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Isotactic−Hemiisotactic Polypropylene from C_1-Symmetric *ansa*-Metallocene Catalysts: A New Strategy for the Synthesis of Elastomeric Polypropylene

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Control of “isotactic−hemiisotactic” alignment, a polypropylene microstructure in which every other stereocenter is of the same configuration and the intervening stereocenters tend to align with their neighbors, has been achieved by R substituent selection in the *ansa*-metallocene catalyst system $R'_2C(\eta^5\text{-3-R-C}_5H_3)(\eta^5\text{-C}_{13}H_8)MCl_2$−MAO (M = Zr, Hf; η^5-$C_{13}H_8$ = fluorenyl; MAO = methylaluminoxane). For R = 2-adamantyl, R′ = Ph, and M = Zr (**4**), α, a parameter equal to the *m* diad fraction, is approximately 0.58, with M_n = 204 000−463 000, and the isotactic−hemiisotactic polypropylene obtained is elastomeric. Typical elongations are between 7 and 14 times the original length, and the residual elongation following a 200% strain is between 1.5% and 9.3%. The elastomeric properties are rationalized by the statistical existence of isotactic stereoblocks among otherwise amorphous hemiisotactic connecting segments. A two-parameter (α and M_n) statistical model has been derived which calculates the isotactic block length distribution and the percent crystallinity, assuming isotactic blocks of 21 monomer units and longer participate in crystallites. The best elastomers are found to have a calculated percent crystallinity in the range of 1.50−4.45% (α = 0.557−0.630).

Introduction

The mechanical properties of a polymer can generally be classified as rigid, flexible, or elastic. While metallocene catalysts are capable of producing polymers that fall into each of these classifications, the most intense efforts have been directed at surpassing existing systems in their aptitude for making rigid isotactic polypropylene and rigid or flexible polyethylene.[1] More recently, growing efforts to devise metallocene catalysts capable of producing elastomeric polymers have revealed several different viable strategies: ethylene−α-olefin copolymers,[2] high-molecular-weight atactic polypropylene,[3] binary isotactic/atactic compatibilized polypropylene,[4] polypropylene with an intermediate isotactic/atactic microstructure,[5] stereoblock isotactic−atactic polypropylene,[6] and isotactic polypropylene with controllable stereoerror sequences.[7] Recent experimental and modeling efforts have treated many of these metallocene catalysts with a unified and quantitative approach.[8] Although the structure−property relationship of each of these regimes is not fully understood, the elastomeric properties undoubtedly rely on the existence of physical cross-links in the presence of an amorphous phase. In

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[3] (a) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998−1005. (b) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. *Organometallics* **1998** *17*, 1502−1510. (c) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640−8646. (d) Kimura, K.; Takaishi, K.; Matsukawa, T.; Yoshimura, T.; Yamazaki, H. *Chem. Lett.* **1998** *7*, 571−572. (e) Xie, B. H.; Wu, Q.; Lin, S. G. *Acta Polym. Sin.* **1999** *1*, 15−19. (f) Xie, B. H.; Wu, Q.; Lin, S. G. *Macromol. Rapid Commun.* **1999** *20*, 167−169.

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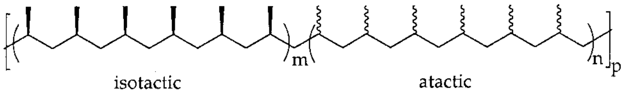
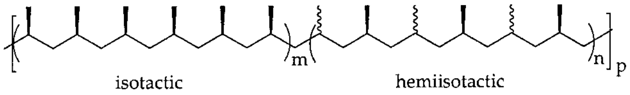
the case of high-molecular-weight materials, the cross-links can be simple chain entanglements. In the other examples, segments from several different polymer chains participate in crystalline regions, which physically connect the chains and provide cross-links in an otherwise amorphous phase.

One of the most studied systems is that initially developed by Coates and Waymouth.[6,9] Their unbridged metallocene (2-phenylindenyl)$_2$ZrCl$_2$, in the presence of methylaluminoxane (MAO), isomerizes between chiral and achiral coordination geometries during the formation of a polypropylene chain. Since the chiral isomer is isospecific and the achiral isomer is aspecific, stereoblock isotactic–atactic polypropylene is obtained:



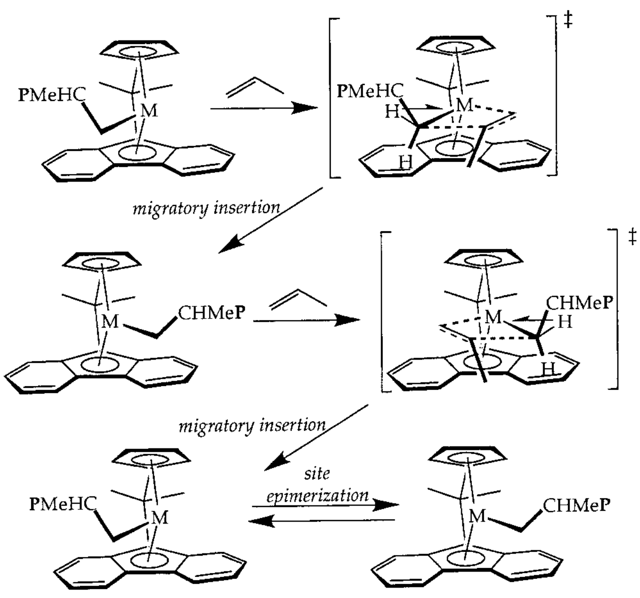
ansa-Metallocene catalysts, those having their cyclopentadienyl ligands connected through linking atoms, tend to be more stable at elevated polymerization temperatures and often behave more predictably when adsorbed on a support. With this in mind, we sought to devise an *ansa*-metallocene catalyst that provided isotactic polypropylene segments to participate in crystallites but formed hemiisotactic polypropylene segments—instead of atactic—to constitute the amorphous phase. As the amorphous phase in an elastomer, hemiisotactic polypropylene might impart new and interesting properties in an elastomeric isotactic–hemiisotactic regime:



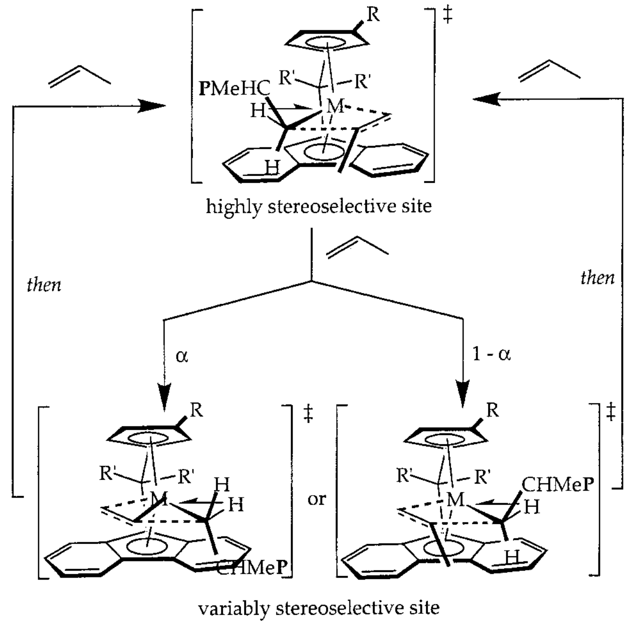
Results and Discussion

Catalyst Design. Chain propagation is best viewed as a migratory insertion step whereby the polymer chain regularly moves from one coordination site of the metallocene to another with each enchainment. With C_s-symmetric metallocenes, particularly with syndiospecific Me$_2$C(η^5-C$_5$H$_4$)(η^5-C$_{13}$H$_8$)ZrCl$_2$/MAO ((η^5-C$_{13}$H$_8$) = fluorenyl) in liquid propylene, inversion at metal ("site epimerization") is much slower than chain propagation (Scheme 1). Regularly alternating propylene enantiofaces are enchained from regularly alternating (enantiotopic) sides of the metallocene wedge, and highly syndiotactic polypropylene is produced.[10]

Scheme 1



Scheme 2



Incorporation of alkyl substituents (R) at the 3-position of the cyclopentadienyl ligand lowers the symmetry from C_s to C_1. With this catalyst system several possible polypropylene microstructures are possible, depending primarily on the size of R. When site epimerization does not compete with propagation, and hence both propylene coordination sites are used, isotactic polypropylene is obtained when monomer insertions occur via the same enantioface (Scheme 2; α = 1). Hemiisotactic polypropylene is obtained when every other monomer inserts with the same enantioface and the intervening monomers insert aspecifically (α = 0.5). Finally, syndiotactic polypropylene is obtained when every other monomer inserts with the same enantioface and the intervening monomers insert via the opposite enantioface (α = 0).

