Highly Stereoregular Syndiotactic Polypropylene Formation with Metallocene Catalysts via Influence of Distal Ligand Substituents

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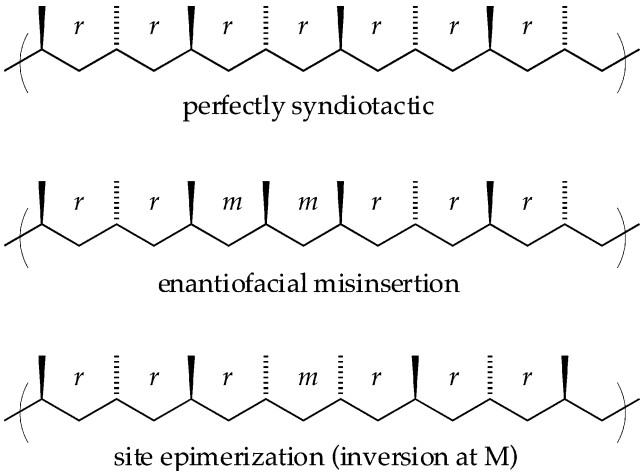
Highly stereoregular syndiotactic polypropylene is obtained with the catalyst systems $Ph_2C(Oct)(C_5H_4)ZrCl_2$/MAO (**8**/MAO) (Oct = octamethyloctahydrodibenzofluorenyl; MAO = methylaluminoxane) and $Me_2C(Oct)(C_5H_4)ZrCl_2$/MAO (**12**/MAO). The syndiotactic polypropylenes obtained are largely devoid of stereoerrors by ^{13}C NMR analysis ([*r*] > 98%), and melting temperatures as high as 153 or 154 °C (from **8** and **12**, respectively) are found for the thermally quenched polymers (without annealing). A related hafnium catalytic system, $Ph_2C(Tet)(C_5H_4)HfCl_2$/MAO (**11**/MAO) (Tet = tetramethyltetrahydrobenzofluorenyl), was found to be the most syndioselective of the hafnocenes tested (T_m = 141 °C). The metallocene dichloride precatalysts represent the first examples of transition metal complexes containing the Oct or Tet ligands. Reported are the solid state crystal structures of **8**, the diprotio ligand precursor of **8** ($Ph_2C(OctH)(C_5H_5)$), and the zirconium analogue of **11**, $Ph_2C(Tet)(C_5H_4)ZrCl_2$ (**10**). Distal ligand influences are thus demonstrated to have a dramatic effect on polymer stereochemistry.

Introduction

The first highly efficient syndiotactic polypropylene polymerization system was reported by Ewen et al. in 1988.[1] The original design employed *ansa* fluorenylcyclopentadienyl precatalysts of the type $Me_2C(C_{13}H_8)(C_5H_4)MCl_2$ (M = Zr, Hf; $C_{13}H_8$ = fluorenyl) activated by methylaluminoxane (MAO). Perfectly syndiotactic polypropylene arises from a regularly alternating insertion mechanism that employs sequentially opposite enantiofaces of the propylene monomer.[2] The $Me_2C(C_{13}H_8)(C_5H_4)MCl_2$/MAO system—as well as other syndioselective catalyst systems that incorporate propylene in a 1,2 fashion[3]—suffers from two kinds of stereoerrors that decrease the syndiotacticity of the produced polymer: enantiofacial misinsertions, giving rise to a double *m*, i.e., a [...*rrmmrr*...] stereoerror sequence, and site epimerizations (inversion at the stereogenic metal center by polymeryl chain swinging), giving rise to an isolated *m*, i.e., a [...*rrmrrr*...] stereoerror sequence (Scheme 1).[4]

Scheme 1



After Ewen's initial discovery, several metallocene-based systems have been devised that exceed the original with respect to syndioselectivity, activity, molecular weight, and polymer melting temperature (T_m) (Scheme 2).[3,4] Following reports of the original singly bridged metallocenes **1** and **2**,[1] Razavi et al. developed bridge-modified analogues **3** and **4**.[5] Alt, Zenk, et al. and Ewen et al. have prepared several fluorenyl-substituted metallocenes, including **5**.[6,7] We have reported doubly [$SiMe_2$]-bridged, syndioselective metallocenes; examples

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(1) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256. (b) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253−295.

(2) (a) Price, F. P. *J. Chem. Phys.* **1962**, *36*, 209. (b) Frisch, H. L.; Mallows, C. L.; Bovey, F. A. *J. Chem. Phys.* **1966**, *45*, 1565. (c) Bovey, F. A. *Acct. Chem. Res.* **1968**, *1*, 175.

(3) For reviews on Ziegler−Natta polymerization see: (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., Int. 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.

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(5) (a) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117−123. (b) Razavi, A.; Peters, L.; Nafpliotis, L. *J. Mol. Catal. A Chem.* **1997**, *115*, 129−154.

(6) (a) Alt, H. G.; Zenk, R.; Milius, W. *J. Organomet. Chem.* **1996**, *514*, 257−270. (b) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *518*, 7−15. (c) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *526*, 295−301.

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Scheme 2

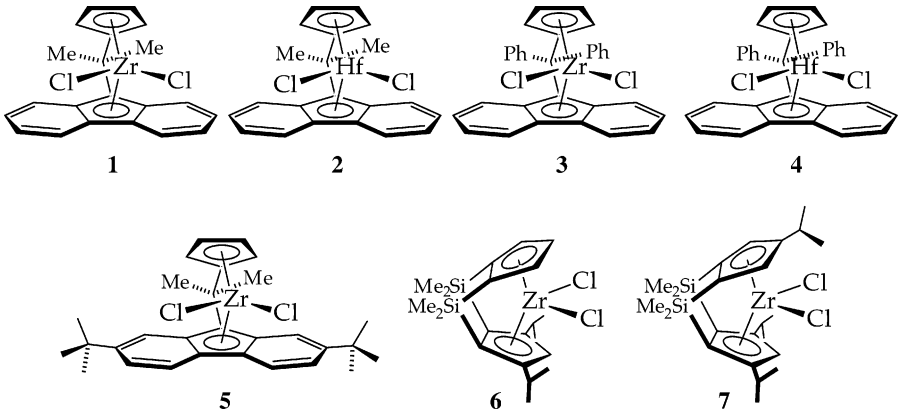


Table 1. MAO-Cocatalyzed Propylene Polymerization Results with 1−7

metallocene	T_p (°C)	[*r*] (%)	[*rrrr*] (%)	T_m (°C)	ref
1	50	96.0		138	5
2	50	74.0		118	5
3	50	97.5		139	5
4	50	90.3		101	5
5	60	99.1	98.7 [*rr*]	141	7
6	20	97.1	93.4	151	8
7	20	99.4	97.5	151	8

are given by **6** and **7**.[8] Table 1 presents representative data regarding polymers made by MAO-cocatalyzed polymerizations. The doubly bridged metallocenes produce the most stereoregular and highest melting syndiotactic polypropylene. For a given ligand system, the hafnium analogues generally provide polymers of lower syndiotacticity. In this report we describe new singly [CR_2]-bridged zirconocene catalysts having cyclopentadienyl linked to sterically expansive substituted fluorenyl ligands, i.e., those with mono- and bis(tetramethyltetrahydrobenzo) substituents on the flourenyl ligand. These new catalyst systems afford syndiotactic polypropylenes with very high [*rrrr*] pentad contents and the highest melt transition temperatures reported to date for thermally quenched polymers (no annealing).

Results and Discussion

Synthesis of Zirconocene and Hafnocene Dichorides. According to the current understanding of propagative stereocontrol,[9] enantiofacial misinsertions occur in parent fluorenyl systems whenever the growing polymer chain is directed toward the fluorenyl ligand during the transition state for insertion. The more three-dimensional nature of the lower cyclopentadienyl ligand having the isopropyl substituents (*vis-à*-vis the flatter fluorenyl ligand of **1**−**4**) of the doubly bridged metallocenes **6** and **7** apparently disfavors the analogous transition state for misinsertion, as these provide polymers containing fewer enantiofacial misinsertions ([*rmmr*] typically <1%).[4a] Thus, the initial goal of this study was to prepare a fluorenyl-based metallocene with similar steric properties such that enantiofacial misinsertions would be minimized.

Metallocene **5** bears added steric bulk in the form of two *tert*-butyl groups at the 2 and 7 positions of the fluorenyl ligand. However, only a modest increase in syndioselectivity is observed over that of the parent system.[6,7] A simple steric analysis suggests that steric bulk placed at the 3 and 6 positions of the fluorenyl ligand might better approximate the steric situation present in the doubly bridged metallocenes. Therefore, the sterically expansive substituted fluorenes 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]-fluorene (OctH) and 1,1,4,4-tetramethyl-1,2,3,4-tetrahydrobenzo[*b*]fluorene (TetH) were prepared according to Scheme 3.[10]

This improved synthesis, the Friedel−Crafts double cycloalkylation[11] of fluorene, which proceeds in high isolated yields (up to 95%), allows the large-scale (ca. 100 g) preparation of sterically loaded fluorene OctH. All starting materials are inexpensive and commercially available with the exception that 2,5-dichloro-2,5-dimethylhexane must be prepared in one step from the corresponding, inexpensive diol (see Experimental Section). TetH is prepared by the analogous single cycloalkylation and must be separated from residual fluorene and OctH, which forms competitively. Nonetheless, acceptable yields (43%) of pure TetH can readily be prepared in multigram quantities (10−20 g).

(7) (a) Ewen, J. A. *Macromol. Symp.* **1995**, *89*, 181−196. (b) Shiomura, T.; Kohno, M.; Inoue, N.; Asanuma, T.; Sugimoto, R.; Iwatani, T.; Uchida, O.; Kimura, S.; Harima, S.; Zenkoh, H.; Tanaka, E. *Macromol. Symp.* **1996**, *101*, 289.

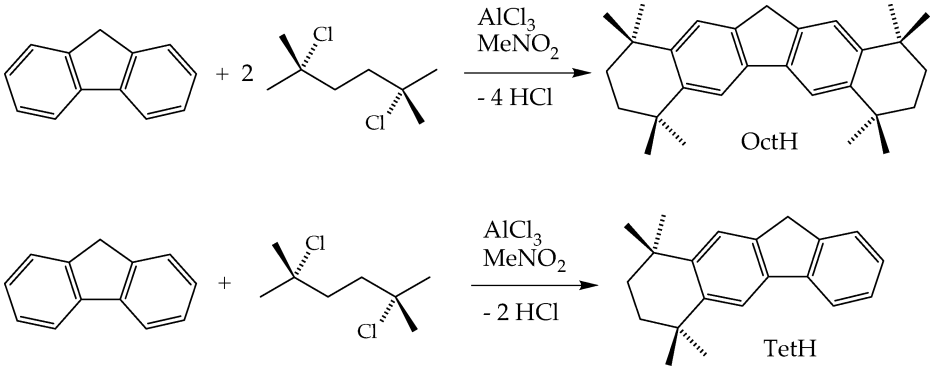
(8) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988−11989.

(9) (a) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015. (b) Cavallo, L.; Guerra, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1991**, *24*, 1784. (c) Corradini, P.; Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, 1995; pp 237−249. (d) Guerra, G.; Corradini, P.; Cavallo, L.; Vacatello, M. *Macromol. Symp.* **1995**, *89*, 307. (e) Gilchrist, J. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 12021−12028. (f) Janiak, C. In *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; pp 547−623.

