mixture. Distillation was continued until all methanol was removed, and the product alcohol was then vacuum distilled. (*rac*)-3,3-Dimethyl-2-butanol was synthesized by the $LiAlH_4$ reduction of pinacolone using standard conditions.

(*R*)-3,3-Dimethylbutyl-2-*p*-toluenesulfonate. (*S*)-3,3-Dimethyl-2-butanol (15.0 g, 147 mmol) was dissolved in methylene chloride (100 mL) in a 250 mL round-bottom flask. Pyridine (35.5 mL, 440 mmol) and DMAP (250 mg) were added, and the reaction mixture was stirred for 48 h at room temperature. Thin-layer chromatography (4:1 hexanes: ethyl acetate eluant) indicated that the reaction had gone to completion. The reaction mixture was subjected to subsequent washings with water, 1 N potassium bisulfate, saturated sodium bicarbonate, and brine. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo to give 35.0 g of a thick light-yellow oil (99.6% from the alcohol). ^{1}H NMR ($CDCl_3$): $\delta = 0.70$ (s, 9H), 1.42 (d, 3H), 4.38 (q, 1H, $J = 7.8$ Hz), 7.35 (d, 2H), 7.75 (d, 2H, $J = 8.4$ Hz). (*rac*)-3,3-Dimethylbutyl-2-*p*-toluenesulfonate was synthesized according to the same procedure (90.3%).

(*S*)-Methylneopentylcyclopentadiene. Lithium cyclopentadienide (41.1 g, 571 mmol) was weighed into a 1 L flask in a nitrogen glovebox. Dry tetrahydrofuran (500 mL) was added, and the flask was cooled in an ice bath. (*R*)-3,3-Dimethylbutyl-2-*p*-toluenesulfonate (94.1 g, 393 mmol) was added as a 1:1 solution with THF. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (172 mL, 1140 mmol) was added, and the solution was allowed to warm to room temperature. The solution was refluxed for 2 days under an argon atmosphere. An aliquot, taken after 24 h, showed (GC) a 1:1 ratio of (*S*)-methylneopentylcyclopentadiene: tosylate; after 48 h, the ratio was 14:1. Low boiling petroleum ether (250 mL) was added, and excess LiCp was quenched by the slow addition of water (10 mL). The solution was treated to washings with water, 1 N $KHSO_4$, saturated $NaHCO_3$, and brine. The solution was dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. The (*S*)-methylneopentylcyclopentadiene was then vacuum transferred from the reaction mixture to give 38.3 g of a colorless liquid (57% from tosylate). As expected, the ^{1}H NMR spectrum was complex, indicating a mixture of double bond isomers.

Li[(*S*)-methylneopentylcyclopentadienide]. (*S*)-Methylneopentylcyclopentadiene (19.2 g, 128 mmol) was dissolved in dry diethyl ether (250 mL) in a 500 mL flask attached to a swivel frit assembly. The flask was cooled to −78 °C, and *n*-butyllithium (1.6 M in hexanes, 95.6 mL, 153 mmol) was added by syringe via the sidearm of the swivel frit. The cold bath was removed, and the solution was allowed to warm to room temperature under an atmosphere of argon open to a mercury bubbler. The reaction was stirred for 12 h at room temperature, and the solvent was then removed in vacuo. Petroleum ether (200 mL) was then vacuum transferred onto the solid material, the resulting suspension was filtered, and the solid was washed twice with petroleum ether. The white solid was dried in vacuo and stored in a nitrogen glovebox. Yield: 17.4 g, 87% from methylneopentylcyclopentadiene. ^{1}H NMR (THF-d_8): $\delta = 0.79$ (s, 9H), 1.13 (d, 3H), 2.39 (q, 1H, $J = 7.14$ Hz), 5.47 (d, 2H), 5.49 (d, 2H, $J = 2.5$ Hz).

(*rac/meso*)-Iron Bis(methylneopentylcyclopentadienide), 3. Iron(II) chloride (81 mg, 0.64 mmol) and lithium (*rac*)-methylneopentylcyclopentadienide (200 mg, 1.28 mmol) were weighed into a 50 mL flask under a nitrogen atmosphere. The flask was evacuated, and dry THF (15 mL) was vacuum transferred into the flask at −78 °C. The flask was allowed to warm to room temperature and stirred for 3 h. The contents of the flask were then poured into water (50 mL), and petroleum ether (50 mL) was added to aid in separation of the organic and aqueous layers. The aqueous layer was washed twice with diethyl ether, and the organic fractions were combined and dried with anhydrous $MgSO_4$. The resulting orange solution was filtered through silica, and the solvent was removed in vacuo to give a viscous orange-brown liquid (188 mg, 91.2%). The ^{1}H NMR spectrum shows a 1:1 ratio of two compounds, the racemic and meso forms of the ferrocene. ^{1}H NMR (*meso*, $CDCl_3$): $\delta = 0.77$ (s, 18H), 1.33 (d, 6H), 2.22 (q, 2H, $J = 7.12$ Hz), 3.98 (m, 8H). ^{13}C NMR (*meso*, $CDCl_3$): $\delta = 16.00$, 28.08, 33.97, 43.48, 67.55, 67.65, 67.99, 71.60, 93.39. ^{1}H NMR (*rac*, $CDCl_3$): $\delta = 0.77$ (s, 18H), 1.31 (d, 6H), 2.22 (q, 2H, $J = 7.09$ Hz), 3.97 (m, 8H). ^{13}C NMR (*rac*, $CDCl_3$): $\delta = 15.86$, 28.06, 34.02, 43.74, 67.31, 67.75, 71.38, 93.01. (*S*,*S*)-Iron bis(methylneopentylcyclopentadienide) was synthesized by the same procedure using (*S*)-lithium

(33) Burger, B. J.; Bercaw, J. E. In *New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds*; Wayda, A., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Vol. 357.
(34) Vasi, I. G.; Desai, K. R. *J. Indian Chem. Soc.* **1975**, *52*, 837.
(35) (a) Parker, D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 83. (b) Chataigner, I.; Lebreton, J.; Durand, D.; Guingant, A.; Villiéras, J. *Tetrahedron Lett.* **1998**, *39*, 1759.

methylneopentylcyclopentadienide as the starting material (yield 99%). The ^{1}H NMR ($CDCl_3$) spectrum shows 5.1% *meso* compound, as compared to (*S*,*S*)-**3** which makes up 94.9% of the observed signal.

