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Ancillary Ligand Effects in Chiral C_1-Symmetric *ansa*-Metallocene Catalysts for Stereoregular α-Olefin Polymerization. "Wingspan" Modification with Octahydrofluorene

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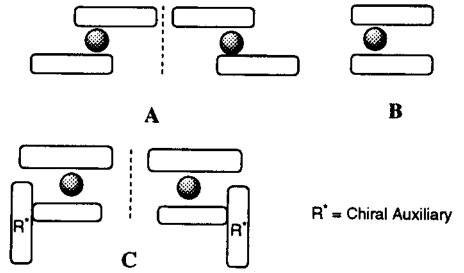
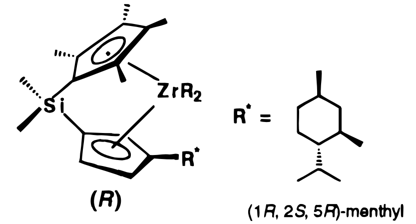
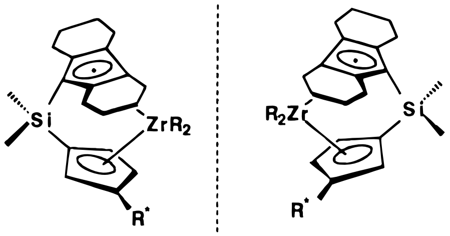
Summary: The synthesis and activity as precatalysts for stereoregular α-olefin polymerization of the chiral C_1-symmetric zirconocene complexes (R)- and (S)-$Me_2Si(\eta^5$-$C_{13}H_{16})(\eta^5$-$C_5H_3R^*)ZrR_2$, where $C_{13}H_{16}$ = octahydrofluorenyl, R = NMe_2, Cl, or Me, and R = (1R,2S,5R)-trans-5-methyl-cis-2-(2-propyl)cyclohexyl ((−)-menthyl), are described.*

Intense research focused on mechanisms of stereoregular α-olefin polymerization mediated by chiral[1,2] C_2-symmetric cationic[3] group 4 metallocene catalysts (**A**, **B**) reveal much about the role of ancillary ligand steric and electronic characteristics[1,2] as well as of counteranions[4,5] in olefin enantiofacial discrimination. Less studied chiral C_1-symmetric[6] *ansa*-metallocenes[5,6] (e.g., **C**, where chiral R* "blocking groups" facilitate separation of metal-centered antipodes)[7] offer an informative contrast with regard to chirality transfer mechanisms, and neither separation of undesired meso isomers (**B**) nor subsequent derivatization/resolution is required for synthesis of configrationally pure products. The efficacy of ligation **C** in enantioselective organolanthanide-centered transformations[7] and, more recently, of (*R*)- and (*S*)-$Me_2Si(Me_4C_5)(C_5H_3R^*)MR_2$ complexes (M = Zr, Hf; R* = (−)−menthyl; R= Cl, Me; **1**) in isoselective propylene polymerization[5,8] raises the intriguing question of whether greater top/bottom discrimination in substrate activation might be achieved by incrementally expanding the "wingspan" of the uppermost η^5 ligand





1a, R = Cl
1b, R = Me



(*S*) **2a**, R = Cl (*R*)
2b, R = Me

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1997.

[1] For recent reviews see: (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144−187. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (c) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (d) Soga, K., Terano, M., Eds. *Catalyst Design for Tailor-Made Polyolefins*; Elsevier: Tokyo, 1994. (e) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29.

[2] For representative recent isotactic polypropylene work, see ref 1 and: (a) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Backmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954−963. (b) Razavi, A.; Atwood, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 7529−7530. (c) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347−1349. (d) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571.

[3] (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (b) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29 and references therein. (c) Kaminsky, W. *Catal. Today* **1994**, *20*, 257−271 and references therein. (d) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65, and references therein. (e) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112−1114. (f) Bochmann, M.; Jagger, A. J. *J. Organomet. Chem.* **1992**, *424*, C5−C7, and references therein. (g) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413−1416 and references therein. (h) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387 and references therein.