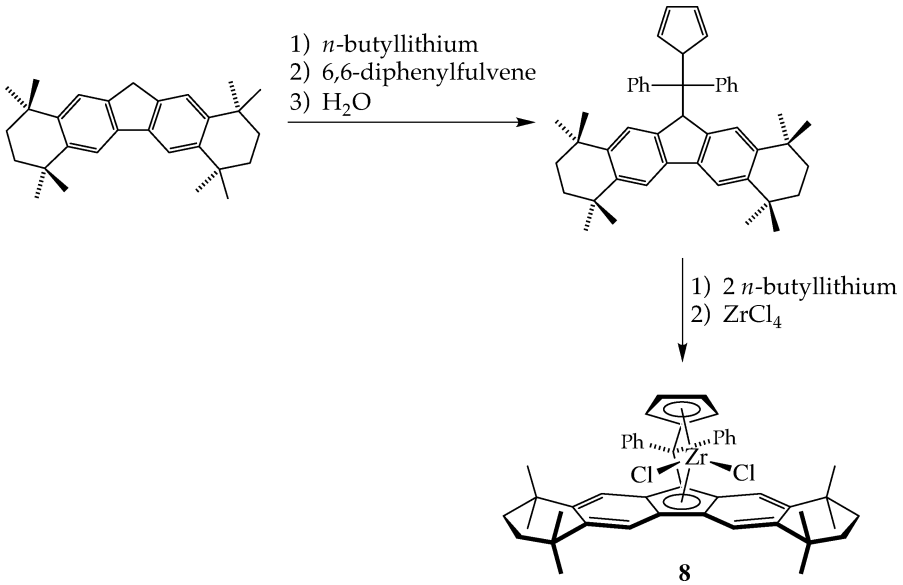
(10) The syntheses of OctH and TetH have been reported: (a) Guilhemat, R.; Pereyre, M.; Petraud, M. *Bull. Soc. Chim. Fr.* **1980**, *2*, 334−344. (b) Gverdtsiteli, D. D.; Revazishvili, N. S.; Tsitsishvili, V. G.; Kikoladze, V. S. *Soobshch. Akad. Nauk. Gruz. SSR* **1989**, *133* (1), 77−80; *Chem. Abstr.* **1989**, *111*, 214206. For the first reports of Oct-containing metallocenes, see ref 19 and: (c) Miller, S. A.; Bercaw, J. E. U.S. Patent 6,469,188, 2002 (application date: 1/20/00). (d) Miller, S. A.; Bercaw, J. E. U.S. Patent 6,693,153, 2004. (e) Kawai, K.; Yamashita, M.; Tohi, Y.; Kawahara, N.; Michiue, K.; Kaneyoshi, H.; Mori, R. PCT Int. Appl. WO 01/27124, 2001 (application date 10/5/00). Additionally, two of our Oct-containing metallocenes have been cited in recent reviews (**8** in ref 3c and **12** in ref 3d).

(11) For Friedel−Crafts cycloalkylation reactions employing 2,5-dichloro-2,5-dimethylhexane, see: (a) Bruson, H. A.; Kroeger, J. W. *J. Am. Chem. Soc.* **1940**, *62*, 36−44. (b) Roberts, R. M.; Khalaf, A. A. *Friedel−Crafts Alkylation Chemistry. A Century of Discovery*; Dekker: New York, 1984. (c) Olah, G. A.; Krishnamurti, R.; Prakash, G. K. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, pp 292−339.

Scheme 3



Scheme 4



Zirconocene and hafnocene dichlorides incorporating the Oct and Tet ligands are prepared according to Scheme 4. A single crystal of the intermediate diprotio ligand $Ph_2C(OctH)(C_5H_5)$ was subjected to X-ray diffraction analysis (Figure 1),[12] revealing the presence of four different molecules residing in the asymmetric unit. These varied because of alternate positioning of the sp^3 carbon in the cyclopentadienyl ring and because of different conformers possible for the 2,5-dimethylhexane-2,5-diyl substituents (Table 2). For example, Figure 1 shows the structure with the proximal (same side of the fluorene ring as 9-H) methyl groups near the 3 and 6 positions of fluorene occupying axial (left) and equatorial (right) positions.

Structural Characterization of the Zirconocene and Hafnocene Dichlorides. Using the procedures similar to that shown in Scheme 4, zirconocene and hafnocene dichlorides having the Oct or Tet ligands were prepared (Scheme 5). Compounds **8**, **9**, and **12** display time-averaged C_s symmetry in solution (^{1}H NMR, 25 °C), suggesting rapid interconversion of the two chairlike conformers possible for the tetramethyltetrahydrobenzo substituents. Additionally, compounds **10** and **11**—a racemic mixture of enantiomers—behave as single, C_1-symmetric species in solution. As seen for the parent fluorenyl complexes **3** and **4**,[5] rotation around the C−phenyl bonds of **8**−**11** is slow on the NMR time scale.

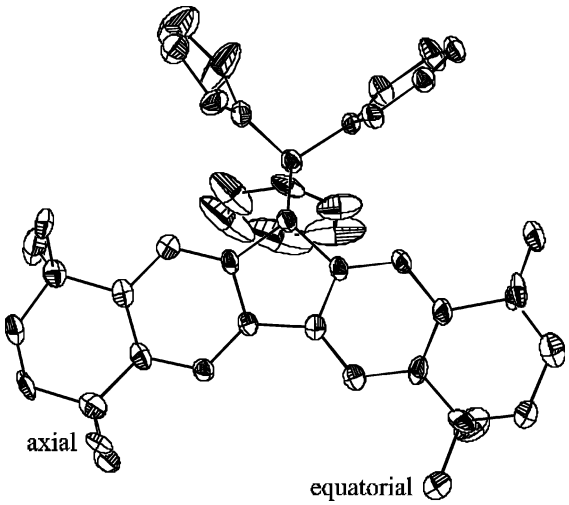


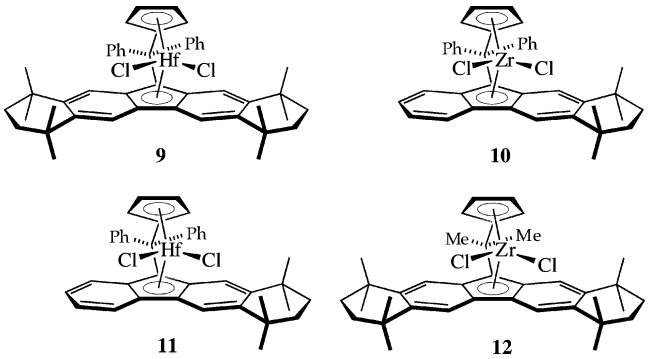
Figure 1. X-ray crystal structure of $Ph_2C(OctH)(C_5H_5)$. Thermal ellipsoids are shown with 50% probability.

(12) The diprotio ligand $Ph_2C(OctH)(C_5H_5)$ (crystallized from ethanol) is monoclinic $C2/c$, a = 39.813(15) Å, b = 12.631(6) Å, c = 29.671(15) Å, β = 98.34(4)°, V = 14763(12) Å^3, Z = 16, T = 85 K. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 105607.

Table 2. Description of Four Solid State Structures for $Ph_2C(OctH)(C_5H_5)$

molecule	position of Cp sp^3 carbon	position of left proximal methyl group	position of right proximal methyl group
A (Figure 1)	3	axial	equatorial
B	3	axial	axial
C	4	axial	equatorial
D	4	equatorial	axial

Scheme 5



The solid state crystal structures of zirconocene dichlorides **8** (Figure 2) and **10** (Figure 3) have been determined by X-ray crystallography.[13,14] These were each crystallized from 1,2-dichloroethane and have empirical formulas of **8**·$(C_2H_4Cl_2)_{1.5}$ and **10**·$(C_2H_4Cl_2)_{1.5}$. In contrast to the several conformations found in the solid state for the diprotio ligand $Ph_2C(OctH)(C_5H_5)$, metallocenes **8** and **10** present only single conformations. The proximal methyl groups of **8** are described as axial/equatorial (Figure 2), and the proximal methyl group of **10** is described as axial (Figure 3).

Polymerization Results. The five metallocene precatalysts shown in Schemes 4 and 5 were subjected to MAO-cocatalyzed polymerizations of propylene. The polymerization results are summarized in Table 3. Figure 4 depicts the ^{13}C NMR spectrum of the methyl region for two polymers made by metallocene **8**/MAO (entry 1 and entry 2), and at the signal-to-noise level of this spectrum, no pentads other than [*rrrr*] are observed.[15] In addition to these precatalysts, **3**, **4**, and those shown in Scheme 6 were also prepared and tested, primarily for obtaining comparative data. Precatalysts **3**, **4**,[5] and **14**[16] have been reported, while **13** is the diphenylmethylidene-bridged variant of the reported isopropylidene-bridged compound **5**.[7] Precatalyst **15** is a C_s-symmetric Oct-containing analogue of **14**.

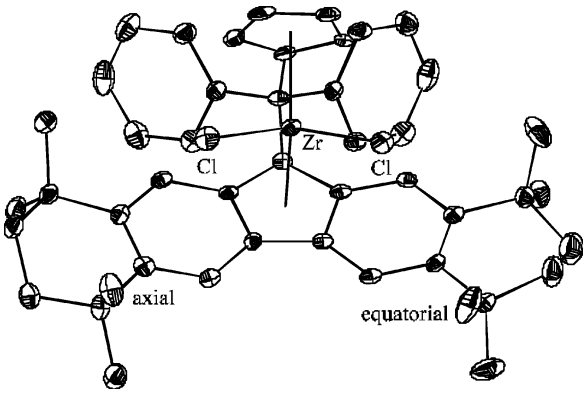


Figure 2. X-ray crystal structure of **8**. Thermal ellipsoids are shown with 50% probability.

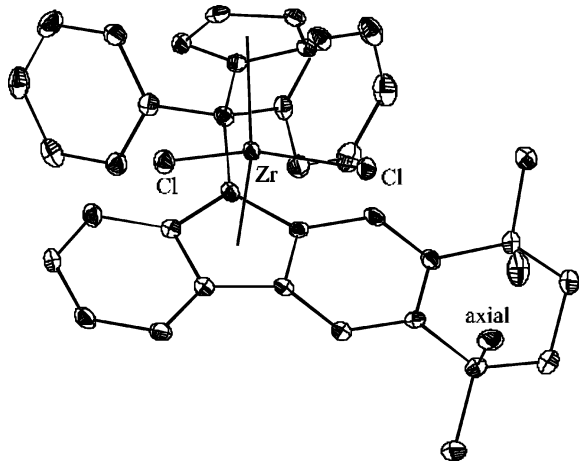


Figure 3. X-ray crystal structure of **10**. Thermal ellipsoids are shown with 50% probability.

Since the thermal history of a syndiotactic polypropylene sample can often impact its melting behavior, polymer melting temperature for several polymers was monitored as a function of thermal history, as described in Table 4.[17] Generally, the first melting temperature is significantly higher than that obtained during subsequent scans. Those values measured during the second, third, and fourth scans correspond to the melting temperature of the thermally quenched polymer and are quite similar. Annealing processes can often lead to unusually high melting temperatures,[18] as shown for entry 3 following annealing for 16 h at 145 °C. The highest melting thermally quenched polymer reported

(13) $Ph_2C(C_{29}H_{36})(C_5H_4)ZrCl_2$ (**8**) (crystallized from 1,2-dichloroethane) is monoclinic $P2_1/n$, a = 13.898(8) Å, b = 13.698(10) Å, c = 23.275(16) Å, β = 96.91(6)°, V = 4399(5) Å^3, Z = 4, T = 85 K. CCDC deposition number 112475.

(14) $Ph_2C(C_{21}H_{22})(C_5H_4)ZrCl_2$ (**10**) (crystallized from 1,2-dichloroethane) is triclinic $P1$, a = 9.1631(10) Å, b = 12.4550(13) Å, c = 16.7351(18) Å, α = 70.655(2)°, β = 87.699(2)°, γ = 87.820(2)°, V = 1800.0(3) Å^3, Z = 2, T = 98 K. CCDC deposition number 137697.

(15) The polymer described by entry 15 has been analyzed by L. Resconi at Montell Polyolefins, and its ^{13}C NMR data are reported in ref 3d. The pentad distribution (^{13}C NMR, 120 °C, $C_2D_2Cl_4$): *mmmm* = 0.0%; *mmmr* = 0.0%; *rmmr* = 0.6%; *mmrr* = 1.2%; *mmrm* + *rrmr* = 2.7%; *mrmr* = 0.1%; *rrrr* = 91.7%; *rrrm* = 3.8%; *mrrm* = 0.0%. The intrinsic viscosity in tetrahydronaphthalene was determined at 135 °C: 4.21 dL/g. This corresponds to a viscosimetric molecular weight (M_v) of 730 000. DSC measurements were identical to those reported in Table 3 (T_m = 154.3 °C). It was suggested that these polypropylenes are too syndiotactic to obtain reliable tacticity information. Therefore, polymer melting temperature is often taken as an alternative measure of syndiotacticity for the polymers reported herein.

(16) Razavi, A.; Vereecke, D.; Peters, L.; Den Dauw, K.; Nafpliotis, L.; Atwood, J. L. In *Ziegler Catalysts: Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; pp 111−147.

(17) Thermal analyses were performed with a Perkin-Elmer DSC 7 with a scan rate of 10 °C/min. Following a scan from 50 °C to 200 °C, the sample was brought to 20 °C at a rate of 200 °C/min.

(18) Caution is advised in comparing melting temperatures of syndiotactic PP, because annealed and thermally quenched polymers typically afford widely different values. (a) Annealing at 140 °C for 2 h provided a T_m of 170 °C: Grisi, F.; Longo, P.; Zambelli, A.; Ewen, J. A. *J. Mol. Catal. A-Chem.* **1999**, *140* (3), 225−233. (b) Annealing at 140 °C provided a T_m of 161.2 °C. The thermally quenched polymer melted at 146.3 °C: Lovinger, A. J.; Lotz, B.; Davis, D. D.; Schumacher, M. *Macromolecules* **1994**, *27*, 6603−6611. (c) A recent report of syndiotactic polypropylenes prepared via chain-end control with nonmetallocene titanium-based catalysts indicated melting temperatures up to 156 °C. The reported triad content of [*rr*] = 94% suggests that these polymers were annealed. See: Mitani M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 7888−7889.