{(SiMe$_2$)$_2$[η^5-C$_5$H(CHMe$_2$)$_2$][η^5-C$_5$H$_2$((*R*/*S*)-CHMeCMe$_3$)]}Zr[(*S*)-2-methylbutane-1-thiolate]$_2$, (*R*/*S*,*S*,*S*)-4. *rac*-**2** (100 mg, 0.197 mmol) and lithium (*S*)-2-methylbutane-1-thiolate (43.3 mg, 0.393 mmol), prepared by reaction of (*S*)-2-methylbutane-1-thiol with 1 equiv of butyllithium (1.6 M in hexanes) in diethyl ether and precipitated by addition of petroleum ether, were placed in a 25 mL flask and attached to a swivel frit assembly. Diethyl ether (15 mL) was vacuum transferred onto the solids at −78 °C. The flask was allowed to warm to room temperature and was stirred for 3 h, resulting in a yellow solution and a white precipitate. The solvent was removed in vacuo, and petroleum ether (15 mL) was transferred into the flask. The suspension was filtered, the solid was washed with petroleum ether, and the solvent was removed in vacuo to give a yellow oil. Hexamethyldisiloxane (10 mL) was added and removed in vacuo, leaving the product as a yellow solid (73% isolated). The ^{1}H NMR spectrum shows a 1:1 mixture of (*S*,*S*,*S*)-**4** and (*R*,*S*,*S*)-**4**. ^{1}H NMR [(*S*,*S*,*S*), benzene-d_6]: δ = 0.56 (s, 3H), 0.58 (s, 3H), 0.59 (s, 3H), 0.64 (s, 3H), 0.91 (s, 9H), 0.82−1.02 (m, 6H), 0.94 (d, 3H, J = 5.13 Hz), 1.04 (d, 3H, J = 7.19 Hz), 1.05 (d, 3H, J = 5.95 Hz), 1.06 (d, 3H, J = 5.13 Hz), 1.28 (m, 2H), 1.38 (d, 3H, J = 6.60), 1.60 (d, 3H, J = 6.59 Hz), 1.67 (m, 2H), 1.90 (d, 3H, J = 7.03 Hz), 2.8−3.5 (m, 9H), 6.62 (s, 1H), 6.70 (d, 1H), 6.77 (d, 1H, J = 1.95 Hz). ^{1}H NMR [(*R*,*S*,*S*), benzene-d_6]: δ = 0.56 (s, 3H), 0.58 (s, 3H), 0.59 (s, 3H), 0.64 (s, 3H), 0.91 (s, 9H), 0.82−1.02 (m, 6H), 0.94 (d, 3H, J = 5.13 Hz), 1.04 (d, 3H, J = 7.19 Hz), 1.05 (d, 3H, J = 5.95 Hz), 1.06 (d, 3H, J = 5.13 Hz), 1.28 (m, 2H), 1.38 (d, 3H, J = 6.60), 1.60 (d, 3H, J = 6.59 Hz), 1.67 (m, 2H), 1.90 (d, 3H, J = 7.03 Hz), 2.85−3.40 (m, 9H), 6.61 (s, 1H), 6.69 (d, 1H), 6.75 (d, 1H, J = 1.47 Hz). (*S*,*S*,*S*)-**4** (70% yield) was made using the same procedure.

{(SiMe$_2$)$_2$[η^5-C$_5$H(CHMe$_2$)$_2$][η^5-C$_5$H$_2$((*S*)-CHMeCMe$_3$)]}Zr(SC$_6$H$_5$)$_2$, (*S*)-5. Compound **5** was made analogously to **4**, but from the reaction of (*S*)-**2** with 2 equiv of lithium thiophenoxide (74% yield). ^{1}H NMR (benzene-d_6): δ = 0.08 (s, 3H), 0.31 (d, 3H, J = 6.60 Hz), 0.54 (s, 3H), 0.55 (s, 3H), 0.67 (s, 9H), 0.69 (s, 3H), 0.88 (d, 3H, 7.03 Hz), 1.05 (d, 3H, J = 7.03), 1.49 (d, 3H, J = 7.03 Hz), 1.59 (d, 3H, J = 6.60 Hz), 2.85−3.0 (m, 2H), 3.28 (quintet, 1H), 6.45 (s, 1H), 6.55 (s, 1H), 6.63 (s, 1H), 6.75−6.98 (m, 4H), 7.05 (t, 2H, J = 7.47 Hz), 7.53 (s, 1H), 7.55 (s, 1H), 8.03 (s, 1H), 8.06 (s, 1H).

6,6-Diethylfulvene. Into a 500 mL flask containing a methanol (250 mL) solution of CpH (50 g, 751 mmol) were added 3-pentanone (65 g, 751 mmol) and pyrrolidine (8.01 g, 113 mmol) at room temperature. The bright yellow solution was allowed to stir overnight at room temperature. The resulting dark orange reaction mixture was neutralized with 50% (v/v) acetic acid and was transferred to a separatory funnel containing 100 mL of water. After the layers were separated, the aqueous layer was extracted with ether (3 × 100 mL). The combined organic layers were washed with water (2 × 100 mL), sat. $NaHCO_3$ (1 × 100 mL), and brine (1 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$, concentrated, and Kugel−Röhr distilled (25 °C, <10^{-3} Torr) to yield 68.14 g (68%) of bright yellow oil. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.9 (t, J = 7.8 Hz, 6H, CH_3), 2.3 (q, J = 7.8 Hz, 4H, CH_2), 6.5 (s, 4H, C$_5H_4$).

1-(3-Pentyl)cyclopentadiene and Isomers, "(3-pentyl)CpH". Under an atmosphere of Ar, an ether (330 mL) slurry of $LiAlH_4$ (1 equiv) was prepared and was equipped with a condenser and an addition funnel. 6,6-Diethylfulvene (30 g, 223 mmol) was dissolved in 100 mL of ether, and the solution was added dropwise to the $LiAlH_4$ slurry over 1 h. The solvent refluxed very gently during the addition. The reaction was stirred at room temperature for 4 h. While the flask was cooled with a dry ice bath, the reaction was quenched slowly with 9 g of water, followed by 9 g of 15% NaOH and 27 g of water. On warming to room temperature, the gray slurry became white in color. The solution was filtered, concentrated, and Kugel−Röhr distilled (30 °C, <10^{-3} Torr) to give 31 g (83%) of a pale yellow oil. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.80, 0.87 (t's, 6H, CH_3), 1.3, 1.5 (m's, 4H, CH_2), 2.2 (m, 1H, C*H*), 2.64, 2.8, 5.93, 6.15, 6.23, 6.34, 6.45 (m's, 5H, C$_5H_5$).

3-(3-Pentyl)-6,6-diethylfulvene. The desired product was prepared by reaction of (3-pentyl)CpH (15.52 g, 114 mmol), 3-pentanone (10.79 g, 126 mmol), and pyrrolidine (10.54 g, 148 mmol) in 100 mL of methanol. The reaction was refluxed overnight. The workup was the same as that for 6,6-diethylfulvene. 17.22 g (74%) of bright orange oil was obtained via Kugel−Röhr distillation (80 °C, <10^{-3} Torr). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.93 (q, J = 7.8 Hz, 12H, CH_3), 1.58 (m, 4H, (CH_2)$_2$CH), 2.25 (m, 1H, C*H*), 2.25 (m, 1H, C*H*), 2.3 (q, J = 7.8 Hz, 4H, (CH_2)$_2$C═), 6.24 (t, J = 2.4 Hz, 1H, C$_5H_3$), 6.46 (dd, J = 5.4, 1.8 Hz, 1H, C$_5H_3$), 6.57 (dd, J = 5.4, 1.8 Hz, 1H, C$_5H_3$).