[4] (a) Chen, Y.-X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582−2583. (b) Chen, Y.−X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451−12452. (c) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128−6129. (d) Jia, L.; Yang, X.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135−3137. (e) Eisch, J. J.; Pombrik, S. I.; Gürtzgen, S.; Rieger, R.; Uzick, W. In ref 1d, pp 221−235. (f) Chien, J. C. W.; Song, W.; Rausch, M. D. *J. Polym. Sci., A: Polym. Chem.* **1994**, *32*, 2387−2393. (g) Eisch, J.; Pombrik, S. I.; Zheng, G.-X. *Organometallics* **1993**, *12*, 3856−3863.

[5] (a) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114−12129. (b) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3326−3327.

[6] (a) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1996**, *520*, 115−120. (b) Ewen, J. A. *Macromol. Symp.* **1995**, *89*, 181−196 and references cited therein.

[7] (a) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168. (b) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276−3277. (c) Giardello, M. A.; Sabat, M.; Rheingold, A. L.; Stern, C. L. *J. Am. Chem. Soc.* **1994**, *116*, 10212−10240. (d) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254.

[8] Symmetry labels refer to the planar chirality element associated with transition-metal bonding to the appropriate η^5 stereoface. See: (a) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1−36. (b) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598−6599.

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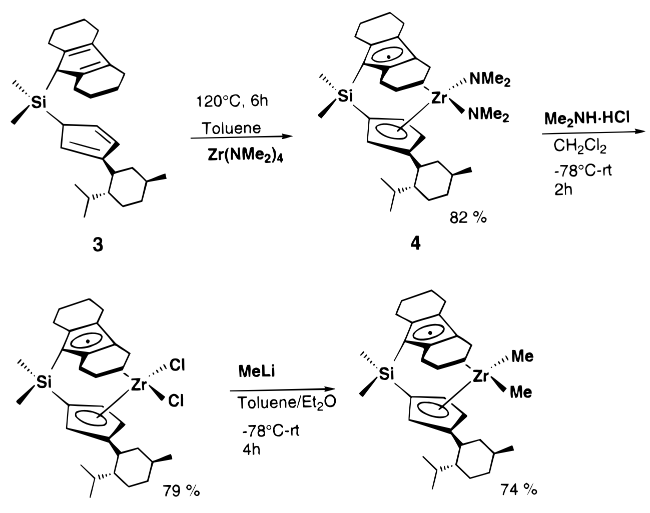
Scheme 1. Preparation of C_1-Symmetric Zirconocene Complexes



in **C**. We report here the successful introduction of the stereodemanding, electron-donating octahydrofluorenyl (Ohf)[9-11] ancillary ligand in *ansa*-metallocene polymerization catalysis. We report the synthesis and spectroscopic/structural characterization of C_1-symmetric complexes **2**, as well as evidence vis-à-vis **1** and the fluorenyl analogue, for enhanced enantiofacial discrimination in olefin polymerization.[9-12]

Ligand **3** (Scheme 1; R*= (−)−menthyl) can be prepared in multigram quantities using octahydrofluorene and procedures similar to those for **1**.[5,13] Highly

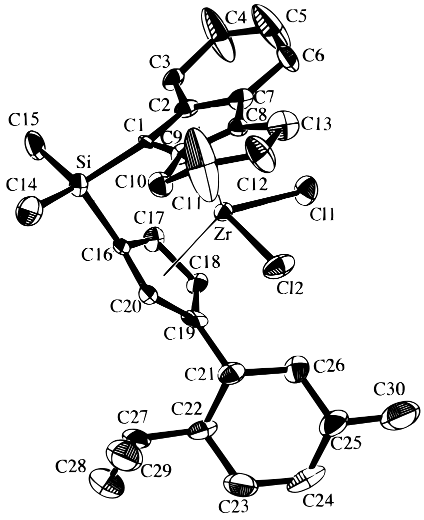
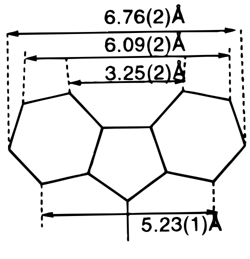
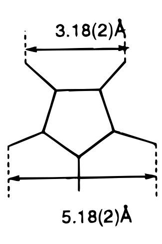