Table 3. MAO-Cocatalyzed Polymerization Results with 8−12, 3, 4, and 13−15

entry	metallocene (mg)	MAO (equiv)	T_p (°C)	toluene (mL)	C_3H_6 (mL)	time (min)	yield (g)	activity[a]	T_m[b] (°C)	[*r*] (%)	M_w	M_w/M_n
1	**8** (0.5)	2000	0	1.0	30	10	0.48	5700	153	>99	961 000	2.1
2	**8** (0.5)	2000	20	1.0	30	10	1.16	14 000	148	>98	843 000	1.8
3	**8** (2.0)	1000	0	2.0	30	10	0.82	2500	149			
4	**8** (2.0)	1000	20	2.0	30	10	1.44	4300	146			
5	**8** (2.0)	1000	0	30.0	3	20	1.44	2200	146	>98		
6	**8** (2.0)	1000	20	30.0	3	5	1.68	10 000	140			
7	**9** (3.0)	1000	0	2.0	30	15	0.25	330	111	88.6		
8	**9** (3.0)	1000	20	2.0	30	10	0.98	2000	88	89.8		
9	**10** (2.0)	1000	0	2.0	30	10	0.27	800	140	>98		
10	**10** (2.0)	1000	20	2.0	30	5	1.60	9600	137			
11	**11** (3.0)	1000	0	2.0	30	60	0.27	90	141	92.2		
12	**11** (3.0)	1000	20	2.0	30	20	1.27	1300	120	89.7		
13	**12** (0.5)	2000	0	1.0	30	10	0.26	3100	151	>98		
14	**12** (0.5)	2000	20	1.0	30	10	0.26	3100	147			
15[c]	**12** (2.0)	1000	0	2.0	30	10	1.16	3500	154	97.5	535 000	2.0
16	**12** (2.0)	1000	20	2.0	30	10	4.79	14 000	153		310 000	2.0
17	**3** (1.0)	1000	0	2.0	30	10	0.31	1900	142			
18	**3** (1.0)	1000	20	2.0	30	10	1.13	6800	136			
19	**4** (3.0)	1000	0	2.0	30	30	0.16	110	124			
20	**4** (3.0)	1000	20	2.0	30	15	0.70	940	119			
21	**13** (2.0)	1000	0	2.0	30	5	1.12	6700	144			
22	**13** (2.0)	1000	20	2.0	30	3	2.24	22 000	139			
23	**14** (0.5)	2000	0	1.0	30	5	3.00	72 000	n.o.	50.2		
24	**14** (0.5)	2000	20	1.0	30	5	5.09	120 000	n.o.	50.5		
25	**15** (0.5)	2000	0	1.0	30	5	1.09	26 000	n.o.	81.3		
26	**15** (0.5)	2000	20	1.0	30	5	2.85	68 000	n.o.	74.1		

[a] Reported in g PP/(g metal·h). [b] n.o. = not observed. [c] See ref 15.

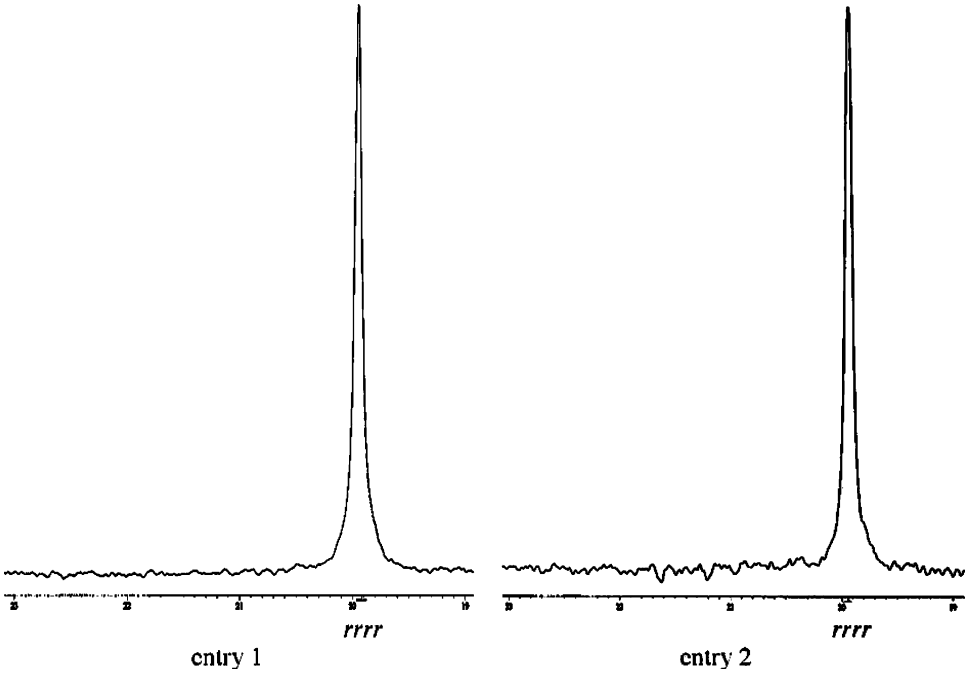
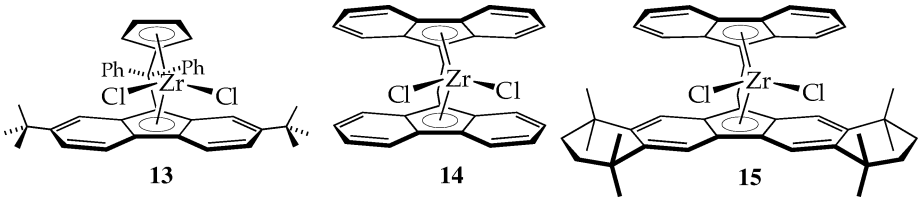


Figure 4. ^{13}C NMR spectrum of the methyl region for polypropylenes made by **8**/MAO (entry 1 and entry 2).

Scheme 6



here is that produced by metallocene **12**/MAO, which is capable of producing syndiotactic polypropylene with a melting temperature of 154.3 °C (entry 15). On the basis of comparing melting points of the polypropylenes produced by this series of zirconocene dichlorides, the syndioselectivity of the Oct complex **8** is higher than that of **10**, **3**, and **13**, which contain Tet, Flu, and 2,7-di-*tert*-butylfluorenyl, respectively. For the hafnium analogues, it is the Tet-containing catalyst system (**11**/MAO) that produces the highest melting polymer.

Table 4. Polymer Melting Temperatures Depend on the Thermal History of the Sample[a]

entry		first scan	second scan	third scan	fourth scan		fifth scan	sixth scan	seventh scan	eighth scan
2	T_m (°C)	160.6	148.0	148.0	148.0					
	H_m (J/g)	83.2	38.2	36.1	37.2					
3	T_m	165.1	148.9	148.9	148.9	anneal at	168.6	148.7	148.7	148.7
	H_m	80.2	48.2	47.0	47.6	145 °C	65.7	48.2	47.0	48.0
4	T_m	157.3	146.1	146.1	146.1					
	H_m	73.6	43.1	44.3	44.9					
15	T_m	159.9	154.3	154.3	154.3					
	H_m	78.8	52.1	53.2	52.9					
16	T_m	156.6	153.1	153.4	153.4					
	H_m	81.1	47.2	47.9	48.1					
17	T_m	148.7	141.6	141.6	141.6					
	H_m	61.0	37.9	37.9	37.6					

[a] Entry numbers correspond to those of Table 3.

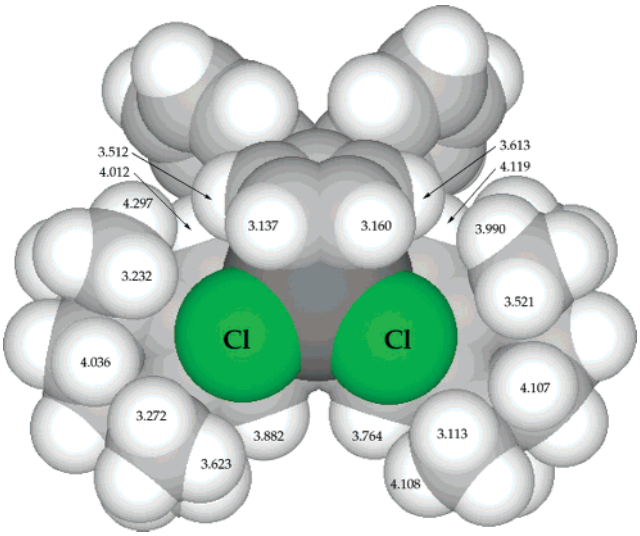


Figure 5. Space-filling model of **8** and H−Cl interatomic distances (in Å).

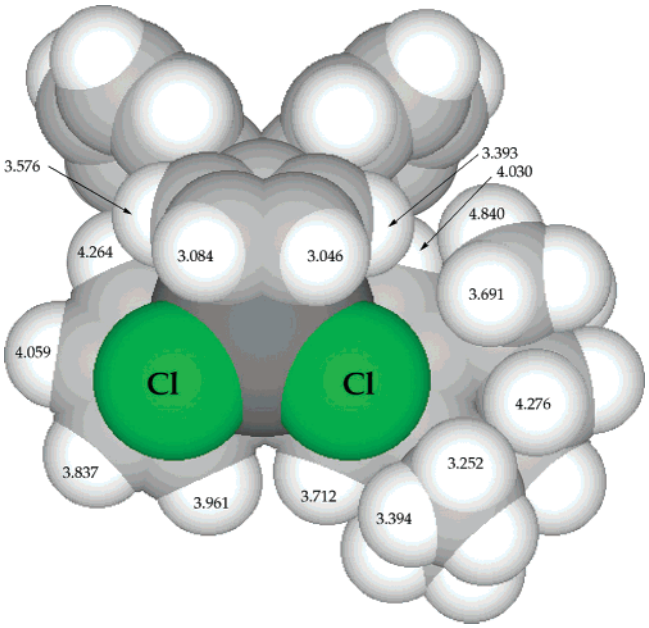


Figure 6. Space-filling model of **10** and H−Cl interatomic distances (in Å).

The magnitude of the effects of the (seemingly distal) tetramethyltetrahydrobenzo substitutents for the Oct and Tet ligands on polypropylene tacticity might seem rather unexpected. On the other hand, inspection of space-filling models derived from the X-ray crystal structures of **8** and **10** reveals surprisingly close contacts between the chloride ligands and the "distal" 2,5-dimethyl-2,5-hexanediyl substituents. Figure 5 depicts metallocene **8** and provides the interatomic H−Cl distances. Remarkably, the shortest H−Cl distance—3.113 Å—is that between chlorine and a hydrogen on the equatorially positioned methyl group of the Oct ligand. In fact, the only other *atom* in the molecule closer to chlorine is zirconium (to which it is covalently bound with Zr−Cl = 2.416 Å), despite the fact that the H−Cl interaction is separated by seven covalent bonds (H−C−C−C−C−C−Zr−Cl). Figure 6 depicts metallocene **10** and provides the interatomic H−Cl distances. In this molecule, the H−Cl distances for the axial methyl group are slightly shorter than those for the axial methyl group of **8** (3.252 vs 3.272 Å). Notwithstanding the shorter zirconium−α-carbon bond present in the active polymerization species, it is probable that there exist significant steric interactions between the distal substituents and the β- and γ-carbons of the growing polymer chain.[19]

An alternative explanation for enhanced catalyst stereoselectivity may be found upon consideration of subtle ion-pairing effects (vide infra). The size of the (MAO) counteranion(s) in olefin polymerization catalysts is not established and likely variable,[20] and its ability to coordinate has been shown to impact relative rates of stereochemically important events.[21] On the other hand, little has been reported on how the size of the cationic transition metal species can affect ion-pairing phenomena. Thus the varying sizes of the Flu, Tet, and Oct ligands may significantly alter the ion-pairing dynamics and result in different stereoselectivities.