By modifying the hemiisospecific metallocene precatalyst Me$_2$C(η^5-3-Me-C$_5$H$_3$)(η^5-C$_{13}$H$_8$)ZrCl$_2$ (**1**) developed by Ewen and Razavi,[11] it is possible to arrive at the desired isotactic–hemiisotactic microstructure. There are two important catalyst design features.

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(9) (a) Petoff, J. L. M.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316–11322. (b) Hu, Y. R.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908–6916. (c) Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707–2715. (d) Madkour, T. M.; Mark, J. E. *Macromol. Theor. Sim.* **1998**, *7*, 69–77.

(10) (a) Ewen, J. A.; Elder, M. J. *Makromol. Chem., Makromol. Symp.* **1993**, 66. (b) Farina, M.; DiSilvestro, G.; Sozzani, P. *Macromolecules* **1993**, *26*, 946. (c) Veghini, D., Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564.

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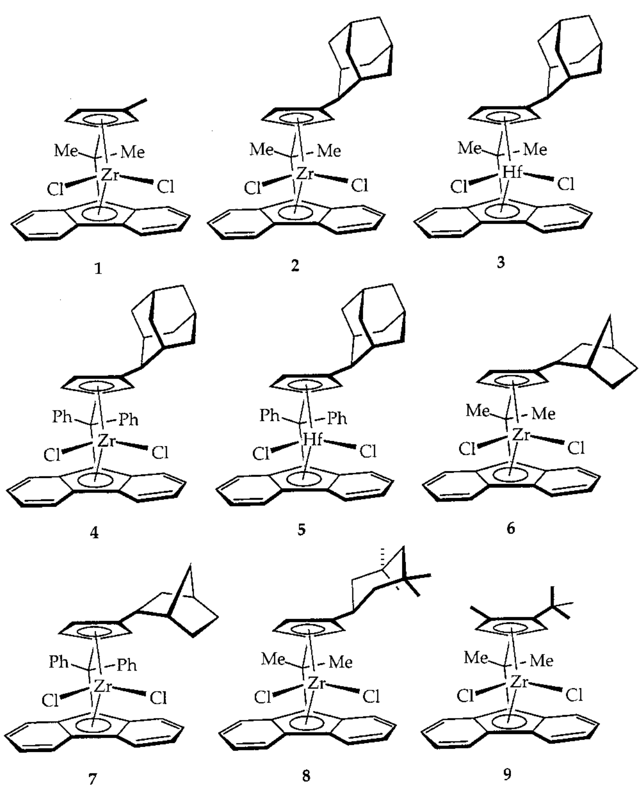
Chart 1



The first is proper selection of the R substituent at the 3-position of the cyclopentadienyl ring (Chart 1). This allows one to control the stereoselectivity at the variably stereoselective site.[12]

For R = methyl (**1**), the parameter α is approximately 0.50 and the intervening stereocenters tend to be stereorandom with respect to their neighbors, yielding amorphous hemiisotactic polypropylene.[13] For R = 3,3,5,5-tetramethylcyclohexyl (**8**), α is found to be approximately 0.75 and the intervening stereocenters tend to be substantially aligned with their neighbors, resulting in a predominantly crystalline, rigid material (T_m = 98 °C). However, if R = 2-adamantyl (**2**−**5**), α has an intermediate value near 0.60, the intervening stereocenters are moderately aligned with their neighbors, and polypropylene with intermediate properties is acquired. The second important design feature is the metallocene bridge, as this impacts the molecular weight of the polymer.[14]

Several of the metallocene dichloride catalyst precursors described in Scheme 3, when combined with MAO, are capable of producing isotactic−hemiisotactic polypropylene with α in the vicinity of 0.60. The structure of $Ph_2C\{\eta^5\text{-}3\text{-}(2\text{-adamantyl})\text{-}C_5H_3\}(\eta^5\text{-}C_{13}H_8)ZrCl_2$ (**4**), as established by a single-crystal X-ray structure determination, is shown in Figure 1.[15]

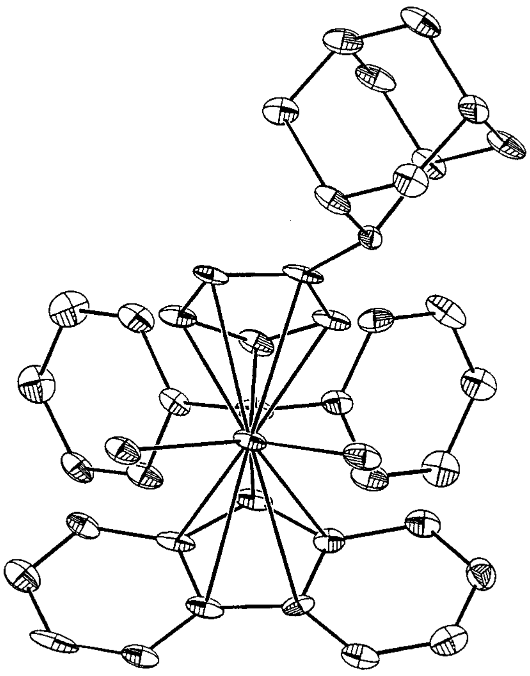


Figure 1. ORTEP drawing from the X-ray crystal structure of $Ph_2C\{\eta^5\text{-}3\text{-}(2\text{-adamantyl})\text{-}C_5H_3\}(\eta^5\text{-}C_{13}H_8)ZrCl_2$ (**4**). Ellipsoids are shown with 50% probability. Hydrogen atoms are omitted.

Synthesis and Characterization of Elastomeric Isotactic−Hemiisotactic Polypropylene. Table 1 summarizes the polymerization results, and Table 2 provides data from the thermal[16] and mechanical property testing. In contrast to isotactic polypropylene, these polymers can be elongated 7−14 times their original length. In contrast to hemiisotactic polypropylene, these polymers are capable of excellent recovery to their original lengths, as the residual elongation following a 200% strain falls between 1.5% (excellent recovery) and 9.3%.

Figure 2 depicts the ^{13}C NMR spectrum of the methyl region for the polymer given by entry 8 (from **4**/MAO, R = 2-adamantyl). Marked deviation from the ideal hemiisotactic pentad distribution[17] (18.75:12.5:6.25:25:0:0:18.75:12.5:6.25) is apparent; nonetheless, the *mmrm*,

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[12] For metallocene **9** it is presumed that the more stereoselective insertion occurs while the chain is in the proximity of the *tert*-butyl group but is directed away from it, toward the benzo substituent of the fluorenyl ligand. A more detailed report on propylene polymerization with this metallocene, along with confirmation of the shown isomer by a single-crystal X-ray diffraction study (CCDC deposition No. 137698), will be reported elsewhere. See also: Miller, S. A. Ph.D. Thesis, California Institute of Technology, 2000; Chapter 6.

[13] The parameter α is equivalent to the *m* dyad percentage, since the α insertion provides an *mm* triad and the 1 − α insertion provides an *rr* triad.

[14] (a) Winter, A.; Rohrmann, J.; Antberg, M.; Dolle, V.; Spaleck, W. Eur. Patent 387690, priority 11.3.89. (b) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993** *459*, 117−123. (c) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996** *518*, 7−15. (d) Patsidis, K.; Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1996** *509*, 63−71.