1,3-Bis(3-pentyl)cyclopentadiene Isomers, "(3-pentyl)$_2$CpH". The product was obtained by reaction of 3-(3-pentyl)-6,6-diethylfulvene (12.54 g, 61.04 mmol) in ether (80 mL) and the 150 mL ether slurry of $LiAlH_4$ (3.48 g, 91.7 mmol). The reaction was quenched with 3.5 g of water, followed by 3.5 g of 15% NaOH and 10.5 g of water. Filtration, concentration, and Kugel−Röhr distillation (90 °C, <10^{-3} Torr) yielded 10.47 g (83%) of pale yellow oil. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.82 (t, J = 7.1 Hz, 6H, CH_3), 0.90 (t, J = 7.4 Hz, 6H, CH_3), 1.35−1.50 (m, 8H, CH_2), 2.12 (m, 1H, C*H*), 2.55, 2.7, 5.87, 6.09, 6.12 (s's, 4H, C$_5H_4$).

Lithium [1,3-Bis(3-pentyl)cyclopentadienide]·DME, "Li[(3-pentyl)$_2$Cp]·DME". Pentane (125 mL) was vacuum transferred onto (3-pentyl)$_2$CpH (20.5 g, 98.7 mmol) in a swivel frit assembly. *n*-BuLi (67.9 mL, 1.6 M in hexane, 108.6 mmol) was added via syringe over 5 min at −78 °C. The solution was allowed to warm slowly to room temperature and was stirred for 6 h. DME (11.3 mL, 108.6 mmol) was vacuum transferred onto the reaction mixture to facilitate the precipitation of the salt product. After being stirred for 2 h at room temperature, the solution was cooled with an ice bath, and the resulting white solid was filtered and washed with pentane (3 × 75 mL). The white solid was dried in vacuo resulting in a fine white powder; 21.9 g (99%). ^{1}H NMR (300 MHz, THF-d_8): δ 0.81 (t, J = 7.5 Hz, 12H, CH_3), 1.45, 1.58 (m's, 8H, CH_2), 2.19 (m, 2H, C*H*), 3.27 (s, 6H, DME CH_3), 3.43 (s, 4H, DME CH_2), 5.40 (m, 3H, C$_5H_3$).

{C$_5$H$_3$(CHEt$_2$)$_2$}SiMe$_2$Cl Isomers. THF (150 mL) was vacuum transferred onto Li[(3-pentyl)$_2$Cp]·DME (10.0 g, 43.0 mmol) in a swivel frit assembly. While the solution was cooling at −78 °C, dichlorodimethylsilane (9.0 mL, 74.2 mmol) was added by vacuum transfer. The reaction mixture was allowed to warm slowly to room temperature overnight. The reaction was stirred at 25 °C for another 24 h. The solvent was removed in vacuo, leaving a white paste. Petroleum ether (150 mL) was added by vacuum transfer, and the product was extracted away from LiCl salts. The solvent was removed in vacuo, leaving a yellow oil (11.69 g, 92%) which was used in the next step without further purification. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.15 (s, 3H, Si(CH_3)$_2$), 0.30 (s, 3H, Si(CH_3)$_2$), 0.88 (m, 12H, CH_3), 1.50 (m, 8H, CH_2), 2.16 (m, 1H, C*H*), 2.60 (m, 1H, C*H*), 3.35, 5.87, 6.2 (s's, 3H, C$_5H_3$).

{C$_5$H$_3$(CHEt$_2$)$_2$}SiMe$_2${C$_5$H$_4$((*S*)-CHMeCMe$_3$)}. THF (100 mL) was vacuum transferred onto Li (*S*)-MNCp (6.17 g, 39.5 mmol) in a swivel frit assembly. THF (25 mL) was vacuum transferred onto {C$_5$H$_3$-(CHEt$_2$)$_2$}SiMe$_2$Cl in a 50 mL flask. The solution of the silyl compound was added to the Li[(*S*)-MNCp] solution via cannula transfer at 0 °C. The mixture was stirred at room temperature overnight. Solvent was removed in vacuo, and petroleum ether was vacuum transferred onto the white paste. The product was extracted away from the LiCl with petroleum ether (3 × 100 mL). The solvent was removed in vacuo, resulting in an orange oil, which was Kugel−Röhr distilled (110 °C, <10^{-3} Torr) to give 16.10 g (99%) of product. ^{1}H NMR (300 MHz, benzene-d_6): δ −0.14, −0.04 (br s, 6H, Si(CH_3)$_2$), 0.924 (m, 12H, CH$_2$CH_3), 0.98 (s, 9H, C(CH_3)$_3$), 1.20 (d, J = 7.2 Hz, 3H, CH_3), 1.56 (m, 8H, CH_2), 2.12−2.58 (m, 3H, C*H*), 2.96−3.6, 6.01−6.61 (m, 7H, C$_5H_3$, C$_5H_4$).

$Li_2[\{C_5H_2(CHEt_2)_2\}SiMe_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}]\cdot DME$. Ether (150 mL) was vacuum transferred onto $\{C_5H_3(CHEt_2)_2\}SiMe_2\{C_5H_4((S)\text{-}CHMeCMe_3)\}$ (16.1 g, 39.2 mmol) in a swivel frit assembly. *n*-BuLi (54.0 mL, 1.6 M in hexane, 86.4 mmol) was syringed onto the solution while it was cooled at −78 °C. The clear solution was stirred overnight at room temperature. The solvent was removed in vacuo, and petroleum ether (125 mL) and DME (9.0 mL, 86.4 mmol) were added by vacuum transfer, producing a copious amount of white precipitate. After cooling in an ice bath, the solution was filtered. The solid was dried in vacuo, resulting in a fine white powder (32.5 g, 90%). ^{1}H NMR (300 MHz, THF-d_8): δ 0.29, 0.30 (s, 6H, Si(CH_3)$_2$), 0.81 (t, J = 7.2 Hz, 12H, CH_2CH_3), 0.85 (s, 9H, C(CH_3)$_3$), 1.21 (d, J = 7.2 Hz, 3H, MN CH_3), 1.36−1.64 (m, 8H, CH_2), 2.21 (quint, J = 7.2 Hz, 1H, CH(CH$_2$)$_2$), 2.47 (q, J = 7.2 Hz, 1H, MN CH), 2.67 (quint, J = 7.2 Hz, 1H, CH(CH$_2$)$_2$), 3.27 (s, 6H, DME CH_3), 3.43 (s, 4H, DME CH_2), 5.55 (d, J = 3.0 Hz, 1H, C_5H_2), 5.67 (t, J = 2.7 Hz, 1H, C_5H_3), 5.71 (d, J = 2.7 Hz, 1H, C_5H_2), 5.81 (m, 1H, C_5H_3), 5.86 (m, 1H, C_5H_3).