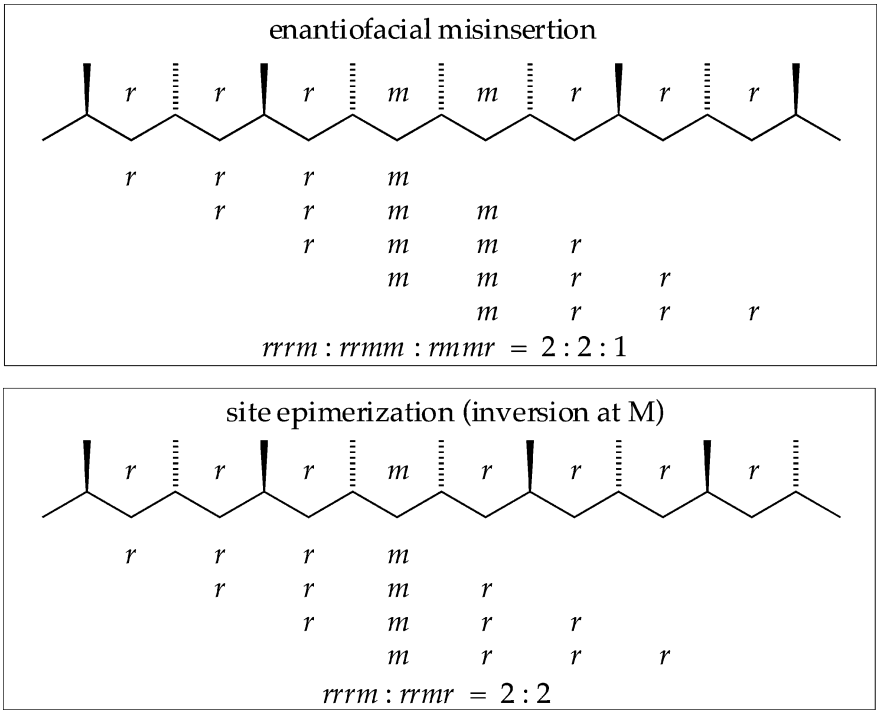
Stereoerror Analysis. As shown in Scheme 7 an isolated enantiofacial misinsertion will produce pentads of the type *rrrm*, *rrmm*, and *rmmr* in a 2:2:1 ratio. A

(19) (a) It is proposed that nonbonded repulsive interactions in the propagative transition state greatly disfavor enantiofacial misinsertions for Oct-containing metallocenes. At the same time, ground state attractive interactions possible between the growing polymer chain and the Oct ligand may increase the barrier to site epimerization. These combined effects result in the highest apparent syndioselectivity observed for a fluorenyl-based metallocene polymerization catalyst. For details on this preliminary theoretical model see: (a) Miller, S. A.; Bercaw, J. E. 217th Am. Chem. Soc. Nat. Meet., Anaheim 1999, INOR 151. (b) Miller, S. A. Ph.D. Thesis, California Institute of Technology, 2000; Chapter 3.

(20) Babushkin, D. E.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2002,** *124*, 12869−12873.

(21) (a) Mohammed, M.; Nele, M.; Al-Humydi, A.; Xin, S.; Stapleton, R. A.; Collins, S. *J. Am. Chem. Soc.* **2003,** *125*, 7930−7941. (b) Chen, M.-C.; Marks, T. J. *J. Am. Chem. Soc.* **2001,** *123*, 11803−11804.

Scheme 7



single, isolated site epimerization will lead to pentads *rrrm* and *rrmr* in a 2:2 ratio.[22] Assuming that stereoerrors are isolated (separated by 4 or more correctly inserted monomer units),[23] one can calculate the relative likelihood of enantiofacial misinsertion versus site epimerization. If the relative probability of enantiofacial misinsertion is defined as $P_{\text{e.m.}}$ and the relative probability of site epimerization is defined as $P_{\text{s.e.}}$, then the following relationships can be written, where I_{xxxx} is the measured intensity for the xxxx pentad:

$$I_{rrrm} = 2P_{\text{e.m.}} + 2P_{\text{s.e.}}$$

$$I_{rmmr} = P_{\text{e.m.}}$$

$$I_{mmrr} = 2P_{\text{e.m.}}$$

$$I_{rmrr} = 2P_{\text{s.e.}}$$

A least-squares calculation[24] was performed on the relevant pentad intensities for entries 7, 8, 11, and 12 for polymers made with Oct-containing (**9**, entries 7 and 8) and Tet-containing (**11**, entries 11 and 12) hafnocene catalysts. The same calculation was performed for entry 15, which is a polymer made with an Oct-containing zirconocene (**12**). The results are summarized in Table 5. For catalyst systems **9**/MAO and **11**/MAO, an increase in polymerization temperature results in an increase in $P_{\text{s.e.}}$. This outcome is anticipated because the rate for the unimolecular site epimerization process is more temperature dependent ($\Delta S^{\ddagger}$ is near zero; $\Delta H^{\ddagger}$ relatively large), while that for the bimolecular propagation step increases more slowly with increasing temperature ($\Delta S^{\ddagger}$ is large and negative; $\Delta H^{\ddagger}$ thus relatively small). The unimolecular process is therefore expected to become increasingly more prevalent at higher temperatures. Less clear is why the Tet-containing hafnocene catalyst derived from **11** is less likely than the Oct-containing analogue **9** to undergo site epimerization. This result is contrary to that observed for the zirconocene series. An additional apparent discrepancy is that **9** allows a considerable fraction of enantiofacial misinsertions, while the isosteric zirconium analogue **12** practically forbids them. It is possible that the hafnium catalyst allows chain epimerizations,[25] producing *mm* stereo-

Table 5. Least-Squares Determination of the Relative Probabilities of Enantiofacial Misinsertion ($P_{\text{e.m.}}$) and Site Epimerization ($P_{\text{s.e.}}$)[a]

entry	7	8	11	12	15
metallocene dichloride	**9**	**9**	**11**	**11**	**12**
T_p (°C)	0	20	0	20	0
pentad (%)					
[*mmmm*]	0.0	0.0	0.0	0.0	0.0
[*mmmr*]	0.0	0.0	0.0	0.0	0.0
[*rmmr*]	3.0	2.0	2.8	3.4	0.6
[*mmrr*]	7.0	4.2	5.1	7.1	1.2
[*mrmm*] + [*rmrr*]	9.9	12.2	4.9	6.7	2.7
[*mrmr*]	0.0	0.0	0.0	0.0	0.1
[*rrrr*]	69.6	66.0	76.4	69.2	91.7
[*rrrm*]	10.6	15.7	10.9	13.6	3.8
[*mrrm*]	0.0	0.0	0.0	0.0	0.0
$P_{\text{e.m.}}$	0.025	0.020	0.027	0.035	0.006
$P_{\text{s.e.}}$	0.039	0.060	0.026	0.033	0.013
$P_{\text{s.e.}}/P_{\text{e.m.}}$	1.53	3.03	0.95	0.94	2.21
% rms error	1.83	0.21	0.25	0.09	0.04

[a] Entry numbers correspond to those of Table 3.

(22) (a) Farina, M. *Top. Stereochem.* **1987**, *17*, 1−111. (b) Price, F. P. In *Markov Chains and Monte Carlo Calculations in Polymer Science*; Lowry, G. G., Ed.: Marcel Dekker: New York, 1970; Chapter 7. (c) Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1972. (d) Randall, J. C. *Polymer Sequence Determination: Carbon-13 NMR Method*; Academic Press: New York, 1977. For leading references, see (e) Randall, J. C. *Macromolecules* **1997**, *30*, 803−816.

(23) For example, for entry 7 (Hf catalyst), 11.4% of the dyads are *m* dyads (dyads resulting from mistakes). The probability of sequential *m* dyads is about (0.114)(0.114) = 1.3%. We considered this number to be comparatively small (close to the experimental error of the ^{13}C NMR analysis), and thus the assumption that stereoerrors are isolated was retained.

Table 6. Polypropylene Pentad Distributions from Entries 23, 24, 25, and 26[a]

entry	23	24	25	26
metallocene dichloride	**14**	**14**	**15**	**15**
T_p (°C)	0	20	0	20
pentad	(%)	(%)	(%)	(%)
[*mmmm*]	4.8	5.9	1.4	2.7
[*mmmr*]	11.2	10.5	2.3	3.9
[*rmmr*]	8.8	7.1	4.9	5.9
[*mmrr*]	12.2	13.7	11.8	12.2
[*mrmm*] + [*rmrr*]	24.3	23.9	4.7	9.4
[*mrmr*]	13.6	14.4	3.7	5.3
[*rrrr*]	6.3	6.6	49.1	41.9
[*rrrm*]	13.3	11.4	16.0	15.2
mrrm]	5.5	6.5	6.1	3.5
[*r*]	50.1	50.5	81.3	74.1
[*m*]	49.9	49.5	18.7	25.9

[a] Entry numbers correspond to those of Table 3.

errors, the same stereochemical defects produced by isolated enantiofacial misinsertions. Admittedly, the calculated value for $P_{e.m.}$ is a combination of unimolecular chain epimerization and bimolecular enantiofacial misinsertion. Since the calculated value for $P_{e.m.}$ is not significantly altered over the narrow temperature range studied, the relative contributions of these two processes cannot presently be disentangled.

Distal Desymmetrization of a C_{2v}-Symmetric Metallocene Catalyst. In the above catalytic systems that incorporate the Oct or Tet ligands, the distal ligand perturbation has been applied to a parent metallocene of C_s symmetry. An alternative approach is to apply the steric perturbation to a C_{2v}-symmetric metallocene. To this end, C_{2v}-symmetric metallocene **14**[16] was desymmetrized to the C_s-symmetric metallocene **15** by incorporation of one Oct ligand.[26] The polymerization results are reported in Table 3 in entries 23 and 24 (**14**) and in entries 25 and 26 (**15**); the pentad distributions are reported in Table 6. It is immediately apparent that the distal ligand perturbations have a pronounced effect on polymer stereochemistry. Whereas the polymers made from **14** are atactic with [*rrrr*] pentad fractions of approximately 6%, this pentad constitutes well over 40% of the polymers made from **15**. A stereochemical analysis of the pentad distributions[22,27] suggests that the latter polymers are made primarily via syndioselective enantiomorphic site control (Table 7) and not by chain end control, although a competing site epimerization process likely contributes to a nonideal statistical fit.

UV/Visible Spectra of MAO-Activated Dichlorides *vis-à-vis* Propylene Polymerization Activity. The variety of color changes observed during polymerizations with fluorenyl-containing metallocenes prompted a UV/visible spectroscopic analysis of these new Tet and Oct derivatives for comparison. While addition of MAO (500 equiv) to a toluene solution of the "parent" fluorenyl-cyclopentadienyl complex, the "Flu" complex **3** (Scheme 6), results in a small red shift of the absorption band (λ_{max} from 498 to 518 nm; $\Delta E = -775$ cm^{-1}), an exceptionally large red shift is observed following addition of MAO (500 equiv) to a toluene solution of **8** (λ_{max} from 520 to 612 nm; $\Delta E = -2890$ cm^{-1}). The intensity of these bands strongly suggests a ligand to zirconium(IV) charge transfer transition. Quite possibly, the large red shift observed for activated **8** could arise from the sterically demanding Oct ligand, disfavoring associated ion pairs; thus the transition involves a more nearly true cationic zirconium. Dichloride **10**, which contains the Tet ligand, undergoes MAO-induced color transitions which are very similar to those observed with Flu compound **3** (purple polymerization reactions), suggesting that extensive substitution on *both* sides of metallocene **8** is requisite for observing drastic shifts in the LMCT band. Although it is rare for d^0 complexes to emit,[28] several fluorenyl-containing complexes studied gave emission spectra; for example, irradiation of $Ph_2C(Oct)(C_5H_4)ZrCl_2$ (**8**, $\lambda_{max} = 520$) causes emission with a maximum near 590 nm. Although the lifetime of the zirconium species is apparently very short, the fluorescence lifetime for $Ph_2C(Oct)(C_5H_4)HfCl_2$ (**9**, $\lambda_{max} = 492$) was determined (in methylcyclohexane): $\tau = 155$ ns ($\lambda_{EM} = 610$ nm).[29]

To the extent that the red shift is proportional to counterion dissociation, one might expect catalyst activity to correlate with the magnitude of the red shift. This phenomenon has been reported with the indenyl-containing complex *rac*-$C_2H_4(1\text{-}C_9H_6)_2ZrCl_2$ following the addition of varying amounts of MAO.[30] The same correlation between propylene polymerization activity and the observed red shift is also found for the Flu-, Tet-, and Oct-containing metallocene series. Table 8 shows that Oct-containing metallocenes **8** and **9** are the most active (1000 equiv of MAO, units = kg polymer/(mol M·h)), despite being the most sterically crowded.

Conclusions

For the series of syndioselective polymerization catalysts of the type $R_2C(Flu')(C_5H_4)ZrCl_2$/MAO, it was found that the catalyst system with Flu′ = octamethyloctahydrodibenzofluorenyl (Oct) provided polypropylene of significantly higher melting temperature as compared to metallocene dichlorides containing other substituted

(24) The least-squares minimization was performed for four pentads (*rmmr*, *mmrr*, *rmrr*, and *rrrm*) according to % rms error = $(((\sum(I_{obs} - I_{calc})^2)/4)^{0.5}) \times 100$.

(25) (a) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329. (b) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667. (c) Reference 9f, p 596. (d) Yoder, J. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 2548.