Figure 1. Perspective ORTEP drawing of the molecule (S)-$Me_2Si(C_{13}H_{16})$[(−)-menthylCp]$ZrCl_2$ ((***S***)**-2a**). All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability. Important bond distances (Å) and angles (deg) are as follows: Zr−Cl(1) = 2.423(3), Zr−Cl(2) = 2.419(3), Zr−C(1) = 2.467(9), Zr−C(2) = 2.478(9), Zr−C(7) = 2.603(9), Zr−C(16) = 2.47(1), Zr−C(17) = 2.468(9), Zr−C(18) = 2.573(10); Cl(1)−Zr−Cl(2) = 97.2(1), C(1)−Si−C(16) = 95.0(4), C(14)−Si−C(15) = 110.2(5), Zr−C(2)−C(3) = 121.5(7), Zr−C(7)−C(6) = 128.8(8), Zr−C(1)−Si = 98.3(4), Zr−C(19)−C(21) = 125.3(7).

S-enriched dichloride **2a** (S:R ≈ 85:15) is prepared by protonolysis of the corresponding bis(dialkylamide) (from **3** + $Zr(NMe_2)_4$) with $Me_2NH{\cdot}HCl$.[13-15] Two recrystallizations afford S:R ≥ 90:10.[16] Subsequent alkylation of **2a** proceeds with retention of configuration to yield dimethyl derivative **2b**.[16] The new complexes were characterized by standard analytical/spectroscopic techniques,[13,16,17] and absolute configurations established by X-ray diffraction and CD spectroscopy.[5,8,13,18] The structure of complex **2a** (Figure 1) exhibits typical "bent metallocene" Zr−ligand metrical parameters, similar to those in **1a**.[5] Space-filling models reveal the greater lateral spatial expanse of Ohf vs Me_4C_5 (Figure 2), as does comparison of C−C wingspan dimensions (**D** vs **E**).



D



E

Cationic catalysts were generated by standard methodologies:[1-4,5] **2a** + methylalumoxane (MAO); **2b** + MAO, $B(C_6F_5)_3$, or $Ph_3C^+B(C_6F_5)_4^-$. Polymerizations were carried out using rigorously anhydrous/anaerobic procedures described previously.[2e,4,5] Polymer microstructures were characterized by NMR using the standard tacticity analysis[19] and melting temperatures (T_m) were measured by DSC. Results are shown in Table 1, and it can be seen that the Ohf catalysts (entries 1−6)

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[9] Communicated in part: Obora, Y.; Stern, C. L.; Marks, T. J. *Abstracts of Papers*, 212th National Meeting of the American Chemical Society, Orlando, FL, August 1996; American Chemical Society: Washington, DC, 1996; INOR 378.

[10] (a) Rieger recently reported a complementary synthetic approach to enantiomerically pure *ansa*-octahydrofluorenyl zirconocenes (submitted after ref 9 appeared);[10b] however, olefin polymerization results were not reported. (b) Jany, G.; Fawzi, R.; Steimann, M.; Rieger, B. *Organometallics* **1997**, *16*, 544−550. (c) See also: Rieger, B.; Jany, G. *Chem. Ber.* **1994**, *127*, 2417−2419 (synthesis of racemic *ansa*-octahydrofluorenyl zirconocenes, without polymerization results).

[11] For patents claiming other types of achiral octahydrofluorenyl ligation, see: (a) Nickias, P. N.; Devore, D. D.; Wilson, D. R. PCT Int. Appl. WO 93-08199, 1993. (b) Bichop, C. E.; Johnes, R. L.; Raman, K.; Dang, V.; Yu, L.-C.; Resconi, L.; Dall'Occo, T.; Galimberti, M. PCT Int. Appl. WO 95 27717, 1995.

[12] For polymerization studies with various unsaturated, achiral fluorene-based ligation see ref 6 and: (a) Chen, Y.-X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1−9. (b) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1995**, *501*, 101−106. (c) Patsidis, K.; Alt, H. G. *J. Organomet. Chem.* **1995**, *501*, 31−35. (d) Ewen, J. A.; Johns, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.