$\{C_5H_2(CHEt_2)_2\}(SiMe_2)_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}$. THF (150 mL) was vacuum transferred onto the dilithio salt $Li_2[\{C_5H_2(CHEt_2)_2\}SiMe_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}]\cdot$DME (10.0 g, 19.5 mmol). At −78 °C, $SiMe_2Cl_2$ (1 equiv) was added by vacuum transfer, and the solution was allowed to warm to room temperature overnight. All volatiles were removed in vacuo. The ligand was extracted away from LiCl with petroleum ether. After the ligand was dried under vacuum, it was Kugel−Röhr distilled (130 °C, $<10^{-3}$ Torr) to give a pale yellow oil (85%).

$\{(SiMe_2)_2[\eta^5\text{-}C_5H(CHEt_2)_2][\eta^5\text{-}C_5H_2((S)\text{-}CHMeCMe_3)]\}ZrCl_2$, (*S*)-6. In a swivel frit apparatus, the ligand $\{C_5H_2(CHEt_2)_2\}(SiMe_2)_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}$ (0.95 g, 2.0 mmol) was dissolved in 50 mL of ether. *n*-BuLi (2.78 mL, 4.45 mmol) was added by syringe to the flask. The solution was allowed to stir for 24 h at room temperature under Ar. In a separate flask, $ZrCl_4$ (541 mg, 2.3 mmol) was dissolved in ether, and the solution was cannula transferred to the solution containing the ligand. The resulting mixture was allowed to stir at room temperature under Ar for 24 h. The solution was filtered, and the solvent was removed in vacuo. Hexamethyldisiloxane (40 mL) was added by vacuum transfer to precipitate a white solid, which was collected by filtration, washed, and dried under vacuum. The product was recrystallized from cold toluene. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.52, 0.54, 0.59, 0.62 (s, 4H, Si(CH_3)$_2$), 0.58 (td, J = 1.7, 7.2 Hz, 6H, CH_2CH_3), 0.81 (s, 9H, C(CH_3)$_3$), 1.02 (m, 6H, CH_2CH_3), 1.37 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.64 (d, J = 7.2 Hz, MN CH_3), 1.69 (m, 2H, CH_2), 2.38 (m, 2H, CH_2), 2.68 (m, 2H, CH_2), 2.90 (q, J = 7.2 Hz, 1H, MN CH), 6.45 (s, 1H, C_5H_1), 6.67 (d, J = 1.8 Hz, 1H, C_5H_2), 6.79 (d, J = 1.8 Hz, 1H, C_5H_2). Anal. Calcd for $C_{30}H_{50}Si_2ZrCl_2$: C, 57.28; H, 8.01. Found: C, 56.57; H, 8.40.

6-Cyclohexylfulvene. The product was prepared from reaction of cyclopentadiene and cyclohexanone, using the same method as described for 6,6-diethylfulvene (85%). ^{1}H NMR (300 MHz, benzene-d_6): δ 1.29 (m, 2H, CH_2), 1.41 (m, 1H, CH_2), 2.34 (t, 4H, CH_2), 6.62 (m, 4H, C_5H_4).

Cyclohexylcyclopentadiene Isomers, "CyCpH". The product was prepared from 6-cyclohexylfulvene in a manner similar to that of (3-pentyl)CpH (91%). ^{1}H NMR (300 MHz, benzene-d_6): δ 1.2 (m, 5H, CH_2), 1.64 (m, 3H, CH_2), 1.80 (m, 1H, CH_2), 1.92 (m, 1H, CH_2), 2.22 (m, 1H, CH), 2.73, 2.80, 5.95, 6.18, 6.24, 6.35, 6.5, 6.55 (m, 5H, C_5H_5).

3,6-Dicyclohexylfulvene. The product was prepared from CyCpH and cyclohexanone using the same method described for (3-pentyl)-6,6-diethylfulvene. The crude oil was Kugel−Röhr distilled (130 °C, $<10^{-3}$ Torr) to yield a yellow oil (70%). ^{1}H NMR (300 MHz, benzene-d_6): δ 1.1−2.4 (m, 21H, CH_2), 6.29 (m, 1H, C_5H_3), 6.55 (dd, J = 1.6, 5.3, 1H, C_5H_3), 6.63 (dd, J = 1.6, 5.3, 1H, C_5H_3).

1, 3-Dicyclohexylcyclopentadiene Isomers, "Cy_2CpH". The preparation of this compound was analogous to that described for (3-pentyl)$_2$CpH to yield a pale yellow oil (94%). ^{1}H NMR (300 MHz, benzene-d_6): δ 1.1−2.3 (m, 22H, CH_2), 2.72, 2.81, 5.84, 6.15, 6.22 (m, 3H, C_5H_3).

$Li[(C_5H_3Cy_2)]\cdot$DME. The synthesis of the target compound from Cy_2CpH was analogous to that used in the preparation of Li[(3-pentyl)$_2$Cp]·DME (85%). ^{1}H NMR (300 MHz, THF-d_8): δ 1.30 (m, 10H, Cy CH_2), 1.6 (m, 10H, Cy CH_2), 1.9 (m, 10H, Cy CH_2), 2.35 (m, 1H, Cy CH_2), 3.3 (s, 6H, DME CH_3), 3.4 (s, 4H, DME CH_2), 5.35, 5.4 (m's, 3H, C_5H_3).

$(C_5H_3Cy_2)SiMe_2Cl$ Isomers. The desired compound was prepared as a white fluffy solid in a manner similar to that used for $\{C_5H_3(CHEt_2)_2\}SiMe_2Cl$ (90%). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.10, 0.25 (s, 6H, $SiMe_2$), 1.25 (m, 10H, Cy CH_2), 1.65 (t, 6H, Cy CH_2), 1.90 (m, 4H, Cy CH_2), 2.27 (m, 1H, Cy CH), 2.50 (m, 1H, Cy CH), 3.45 (br s, 1H, C_5H_3), 5.87 (br s, 1H, C_5H_3), 6.28 (s, 1H, C_5H_3).