(26) A similar desymmetrization has been reported to arrive at the C_s-symmetric 2,7-disubstituted metallocene: $Me_2Si(C_{13}H_8)$(2,7-di-*tert*-butyl-$C_{13}H_6)ZrCl_2$. Patsidis, K.; Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1996**, *509*, 63−71. For a propylene polymerization conducted at 70 °C (1000 equiv of MAO), the resulting polymer contained 32.46% *rr* triads. The unsubstituted analogue **14** provides polymers with *rr* triad contents of 25.1% and 24.5% (Table 8, entries 23 and 24), while the Oct-containing analogue **15** provides polymers with *rr* triad contents of 71.2% and 60.6% (Table 8, entries 25 and 26). These results highlight the importance of substitution at the 3 and 6 positions of fluorenyl for effecting a significant change in polymer stereochemistry.

(27) The least-squares minimization was performed on the nine resolvable pentad intensities according to rms error = $(((\sum(I_{obs} - I_{calc})^2)/9)^{0.5})$.

(28) (a) Heinselman, K. S.; Hopkins, M. D. *J. Am. Chem. Soc.* **1995**, *117*, 12340−12341. (b) Williams, D. S.; Thompson, D. W.; Korolev, A. V. *J. Am. Chem. Soc.* **1996**, *118*, 6526−6527.

(29) Rack, J. R.; Gray, H. B.; Miller, S. A.; Bercaw, J. E. Unpublished results.

(30) (a) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 1451−1457. (b) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 1459−1464. (c) Pieters, P. J. J.; Vanbeek, J. A. M.; Vantol, M. F. H. *Macromol. Rapid Commun.* **1995**, *16*, 463−467. (d) Wieser, U.; Brintzinger, H.-H. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer: Berlin, 2001; pp 3−13. (e) Paczkowski, N.; Gregorius, H.; Kristen, M. O.; Sueling, C.; Suhm, J.; Brintzinger, H.-H.; Wieser, U. PCT Int. Appl., WO 03/06961, 2003.

Table 7. Statistical Fits of Polymers from Entries 25 and 26 for Catalyst 15 to the Chain End Control Model and the Syndioselective Enantiomorphic Site Control Model[a]

	entry 25 (T_p = 0 °C)			entry 26 (T_p = 20 °C)		
pentad	observed (%)	chain end control (%)	site control (%)	observed (%)	chain end control (%)	site control (%)
[*mmmm*]	1.4	0.1	1.5	2.7	0.1	1.8
[*mmmr*]	2.3	0.6	3.1	3.9	1.1	3.7
[*rmmr*]	4.9	1.7	7.8	5.9	2.4	8.0
[*mmrr*]	11.8	3.3	15.6	12.2	4.7	16.1
[*mrmm*] + [*rmrr*]	4.7	19.1	6.1	9.4	21.3	7.4
[*mrmr*]	3.7	3.3	3.1	5.3	4.7	3.7
[*rrrr*]	49.1	51.7	45.8	41.9	43.2	41.3
[*rrrm*]	16.0	18.5	15.6	15.2	20.2	16.1
[*mrrm*]	6.1	1.7	1.5	3.5	2.4	1.8
[*r*]	81.3	84.8	75.3	74.1	81.1	72.9
[*m*]	18.7	15.2	24.7	25.9	18.9	27.1
σ		0.152			0.189	
α			0.855			0.838
rms error		6.03	2.52		5.29	1.87

[a] Entry numbers correspond to those of Table 3.

Table 8. Activity Comparisons for Flu-, Tet-, and Oct-Containing Metallocene Dichloride/MAO Catalyst Systems[a]

	Flu		Tet		Oct	
T_p (°C)	Zr (**3**)	Hf (**4**)	Zr (**10**)	Hf (**11**)	Zr (**8**)	Hf (**9**)
0	1000	70	540	69	1700	280
20	3800	600	6400	960	7800	1700

[a] Activity measured in units of kg polypropylene/(mol metal·h).

fluorenyl ligands, including parent fluorenyl, tetramethyltetrahydrobenzofluorenyl (Tet), and 2,7-di-*tert*-butylfluorenyl. For the Oct-containing zirconocene dichlorides, melting temperatures as high as 153 °C (**8**, R = Ph) or 154 °C (**12**, R = Me) were measured for the thermally quenched polymer. These results underscore the importance of bulky substituents in the 3 and 6 positions of the fluorenyl ligand.

For the hafnocene dichlorides, it is found that $Ph_2C(Tet)(C_5H_4)HfCl_2$/MAO (**11**/MAO) produces syndiotactic polymer with the highest melting temperature (141 °C), surpassing both the fluorenyl and Oct analogues. This results from the unexpected and diminished propensity of the Tet-containing catalyst to perform site epimerizations. That this is contrary to the results obtained from the zirconocenes warrants further investigation, perhaps by molecular modeling studies.

The switch in polymer microstructure on replacement of a fluorenyl of C_{2v}-symmetric catalyst **14** with an Oct ligand is clearly the most compelling evidence of the importance of the distal substituents. While the parent catalyst $C_2H_4(Flu)_2ZrCl_2$/MAO produces essentially atactic polypropylene ([*rrrr*] = 6.3%), the distal substituents of $C_2H_4(Oct)(Flu)ZrCl_2$/MAO (**15**/MAO) yield a moderately syndiotactic polypropylene with an [*rrrr*] pentad content of 49.1%.

Finally, despite the added steric bulk, the activities of Oct-containing metallocenes generally exceed those of less substituted catalyst systems. Evidence that this might be related to diminished ion pairing is found in an exceptionally large red shift of the LMCT band upon exposure of $Ph_2C(Oct)(C_5H_4)ZrCl_2$ (**8**) to MAO (ΔE = −2890 cm^{-1}).

Experimental Section

General Considerations. Unless otherwise noted, all reactions and procedures are carried out under an inert atmosphere of argon or nitrogen using standard glovebox, Schlenk, and high-vacuum line techniques.[31] Solvents are dried according to standard procedures. The following were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%); fluorene (98%); *n*-butyllithium (1.6 M in hexanes); zirconium tetrachloride (99.5%); aluminum chloride (99.99%); 2,5-dimethyl-2,5-hexanediol (99%); benzophenone (99%); and nitromethane (96%). Dicyclopentadiene was obtained from Aldrich and cracked following standard procedures prior to use. Crystalline $LiCH_2Si(CH_3)_3$ (Aldrich, solution in pentane) is obtained by condensing the pentane solution. 1,2-Dibromoethane (Aldrich) was dried over calcium hydride and isolated by vacuum transfer. Hafnium tetrachloride (99%) was obtained from Cerac and used as received.

Instrumentation. NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC−MS were acquired with a Hewlett-Packard 5890 Series II gas chromatograph connected to a Hewlett-Packard 5989A mass spectometer. The GC was equipped with a column of dimensions 7.1 m × 0.1 μm having an HP-1 phase (cross-linked methyl silicone gum). LC-MS were acquired with a Hewlett-Packard 1090 Series II liquid chromatograph with a toluene phase (solvent dried over sodium/benzophenone). The LC was connected to a Hewlett-Packard 59980B particle beam interface, and this was connected to a Hewlett-Packard 5989A mass spectrometer.

Metallocene Dichloride Syntheses. 6,6-Diphenylfulvene. (Synthesis modified from that previously reported.[32]) Sodium methoxide (41.00 g, 759.0 mmol), ethanol (500 mL), and benzophenone (125.00 g, 686.0 mmol) were added to a 1 L vessel. Cyclopentadiene (100.0 mL, 1213 mmol) was poured in, giving a red solution. After stirring for 7 days, the orange precipitate was collected by filtration and rinsed with 50 mL of ethanol. The solid was refluxed in 200 mL of methanol for 1 h. Upon cooling the solid was collected, rinsed with 75 mL of methanol, and dried in vacuo for 48 h to provide the product as an orange powder: 136.18 g (86.2%). MS (GC−MS): *m*/*z* 230.3 (M^+). Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 92.60, 92.59; H, 5.37, 5.19.

2,5-Dichloro-2,5-dimethylhexane. A 2 L argon-purged vessel was charged with 2,5-dimethyl-2,5-hexanediol (200.00 g, 1.368 mol), and concentrated aqueous hydrochloric acid (1.00 L, 12.2 mol HCl) was poured in. The white slurry was shaken and stirred for 17 h. The white solid was collected by suction filtration and rinsed with 500 mL of water. The solid was dissolved in 1.00 L of diethyl ether, the small water layer was removed, and the organic layer was dried over $MgSO_4$. The

(31) Burger, B. J.; Bercaw, J. E. *New Developments in the Synthesis, Manipulation, and Characterization of Organometallic Compounds*; 1987; ACS Symposium Series 357.

(32) Thiele, J. *Chem. Ber.* **1900**, *33*, 666.

solution was forced through a short column of alumina, solvent was removed from the filtrate by rotary distillation, and the white crystalline solid was briefly (30 min) dried in vacuo to provide the product: 237.96 g (95.0%). ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 12H, C*H*$_3$), 1.90 (s, 4H, C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 32.59 (*C*H$_3$), 41.21 (*C*H$_2$), 70.13 (*C*H$_0$). Analysis Calcd for $C_8H_{16}Cl_2$: C, 52.47; H, 8.81. Found: C, 52.65, 52.35; H, 9.74, 9.39.

Octamethyloctahydrodibenzofluorene. A 2 L argon-purged vessel was charged with fluorene (36.00 g, 216.6 mmol) and 2,5-dichloro-2,5-dimethylhexane (80.00 g, 436.9 mmol). The solids were dissolved in 600 mL of nitromethane, and the vessel was equipped with an addition funnel, which was charged with $AlCl_3$ (38.50 g, 289 mmol) dissolved in 100 mL of nitromethane. The solution was added over 10 min, and the purple reaction was stirred for 20 h before it was slowly poured into 700 mL of ice water. The precipitate was collected by filtration and refluxed in 500 mL of ethanol for 2 h. Upon cooling, the solid was collected by filtration, and this was refluxed in 300 mL of hexanes for 2 h. After cooling, the solid was collected by filtration and dried in vacuo, giving the product as a white powder: 62.53 g (74.7%). MS (GC−MS): *m*/*z* 386.5 (M$^+$). ^{1}H NMR ($Cl_2DCCDCl_2$): δ 1.38, 1.43 (s, 24H, C*H*$_3$), 1.77 (apparent s, 8H, C*H*$_2$), 3.82 (s, 2H, C*H*$_2$), 7.49, 7.71 (s, 4H, Flu-*H*). ^{13}C NMR ($Cl_2DCCDCl_2$): δ 32.37, 32.53 (*C*H$_3$), 34.68, 34.71 (*C*H$_0$), 35.50, 35.55 (*C*H$_2$), 36.47 (*C*H$_2$), 117.48, 123.31(*C*H$_1$), 139.20, 140.80, 143.50, 143.66 (*C*H$_0$). Anal. Calculated for $C_{29}H_{38}$: C, 90.09; H, 9.91. Found: C, 89.07, 89.16; H, 8.94, 8.85.

Alternative Preparation of Octamethyloctahydrodibenzofluorene. An argon-purged 2 L vessel was charged with fluorene (45.30 g, 0.2725 mol), 2,5-dichloro-2,5-dimethylhexane (100.00 g, 0.5461 mol), and nitromethane (800 mL). The solids were dissolved by gentle heating. A solution of $AlCl_3$ (44.65 g, 0.335 mol) in 60 mL of nitromethane was syringed in over 6 min. During the addition, much HCl evolved through an oil bubbler and precipitate was rapidly formed. After stirring for 18 h, the steel blue reaction was filtered and the solid collected on filter paper. Water (300 mL) was slowly added to the filtrate, and the formed precipitate was collected by suction filtration. The combined precipitates were added slowly to 400 mL of water. Hexanes (200 mL) were added to this, and the slurry was stirred overnight to quench the aluminum chloride. The water layer was removed and the solvent removed from the remaining slurry by rotary evaporation. The solid was extracted over a period of 3 days with 300 mL of diethyl ether from a cellulose extraction thimble. Diethyl ether was removed by rotary evaporation and the remaining solid boiled in 100 mL of hexanes, cooled, filtered, and washed with 50 mL of hexanes. In vacuo drying afforded 87.75 g of octamethyloctahydrodibenzofluorene as a white powder (83.3%). MS (GC−MS): *m*/*z* 386.5 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 1.32, 1.38 (s, 24H, C*H*$_3$), 1.72 (apparent s, 8H, C*H*$_2$), 3.77 (s, 2H, C*H*$_2$), 7.43, 7.66 (s, 4H, Flu-*H*).