[15] X-ray analysis was performed on two crystals of **4**. For the structure shown, the asymmetric unit contains one metallocene and 1.5 molecules of benzene. The dihedral angle between the cyclopentadienyl plane and the plane that divides the adamantyl group into two equivalent hemispheres is 56.9°. The asymmetric unit of the second crystal contained two metallocenes and four molecules of benzene. The corresponding dihedral angles were found to be 73.0 and 112.3°. The former crystal is triclinic, $P\bar{1}$, with a = 9.4262(18) Å, b = 13.514(3) Å, c = 15.357(3) Å, α = 103.984(3)°, β = 90.944(3)°, γ = 90.162(3)°, V = 1898.0(6) Å^3, Z = 2, and T = 98 K. The latter crystal is triclinic, $P\bar{1}$, with a = 13.242(6) Å, b = 17.098(10) Å, c = 21.311(5) Å, α = 82.67(3)°, β = 73.29(3)°, γ = 67.26(5)°, V = 4261(3) Å^3, Z = 4, and T = 84 K. CCDC deposition No. 137247.

[16] The DSC traces obtained—except those for entries 20 and 21, which are typical for moderately isotactic specimens—generally show very faint (H_m < 1 J/g) and narrow (5−20 °C) melting temperatures which vary by several degrees on the temperature axis, depending on the thermal history of the sample. Where these were widely erratic, unusually broad, or absent, a designation of “not observed” is employed.

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Table 1. Polymerization Data with 1−9/MAO in Liquid Propylene

entry	metallocene (amt (mg))	T_p (°C)	amt of C_3H_6 (mL)	time (min)	yield (g)	activity[d]	T_m[e] (°C)	*m* (%)	*mmmm* (%)	M_w	M_w/M_n
1	**1** (1.0)[a]	0	30	15	1.43	5 710	n.o.	50.4	21.6	80 000	1.81
2	**1** (1.0)[a]	20	30	10	4.95	29 700	n.o.	49.6	18.3		
3	**2** (0.5)[b]	0	30	30	1.50	6 020	n.o.	62.3	28.4	134 000	3.15
4	**2** (0.5)[b]	20	30	10	1.08	12 900	88	62.7	31.4	81 900	4.38
5	**2** (2.0)[a]	0	55	60	9.96	5 000	n.o.	61.0	28.0		
6	**3** (5.0)[a]	0	30	60	0.15	30	n.o.	64.4	32.0		
7	**3** (5.0)[a]	20	30	60	2.34	470	n.o.	66.4	34.0		
8	**4** (15)[a]	0	350	90	23.22	1 030	115	57.8	27.2	638 000	2.33
9	**4** (15)[a]	20	350	30	27.76	3 700	125	55.7	25.3	435 000	2.14
10	**4** (2.0)[a]	0	180	180	11.27	1 900	147	57.9	25.9	1 081 000	2.33
11	**4** (6.0)[a]	0	200	70	26.02	3 700	146	58.7	26.6	1 006 000	2.42
12	**4** (2.0)[a]	0	200	360	13.85	1 200	125	58.8	27.7	802 000	2.43
13	**5** (5.0)[a]	0	55	60	0.19	38	134	58.8	26.6		
14	**5** (5.0)[a]	20	55	60	1.92	384	n.o.	58.8	28.1		
15	**5** (15)[a]	20	55	60	8.03	540	135	57.6	24.0	806 000	1.93
16	**6** (1.0)[a]	0	30	15	1.31	5 220	122	57.6	27.5	105 000	1.93
17	**6** (1.0)[a]	20	30	10	3.74	22 500	n.o.	58.4	28.0		
18	**7** (2.0)[a]	0	55	60	8.38	4 190	148	43.8	14.7	572 000	2.55
19	**7** (2.0)[a]	20	55	30	12.50	12 500	147	50.6	18.5	390 000	2.32
20	**8** (2.0)[a]	0	30	30	1.57	1 570	98	75.3	49.3	77 400	2.01
21	**8** (2.0)[a]	20	30	15	3.54	7 070	91	75.0	47.9		
22	**9** (1.0)[a]	0	30	3	1.23	24 600	n.o.	57.5	26.9	653 000	1.87
23	**9** (0.5)[c]	20	30	3	1.12	44 700	n.o.	61.0	30.0	397 000	2.31
24	**9** (1.0)[a]	20	55	15	10.22	41 000	149	63.0	31.8	535 000	2.21

[a] 1000 equiv of MAO and 2.0 mL of toluene used. [b] 2000 equiv of MAO and 1.0 mL of toluene used. [c] 1000 equiv of MAO and 1.0 mL of toluene used. [d] In units of g of polypropylene/((g of metal) h). [e] n.o. = melting temperature not observed.

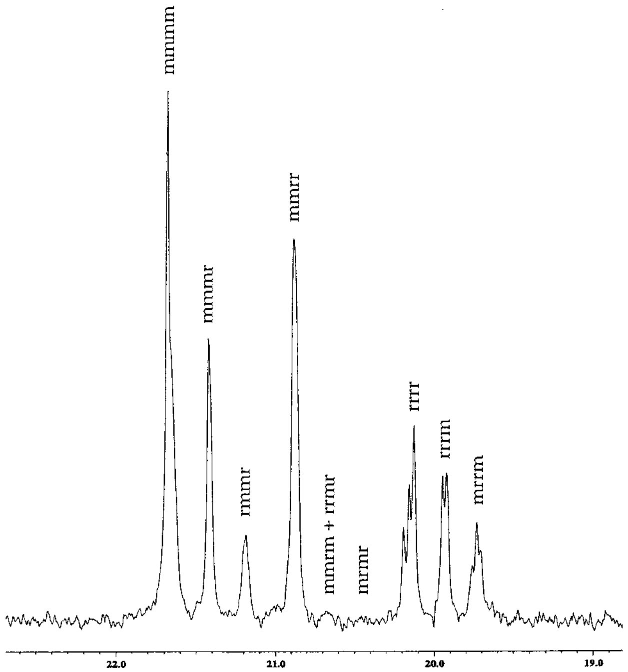

Figure 2. ^{13}C NMR spectrum of the methyl region for polypropylene prepared with **4**/MAO at 0 °C (entry 8). The pentad distribution was determined: 27.2% *mmmm*; 13.2% *mmmr*; 5.5% *rmmr*; 22.2% *mmrr*; 1.2% *mmrm* + *rrmr*; 0.6% *mrmr*; 12.5% *rrrr*; 9.1% *rrrm*; 8.5% *mrrm*.

rrmr, and *mrmr* pentads are still virtually absent. As shown in Table 3, the forbidden pentads constitute approximately 1−3% of the polymers made by **1**−**8** and 4−7% of the polymers made by **9**.

For the synthesis of elastomeric polypropylene, the ideal α parameter is approximately 0.60 and a molecular weight in the vicinity of M_n = 200 000 is suitable. Except for **9**, those metallocenes with an isopropylidene bridge (R′ = Me) generally produce polymers of lower molecular weight (M_w = 77 400−134 000; entries 1, 3, 4, 16, and 20). However, the metallocenes bearing a diphenylmethylidene bridge (R′ = Ph) provide polymer molecular weights that are significantly higher (M_w = 390 000−1 081 000; entries 8−12, 15, 18, and 19).

Isotactic Block Length Distribution for Isotactic−Hemiisotactic Polypropylene. While simple chain entanglements may be partly or largely responsible for the elastomeric properties observed,[3a,18] one must consider the possibility that the elasticity derives from a biphasic morphology in which there exists a statistical likelihood of obtaining isotactic segments capable of participating in crystallites, as well as a statistical likelihood of obtaining hemiisotactic segments long enough to behave as amorphous connectors of these crystallites.

One can calculate the isotactic block length distribution for an ideal isotactic−hemiisotactic polypropylene. For a hemiisotactic regime, only sequential *rr* and *mm* triads are allowed. Therefore, only isotactic blocks containing an odd number of monomers are allowed and an isotactic block is defined by $(rr)(mm)^s(rr)$, where *s* is the number of repeating *mm* triads.[19] The probability of creating an isotactic block of length *n* is given by $P_n = (0.5)(1 - \alpha)(\alpha)^{(n-1)/2}(1 - \alpha)$, and the number of isotactic blocks with length *n* in a given polymer chain is $N_n = P_n(\mathrm{DP})$, where DP is the degree of polymerization, the number of monomer units per chain (however, $P_1 = (0.5)(1 - \alpha)^2 + (0.5)(1 - \alpha)$; see the Supporting Information).[20]

Using only the parameters α and M_n, the isotactic block length distribution for the elastomeric polymers

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[18] Eckstein, A.; Suhm, J.; Friedrich, C.; Maier, R.-D.; Sassmannshausen, J.; Bochmann, M.; Mülhaupt, R. *Macromolecules* **1998**, *31*, 1335−1340.