$Li_2[(C_5H_2Cy_2)SiMe_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}]\cdot$DME. $(C_5H_2Cy_2)SiMe_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}$ was prepared analogously to the procedure used for $\{C_5H_3(CHEt_2)_2\}SiMe_2\{C_5H_4((S)\text{-}CHMeCMe_3)\}$ to give a dark yellow oil (98%). The dilithio salt of this oil was prepared by deprotonation in the same manner as used for $Li_2[\{C_5H_3(CHEt_2)_2\}SiMe_2\{C_5H_4((S)\text{-}CHMeCMe_3)\}]$ (95%). ^{1}H NMR (300 MHz, THF-d_8): δ 0.28 (s, 6H, Si(CH_3)$_2$), 0.84 (s, 9H, C(CH_3)$_3$), 1.18 (d, 3H, MN CH_3), 1.32 (m, 10H, Cy CH_2), 1.70 (m, 6H, Cy CH_2), 1.88 (m, 4H, Cy CH_2), 2.36 (m, 1H, Cy CH), 2.46 (qt, 1H, MN CH), 2.78 (m, 1H, Cy CH), 3.27 (s, 6H, DME CH_3), 3.42 (s, 4H, DME CH_2), 5.63 (m, 3H, C_5H_3), 5.82 (m, 2H, C_5H_2).

$(C_5H_2Cy_2)(SiMe_2)_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}$. THF (50 mL) was added by vacuum transfer to a swivel frit assembly containing the dilithio salt $Li_2[(C_5H_2Cy_2)SiMe_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}]\cdot$DME (3.32 g, 7.4 mmol). At −78 °C, $SiMe_2Cl_2$ (1 mL, 8 mmol) was added by vacuum transfer. The resulting slurry was stirred at −78 °C and allowed to warm slowly to room temperature overnight. All volatiles were removed in vacuo. Petroleum ether was added by vacuum transfer, and the solution was filtered to give a yellow filtrate. All volatiles were removed in vacuo, and the yellow oil obtained was pumped down under high vacuum until a solid formed (73%). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.55 (s, 6H, Si(CH_3)$_2$), 0.62 (s, 6H, Si(CH_3)$_2$), 1.03 (s, 9H, C(CH_3)$_3$), 1.28 (d, 3H, MN CH_3), 1.28−2.8 (m, 20H, Cy CH_2), 2.32 (t, 1H, Cy CH), 2.56 (m, 1H, MN CH), 2.82 (t, 1H, Cy CH), 3.5 (m, 1H, Cp), 6.46 (m, 2H, Cp), 7.02 (d, 1H, Cp).

$\{(SiMe_2)_2[\eta^5\text{-}C_5HCy_2][\eta^5\text{-}C_5H_2((S)\text{-}CHMeCMe_3)]\}ZrCl_2$, (*S*)-7. To a 50 mL flask were added $(C_5H_2Cy_2)(SiMe_2)_2\{C_5H_3((S)\text{-}CHMeCMe_3)\}$ (0.93 g, 1.9 mmol), $Zr(NMe_2)_4$ (0.51 g, 1.9 mmol), and dry xylenes (25 mL). The resulting yellow solution was refluxed under a strong Ar purge to vent product $HNMe_2$. When the vented gas showed a neutral reading on pH paper, all volatiles were removed in vacuo. The reaction vessel was attached to a swivel frit assembly, and the residue was dissolved in toluene (25 mL). To this solution was added TMSCl (2.2 equiv) by vacuum transfer. After the solution was stirred overnight at room temperature, the volatiles were removed, and the residue was washed with $(TMS)_2O$ (61%). Crystals were obtained from CH_2Cl_2. ^{1}H NMR (300 MHz, benzene-d_6): δ 0.48 (s, 3H, Si(CH_3)$_2$), 0.50 (s, 3H, Si(CH_3)$_2$), 0.54 (s, 3H, Si(CH_3)$_2$), 0.58 (s, 3H, Si(CH_3)$_2$), 0.78 (s, 9H, C(CH_3)$_3$), 1.0−1.4 (m, 10H, Cy CH_2), 1.61 (d, 3H, MN CH_3), 1.6 (m, 6H, Cy CH_2), 1.73 (m, 4H, Cy CH_2), 2.5−2.7 (m, 2H, Cy CH), 2.87 (qt, 1H, MN CH), 6.42 (s, 1H, Cp), 6.64 (s, 1H, Cp), 6.75 (s, 1H, Cp). Anal. Calcd for $C_{32}H_{50}Si_2ZrCl_2$: C, 58.20; H, 7.72. Found: C, 58.20; H, 7.93.

(*R*)-1-Cyclohexylethanol. *rac*-1-Cyclohexylethanol (50 mL, 390 mol) and (*S*)-ethyl thiooctanoate (73.4 mL, 390 mmol) were combined in a 250 mL round-bottom flask. Two grams of the Novozyme-435 enzyme were added. With the flask venting properly in a fume hood (ethanethiol evolution!), the temperature was increased to 43 °C with constant stirring. The reaction was stopped short of 50% conversion (5.5 h; % conversion by GC) followed by removal of the enzyme by filtration. The product (*R*)-cyclohexylethyloctanoate (43 g) was isolated from the reaction mixture by fractional distillation under reduced

pressure. The (*R*)-cyclohexylethyloctanoate was hydrolyzed in a 1 M solution of NaOH in MeOH (400 mL) for 3 d. The product alcohol was then extracted with ether. This required the addition of water and brine to get two layers. The combined ether layers were washed with water and brine and then dried over $MgSO_4$. Evaporation of the ether gave 18 g of pure alcohol, $ee_R > 96\%$, by enantioselective GC of the trifluoroacetyl derivative.

(*R*)-1-Cyclohexylethylmethanesulfonate. (*R*)-1-Cyclohexylethanol (5 g, 39 mmol) was dissolved in dry CH_2Cl_2 (200 mL). Triethylamine (8.2 mL, 59 mmol) was added, and the resulting solution was cooled to 0 °C. Methanesulfonyl chloride was added dropwise over 5−10 min. The solution was stirred further for 1 h at 0 °C, and then was washed with water, HCl (10%), $NaHCO_3$, and brine. The solution was dried over $MgSO_4$, and the solvent was removed in vacuo to give a light yellow oil (95%). ^{1}H NMR ($CDCl_3$): $\delta = 0.9-1.3$ (br m), 1.35 (d, 3H), 1.44−1.84 (br m), 2.96 (s, 3H), 4.55 (q, 1H).

(*S*)-1-Cyclohexylethylcyclopentadiene. Lithium cyclopentadienide (6.9 g, 96 mmol) was weighed into a 200 mL Schlenk tube in a nitrogen glovebox. On a Schlenk line, dry THF was added (60 mL) to give an amber solution. (*R*)-1-Cyclohexylethylmethanesulfonate (15.3 g, 74 mmol) was added via cannula as a solution in dry THF (30 mL), changing the solution color to orange. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (29.1 mL, 193 mmol) was then added via syringe. The solution was heated to reflux under an argon atmosphere for 12 h and then stirred at room temperature for a further 12 h to effect reaction completion. During this time, the solution became cloudy and brown in color. Once the reaction was complete, excess LiCp was quenched by the slow addition of water. The solution was then treated to washings with water, 1 M $KHSO_4$, saturated $NaHCO_3$, and then brine. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo to give a dark brown oil. The product could be purified by Kugel−Röhr distillation at 65−80 °C under high vacuum to give a light yellow oil (70%). The ^{1}H NMR spectrum is complex, consistent with a mixture of double bond isomers.