$Ph_2C(C_5H_4)(C_{29}H_{36})H_2$. A 300 mL flask was charged with octamethyloctahydrodibenzofluorene (12.00 g, 31.04 mmol), equipped with a 180° needle valve, evacuated, and charged with diethyl ether (120 mL) by vacuum transfer. At 0 °C, *n*-butyllithium (21.0 mL, 33.6 mmol, 1.6 M in hexanes) was syringed in over 3 min, giving much yellow precipitate. After 21 h, the solvent was removed and 6,6-diphenylfulvene (7.148 g, 31.04 mmol) was added. Diethyl ether (150 mL) was condensed in and the reaction stirred at room temperature for 5 days before 60 mL of aqueous NH_4Cl was added slowly at 0 °C. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (4 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the crude product in quantitative yield (19.15 g). The material can be recrystallized from ethanol. MS (GC−MS): *m*/*z* 616.8 (M$^+$). Major isomer (76%): ^{1}H NMR ($Cl_2DCCDCl_2$, 100 °C): δ 1.02, 1.22, 1.33, 1.36 (s, 24H, C*H*$_3$), 1.71 (m, 8H, C*H*$_2$), 3.00 (s, 2H, Cp-C*H*$_2$), 5.54 (s, 1H, 9-Oct-*H*), 6.24, 6.24, 6.28 (m, 3H, Cp-C*H*$_1$), 7.11−7.18 (m, 10H, phenyl-*H*), 7.35, 7.35 (s, 4H, Oct-*H*). ^{13}C NMR ($Cl_2DCCDCl_2$, 100 °C): δ 32.00, 32.03, 32.12, 32.39 (*C*H$_3$), 34.37, 34.50 (*C*H$_0$), 35.74, 35.85 (*C*H$_2$), 40.85 (Cp-*C*H$_2$), 53.16 (9-Oct-*C*H$_1$), 60.08 (*C*(Oct)-(Cp)(Ph)$_2$), 116.14, 125.40, 125.82 (Cp-*C*H$_1$), 127.04, 130.18 (Oct-*C*H$_1$), 126.76, 128.84, 130.31, 131.08, 135.93 (phenyl-*C*H$_1$), 140.04, 142.34, 142.38, 143.59 (Oct-*C*H$_0$), other *C*H$_0$ not determined. Minor isomer (24%): ^{1}H NMR ($Cl_2DCCDCl_2$, 100 °C): δ 1.08, 1.25, 1.33, 1.36 (s, 24H, C*H*$_3$), 1.72 (m, 8H, C*H*$_2$), 2.94 (s, 2H, Cp-C*H*$_2$), 5.49 (s, 1H, 9-Oct-*H*), 6.36, 6.49, 6.58 (m, 3H, Cp-C*H*$_1$), 7.11−7.18 (m, 10H, phenyl-*H*), 7.29, 7.29 (s, 4H, Oct-*H*). Anal. Calcd for $C_{47}H_{52}$: C, 91.50; H, 8.50. Found: C, 90.36, 90.47; H, 7.72, 7.76.

$Ph_2C(C_5H_4)(C_{29}H_{36})ZrCl_2$ (8). A 250 mL flask was charged with $Ph_2C(C_5H_4)(C_{29}H_{36})H_2$ (10.00 g, 16.21 mmol) and $LiCH_2Si(CH_3)_3$ (3.053 g, 32.42 mmol) and equipped with a 180° needle valve. Diethyl ether (75 mL) was condensed in at −78 °C and the cold bath removed. Upon warming, 25 mL of tetrahydrofuran was condensed in. After 45 h, solvent was removed and $ZrCl_4$ (3.78 g, 16.2 mmol) was added. Petroleum ether (75 mL) was condensed in at −78 °C, and the cold bath was removed. After 47 h, solvent was removed and the pink material was extracted in a cellulose extraction thimble with 200 mL of diethyl ether for 2 days. The volume was reduced to 100 mL, and the precipitate was collected and dried in vacuo: 5.03 g (39.9%). Two additional crops were obtained for a total mass of 5.519 g (43.8%). MS (LC-MS): *m*/*z* 776.8 (M$^+$). ^{1}H NMR (C_6D_6): δ 1.01, 1.07, 1.35, 1.51 (s, 24H, Oct-C*H*$_3$), 1.61 (m, 8H, Oct-C*H*$_2$), 5.68, 6.21 (s, 4H, Cp-*H*), 6.42, 8.42 (s, 4H, Oct-*H*), 6.97, 7.08, 7.12 (t, $^3J_{HH}$ = 7.0, 7.3, 8.1 Hz, 6H, phenyl-*H*), 7.70, 7.74 (d, $^3J_{HH}$ = 7.7, 7.7 Hz, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 30.97, 31.75, 32.42, 33.50 (*C*H$_3$), 34.56, 34.80, 34.83, 35.05 (*C*H$_0$ and *C*H$_2$), 57.92 (Ph*C*Ph), 74.25, 108.78, 119.78, 121.09, 144.90, 146.12, 146.81 (Cp-, phenyl-, and Oct-*C*H$_0$), 102.05, 117.83 (Cp-*C*H$_1$), 121.61, 122.18, 126.71, 127.17, 129.01, 129.10, 129.46 (phenyl- and Oct-*C*H$_1$). Anal. Calcd for $C_{47}H_{50}Zr_1Cl_2$: C, 72.65; H, 6.49. Found: C, 69.93; H, 6.10.

$Ph_2C(C_5H_4)(C_{29}H_{36})HfCl_2$ (9). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{29}H_{36})H_2$ (3.500 g, 5.637 mmol) and $LiCH_2Si(CH_3)_3$ (1.100 g, 11.68 mmol) and equipped with a 180° needle valve. Diethyl ether (50 mL) was condensed in at −78 °C and the cold bath removed. Upon warming, 5 mL of tetrahydrofuran was condensed in. After 45 h, solvent was removed and $HfCl_4$ (2.00 g, 6.244 mmol) was added. Petroleum ether (50 mL) was condensed in at −78 °C, and the cold bath was removed. After 43 h, solvent was removed and the yellow material was extracted in a cellulose extraction thimble with 150 mL of diethyl ether overnight. The volume was reduced to 50 mL, and the precipitate was collected and dried in vacuo: 0.975 g (19.9%). MS (LC-MS): *m*/*z* 864.5 (M$^+$). ^{1}H NMR (C_6D_6): δ 1.02, 1.08, 1.35, 1.51 (s, 24H, Oct-C*H*$_3$), 1.61 (m, 8H, Oct-C*H*$_2$), 5.65, 6.16 (t, $^3J_{HH}$ = 2.6, 2.7, 4H, Cp-*H*), 6.47, 8.40 (s, 4H, Oct-*H*), 6.98, 7.08, 7.13 (t, $^3J_{HH}$ = 7.4, 7.6, 9.0 Hz, 6H, phenyl-*H*), 7.70, 7.77 (d, $^3J_{HH}$ = 7.8, 7.9 Hz, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 31.13, 31.81, 32.47, 33.64 (*C*H$_3$), 34.59, 34.78, 34.78, 35.07 (*C*H$_0$ and *C*H$_2$), 57.73 (Ph*C*Ph), 74.03, 111.64, 118.78, 119.55, 145.18, 145.55, 146.54 (Cp-, phenyl-, and Oct-*C*H$_0$), 99.66, 116.96 (Cp-*C*H$_1$), 121.23, 121.93, 126.72, 127.15, 128.97, 129.10, 129.49 (phenyl- and Oct-*C*H$_1$). Anal. Calcd for $C_{47}H_{50}Hf_1Cl_2$: C, 65.31; H, 5.83. Found: C, 63.53; H, 5.33.

Tetrahydrotetramethylbenzofluorene. A 2 L argon-purged vessel was charged with fluorene (200.0 g, 1203 mmol), 2,5-dichloro-2,5-dimethylhexane (25.00 g, 136.5 mmol), and 1000 mL of nitromethane. The solids were dissolved by heating to 60 °C, and when the vessel had cooled to 50 °C, a solution of $AlCl_3$ (25.00 g, 187.5 mmol) in nitromethane (40 mL) was syringed in over 2 min, giving a dark green homogeneous solution. After 15 min, 60 mL of water was syringed in very slowly, followed by addition of 100 mL of water. The formed precipitate (>99% fluorene by GC) was removed by filtration.

The filtrate (77.5:22.5 ratio of FluH:TetH) was extracted with hexane (7 × 100 mL). Solvent was removed by rotavap from the combined hexane extracts, giving 64.7 g of FluH and TetH. This material was subjected to Kugelrohr distillation under high vacuum. Several fractions were removed at 100 °C until 22.54 g of material remained. This material was dissolved in 300 mL of boiling ethanol, hot filtered, and slowly cooled. The pure product was obtained by collection of the precipitate and in vacuo drying: 16.06 g (42.5%). Essentially pure fluorene was recovered from several of the removed fractions and by Kugelrohr distillation of the original filtrate: 133.7 g, 75.4% of the theoretically recoverable amount of 177.3 g. MS (GC−MS): *m/z* 276.3 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.38, 1.42 (s, 12H, C*H*$_3$), 1.78 (apparent s, 4H, C*H*$_2$), 3.88 (s, 2H, C*H*$_2$), 7.29 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Flu-*H*), 7.38 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Flu-*H*), 7.53 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Flu-*H*), 7.54 (s, 1H, Flu-*H*), 7.78 (s, 1H, Flu-*H*), 7.80 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Flu-*H*). ^{13}C NMR ($CDCl_3$): δ 32.27, 32.40 (*C*H$_3$), 34.66, 34.73 (*C*H$_0$), 35.40, 35.40 (*C*H$_2$), 36.69 (*C*H$_2$), 117.67, 119.65, 123.05, 125.03, 126.33, 126.65 (*C*H$_1$), 139.47, 140.65, 141.98, 143.54, 143.68, 143.90 (*C*H$_0$). Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.51, 90.17; H, 7.99, 7.65.

$Ph_2C(C_5H_4)(C_{21}H_{22})Li_2$. A 200 mL flask was charged with tetramethyltetrahydrobenzofluorene (4.500 g, 16.28 mmol), equipped with a 180° needle valve, evacuated, and charged with 100 mL of diethyl ether by vacuum transfer. At room temperature, an *n*-butyllithium (11.0 mL, 17.6 mmol, 1.6 M in hexanes) solution was syringed in over 3 min. After 23 h of stirring, solvent was removed and 6,6-diphenylfulvene (3.749 g, 16.28 mmol) was added. Diethyl ether (100 mL) was condensed in, and the homogeneous reaction slowly formed a white precipitate. After stirring for 23 days, 60 mL of water was slowly added. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the volume was reduced to 100 mL. After 48 h at −78 °C, the liquid was decanted from the formed precipitate, which was collected and dried in vacuo (7.05 g, 13.9 mmol, 85.5%). The flask was attached to a swivel frit, and 100 mL of diethyl ether was condensed in before an *n*-butyllithium solution (19.0 mL, 30.4 mmol, 1.6 M in hexanes) was syringed into the white slurry over 3 min at room temperature. The reaction was stirred for 22 h before the orange solid was collected by filtration and dried in vacuo: 7.21 g (quantitative yield).

$Ph_2C(C_5H_4)(C_{21}H_{22})ZrCl_2$ (10). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{21}H_{22})Li_2$ (3.895 g, 7.51 mmol) and $ZrCl_4$ (1.750 g, 7.51 mmol) and equipped with a 180° needle valve. Petroleum ether (60 mL) was condensed in at −78 °C, and the cold bath was removed. The reaction was allowed to warm slowly, and after 18 h the solvent was removed. The solid was placed in a cellulose extraction thimble and extracted with 150 mL of methylene chloride overnight. The filtrate was switched onto a swivel frit, and solvent was removed. Toluene (200 mL) was condensed in and the solution filtered. The filtrate was reduced in volume to 40 mL, and the pink precipitate was collected and dried in vacuo: 2.149 g (42.9%). MS (LC-MS): *m/z* 666.6 (M^+). ^{1}H NMR (CD_2Cl_2): δ 0.83, 0.94, 1.40, 1.46 (s, 12H, C*H*$_3$), 1.61, 1.68 (m, 4H, C*H*$_2$), 5.66, 5.71 (q, $^3J_{HH}$ = 2.6, 2.9 Hz, 2H, Cp-*H*), 6.31, 6.31 (t, $^3J_{HH}$ = 2.6, 2.6 Hz, 2H, Cp-*H*), 6.24, 8.15 (s, 2H, Tet-*H*), 6.39, 8.16 (d, $^3J_{HH}$ = 8.8, 8.8 Hz, 1H, Tet-*H*), 6.96, 7.23 (t, $^3J_{HH}$ = 7.7, 7.3 Hz, 2H, Tet-*H*), 7.33, 7.49 (m, 6H, phenyl-*H*). 7.86, 7.88, 7.93, 7.96 (d, $^3J_{HH}$ = 8.8, 7.7, 6.6, 6.6, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 30.95, 31.75, 32.41, 33.53 (*C*H$_3$), 34.53, 34.53, 34.86, 34.95 (*C*H$_0$ and *C*H$_2$), 102.90, 103.13, 117.88, 118.67 (Cp-*C*H$_1$), 121.58, 122.17, 123.98, 124.63, 125.01, 126.60, 126.77, 127.22, 127.29, 127.93, 128.18, 129.07, 129.10, 129.18, 129.21, 129.49 (Tet-*C*H$_1$ and phenyl-*C*H$_1$), 144.76, 145.02, 146.62, 147.35 (Tet-*C*H$_0$ and phenyl-*C*H$_0$), remaining *C*H$_0$ not determined. Anal. Calcd for $C_{39}H_{36}Zr_1Cl_2$: C, 70.25; H, 5.44. Found: C, 71.46; H, 5.55.