[19] This idealized model assumes that no site epimerization is operating and that the stereoselectivity of the more stereoselective site is perfect. While these assumptions are not strictly true, the presented analysis does not deviate greatly from the case where these mistakes do occur to a very minor degree, as seen with the catalysts presented (typically [*mmrm*] + [*rrmr*] + [*mrmr*] = 1−3%, except for **9**, 4−7%).

Table 2. Thermal and Mechanical Properties of Elastomeric Polypropylenes

	entry (from Table 1)/metallocene dichloride precatalyst									
	5/**2**	8/**4**	9/**4**	10/**4**	11/**4**	12/**4**	15/**5**	18/**7**	19/**7**	24/**9**
Thermal Properties										
melt flow rate[a]		0.1	0.41							
T_g (°C)		−3	−3							
T_m (°C)	n.o.	115	125	147	146	125	135	148	147	149
H_m (J/g)		9.3	6.8	5.4	4.5	0.5	0.7	6.6	6.5	2.2
T_c (°C)		66	62	88	86	78		87	82	79
H_c (J/g)		4.6	2.7	8.7	3.1	1.9		7.1	7.8	3.6
Mechanical Properties										
initial modulus (psi)	1007 ± 44	679	712				509 ± 23	483 ± 23		1100 ± 33
stress (psi)										
at 100% strain	226 ± 2						222 ± 24	155 ± 1		260 ± 4
at 200% strain	249 ± 3						313 ± 7	170 ± 1		305 ± 3
at 300% strain	180 ± 2						415 ± 9	174 ± 1		366 ± 3
at 400% strain	325 ± 3						530 ± 12	181 ± 1		459 ± 6
at 500% strain	379 ± 2						660 ± 14	191 ± 1		586 ± 9
at 1000% strain	895 ± 10						NA	328 ± 8		NA
at break	1233 ± 27	1215	1230				1219 ± 70	642 ± 43		1763 ± 29
strain at break (%)	1245 ± 30	756	813				792 ± 32	1447 ± 45		910 ± 75
recovery (%)										
trial 1	11.3						0.70	3.70		3.60
trial 2	7.60						2.10	5.70		3.40
trial 3	9.10						1.8	5.00		4.9
average[b]	9.33						1.53	4.80		3.97
tensile stress relaxation (%)[c]		27	28							
tensile hysteresis[d]										
cumulative set (%)[e]		6.5	7.3							
retained force (%)[f]		51	49							
[*m*] (%)	61.0	57.8	55.7	57.9	58.7	58.8	57.6	43.8	50.6	63.0
M_n	n.d.[g]	273 000	204 000	463 000	416 000	330 000	417 000	224 000	168 000	242 000

[a] In units of g/600 s at 230 °C. [b] Recovery from 200% strain (%) = ((final length) − (initial length))/(initial length), where initial length = 0.5000 in. [c] 50% elongation stress decay, 5 min. [d] Three cycles, 100% elongation, 30 s hold at extension, 60 s hold at recovery. [e] Two cycles. [f] Second cycle, (stress at 50% on recovery)/(stress at 100% on extension before hold). [g] An estimation of M_n = 43 000 can be made, based on entry 3, performed with the same catalyst at the same temperature.

Table 3. Pentad Distributions (in %) for Polymers Obtained with Metallocene Dichlorides 1−9 as Precatalysts

entry	metallocene	[*mmmm*]	[*mmmr*]	[*rmmr*]	[*mmrr*]	[*mmrm*] + [*rrmr*]	[*mrmr*]	[*rrrr*]	[*rrrm*]	[*mrrm*]
1	**1**	21.6	10.9	6.0	21.8	1.3	0.6	23.1	10.3	4.4
2	**1**	18.3	11.6	5.5	22.5	1.9	0.8	21.3	11.7	6.5
3	**2**	28.4	15.5	5.3	24.7	0.8	0.4	7.9	7.4	9.5
4	**2**	31.4	14.7	4.5	23.1	0.9	0.4	8.2	8.5	8.4
5	**2**	28.0	14.3	5.7	24.6	1.1	0.5	8.1	8.9	9.0
6	**3**	32.0	15.3	4.6	23.5	1.2	0.4	7.5	6.9	8.7
7	**3**	34.0	15.3	5.1	21.5	1.4	0.9	6.6	7.0	8.0
8	**4**	27.2	13.2	5.5	22.2	1.2	0.6	12.5	9.1	8.5
9	**4**	25.3	13.2	5.0	21.5	2.3	0.6	11.6	11.1	9.3
10	**4**	25.9	13.6	5.8	23.4	1.2	0.6	12.2	9.4	7.8
11	**4**	26.6	13.9	5.5	23.5	1.3	0.7	11.4	9.4	7.8
12	**4**	27.7	13.4	5.2	22.6	1.4	0.8	12.3	9.0	7.5
13	**5**	26.6	13.2	6.3	23.1	1.3	0.7	12.7	8.9	7.2
14	**5**	28.1	13.5	5.0	22.3	1.6	0.5	11.1	10.2	7.7
15	**5**	24.0	14.9	6.1	24.0	1.0	0.2	11.8	9.4	8.5
16	**6**	27.5	12.9	5.1	21.3	2.0	1.1	13.6	8.8	7.8
17	**6**	28.0	13.3	4.8	21.7	2.2	1.0	12.3	9.4	7.3
18	**7**	14.7	9.8	6.1	22.7	2.9	0.6	21.1	13.4	8.6
19	**7**	18.5	13.4	6.7	21.6	1.6	0.8	20.4	10.6	6.5
20	**8**	49.3	13.2	3.2	15.5	2.6	1.0	3.5	4.3	7.3
21	**8**	47.9	14.3	2.8	16.8	2.0	1.2	4.0	4.1	6.9
22	**9**	26.9	13.4	4.8	20.4	4.2	0.2	11.7	10.8	7.6
23	**9**	30.0	15.1	3.1	19.2	5.2	1.2	8.9	8.7	8.6
24	**9**	31.8	15.3	3.0	19.3	5.4	1.4	8.0	7.8	8.1

can be calculated. The polymer from entry 8 (from **4**/MAO, $\alpha = 0.578$, $M_n = 273\,000$, DP = 6488) is representative, and its distribution is shown in Table 4. N_n is the number of isotactic blocks of length n present and $(N_n)n$ is the total number of monomers present in all isotactic blocks of length n ($\sum(N_n)n = 6488$). As required for a stereoblock elastomer,[6] this polymer contains at least two blocks of crystallizable length (approximately ≥ 21)[21] and, in fact, is calculated to contain 5.70 isotactic blocks of length 21 or greater ($5.70 = \sum(N_n)|n \geq 21$) per polymer chain. The measured values for M_n and α precisely determine the calculated

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[20] The relationship between s and n is given by $s = (n - 1)/2$. For example, the sequence $(rr)(mm)^{10}(rr)$ contains $n = 21$ monomers in its isotactic stereoblock. DP = M_n/(monomer molecular weight; 42.08 for polypropylene).