Li[(*S*)-1-cyclohexylethylcyclopentadienide]. To a solution of (*S*)-1-cyclohexylethylcyclopentadiene (1.2 g, 6.63 mmol) in cold diethyl ether (20 mL, −78 °C) was added 1.6 M *n*-BuLi (5 mL, 7.3 mmol) in hexanes. The mixture was allowed to warm to room temperature, and a white precipitate formed over the next 1 h. The solvent was evaporated and replaced with petroleum ether. The white product (1.1 g, 92%) was isolated after filtration and further washing with petroleum ether. ^{1}H NMR (THF-d_8): $\delta = 0.84-1.38$ (br m, 6H), 1.15 (d, 3H), 1.42−1.80 (br m, 5H), 2.43 (q, 1H), 5.5 (m, 4H). ^{13}C NMR (THF-d_8): $\delta =$ 18.5 (CH_3), 26.1 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 29.8 (CH_2), 30.5 (CH_2), 39.5 (CH), 45.1 (CH), 99.7 (Ar), 100.4 (Ar), 123.0 (Ar).

(*rac*/*meso*)-Iron Bis(1-cyclohexylethylcyclopentadienide). The iron complexes were prepared as described above for iron bis(methylneopentylcyclopentadienide). The ^{1}H NMR spectrum was less informative in this case, as the *rac* and *meso* forms showed essentially the same set of resonances. Instead, ^{13}C NMR data were used to assess enantiopurity. (*S*,*S*)-Iron bis(1-cyclohexylethylcyclopentadienide) was synthesized from lithium (*S*)-1-cyclohexylethylcyclopentadienide. ^{13}C NMR [(*S*,*S*), $CDCl_3$]: $\delta = 16.65$ (CH_3), 26.72 (CH_2), 26.81 (CH_2), 26.86 (CH_2), 29.76 (CH_2), 30.56 (CH_2), 38.80 (CH), 45.36 (CH), 66.29 (Cp), 67.33 (Cp), 67.61 (Cp), 69.59 (Cp), 93.90 (Cp). A 1:1 mixture of *rac* and *meso* forms was made from lithium (*S*/*R*)-1-cyclohexylethylcyclopentadienide. ^{13}C NMR (*rac*/*meso*, $CDCl_3$): $\delta = 16.6$ (CH_3), 16.7 (CH_3), 26.7 (coincident CH_2's), 26.8 (coincident CH_2's), 26.9 (coincident CH_2's), 29.6 (CH_2), 29.8 (CH_2), 30.58 (CH_2), 30.57 (CH_2), 38.66 (CH), 38.78 (CH), 45.34 (coincident CH's), 66.38 (CpH), 66.86 (Cp), 67.27 (Cp), 67.42 (coincident Cp's), 67.70 (Cp), 69.18 (Cp), 69.68 (Cp), 94.05 (Cp), 94.16 (Cp).

$C_5H_3CMe_2$((*S*)-1-Cyclohexylethyl), "6,6-dimethyl,(*S*)-1-cyclohexylethylfulvene". To a solution of (*S*)-1-cyclohexylethylcyclopentadiene (9 g, 52 mmol) and acetone (5.7 mL, 78 mmol) in MeOH (350 mL) was added pyrrolidine (6.9 mL, 82 mmol). The brown solution was stirred for 15 h and then neutralized by addition of CH_3COOH. Water and ether were added, and the layers were separated. The aqueous layer was extracted with ether, and the combined ether fractions were washed with water and brine. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed to give the product as a light brown liquid (10 g, 90%). ^{1}H NMR ($CDCl_3$): $\delta = 0.84-1.00$ (br m, 5H), 1.02−1.79 (br m, 6H), 1.13 (d, 3H), 2.14 (s, 6H), 2.36 (q, 1H), 6.11 (m, 1H), 6.39 (dd, 1H), 6.49 (dd, 1H).

$C_5H_4(CHMe_2)$((*S*)-1-cyclohexylethyl). In a three neck flask fitted with an addition funnel and an efficient reflux condenser, $LiAlH_4$ (2.1 g, 54 mmol) was suspended in ether (350 mL). A solution of (*S*)-1-cyclohexyl-6,6-dimethylethylfulvene (9.8 g, 45.1 mmol) in ether (100 mL) was added dropwise over 30 min. Stirring for 15 h gave a yellow mixture that was carefully quenched by dropwise addition of water (5 mL), followed by 7.5 mL of 15% NaOH(aq). This caused a granular white solid to form. Once H_2 evolution had ceased, a further 250 mL of water was added. The ether layer was then separated and washed with water. The yellow solution was dried over $MgSO_4$ and filtered, and the solvent was evaporated to give a light yellow oil (9.3 g, 95%). The ^{1}H NMR spectrum is complex, consistent with a mixture of double bond isomers.

Li[$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl)]. In a large swivel frit assembly, $C_5H_4(CHMe_2)$((*S*)-1-cyclohexylethyl) (6.6 g, 30 mmol) was dissolved in pentane (130 mL), and the solution was cooled to −78 °C. To this was added 1.6 M *n*-BuLi in hexanes (21 mL, 33 mmol) via syringe. The solution was warmed to room temperature and stirred for 24 h, during which time the color changed from orange to very pale yellow. Addition of a small excess of DME (1.3 mL) and further pentane (50 mL), followed by stirring at low temperature (>1 h), gave a white precipitate. The mixture was filtered while cold to give an off-white powder which was dried under vacuum (6.1 g, 90%). ^{1}H NMR (THF-d_8): $\delta = 0.86-1.37$ (br m, 6H), 1.14 (m, 9H), 1.53−1.81 (br m, 5H), 2.37 (q, 1H), 2.75 (q, 1H), 5.31 (m, 1H), 5.35 (m, 2H).

{$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl)}$SiMe_2Cl$. In a swivel frit assembly, an excess of $SiMe_2Cl_2$ (3.4 mL, 28 mmol) was added to a cold (−78 °C) solution of Li[$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl)] (4.2 g, 19 mmol) in THF (80 mL) via syringe. The initially cloudy mixture was very slowly warmed to room temperature (>5 h) and was stirred for a total of 24 h to give a clear yellow solution. The solvent was evaporated, and the product was extracted into petroleum ether followed by filtration to remove LiCl. Removal of the petroleum ether solvent gave a dark yellow oil (4.3 g). The ^{1}H NMR spectrum is complex, consistent with a mixture of double bond isomers.