[13] See the Supporting Information for additional synthetic and characterization information.

[14] (a) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5−7. (b) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857−3858.

[15] A 100 mL flask was charged with (Ohf-Me_2Si-MCp)Zr(NMe_2)$_2$ (0.50 g, 0.82 mmol) in the glovebox. The flask was removed from the glovebox, and under an inert atmosphere, CH_2Cl_2 (20 mL) was transferred into the reaction flask at −78 °C. Then a solution of $Me_2NH{\cdot}HCl$ (150 mg, 1.80 mmol) was added dropwise at −78 °C. The resulting solution was stirred at room temperature for 1 h. Removal of solvent was followed by extraction with pentane (50 mL). Pale yellow solid (620 mg, 79%) was obtained by removal of the solvent. Two recrystallizations from pentane yielded an ≥ 90:10 S:R diastereomeric mixture of products (20%). ^{1}H NMR: δ 0.21 (s, 3H), 0.25 (s, 3H), 0.61 (d, 3H), 0.74 (d, 3H), 0.83 (d, 3H), 1.14−1.36 (m, 6H), 1.46 (t, 1H), 1.56−2.06 (m, 8H), 2.07−2.15 (m, 6H), 2.76−3.05 (m, 5H), 5.24 (t, 1H), 5.38 (t, 1H), 6.80 (t, 1H). ^{13}C NMR (C_6D_6): δ −2.16, −1.13, 14.27, 15.89, 21.75, 22.06, 22.29, 22.65, 22.87, 22.96, 25.19, 26.98, 27.29, 27.63, 33.30, 34.40, 35.77, 41.56, 50.83, 96.17, 104.20, 112.08, 114.87, 125.59, 127.19, 130.68, 134.21, 137.28, 143.58. CD (pentane); λ_{max} ([θ]): 272 (−49 440), 312 (+13 760), 328 (+8 680), 377(+26 760) nm. Anal. Calcd for $C_{30}H_{44}Cl_2SiZr$: C, 60.57; H, 7.46; N, 0.00. Found: C, 60.83; H, 7.77; N, 0.00.

[16] In contrast, the reaction of the dilithio salt of **3** with $ZrCl_4$ under a variety of conditions proceeds with poor diastereoselectivity.

Table 1. Activity, Polymer Molecular Weight, Polymer Isotacticity, and Polymer Melting Temperature Data for Propylene Polymerization by Chiral C_1-Symmetric Organozirconium Complexes

entry no.	cat.[a]	cocat.	[cocat.][c]	T (°C)	[mon][d]	M_n[e,i]	M_w[e,i]	activity[f]	time (h)	yield (g)	Tm (°C)[g]	% mmmm[h,j]
1	2a	MAO[b]	180	25	0.8	7 130	25 000	7.6×10^4	2.0	1.71	142.7	83
2	2a	MAO[b]	180	0	1.6	9 680	39 300	1.2×10^4	3.0	0.78	142.8	90
3	2b	MAO[b]	180	25	0.8	6 310	18 900	2.3×10^5	2.0	5.25	142.4	85
4	2b	$B(C_6F_5)_3$	0.7	0	1.6	5 110	13 000	8.9×10^3	2.0	0.40	144.1	90
5	2b	$Ph_3C^+B(C_6F_5)_4^-$	0.7	0	1.6	24 300	70 400	1.6×10^5	0.5	1.82	150.4	89
6	2b	$Ph_3C^+B(C_6F_5)_4^-$	0.7	−50	5.0	69 500	274 800	6.0×10^3	0.5	0.21	143.2	90
7	1a	MAO[b]	700	25	0.8	1 740	2 170	5.4×10^4	3.0	2.32		35
8	1a	MAO[b]	700	−5	2.4	6 750	9 940	2.0×10^4	3.0	2.60		70
9	1b	MAO[b]	700	25	0.8	2 850	13 510	4.6×10^4	3.0	2.00		35
10	1b	$B(C_6F_5)_3$	0.7	25	0.8	190[i]		5.4×10^4	3.0	2.34		
11	1b	$Ph_3C^+B(C_6F_5)_4^-$	0.7	0	1.6	15 100	31 200	1.6×10^4	0.50.5	0.23		64