Table 4. Calculated Isotactic Block Length Distribution for Entry 8 ($\alpha = 0.578$, $M_n = 273\,000$)

n	N_n	$(N_n)n$	n	N_n	$(N_n)n$
1	1946.57	1946.57	27	0.46	12.53
3	333.89	1001.68	29	0.27	7.78
5	192.99	964.96	31	0.16	4.81
7	111.55	780.84	33	0.09	2.96
9	64.48	580.28	35	0.05	1.81
11	37.27	409.93	37	0.03	1.11
13	21.54	280.02	39	0.02	0.68
15	12.45	186.75	41	0.01	0.41
17	7.20	122.34	43	0.01	0.25
19	4.16	79.03	45	0.00	0.15
21	2.40	50.49	47	0.00	0.09
23	1.39	31.96	49	0.00	0.05
25	0.80	20.08	51	0.00	0.03

Table 5. Comparison of Calculated Isotactic Block Length Distribution Data for Entries 1, 8, and 20

	entry (from Table 1)/α/M_n		
	1/0.504/ 44 200	8/0.578/ 273 000	20/0.753/ 38 500
longest isotactic segment with $N_n \geq 1$	15	23	23
N_{11}	4.20	37.27	6.76
N_{21}	0.14	2.40	1.64
N_{31}	0.00	0.16	0.40
N_{41}	0.00	0.01	0.10
$\sum(N_n)$ for $n \geq 21$	0.28	5.70	6.62
degree of polymerization (DP = M_n/42.08)	1050.4	6487.6	914.9
monomers in blocks with $n \geq 21$ ($\sum((N_n)n)$)	6.35	135.24	179.43
percent in blocks with $n \geq 21$	0.60	2.08	19.61

value of $\sum(N_n)|n \geq 21$ for a given polymer sample. This number approximates the statistical number of crystallizable isotactic blocks present per polymer chain and has been calculated for the elastomeric samples described in Table 2: entry 5, 1.42; entry 8, 5.70; entry 9, 3.09; entry 10, 9.81; entry 11, 9.92; entry 12, 7.98; entry 15, 8.45; entry 18, 0.39; entry 19, 1.09; entry 24, 10.48.

It is important to note that the elastomeric polymers reported herein have *sufficiently large M_n values* and *intermediate α parameters* such that the derived model predicts isotactic stereoblocks of appropriate number and length to form crystalline regions in an amorphous network. This is in contrast to previously reported[10] hemiisotactic polymers, which generally have modest molecular weights (ca. 50 000) and $\alpha \approx 0.50$. As calculated for entry 1 in Table 5, such hemiisotactic polymers likely do not contain isotactic blocks in great enough number or length to form the crystalline regions necessary for elastomeric polypropylene. For example, only one in 3.6 chains (=1/0.28) contains an isotactic block of length 21 or greater. At the other extreme, a polymer with $\alpha = 0.753$ and $M_n = 38\,500$ (entry 20, Table 5) contains lengthy and abundant isotactic blocks at the expense of amorphous hemiisotactic segments; a rigid polymer results (T_m = 98 °C), since almost 20% of the monomers reside in isotactic blocks with $n \geq 21$.

Conclusions

Fine-tuning of the metallocene structure $R'_2C(\eta^5\text{-}3\text{-}R\text{-}C_5H_3)(\eta^5\text{-}C_{13}H_8)MCl_2$ (M = Zr, Hf) has produced several metallocene/MAO catalyst systems capable of polymerizing propylene to elastomeric polypropylene having an isotactic–hemiisotactic structure. A statistical model was developed to quantify the isotactic block length distribution and rationalize the elastomeric properties. For an isotactic–hemiisotactic polypropylene with $[m] = \alpha = 0.578$ and $M_n = 273\,000$, the statistical model predicts the presence of 5.70 isotactic stereoblocks per chain with sufficient length (≥21 monomer units) to participate in crystallites, thereby providing physical cross-links in an otherwise hemiisotactic, amorphous phase. The model also provides an estimation of the percent crystallinity, as measured by the fraction of monomers that exist in isotactic stereoblocks of 21 monomer units or longer. Elastomeric isotactic–hemiisotactic polypropylene is calculated to have a percent crystallinity in the range of 1.50–4.45% (α = 0.557–0.630).[22]

It may be argued that these polypropylenes have structures—and certainly properties—similar to those of previously prepared elastomeric polypropylenes. It should be emphasized that the unique feature of the catalysts investigated here is their fidelity with respect to site epimerization. Essentially devoid of stereoerrors arising from this mistake process, many of the polymers are suitably described by a *single stereochemical parameter*. Hence, the tacticity is statistically simple and appropriately classified as isotactic–hemiisotactic. This situation is contrasted with the action of other metallocene catalysts that produce polypropylene microstructures that must be modeled by several stereochemical parameters.[5–8]

It is evident that the isotactic block length distribution for isotactic–hemiisotactic polypropylene is quite sensitive to the polymer stereochemistry (as quantified by the parameter α) and to the polymer molecular weight (M_n). The effects of altering these parameters, the mechanistic processes (including mistake processes) of forming isotactic–hemiisotactic polypropylene, and the detailed origin of the elastomeric properties are topics of further investigation.

Experimental Section

General Methods. Unless otherwise noted, all reactions and procedures were carried out under an inert atmosphere of argon or nitrogen using standard glovebox, Schlenk, and high-vacuum-line techniques.[23] Solvents were dried according to standard procedures. The following reagents were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%), 2-adamantanone (99%), fluorene (98%), *n*-butyllithium (1.6 M in hexanes), zirconium tetrachloride (99.5%),

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[21] The lamellar thickness of the isotactic crystallites in certain elastomeric PP samples has been estimated by transmission electron microscopy (TEM) and corresponds to a minimum of 11–15 monomer units per crystallized stereoblock. See: Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858. It has been pointed out that a few monomer units in each isotactic sequence are likely located in diffuse phase boundaries and thus do not participate in the cocrystallization. A reasonable assumption was advanced that crystallites are made of isotactic sequences 21 propylene units or longer.[5e]

[22] The calculated percent crystallinity is a function solely of α and is addressed more thoroughly in the Supporting Information. Preliminary efforts to correlate thermal and mechanical properties (such as T_m, H_m, H_c, or strain at break) with the calculated percent crystallinity provided no obvious correlations. Thermal history considerations have not been fully investigated and may significantly influence the thermal and mechanical properties. However, thermal history does not influence the calculated percent crystallinity, since this is a function of α, which equals $[m]$.

[23] Burger, B. J.; Bercaw, J. E. *New Developments in the Synthesis, Manipulation, and Characterization of Organometallic Compounds*; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

norcamphor (98%), and 3,3,5,5-tetramethylcyclohexanone (98%). Dicyclopentadiene and di(methylcyclopentadiene) were obtained from Aldrich and cracked following standard procedures prior to use. 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 spectrometer. 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 Syntheses. Preparation of 1. The synthesis of **1** was performed as described in the literature.[24]

6,6-Adamantylidenefulvene. The procedure was modified from that reported earlier.[25] Pyrrolidine (10.0 mL, 0.116 mol) was syringed into a solution of 2-adamantanone (25.00 g, 0.1664 mol) and cyclopentadiene (30.0 mL, 0.364 mol) in 250 mL of methanol. The reaction mixture was stirred for 92 h before the yellow precipitate was collected by suction filtration, rinsed with a small volume of methanol, and dried in vacuo. A 25.71 g amount (77.9%) of 6,6-adamantylidenefulvene was isolated. MS (GC-MS): *m/z* 198.3 (M$^+$). ^{1}H NMR (CDCl$_3$): δ 1.93−2.08, 3.29 (m, 14H, adamantyl *H*), 6.52, 6.60 (m, 4H, fulvene *H*). ^{13}C NMR (CDCl$_3$): δ 28.30, 37.05, 37.35, 40.25 (adamantyl *C*), 119.47, 130.47 (fulvene *C*H$_1$), 135.81, 167.38 (fulvene *C*H$_0$). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.20, 90.22; H, 8.39, 8.50.

2-Adamantylcyclopentadiene. A 6.00 g portion (30.3 mmol) of 6,6-adamantylidenefulvene was dissolved in 30 mL of tetrahydrofuran and this solution added over 30 min to a stirred slurry of LiAlH$_4$ (1.40 g, 0.0369 mol) at 0 °C. After 5 h of stirring at room temperature, the reaction mixture was cooled to 0 °C and quenched by slow addition of 20 mL of saturated NH$_4$Cl solution. Then 300 mL of H$_2$O, 25 mL of concentrated HCl, and 50 mL of diethyl ether were added, the organic layer was isolated, and the aqueous layer was extracted with additional diethyl ether (3 × 50 mL). The combined organic layers were dried over MgSO$_4$, filtered, and rotavapped to give the product, 2-adamantylcyclopentadiene, in quantitative yield as a light yellow oil. MS (GC-MS): *m/z* 200.3 (M$^+$).