{$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl)}$SiMe_2(C_5H_5)$. A large swivel frit assembly was charged with {$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl)}-$SiMe_2Cl$ (6.7 g, 22 mmol), and THF (100 mL) was added by vacuum transfer. To this was added a solution of lithium cyclopentadienide (1.9 g, 26 mmol) in THF (50 mL) via cannula. The reaction was stirred for 24 h to give an amber solution. The solvent was evaporated to give a thick yellow paste. The product was extracted with petroleum ether, and the solution was filtered to remove LiCl. Removal of petroleum ether gave an orange oil (7.2 g).

Li_2[{$C_5H_2(CHMe_2)$((*S*)-1-cyclohexylethyl)}$SiMe_2(C_5H_4)$]. The dilithio salt was prepared from {$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl}-$SiMe_2(C_5H_5)$ (7.2 g, 21 mmol) and 1.6 M *n*-BuLi (28 mL), in a manner similar to that of Li[$C_5H_3(CHMe_2)$((*S*)-1-cyclohexylethyl)] (see above) (9.2 g, 80%). The ^{1}H NMR (THF-d_8) spectrum is consistent with the presence of two linkage isomers: $\delta = 0.34$ (m, 12H, $SiCH_3$'s), 0.9−1.46 (br m, 12H, Cy), 1.14 (m, 18H, CH_3's), 1.50−1.96 (br m, 10H, Cy), 2.39 (q, 1H, CH), 2.77 (q, 1H, CH), 2.84 (q, 1H, CH), 3.21 (q, 1H, CH), 5.63 (m, 4H, Cp), 5.81 (m, 4H, Cp), 5.97 (m, 4H, Cp).

{$C_5H_2(CHMe_2)$((*S*)-1-cyclohexylethyl)}$(SiMe_2)_2(C_5H_4)$, "(*S*)-1-cyclohexylethylThp", "(*S*)-ceThp". In a swivel frit assembly, 9.2 g of Li_2[{$C_5H_2(CHMe_2)$((*S*)-1-cyclohexylethyl}$SiMe_2(C_5H_4)$] was reacted with $SiCl_2Me_2$ (1.2 equiv) in THF (110 mL). The reaction was stirred for 15 h to give an amber solution. Removal of solvent gave a beige

paste, from which the product was extracted with petroleum ether. Filtration and evaporation of petroleum ether gave the product as a thick orange oil (5.1 g). The ^{1}H NMR spectrum is complex, consistent with a mixture of double bond isomers.

Li_2[{C_5H(CHMe$_2$)((*S*)-1-cyclohexylethyl)}(SiMe$_2$)$_2$(C_5H_3)], "Li_2-[(*S*)-ceThp]". The protio form of the ligand, (*S*)-ceThp (0.98 g, 2.5 mmol), was dissolved in ether (50 mL), and the solution was cooled to −78 °C. To this was added 1.6 M *n*-BuLi in hexanes (3.3 mL, 5.2 mmol) via syringe. After 24 h, the solvent was removed and replaced with petroleum ether. The off-white solid product was recovered by filtration and washed with petroleum ether (2 × 5 mL) (1 g, 95%). ^{1}H NMR (THF-d_8): δ = 0.22 (s, 3H), 0.24 (s, 3H), 0.28 (s, 3H), 0.29 (s, 3H), 0.84−1.82 (br m, 10H, Cy), 2.01 (br d, 1H, Cy), 2.69 (q, 1H, CH), 3.14 (q, 1H, CH), 3.74 (m, 1H), 5.89 (s, 1H), 6.07 (br t, 1H), 6.15 (d, 2H). ^{13}C NMR (THF-d_8): δ = 5.26 (Si*C*H$_3$), 5.75 (Si*C*H$_3$), 5.77 (Si*C*H$_3$), 5.87 (Si*C*H$_3$), 22.59 (*C*H$_3$), 27.27 (*C*H$_3$), 27.77 (*C*H$_3$), 28.10 (*C*H$_2$), 28.22 (*C*H$_2$), 28.34 (*C*H$_2$), 30.45 (*C*H$_2$), 31.66 (*C*H$_2$), 33.79 (*C*H), 41.52 (*C*H), 46.64 (*C*H), 102.45, 110.07, 112.90, 113.01, 113.96, 115.26, 120.37, 120.47, 137.76, 139.78.

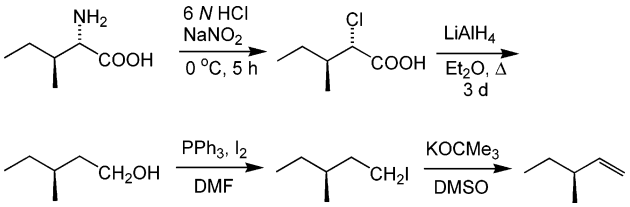
(*S*)-ceThpZrCl$_2$, 8a. Zirconium tetrachloride (0.56 g, 2.5 mmol) and Li_2[(*S*)-ceThp] were loaded into a swivel frit assembly in the glovebox. Toluene (25 mL) was added by vacuum transfer. After being stirred for 20 h, the mixture was filtered (very slowly) to remove LiCl. Removal of solvent gave an oily solid. Addition of petroleum ether (15 mL) gave a powdered product. The mixture was cooled, and the product was filtered off and washed with cold petroleum ether (2 × 5 mL). Drying under vacuum gave a white powder (0.24 g). The ^{1}H NMR (benzene-d_6) spectrum showed that a single diastereomer was isolated: δ = 0.38 (s, 3H, SiCH$_3$), 0.44 (s, 3H, SiCH$_3$), 0.52 (s, 3H, SiCH$_3$), 0.54 (s, 3H, SiCH$_3$), 0.9−1.88 (br m, 10H, Cy), 0.88 (d, 3H, CH$_3$), 0.91 (d, 3H, CH$_3$), 1.39 (d, 3H, CH$_3$), 2.29 (br t, 1H, Cy), 2.78 (q, 1H, CH), 2.89 (sep, 1H, CH), 6.31 (t, 1H), 6.51 (s, 2H), 6.70 (m, 2H). ^{13}C NMR (benzene-d_6): δ = −1.31 (Si*C*H$_3$), −1.14 (Si*C*H$_3$), 3.60 (coincident Si*C*H$_3$'s), 21.08 (*C*H$_3$), 21.24 (*C*H$_3$), 26.96 (*C*H$_3$), 27.74 (CH$_2$), 27.75 (CH$_2$), 28.95 (CH$_2$), 29.14 (CH$_2$), 29.78 (CH$_2$), 34.30 (CH), 40.16 (CH), 109.73, 110.36, 114.67, 115.21, 116.29, 138.12, 138.20, 161.97, 164.59, 165.01. Anal. Calcd for $C_{24}H_{37}Si_2ZrCl_2$: C, 53.92; H, 6.88. Found: C, 53.84; H, 6.98.