$Ph_2C(C_5H_4)(C_{21}H_{22})HfCl_2$ (11). A swivel frit was charged with $Ph_2C(C_5H_4)(C_{21}H_{22})Li_2$ (1.40 g, 2.70 mmol) and $HfCl_4$ (1.000 g, 3.12 mmol). Petroleum ether (60 mL) was condensed in at −78 °C, and the cold bath was removed. The reaction was allowed to warm slowly, and after 40 h, the solvent was removed. Diethyl ether (100 mL) was added by vacuum transfer, and the solution was filtered. The filtrate was condensed to 25 mL, and the product precipitated very slowly. The yellow solid was collected and dried in vacuo: 0.518 g (25.4%). MS (LC-MS): *m/z* 754.7 (M^+). ^{1}H NMR (CD_2Cl_2): δ 0.84, 0.95, 1.39, 1.45 (s, 12H, C*H*$_3$), 1.61, 1.68 (m, 4H, C*H*$_2$), 5.61, 5.67 (q, $^3J_{HH}$ = 2.6, 2.6 Hz, 2H, Cp-*H*), 6.25, 6.25 (t, $^3J_{HH}$ = 2.9, 2.9 Hz, 2H, Cp-*H*), 6.28, 8.12 (s, 2H, Tet-*H*), 6.43, 8.13 (d, $^3J_{HH}$ = 8.8, 8.0 Hz, 2H, Tet-*H*), 6.93, 7.32 (t, $^3J_{HH}$ = 8.8, 6.0 Hz, 2H, Tet-*H*), 7.33, 7.47 (m, 6H, phenyl-*H*), 7.85, 7.87, 7.95, 7.96 (d, $^3J_{HH}$ = 7.7, 8.8, 6.6, 7.0 Hz, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 31.07, 31.80, 32.43, 33.62 (*C*H$_3$), 34.56, 34.78, 34.81, 34.96 (*C*H$_0$ and *C*H$_2$), 100.48, 100.70, 116.91, 117.72 (Cp-*C*H$_1$), 118.71, 119.83, 120.52, 121.41 (Tet-*C*H$_0$), 121.25, 121.92, 123.70, 124.49, 124.56, 126.60, 126.78, 127.18, 127.25, 127.68, 128.99, 128.99, 129.07, 129.16, 129.22, 129.51 (Tet-*C*H$_1$ and phenyl-*C*H$_1$), 145.03, 145.28, 146.09, 147.06 (Tet-*C*H$_0$ and phenyl-*C*H$_0$), remaining *C*H$_0$ not determined. Anal. Calcd for $C_{39}H_{36}Hf_1Cl_2$: C, 62.12; H, 4.81. Found: C, 61.11; H, 5.02.

6,6-Dimethylfulvene (Synthesis modified from ref 33). A 2 L vessel was charged with methanol (875 mL), cyclopentadiene (101.0 g, 1528 mmol), and acetone (230 mL). Pyrrolidine (13.5 mL, 112 mmol) was syringed in over 10 min. The reaction was stirred for 18 h before an aqueous acetic acid solution (50 mL of acetic acid/200 mL of water) was added over 2 min. Diethyl ether (500 mL) and water (1000 mL) were added, and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (3 × 100 mL), and the combined organic layers were extracted with water (5 × 150 mL). The ether layer was dried over $MgSO_4$, filtered, and rotavapped at 40 °C for 2 h. This provided ether-free fulvene (156.81 g, 96.7%). This material was further cleaned by pushing the neat liquid through a short column of alumina: 111.2 g (68.5%).

$Me_2C(C_5H_4)(C_{29}H_{36})H_2$. Octamethyloctahydrodibenzofluorene (9.625 g, 24.89 mmol) was massed into a 250 mL round-bottom Schlenk flask. This was evacuated, backfilled with argon, and charged with 100 mL of tetrahydrofuran via syringe. A solution of *n*-butyllithium in hexanes (16.0 mL, 1.6 M, 25.6 mmol) was syringed in over 10 min, giving initially a red solution, which later formed some red precipitate. After 100 min, 6,6-dimethylfulvene (3.0 mL, 2.64 g, 24.9 mmol) was syringed in, yielding a homogeneous solution. After 22 h, 60 mL of aqueous NH_4Cl was slowly syringed in and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 × 25 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give the product as a yellow crystalline solid, 12.27 g in theoretical yield.

$Me_2C(C_5H_4)(C_{29}H_{36})Li_2$. A 250 mL round-bottom flask was charged with $Me_2C(C_5H_4)(C_{29}H_{36})H_2$ (12.27 g, 24.89 mmol) and attached to a swivel frit before 75 mL of diethyl ether was condensed in. A solution of *n*-butyllithium in hexanes (32.0 mL, 1.6 M, 51.2 mmol) was syringed in over 3 min at 0 °C. After stirring for 17 h at room temperature, solvent was removed and 75 mL of benzene was condensed in. The solution was frozen and lyophilized to give 11.80 g of the dilithio salt as an orange powder (93.9%).

$Me_2C(C_5H_4)(C_{29}H_{36})ZrCl_2$ (12). In the glovebox, a swivel frit apparatus was charged with $Me_2C(C_5H_4)(C_{29}H_{36})Li_2$ (3.246 g, 6.436 mmol) and zirconium tetrachloride (1.500 g, 6.437 mmol). Petroleum ether (50 mL) was condensed in and the reaction stirred at room temperature for 51 h before solvent removal. Dichloromethane (20 mL) was condensed in, stirred, and removed. Then, 30 mL of diethyl ether was condensed in,

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stirred, and removed. In the glovebox, the solid was transferred to a cellulose extraction thimble, and this was extracted overnight with 100 mL of diethyl ether. The obtained slurry was transferred back to the swivel frit and the volume reduced to 30 mL. The orange precipitate (**12**) was collected on the frit and dried in vacuo: 1.649 g (39.2%). MS (LC-MS): *m/z* 653.7 (M^+). ^1H NMR (CD_2Cl_2): δ 1.23, 1.38, 1.39, 1.49 (s, 24H, Oct-C*H*$_3$), 1.73 (m, 8H, Oct-C*H*$_2$), 2.32 (s, 6H, (C*H*$_3$)$_2$C-Oct-Cp), 5.57, 6.20 (t, $^3J_{HH}$ = 2.6, 2.2 Hz, 4H, Cp-*H*), 7.63, 8.04 (s, 4H, Oct-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.60, 31.88, 32.22, 32.37, 33.50 (*C*H$_3$), 34.78, 34.86, 35.03, 35.11 (*C*H$_0$ and *C*H$_2$), 40.06 (Me*C*-Me), 75.23, 112.89, 121.05, 121.50, 145.68, 147.68 (Cp- and Oct-*C*H$_0$), 100.45, 118.44 (Cp-*C*H$_1$), 120.63, 122.06 (Oct-*C*H$_1$). Anal. Calcd for $C_{37}H_{46}Zr_1Cl_2$: C, 68.07; H, 7.10. Found: C, 60.14; H, 6.45.

Preparation of 3 and 4. The syntheses of **3** and **4** were accomplished as follows by slight modification of the literature procedure.[5a]

$Ph_2C(C_5H_4)(C_{13}H_8)H_2$. A 500 mL flask was charged with fluorene (28.87 g, 173.7 mmol), equipped with a 180° needle valve, evacuated, and backfilled with argon before 180 mL of diethyl ether was syringed in. *n*-Butyllithium (110.0 mL, 176 mmol, 1.6 M in hexanes) was syringed in over 8 min at 0 °C. After 15 h, all solvent was removed, 6,6-diphenylfulvene (40.00 g, 173.7 mmol) was added, and 200 mL of diethyl ether was condensed in. After stirring for 6 days, the vessel was cooled to 0 °C and 120 mL of water was very slowly added, followed by 60 mL of aqueous NH_4Cl solution. The slurry was suction filtered, and the crude product was boiled in 400 mL of ethanol for 2 h. This was filtered hot, and the collected solid was dried in vacuo (53.39 g, 77.5%). Three crops were obtained with a total mass of 64.72 g (94.0%). MS (GC−MS): *m/z* 396.4 (M^+). Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 92.30, 92.33; H, 5.27, 5.47.

$Ph_2C(C_5H_4)(C_{13}H_8)Li_2$. A 500 mL flask was charged with $Ph_2C(C_5H_4)(C_{13}H_8)H_2$ (21.00 g, 52.96 mmol) and attached to a swivel frit. Diethyl ether (200 mL) was condensed in before an *n*-butyllithium solution (70.0 mL, 112 mmol, 1.6 M in hexanes) was syringed into the white slurry over 12 min at room temperature. After 18 h, the orange slurry was heated at 40 °C for 5 h, when the orange solid was collected on the frit and dried in vacuo. The product as a diethyl ether adduct (27.71 g) was obtained (theoretical: 21.63 g for ether-free product; 25.55 g for mono diethyl ether adduct; 29.48 g for bis diethyl ether adduct).

$Ph_2C(C_5H_4)(C_{13}H_8)ZrCl_2$ (3). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{13}H_8)Li_2$ (4.381 g, 10.73 mmol) and $ZrCl_4$ (2.500 g, 10.73 mmol) and equipped with a 180° needle valve. Petroleum ether (60 mL) was condensed in at −78 °C and the cold bath removed. After 24 h, solvent was removed from the pink slurry, and the solid was extracted in a cellulose thimble with 150 mL of methylene chloride overnight. The volume of the filtrate was reduced to 50 mL, and the precipitate was collected and dried in vacuo: 1.32 g (22.1%). MS (LC-MS): *m/z* 556.6 (M^+). ^1H NMR (CD_2Cl_2): δ 5.79, 6.36 (t, $^3J_{HH}$ = 3.0, 2.6 Hz, 4H, Cp-*H*), 6.42, 8.19 (d, $^3J_{HH}$ = 8.8, 8.4 Hz, 4H, Flu-*H*), 6.99, 7.31, 7.35 (t, $^3J_{HH}$ = 7.0, 7.3, 7.7 Hz, 6H, phenyl-*H*), 7.45, 7.56 (t, $^3J_{HH}$ = 7.4, 8.1 Hz, 4H, Flu-*H*), 7.86, 7.94 (d, $^3J_{HH}$ = 7.7, 7.7 Hz, 4H, phenyl-*H*). Anal. Calcd for $C_{31}H_{22}Zr_1Cl_2$: C, 66.89; H, 3.98. Found: C, 61.12; H, 3.65.

$Ph_2C(C_5H_4)(C_{13}H_8)HfCl_2$ (4). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{13}H_8)Li_2$ (2.55 g, 6.24 mmol) and $HfCl_4$ (2.000 g, 6.24 mmol) and equipped with a 180° needle valve. Petroleum ether (60 mL) was condensed in at −78 °C and the cold bath removed. After 21 h, solvent was removed from the yellow slurry, and the solid was extracted in a cellulose thimble with 150 mL of methylene chloride for 2 days. The filtrate was switched onto a swivel frit and gravity filtered. The volume of the filtrate was reduced to 40 mL, and the precipitate was collected and dried in vacuo: 1.15 g (28.5%). MS (LC-MS): *m/z* 644.7 (M^+). ^1H NMR (CD_2Cl_2): δ 5.75, 6.30 (t, $^3J_{HH}$ = 3.0, 2.6 Hz, 4H, Cp-*H*), 6.46, 8.16 (d, $^3J_{HH}$ = 8.8, 8.4 Hz, 4H, Flu-*H*), 6.97, 7.31, 7.35 (t, $^3J_{HH}$ = 7.0, 7.4, 7.4 Hz, 6H, phenyl-*H*), 7.45, 7.52 (t, $^3J_{HH}$ = 7.7, 7.4 Hz, 4H, Flu-*H*), 7.86, 7.94 (d, $^3J_{HH}$ = 7.4, 8.1 Hz, 4H, phenyl-*H*). Anal. Calcd for $C_{31}H_{22}Hf_1Cl_2$: C, 57.82; H, 3.44. Found: C, 53.97; H, 3.23.

$Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)H_2. A 250 mL flask was charged with 2,7-di-*tert*-butylfluorene[34] (10.00 g, 35.91 mmol) and equipped with a 180° needle valve. The flask was evacuated, and 125 mL of diethyl ether was condensed in before an *n*-butyllithium solution (23.0 mL, 36.8 mmol, 1.6 M in hexanes) was syringed in over 3 min at room temperature. After 3.5 h, solvent was removed and 6,6-diphenylfulvene (8.271 g, 35.91 mmol) was added. Diethyl ether (100 mL) was condensed in, and the reaction was stirred for 26 days. Water (60 mL) was slowly added, and the white precipitate that slowly formed was collected by suction filtration. A white powder (13.11 g, 71.8%) was isolated after drying in vacuo at 80 °C for several hours. MS (GC−MS): *m/z* 508.6 (M^+). Anal. Calcd for $C_{39}H_{40}$: C, 92.08; H, 7.92. Found: C, 89.42; H, 7.07.

$Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)Li_2. A swivel frit was charged with $Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)H_2 (12.00 g, 23.59 mmol), and 150 mL of diethyl ether was added by vacuum transfer. *n*-Butyllithium solution (32.0 mL, 51.2 mmol, 1.6 M in hexanes) was added over 8 min at room temperature. After 19 h, the orange precipitate was collected by filtration and dried in vacuo: 12.28 g, (quantitative yield).

$Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)$ZrCl_2$ (13). A 100 mL flask was charged with $Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)Li_2 (3.351 g, 6.437 mmol) and $ZrCl_4$ (1.500 g, 6.437 mmol). Petroleum ether (60 mL) was condensed in at −78 °C, and the cold bath was removed. The reaction was allowed to warm slowly, and after 23 h the solvent was removed. The solid was placed in a cellulose extraction thimble and extracted with 150 mL of methylene chloride overnight. The filtrate was switched onto a swivel frit, filtered, and condensed to 10 mL. The orange precipitate was collected and dried in vacuo: 1.271 g (29.5%). MS (LC-MS): *m/z* 668.5 (M^+). ^1H NMR (CD_2Cl_2): δ 1.04 (s, 18H, C(C*H*$_3$)$_3$), 5.69, 6.34 (t, $^3J_{HH}$ = 2.6, 3.7 Hz, 4H, Cp-*H*), 6.34, (s, 2H, Flu-*H*), 7.62, 8.05 (d, $^3J_{HH}$ = 8.8, 8.8 Hz, 4H, Flu-*H*), 7.89, 7.98 (d, $^3J_{HH}$ = 8.1, 8.1 Hz, 4H, phenyl-*H*), 7.31, 7.38, 7.48 (t, $^3J_{HH}$ = 7.3, 7.3, 7.7 Hz, 6H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 30.36 (C(*C*H$_3$)$_3$), 34.98 (*C*(CH$_3$)$_3$), 58.28 (*C*(Cp)(Flu)(Ph)$_2$), 77.82, 110.21, 120.82, 121.63, 144.86, 150.76 (Flu-*C*H$_0$, phenyl-*C*H$_0$, and Cp-*C*H$_0$), 102.86, 118.39, 119.94, 123.95, 124.66, 126.65, 127.26, 129.07, 129.14, 129.47 (Flu-*C*H$_1$ and phenyl-*C*H$_1$). Anal. Calcd for $C_{39}H_{38}Zr_1Cl_2$: C, 70.03; H, 5.73. Found: C, 67.36; H, 5.13.

Preparation of 14. Metallocene **14** was synthesized as reported in the literature.[16] MS (LC-MS): *m/z* 518.5 (M^+). Anal. Calcd for $C_{28}H_{20}Zr_1Cl_2$: C, 64.85; H, 3.89. Found: C, 62.92; H, 3.62.

2-(9-Fluorenyl)bromoethane. A 500 mL Schlenk flask was charged with fluorene (50.00 g, 300.8 mmol), evacuated, backfilled with argon, and charged with 180 mL of tetrahydrofuran via syringe. At 0 °C, an *n*-butyllithium solution (200.0 mL, 320 mmol, 1.6 M in hexanes) was syringed in over 20 min. After 1 h this fluorenyllithium solution was cannulated over 60 min into a 1 L flask containing 1,2-dibromoethane (180 mL, 2090 mmol) and 180 mL of petroleum ether. After stirring for 29 h, all volatiles were removed by vacuum transfer. Then, 300 mL of water and 400 mL of methylene chloride were added. The organic layer was isolated, and the aqueous layer was extracted with methylene chloride (3 × 50 mL). The organic layers were dried over $MgSO_4$, filtered, and rotavapped. The resulting orange oil was stirred in 100 mL of boiling hexanes; this was cooled and filtered. Solvent was removed from the filtrate, and the resulting oil was subjected to Kugelrohr distillation under high vacuum at 80 °C to remove

(34) Kajigaeshi, S.; Kadowaki, T.; Nishida, A.; Fujisaki, S.; Noguchi, M. *Synthesis* **1984**, 335−337.

1 mL of material. The second crop, collected at 110 °C, was dissolved in 100 mL of hexanes; the solution was pushed through a column of alumina, rotavapped, and dried in vacuo to provide 50.55 g (61.5%) of the product as an oil, which crystallized upon standing. MS (GC−MS): *m/z* 272.2 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.49, 3.29 (m, 4H, C*H*$_2$), 4.16 (m, 1H, 9-Flu-*H*), 7.32, 7.38, 7.51, 7.75 (m, 8H, Flu-*H*). Anal. Calcd for $C_{15}H_{13}Br_1$: C, 65.95; H, 4.80. Found: C, 67.35; H, 4.46.

1,2-Ethano($C_{29}H_{36}$)($C_{13}H_8$)H_2. A 250 mL flask was charged with octamethyloctahydrodibenzofluorene (10.00 g, 25.87 mmol), equipped with a 180° needle valve, and evacuated before 80 mL of diethyl ether was condensed in. *n*-Butyllithium (17.0 mL, 27.2 mmol, 1.6 M in hexanes) was syringed in over 3 min, providing a yellow slurry. After 2 h, solvent was removed and 2-(9-fluorenyl)bromoethane (7.066 g, 25.87 mmol) was added in the glovebox. Diethyl ether (80 mL) was condensed in, and the reaction was stirred for 24 days before cooling to 0 °C and addition of 100 mL of water and 150 mL of diethyl ether. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The organic layers were dried over $MgSO_4$, filtered, and condensed to 50 mL. Cooling to −78 °C provided six crops of product, which were further dried in vacuo: 13.36 g (89.2%). MS (GC−MS): *m/z* 578.7 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.30, 1.37, 1.38, 1.42 (s, 24H, C*H*$_3$), 1.74 (apparent s, 8H, Oct-C*H*$_2$), 1.64, 1.72 (m, 4H, C*H*$_2$), 3.71, 3.85 (m, 2H, 9-Flu-*H* and 9-Oct-*H*), 7.20, 7.62 (s, 4H, Oct-*H*), 7.31, 7.38 (t, $^3J_{HH}$ = 7.3, 6.8 Hz, 4H, Flu-*H*), 7.77, 7.77 (d, $^3J_{HH}$ = 7.3, 7.3 Hz, 4H, Flu-*H*). Anal. Calcd for $C_{44}H_{50}$: C, 91.29; H, 8.71. Found: C, 91.01; H, 8.38.

1,2-Ethano($C_{29}H_{36}$)($C_{13}H_8$)$ZrCl_2$ (15). A 100 mL flask was charged with 1,2-ethano($C_{29}H_{36}$)($C_{13}H_8$)H_2 (3.000 g, 5.182 mmol), evacuated, and charged with 50 mL of diethyl ether. *n*-Butyllithium (7.0 mL, 11.2 mmol, 1.6 M in hexanes) was syringed in over 3 min. After 43 h, solvent was removed from the yellow slurry and $ZrCl_4$ (1.300 g, 5.58 mmol) was added. Petroleum ether was condensed in at −78 °C, and the reaction was allowed to warm slowly. After 29 h, solvent was removed, 50 mL of diethyl ether was condensed in, and this was stirred an additional 40 h. Solvent was removed and the pink-red solid was extracted from a cellulose extraction thimble overnight with 150 mL of diethyl ether. The volume of the filtrate was reduced to 30 mL, and the precipitate was collected on a frit and dried in vacuo: 0.779 g (20.3%). MS (LC-MS): *m/z* 738.7 (M^+). ^{1}H NMR (C_6D_6): δ 1.20, 1.36, 1.37, 1.39 (s, 24H, Oct-C*H*$_3$), 1.60 (m, 8H, Oct-C*H*$_2$), 3.93 (m, 4H, ethano-*H*), 6.98, 7.09 (t, $^3J_{HH}$ = 8.4, 8.4 Hz, 4H, Flu-*H*), 7.50, 7.54 (d, $^3J_{HH}$ = 9.2, 8.4 Hz, 4H, Flu-*H*), 7.52, 7.89 (s, 4H, Oct-*H*). ^{13}C NMR (CD_2Cl_2): δ 29.68, 30.00 (*C*H$_2$-*C*H$_2$), 31.61, 32.35, 32.57, 33.87 (*C*H$_3$), 34.87, 34.97, 35.00, 35.07 (*C*H$_0$ and *C*H$_2$), 102.10, 105.40, 120.88, 121.28, 126.55, 127.35, 145.74, 146.91 (Flu- and Oct-*C*H$_0$), 119.59, 121.97, 122.49, 124.39, 124.49, 127.84 (Flu- and Oct-*C*H$_1$). Anal. Calcd for $C_{44}H_{48}Zr_1Cl_2$: C, 71.51; H, 6.55. Found: C, 69.50; H, 6.07.

Propylene Polymerization Procedures. CAUTION: All Polymerization Procedures Should Be Performed Behind a Blast Shield. All polymerization reactions were prepared in nitrogen-filled gloveboxes. Methylaluminoxane (MAO) was purchased as a toluene solution from Albemarle Corporation and used as the dry powder obtained by in vacuo removal of all volatiles. Toluene was dried over sodium and distilled. Propylene from Scott Specialty Gases (>99.5%) was used following drying through a Matheson 6410 drying system equipped with an OXYSORB column. Polymerizations were conducted in a 3 oz. Lab Crest glass reaction vessel and were stirred with a magnetic stir bar. Monomer was condensed into the vessel over several min at 0 °C. The vessel was then equilibrated at either 0 or at 20 °C with an ice or water bath for 10 min. A given reaction commenced upon injection of a toluene solution of the metallocene into the vessel with a 2.5 mL Hamilton syringe rated to 200 psi. Temperature maintenance was monitored by an affixed pressure gauge. Polymerization reactions were vented and quenched with a small volume of methanol/concentrated HCl (12:1), and the polymers were separated from hydrolyzed aluminoxanes by precipitation from methanol, followed by filtration. Residual amounts of toluene and methanol were removed from the obtained polymers by in vacuo drying.

Representative Polymerization Procedures. Entry 1. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.075 g, 1.3 × 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of $Ph_2C(Oct)(C_5H_4)ZrCl_2$ (**8**, 0.0005 g, 6 × 10^{-7} mol) in toluene (1.0 mL) was injected and the reaction stirred in a 0 °C ice/water bath for 10 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 2. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.075 g, 1.3 × 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of $Ph_2C(Oct)(C_5H_4)ZrCl_2$ (**8**, 0.0005 g, 6 × 10^{-7} mol) in toluene (1.0 mL) was injected and the reaction stirred in a 20 °C water bath for 10 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 13. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.089 g, 1.53 × 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of $Me_2C(Oct)(C_5H_4)ZrCl_2$ (**12**, 0.0005 g, 7.7 × 10^{-7} mol) in toluene (1.0 mL) was injected and the reaction stirred in a 0 °C ice/water bath for 10 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 14. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.089 g, 1.53 × 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of $Me_2C(Oct)(C_5H_4)ZrCl_2$ (**12**, 0.0005 g, 7.7 × 10^{-7} mol) in toluene (1.0 mL) was injected and the reaction stirred in a 20 °C water bath for 10 min. The reaction was vented and quenched with dilute HCl/methanol.

Polymer Characterization. Polymer melting temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC 7). The second scan (from 50 to 200 °C at 10 °C/min) was used when subsequent scans were similar. The polymer pentad distributions were determined by integration of the nine resolved peaks in the methyl region (19−22 ppm) of the ^{13}C NMR spectra obtained.[35] Spectra were acquired at 124 °C with tetrachloroethane-d_2 as solvent. A 90° pulse was employed with broadband decoupling. A delay time of 3 s and a minimum of 1000 scans were used.

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Supporting Information Available: X-ray crystal structure data for $Ph_2C(OctH)(C_5H_5)$, $Ph_2C(C_{29}H_{36})(C_5H_4)ZrCl_2$ (**8**), and $Ph_2C(C_{21}H_{22})(C_5H_4)ZrCl_2$ (**10**). This material is available free of charge via the Internet at http://pubs.acs.org.

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