3-(2-Adamantyl)-6,6-dimethylfulvene. To 2-adamantylcyclopentadiene (6.06 g, 30.3 mmol) was added 50 mL of methanol, 50 mL of ethanol, 20 mL of tetrahydrofuran, 36 mL of acetone (0.49 mol) and 0.5 mL of pyrrolidine (0.006 mol). After the mixture was stirred for 48 h, 5 mL of acetic acid was injected, followed by 200 mL of H$_2$O and 200 mL of diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 × 40 mL). The combined organic layers were extracted with H$_2$O (3 × 25 mL) and with 10% aqueous NaOH (3 × 25 mL), dried over MgSO$_4$, filtered, and rotavapped. The obtained yellow solid was further purified by overnight Soxhlet extraction by 150 mL of methanol. The precipitate in the filtrate was isolated by filtration at 0 °C and in vacuo drying, yielding 4.54 g (62.5%) of 3-(2-adamantyl)-6,6-dimethylfulvene as a yellow powder. Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 82.23, 82.23; H, 8.78, 8.82.

Me$_2$C(3-(2-adamantyl)C$_5$H$_3$)(C$_{13}$H$_8$)H$_2$. A 10.5 mL portion of an *n*-butyllithium solution (1.6 M in hexanes, 0.0168 mol) was syringed into a solution of fluorene (2.77 g, 0.0166 mol) in 60 mL of tetrahydrofuran. After the mixture was stirred for 5 h, a solution of 3-(2-adamantyl)-6,6-dimethylfulvene (4.00 g, 0.0166 mol) in 40 mL of tetrahydrofuran was injected over 2 min. After this mixture was stirred for 20 h, 60 mL of a saturated NH$_4$Cl solution was added, the organic layer isolated, and the aqueous layer extracted with diethyl ether (2 × 25 mL). The combined organic layers were dried over MgSO$_4$, filtered, and rotavapped to give the product in quantitative yield as a yellow oil.

Me$_2$C(3-(2-adamantyl)C$_5$H$_3$)(C$_{13}$H$_8$)Li$_2$. The dianion was prepared by treating a solution of Me$_2$C(3-(2-adamantyl)C$_5$H$_3$)(C$_{13}$H$_8$)H$_2$ (6.77 g, 16.6 mmol) in 75 mL of diethyl ether with 22.0 mL of *n*-butyllithium solution (1.6 M in hexanes, 0.0352 mol) at 0 °C. After the mixture was stirred for 21 h, the solvent was removed by vacuum transfer and 50 mL of petroleum ether was condensed in. The dilithio salt was isolated by filtration and in vacuo drying in quantitative yield as an orange powder.

Me$_2$C(η^5-3-(2-adamantyl)-C$_5$H$_3$)(η^5-C$_{13}$H$_8$)ZrCl$_2$ (2). A 2.00 g amount of Me$_2$C(3-(2-adamantyl)C$_5$H$_3$)(C$_{13}$H$_8$)Li$_2$ (0.004 78 mol) and 1.114 g of ZrCl$_4$ (0.00478 mol) were combined in a swivel frit apparatus. A 40 mL portion of petroleum ether was condensed in at −78 °C. This mixture was warmed slowly to room temperature before solvent removal after 14 h of stirring. A 40 mL portion of methylene chloride was condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted in the swivel frit with 50 mL of refluxing diethyl ether. Two crops were obtained for a total of 1.502 g (55.5%) of **2** as an orange powder following collection at 0 °C and in vacuo drying. MS (LC-MS): *m/z* 566.5 (M$^+$). ^{1}H NMR (C$_6$D$_6$): δ 1.36−2.04 (m, 14H, adamantyl *H*), 1.84, 1.86 (s, 6 H, C(C*H*$_3$)$_2$), 3.32 (s, 1H, 2-*H* adamantyl), 5.44, 5.48, 6.18 (m, 3H, Cp *H*), 6.95, 7.03, 7.29, 7.34 (t, $^3J_{\mathrm{HH}} = 7.7, 7.7, 8.0, 8.0$ Hz, 4H, Flu *H*), 7.41, 7.49, 7.84, 7.84 (d, $^3J_{\mathrm{HH}} = 8.8, 9.1, 7.7, 7.7$ Hz, 4H, Flu *H*). ^{13}C NMR (CD$_2$Cl$_2$): δ 28.58, 28.65 (C(*C*H$_3$)$_2$), 27.90, 27.93, 31.98, 32.41, 32.62, 32.66, 37.84, 38.50, 38.66, 43.83 (adamantyl *C*), 102.56, 103.02, 116.65 (Cp *C*H$_1$), 123.41, 123.67, 124.61, 124.67, 124.76, 124.83, 128.81, 128.81 (Flu *C*H$_1$), 139.93 (9-Flu *C*), *C*H$_0$ not determined. Anal. Calcd for $C_{31}H_{32}ZrCl_2$: C, 65.70; H, 5.69. Found: C, 63.46, 61.93; H, 5.57, 5.42.

Me$_2$C(η^5-3-(2-adamantyl)-C$_5$H$_3$)(η^5-C$_{13}$H$_8$)HfCl$_2$ (3). A 2.00 g portion of Me$_2$C(3-(2-adamantyl)C$_5$H$_3$)(C$_{13}$H$_8$)Li$_2$ (4.78 mmol) and 1.531 g of HfCl$_4$ (4.78 mol) were combined in a 100 mL flask equipped with a 180° needle valve. A 50 mL amount of petroleum ether was condensed in at −78 °C. This mixture was warmed slowly to room temperature before solvent removal after 47 h of stirring. A 20 mL portion of methylene chloride was condensed in and removed in order to quench unreacted ligand. Then the yellow solid was extracted in a cellulose extraction thimble with 150 mL of refluxing methylene chloride for 48 h. Solvent was removed from the filtrate, and 30 mL of diethyl ether was condensed in. The yellow solid was collected on the frit and dried in vacuo: 1.771 g (56.7%). MS (LC-MS): *m/z* 654.7 (M$^+$). ^{1}H NMR (C$_6$D$_6$): δ 1.11−2.04 (m, 14H, adamantyl *H*), 1.85, 1.88 (s, 6 H, C(C*H*$_3$)$_2$), 3.37 (s, 1H, 2-*H* adamantyl), 5.40, 5.43, 6.12 (m, 3H, Cp *H*), 6.94, 7.01, 7.27, 7.33 (t, $^3J_{\mathrm{HH}} = 7.0, 7.7, 7.0, 7.3$ Hz, 4H, Flu *H*), 7.46, 7.55, 7.84, 7.84 (d, $^3J_{\mathrm{HH}} = 8.8, 8.8, 8.4, 8.4$ Hz, 4H, Flu *H*). ^{13}C NMR (CD$_2$Cl$_2$): δ 28.82, 28.88 (C(*C*H$_3$)$_2$), 27.90, 27.90, 32.08, 32.40, 32.65, 32.70, 37.86, 38.53, 38.68, 43.77 (adamantyl *C*), 99.90, 100.22, 115.73 (Cp *C*H$_1$), 123.16, 123.42, 124.27, 124.42, 124.54, 124.66, 128.61, 128.64 (Flu *C*H$_1$), 138.42 (9-Flu *C*), *C*H$_0$ not determined. Anal. Calcd for $C_{31}H_{32}HfCl_2$: C, 56.93; H, 4.93. Found: C, 54.80; H, 4.97.

6,6-Adamantylidenefulvene. The procedure was modified from that reported earlier.[25] 2-Adamantanone (40.22 g, 267.7 mmol), methanol (200 mL), cyclopentadiene (51.0 mL, 618.9 mmol), and pyrrolidine (20.0 mL, 239.6 mmol) were added to a 1 L round-bottom flask. After the mixture was stirred for

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[24] Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1995**, *497*, 105−111.

[25] Abrams, M. B.; Yoder, J. C.; Loeber, C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1389−1401.

70 h, the yellow precipitate was collected by suction filtration and washed with 50 mL of methanol. After in vacuo drying, 45.59 g of 6,6-adamantylidenefulvene was obtained (85.9%). MS (GC-MS): *m*/*z* 198.3 (M^+).