[a] [catalyst] = 0.7 mM in toluene. [b] Methylalumoxane, solvent removed from a 20 wt % solution in toluene (Schering). [c] [cocatalyst], mM in toluene. [d] [monomer], M in toluene. [e] By GPC, relative to polystyrene standards. [f] g of polymer/((mol of Zr)(mol L^{-1} of propylene) h) (reproducibility >15 %). [g] By DSC. [h] From pentad analysis in 1,1,2,2-tetrachloroethane-d_2 at 130 °C (reproducibility >3% for large mmmm). [i] By NMR end-group analysis. [j] Pentane-insoluble fraction.

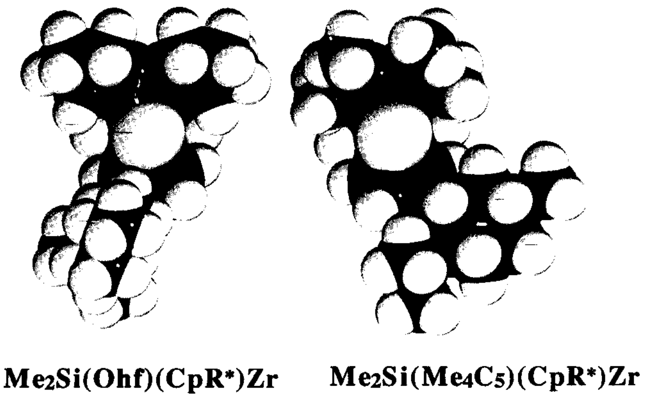

Figure 2. Perspective space-filling models of the molecular structures of (*S*)-$Me_2Si(C_{13}H_{16})$[(−)-menthylCp]$ZrCl_2$ ((***S***)-**2a**; this work) and (*R*)-Me_2SiCp''[(−)-menthylCp]$ZrCl_2$ ((***R***)-**1a**; from ref 5) viewed along the Zr−Si vectors. Chloride ligands are omitted for clarity.

exhibit activities similar to or higher than those of the Me_4C_5 analogues (entries 7−11). More importantly, the Ohf-catalyst-derived polypropylenes exhibit substantially higher isotacticities, contain negligible pentane-soluble fractions, and have melting temperatures as high as 150.4 °C. In addition, polypropylene molecular weights obtained from the Ohf catalysts are ca. 2−10 times higher than from the Me_4C_5 catalysts. As an additional comparison, the C_1-symmetric unsaturated *fluorene* analogue of **2a** (**3a**) was synthesized and examined for propylene polymerization.[13,20] Under catalytic conditions identical with those in Table 1, (entries 1 and 2), the fluorenyl catalyst produces polypropylenes of similar molecular weight characteristics but significantly lower isotacticity (% mmmm = 64% at 25 °C, 72% at 0 °C).[21]

These results indicate that the polymerization catalytic characteristics (isotacticity, molecular weight) of C_1-symmetric catalysts of type **C** can be substantially modified by introducing more sterically demanding, saturated η^5 ancillary ligands. They also suggest that octahydrofluorene is a promising ancillary ligand for asymmetric d- and f-element catalysis.

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Supporting Information Available: Text giving synthetic, spectroscopic, and analytical data and X-ray experimental details, including tables of positional and anisotropic displacement parameters and bond lengths and angles (36 pages). Ordering information is given on any current masthead page.