(*S*)-ceThpZrCl$_2$, 8b. To access the dichloride precatalyst, complex **9b** (0.6 g, 1.1 mmol) was treated with excess TMSCl (0.84, 6.6 mmol) in toluene (20 mL). After 3 h, all volatiles were removed in vacuo to give the product as an oily yellow solid which solidified over time under high vaucuum. Unfortunately, the extreme solubility of **8b** precluded further purification. The ^{1}H NMR spectrum (benzene-d_6) showed only minor impurities (<5%) and that a single diastereomer **8b** was dominant (ca. 10:1 ratio): δ = 0.36 (s, 3H, SiCH$_3$), 0.44 (s, 3H, SiCH$_3$), 0.48 (s, 3H, SiCH$_3$), 0.64 (s, 3H, SiCH$_3$), 0.90 (d, 3H, CH$_3$), 1.26 (d, 3H, CH$_3$), 1.34 (d, 3H, CH$_3$), 2.78 (m, 1H), 2.87 (sep, 1H), 6.3 (t, 1H), 6.42 (s, 1H), 6.72 (m, 2H).

(*S*)-ceThpZr(NMe$_2$)$_2$, 9b. A Schlenk tube fitted with a reflux condenser was charged with the protio ligand, (*S*)-ceThp (0.42 g, 1 mmol), and Zr(NMe$_2$)$_4$ (0.28 g, 1 mmol). THF (25 mL) was then added by vacuum transfer. The solution was heated to 120 °C to ensure gentle refluxing and was stirred for 24 h, while open to a mercury bubbler. Next, a strong argon purge was passed over the flask for a further 24 h, after which time vented gas gave only slightly basic readings. The solvent was removed to give an orange oil which solidified under high vacuum. Further purification was not possible due to the extreme solubility of **9b**. The ^{1}H NMR spectrum (benzene-d_6) showed the presence of mainly diastereomer **9b** (ca. 10:1): δ = 0.52 (s, 3H, SiCH$_3$), 0.60 (s, 3H, SiCH$_3$), 0.69 (s, 3H, SiCH$_3$), 0.80 (s, 3H, SiCH$_3$), 1.03 (d, 3H, CH$_3$), 1.23 (d, 3H, CH$_3$), 1.29 (d, 3H, CH$_3$), 2.83 (s, 6H, NMe$_2$), 2.88 (s, 6H, NMe$_2$), 6.19 (t, 1H), 6.23 (s, 1H), 6.51 (m, 2H).

Polymerization Procedures. A typical polymerization procedure was carried out as follows. MAO (250 mg) and tetradecane (1.5 mL, distilled from Na) were weighed into a 10 mL Schlenk tube in the glovebox, under an atmosphere of nitrogen. A Teflon needle valve was fitted to the Schlenk flask, and it was degassed on the high-vacuum line. Olefin (1.8 mL) was vacuum transferred from $LiAlH_4$ or CaH_2 into a measuring cylinder and then into the flask containing the MAO/tetradecane mixture. The olefin was stirred in the MAO suspension for 1 h to ensure the removal of all traces of moisture. Prior to catalyst injection, an aliquot was taken via the sidearm of the Schlenk flask (fitted with a septum) and was immediately quenched with *n*-butanol. The flask was placed under an atmosphere of argon, and the catalyst solution was added via syringe (0.50 mL of a 3.5 × 10^{-3} M solution in toluene is typical). The solution usually changed from colorless to light yellow upon catalyst addition. When the desired conversion was reached, a final aliquot was taken, and the contents of the flask were immediately frozen at 77 K and degassed under high vacuum. The unreacted olefin was vacuum transferred into a receiving flask, and the purity was checked by ^{1}H NMR. The aliquots were used for the GC determination of conversion, with tetradecane serving as the internal standard for integration. The polymer could be isolated by first quenching the residue with methanol (10 mL) followed by a 1 M solution of HCl in methanol (10 mL). The methanol was removed in vacuo, and the tetradecane was then removed by Kugel−Röhr distillation. The polymer was suspended in methanol, filtered, washed, and dried in vacuo. To more easily isolate the polymer, the polymerization could be carried out in toluene. The solvent was easily removed, precluding the need for the Kugel−Röhr distillation.

Scheme 11



Enantioassay of Recovered Olefins. Optical purity was determined by enantioassay of the methyl ester derivative on a GC column with a chiral stationary phase. A typical procedure for the derivatization follows. Olefin (200 mg) was added to a 25 mL flask containing CCl_4 (4 mL), CH_3CN (4 mL), H_2O (6 mL), and $NaIO_4$ (4 equiv). $RuCl_3 \cdot 3H_2O$ (10 mg) was added, and the biphasic reaction mixture was stirred vigorously for >12 h at room temperature, after which time H_2O (5 mL) and CH_2Cl_2 (5 mL) were added. The organic layer was separated and washed with $Na_2S_2O_3$(aq) (to reduce any I_2 and I_3^- present) and then brine. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo to give a light yellow oil. The methyl esters were prepared by boiling a BF_3/MeOH (15%) solution (5 mL) of the carboxylic acid (~100 mg) for 5−10 min. The methyl ester was extracted into petroleum ether (15 mL) which was dried prior to injection on the GC column with a chiral stationary phase.

(*S*)-3-Methyl-1-pentene. The procedure followed that outlined in Scheme 11. L-Isoleucine was converted to the chloroacid (81%) according to literature precedents (refs 22a,b), modified slightly by adding urea (2.5 equiv) after a 1 d reaction time to remove soluble N_2O_4 gas. The chloroacid was reduced to the alcohol (66%) with $LiAlH_4$ and quenched very carefully with water and 15% NaOH(aq) to give a granular white precipitate. The alcohol was then transformed to the iodide following the procedure in ref 22c. DMF was used as the solvent to increase the yield (72%). In the final step, (*S*)-3-methyl-1-pentene was obtained by dehydrohalogenation, following the procedure in ref 22d (56%).

Mandelic Ester Derivatization of Recovered Olefins. The carboxylic acid was first prepared from the desired olefin as outlined above. The acid (63 μL, 0.50 mmol), (*S*)-methylmandelate (83 mg, 0.50 mmol), and DMAP (10 mg, 0.08 mmol) were combined in a dry 25 mL flask. The flask was flushed with argon and cooled to 0 °C, and dicyclohexylcarbodiimide (0.82 mL of a 0.672 M solution in CH_2Cl_2, 0.55

mmol) was added. After the mixture was stirred at 0 °C for 1 h, the ice bath was removed, and the reaction mixture was stirred for 12 h at room temperature. The resulting slurry was filtered to remove the majority of the dicyclohexyl urea and was diluted with diethyl ether (10 mL). After washings with 1 N $KHSO_4$, saturated $NaHCO_3$, and brine, the organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. The oily material was then dissolved in $CDCl_3$, and ^1H and ^{13}C NMR spectra were taken.

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Supporting Information Available: X-ray data for (*S*)-**2**, (*S*)-**5**, (*S*)-**6**, and (*S*)-**7** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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