2-Adamantylcyclopentadiene. A 500 mL argon-purged round-bottom flask was charged with $LiAlH_4$ (8.20 g, 216 mmol) and 100 mL of tetrahydrofuran. 6,6-Adamantylidenefulvene (30.00 g, 151.3 mmol) was added via a solid addition funnel, followed by another 100 mL of tetrahydrofuran over 2 min at 0 °C. After the reaction mixture was stirred for 22 h at room temperature, it was cooled to 0 °C and 100 mL of water was added dropwise over 60 min. Then, 100 mL of concentrated aqueous HCl in 300 mL of water and 50 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3×50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give 30.30 g of the product in quantitative yield. MS (GC-MS): *m*/*z* 200.3 (M^+).

3-(2-Adamantyl)-6,6-diphenylfulvene. A 250 mL round-bottom flask was charged with 2-adamantylcyclopentadiene (10.24 g, 51.13 mmol), benzophenone (9.32 g, 51.13 mmol), and 100 mL of absolute ethanol. Once the solids had dissolved, sodium methoxide (5.00 g, 92.6 mmol) was added and the reaction mixture was stirred for 5 days. The orange precipitate was collected by suction filtration and washed with 50 mL of ethanol. The air-dried product was stirred in 100 mL of methanol overnight, and the solid was collected by suction filtration and washed with 50 mL of methanol. Drying in vacuo for several hours provided 13.32 g of the desired product (71.5%). MS (GC-MS): *m*/*z* 364.5 (M^+). Anal. Calcd for $C_{28}H_{28}$: C, 92.26; H, 7.74. Found: C, 87.05; H, 6.92.

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$. In the glovebox, a 250 mL round-bottom flask was charged with 3-(2-adamantyl)-6,6-diphenylfulvene (6.000 g, 16.46 mmol) and fluorenyllithium diethyl ether adduct (4.054 g, 16.46 mmol). This was equipped with a 180° needle valve, and 100 mL of diethyl ether was condensed into the reaction vessel. After the mixture was stirred at room temperature for 7 days, 60 mL of aqueous NH_4Cl and 50 mL of water were slowly added. After 2 h, the solid that formed was collected by filtration and washed with 40 mL of diethyl ether. The crude, wet product was dissolved in 250 mL of tetrahydrofuran, dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to give 2.834 g of a waxy solid as the product (32.4%). MS (GC-MS): *m*/*z* 530.6 (M^+).

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (4). A 2.834 g amount of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$ (5.340 mmol) was combined with $LiCH_2$(trimethylsilane) (1.006 g, 10.68 mmol) in a 250 mL round-bottom flask. A 50 mL portion of tetrahydrofuran was condensed in, and this mixture was stirred at room temperature for 17 h, at which point the solvent was removed. In the glovebox, zirconium tetrachloride (1.245 g, 5.343 mmol) was added. A 60 mL portion of petroleum ether was condensed in, and the reaction mixture was stirred at room temperature for 52 h. Solvent was removed, and 20 mL of dichloromethane was condensed in, stirred, and removed. Then, 50 mL of diethyl ether was condensed in, stirred, and removed. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of methylene chloride. The obtained solution was filtered through a frit. Solvent was removed, 15 mL of diethyl ether was condensed in, and the orange solid was broken up, collected at 0 °C, and dried in vacuo to give 0.778 g of product **3** (21.1%). MS (LC-MS): *m*/*z* 690.9 (M^+). Anal. Calcd for $C_{41}H_{36}ZrCl_2$: C, 71.28; H, 5.25. Found: C, 68.78; H, 5.21.

Alternate Preparation of 4. 6,6-Adamantylidenefulvene. The procedure was modified from that reported earlier.[25] 2-Adamantanone (45.00 g, 299.6 mmol), methanol (200 mL), cyclopentadiene (60.0 mL, 728 mmol), and pyrrolidine (20.0 mL, 240 mmol) were added to a 1 L round-bottom flask. After the mixture was stirred for 77 h, the yellow precipitate was collected by suction filtration and washed with 50 mL of methanol. After in vacuo drying, 49.56 g of 6,6-adamantylidenefulvene was obtained (83.4%). MS (GC-MS): *m*/*z* 198.3 (M^+).

2-Adamantylcyclopentadiene. A 500 mL argon-purged round-bottom flask was charged with $LiAlH_4$ (9.00 g, 237 mmol) and 400 mL of diethyl ether. 6,6-Adamantylidenefulvene (31.05 g, 156.6 mmol) was added as a solid over 2 min at 0 °C. After the reaction mixture was stirred for 15 h at room temperature, it was cooled to 0 °C and 60 mL of water was added dropwise over 2 h, along with 300 mL of diethyl ether. The alumina residue was removed by gravity filtration and rinsed with an additional 100 mL of diethyl ether. The organic layer was rotavapped to give 30.18 g of the product (96.2%) as a light yellow oil.

3-(2-Adamantyl)-6,6-diphenylfulvene. In a 500 mL round-bottom flask containing 2-adamantylcyclopentadiene (30.18 g, 150.7 mmol) was added benzophenone (27.50 g, 150.9 mmol) and 300 mL of absolute ethanol. Once the solids had dissolved, sodium methoxide (15.00 g, 278 mmol) was added and the reaction mixture was stirred for 6 days. The orange precipitate was collected by suction filtration, and the air-dried product was then stirred in 100 mL of methanol for 2 days before the solid was collected by suction filtration and washed with 100 mL of methanol. Drying in vacuo for 2 days provided 25.72 g of the desired product (46.8%). A second crop was also obtained: 6.08 g (57.9% for both crops). MS (GC-MS): *m*/*z* 364.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.52−2.23 (m, 14H, adamantyl *H*), 2.80 (s, 1H, 2-*H* adamantyl), 7.30−7.40 (m, 12H, phenyl *H*), 6.05 (m, 1H, fulvene *H*), 6.29, 6.59 (d, $^3J_{HH} = 3.4, 3.7$ Hz, 2H, fulvene *H*). ^{13}C NMR ($CDCl_3$): δ 28.14, 28.14, 31.21, 31.21, 32.72, 32.72, 38.06, 38.92, 38.92 (adamantyl *C*), 45.20 (2-*C* adamantyl), 118.16, 125.01, 133.10 (fulvene CH_1), 127.68, 127.68, 127.77, 127.77, 128.31, 128.31, 132.02, 132.02, 132.08, 132.08 (phenyl CH_1), 141.70, 141.70 (ipso *C*), 144.39, 148.69, 152.27 (fulvene CH_0). Anal. Calcd for $C_{28}H_{28}$: C, 92.26; H, 7.74. Found: C, 83.42; H, 6.59.

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$. In the glovebox, a 250 mL round-bottom flask was charged with 3-(2-adamantyl)-6,6-diphenylfulvene (20.00 g, 54.87 mmol) and fluorenyllithium diethyl ether adduct (13.51 g, 54.86 mmol). This flask was equipped with a 180° needle valve, and 150 mL of diethyl ether was condensed into the reaction vessel. After the mixture was stirred at room temperature for 2 days and at reflux for 7 days, 60 mL of H_2O was slowly added. After 3 h, the solid that formed was collected by filtration. The air-dried product was combined with 100 mL of diethyl ether and stirred for 1 h before collection by suction filtration, rinsing with 25 mL of diethyl ether, and in vacuo drying: yield 14.30 g (49.1%). MS (GC-MS): *m*/*z* 530.6 (M^+). Anal. Calcd for $C_{41}H_{38}$: C, 92.78; H, 7.22. Found: C, 85.14, 84.89; H, 6.04, 6.08.

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$. A large swivel frit was charged with $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$ (14.00 g, 26.38 mmol) and evacuated before 150 mL of diethyl ether was condensed in. A 35.0 mL portion of *n*-butyllithium in hexanes (1.6 M, 56.0 mmol) was syringed in at room temperature over 5 min. The reaction mixture was stirred at room temperature for 22 h and at 40 °C for 5 h. The orange precipitate was collected and dried in vacuo: 11.44 g (79.9%).