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(17) A 100 mL flask was charged with 90:10 (*R*) and (*S*)-$Me_2Si(C_{13}H_{16})$[(-)-menthylCp]$ZrCl_2$ (0.25 g, 0.41 mmol) in the glove box. Toluene (20 mL) was then condensed onto the solid at −78 °C. MeLi (0.61 mL, 0.85 mmol, 1.4 M solution in Et_2O) was added dropwise to the solution, and the mixture was stirred for 4 h at room temperature. The volatiles were then removed and the residue dried in vacuo. Pentane (30 mL) was next condensed onto the residue, and the solution was warmed to ambient temperature. The mixture was then filtered and the LiCl washed thoroughly with pentane (3 × 50 mL). The combined extracts were evaporated, and a colorless solid (173 mg, 73% yield) was obtained. ^1H NMR (C_6D_6): δ −0.05 (s, 3H), −0.01 (s, 3H), 0.40 (s, 3H), 0.44 (s, 3H), 0.88 (d, 3H), 1.00 (d, 3H), 1.22 (d, 3H), 1.10−1.35 (m, 6H), 1.37−2.26 (m, 9H), 2.32−2.73 (m, 9H), 2.87 (t, 1H), 5.32 (t, 1H), 5.54 (t, 1H), 6.87 (t, 1H). ^{13}C NMR (C_6D_6): δ −1.97, −0.72, 15.93, 21.89, 22.56, 22.76, 23.03, 23.14, 23.52, 23.67, 25.27, 26.82, 26.98, 27.48, 33.41. 33.79, 34.84, 35.80, 41.31, 41.90, 51.34, 90.14, 98.02, 111.35, 113.09, 119.09, 124.03, 127.39, 127.56, 128.20, 137.52. CD (pentane); λ_{max} ([θ])): 278 (+9 840), 288 (+8 080), 308 (+9 680) nm. *Anal*. Calcd for $C_{32}H_{50}SiZr$: C, 69.30; H, 9.10; N, 0.00. Found: C, 69.32; H, 8.87; N, 0.00.

(18) Crystal data for $C_{30}H_{44}Cl_2SiZr$: space group $P2_12_12_1$ (No. 19) with $a = 9.652(4)$ Å, $b = 10.632(4)$ Å, $c = 29.357(7)$ Å at −120 °C, $Z = 4$, and $V = 3012(1)$ Å^3. The structure was solved by direct methods (SHELX86) and refined by full-matrix least-squares techniques using 1803 reflections having $I > 3.00\sigma(I)$ to $R = 0.048$ and $R_w = 0.036$.

(19) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982; pp 78−84.

(20) $Li_2Me_2Si(C_{13}H_8)$[(−)-menthylCp] (418 mg, 0.96 mmol) and $ZrCl_4$ (220 mg, 0.94 mmol) was charged in a 100 mL reaction flask in the glove box, the flask was removed from the box, and Et_2O (20 mL) was condensed *in vacuo* at −78 °C. The mixture was warmed to room temperature and stirred for 30 min. The volatiles were then removed, and the residue was vacuum-dried for 3 h. Pentane (30 mL) was next condensed onto the residue, and the solution was warmed to ambient temperature. The solution was filtered, and the LiCl was washed thoroughly with pentane (3 × 50 mL). The combined extracts were concentrated *in vacuo* to yield 260 mg (47%) of colorless solid. ^1H NMR (C_6D_6): δ 0.65−0.70 (m), 0.75−1.81 (m), 2.17−2.26 (m), 2.43−2.75 (m), 5.59−5.63 (m), 5.71 (t), 6.40 (t), 6.48 (t). ^{13}C NMR (C_6D_6): δ −1.71, −1.65, −0.93, −0.88, 15.77, 16.58, 21.68, 21.89, 22.71, 22.83, 25.03, 27.15, 27.63, 32.74, 33.03, 35.20, 35.54, 40.72, 41.20, 41.71, 43.59, 48.13, 50.97, 101.53, 103.12, 110.45, 110.69, 113.63, 113.76, 121.69, 123.78, 124.20, 124.32, 124.54, 124.62, 125.09, 125.20, 125.35, 125.44, 126.19, 126.57, 126.61, 126.76, 129.06, 129.28, 130.29, 130.58, 130.63, 130.97, 143.74, 147.06. Anal. Calcd for $C_{30}H_{36}Cl_2SiZr$: C, 61.39; H, 6.20. Found: C, 60.22; H, 6.14.

(21) Complex **3a** is obtained as a 1:1 *S*:*R* mixture, and attempts at diastereomer separation are still in progress. That diastereoselectivity effects are small in these systems and that these systems and these results can be compared to those for **2a** are supported by the fact that a 1:1 *S*:*R* sample of **2a** affords polypropylene with mmmm = 85% in a Table 1, entry 2 type experiment.