$Ph_2C(\eta^5\text{-}3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(\eta^5\text{-}C_{13}H_8)ZrCl_2$ (4). In the glovebox, 4.657 g of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$ (8.582 mmol) was combined with $ZrCl_4$ (2.000 g, 8.583 mmol) in a 100 mL round-bottom flask. This was equipped with a 180° needle valve, and 60 mL petroleum ether was condensed in by vacuum transfer at −78 °C. The vessel was warmed slowly, and after 46 h of stirring, solvent was removed. The solid was extracted for 2 days in a cellulose extraction thimble with 150 mL of methylene chloride. The obtained solution was filtered through a frit and condensed to 15 mL. After it stood for 1 h, the formed precipitate was collected on the frit and dried in vacuo: 2.443 g of product **3** was obtained (41.2%). MS (LC-MS): *m*/*z* 690.7 (M^+). ^1H NMR (C_6D_6): δ 1.46−2.10 (m, 14H, adamantyl *H*), 3.36 (s, 1H, 2-*H* adamantyl), 5.73, 5.74

(s, 2H, Cp *H*), 6.28 (t, $^3J_{HH}$ = 2.9 Hz, 1H, Cp *H*), 6.93, 6.97, 7.02, 7.04, 7.12, 7.14 (t, $^3J_{HH}$ = 7.3, 7.3, 7.4, 7.4, 7.3, 6.6 Hz, 6H, phenyl *H*), 7.59, 7.60, 7.82, 7.95 (d, $^3J_{HH}$ = 8.1, 8.1, 8.1, 8.4 Hz, 4H, phenyl *H*), 6.49, 6.55, 7.90, 7.90 (d, $^3J_{HH}$ = 8.8, 8.8, 8.4, 8.4 Hz, 4H, Flu *H*), 6.71, 6.77, 7.28, 7.33 (t, $^3J_{HH}$ = 7.0, 7.0, 7.4, 7.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 27.90, 28.03, 32.30, 32.48, 32.51, 32.72, 37.88, 38.48, 38.64 (adamantyl *C*), 43.88 (2-*C* adamantyl), 104.23, 104.57, 116.06 (Cp *C*H$_1$), 121.30, 121.43, 122.98, 123.28 (Flu *C*H$_0$), 123.82, 124.02, 124.53, 124.68, 124.14, 125.28, 126.65, 126.65, 127.20, 127.26, 128.06, 128.06, 129.04, 129.04, 129.13, 129.13, 129.26, 129.39 (phenyl and Flu *C*H$_1$), 139.39 (9-Flu *C*), 145.01, 145.11 (ipso *C*), other *C*H$_0$ not determined. Anal. Calcd for $C_{41}H_{36}ZrCl_2$: C, 71.28; H, 5.25. Found: C, 63.48, 63.71; H, 4.46, 4.57.

$Ph_2C(\eta^5$-3-(2-adamantyl)-$C_5H_3)(\eta^5$-$C_{13}H_8)HfCl_2$ (5). In the glovebox, 3.388 g of Ph_2C(3-(2-adamantyl)C_5H_3)($C_{13}H_8$)Li_2 (6.244 mmol, prepared as given in the alternate preparation of **3**) was combined with $HfCl_4$ (2.000 g, 6.244 mmol) in a 100 mL round-bottom flask. This was equipped with a 180° needle valve, and 60 mL of petroleum ether was condensed in by vacuum transfer at −78 °C. The vessel was warmed slowly, and after 30 h of stirring, the solvent was removed. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of methylene chloride. The obtained solution was filtered through a frit and condensed to 30 mL. After it stood for 1 h, the formed precipitate was collected on the frit and dried in vacuo: 1.547 g of product **5** was obtained (31.8%). A second crop was obtained from toluene: 1.237 g (57.3% for both crops). MS (LC-MS): *m*/*z* 778.8 (M$^+$). ^{1}H NMR (C_6D_6): δ 1.45−2.09 (m, 14H, adamantyl *H*), 3.41 (s, 1H, 2-*H* adamantyl), 5.68, 5.69 (s, 2H, Cp *H*), 6.21 (t, $^3J_{HH}$ = 3.0 Hz, 1H, Cp *H*), 6.93, 6.98, 7.02, 7.04, 7.12, 7.14 (t, $^3J_{HH}$ = 7.3, 7.3, 7.7, 7.7, 8.0, 8.0 Hz, 6H, phenyl *H*), 7.60, 7.60, 7.83, 7.96 (d, $^3J_{HH}$ = 7.4, 7.4, 8.1, 7.7 Hz, 4H, phenyl *H*), 6.54, 6.60, 7.89, 7.89 (d, $^3J_{HH}$ = 8.8, 9.2, 8.4, 8.4 Hz, 4H, Flu *H*), 6.71, 6.77, 7.26, 7.31 (t, $^3J_{HH}$ = 7.7, 7.7, 7.3, 7.0 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 27.91, 28.01, 32.42, 32.47, 32.59, 32.72, 37.93, 38.53, 38.67 (adamantyl *C*), 43.83 (2-*C* adamantyl), 101.61, 101.92, 115.20 (Cp *C*H$_1$), 120.19, 120.27, 121.51, 121.87 (Flu *C*H$_0$), 123.62, 123.83, 124.45, 124.57, 124.79, 124.92, 126.68, 126.68, 127.18, 127.24, 127.84, 127.85, 128.99, 128.99, 129.12, 129.12, 129.29, 129.41 (phenyl and Flu *C*H$_1$), 137.91 (9-Flu *C*), 145.28, 145.38 (ipso *C*), other *C*H$_0$ not determined. Anal. Calcd for $C_{41}H_{36}HfCl_2$: C, 63.29; H, 4.66. Found: C, 66.36, 66.16; H, 4.66, 4.69.

6,6-Norbornylidenefulvene. Norcamphor (10.00 g, 90.8 mmol), sodium methoxide (12.0 g, 222 mmol), and 100 mL of methanol were added to a 250 mL flask. The solids were dissolved before addition of cyclopentadiene (12.0 g, 182 mmol). After the mixture was stirred for 68 h, 200 mL of water and 100 mL of diethyl ether were added to the deep red solution. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to yield the crude product in quantitative yield.

Norbornylcyclopentadiene. 6,6-Norbornylidenefulvene (14.37 g, 90.8 mmol) dissolved in 100 mL of tetrahydrofuran was cooled to 0 °C before $LiAlH_4$ (5.00 g, 132 mmol) was added over 2 min. After the reaction mixture was stirred at room temperature for 17 h, it was cooled to 0 °C and 100 mL of water was added dropwise over 1 h. Then, 200 mL of water/50 mL of concentrated aqueous HCl and 100 mL of diethyl ether were added. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the crude product as a light yellow oil in quantitative yield. The stereochemistry is assumed to be endo on the basis of reduction of 2-methylenenorbornane and norbornan-2-one at the exo face to give predominantly endo products.[26]

3-(2-Norbornyl)-6,6-dimethylfulvene. Sodium methoxide (4.00 g, 74.0 mmol) was added to a solution of norbornylcyclopentadiene (8.00 g, 49.9 mmol) in 50 mL of methanol. Acetone (15.8 g, 270 mmol) was added, and the reaction mixture stirred for 48 h when 200 mL of water and 100 mL of diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (4 × 50 mL). The organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the crude product as a yellow oil, which was purified by in vacuo drying and passing through a short column of alumina: 8.18 g (81.8%). MS (GC-MS): *m*/*z* 200.3 (M$^+$).

Me_2C(3-(2-norbornyl)C_5H_3)($C_{13}H_8$)H_2. A 250 mL flask was charged with fluorene (3.32 g, 20.0 mmol), evacuated, and back-filled with argon before 60 mL of tetrahydrofuran and 13.0 mL of *n*-butyllithium in hexanes (1.6 M, 20.8 mmol) were syringed in. The orange solution was stirred for 30 min before 3-(2-norbornyl)-6,6-dimethylfulvene (4.00 g, 20.0 mmol) was syringed in. Following an additional 20 h, the stirred reaction mixture was quenched by addition of 60 mL of aqueous NH_4Cl. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to give 7.32 g of product as a light yellow oil in quantitative yield.

Me_2C(3-(2-norbornyl)C_5H_3)($C_{13}H_8$)Li_2. A swivel frit was charged with Me_2C(3-(2-norbornyl)C_5H_3)($C_{13}H_8$)H_2 (7.32 g, 20.0 mmol) and evacuated before 50 mL of diethyl ether was condensed in. To the solution was added 26.0 mL of *n*-butyllithium in hexanes (1.6 M, 41.6 mmol) at 0 °C over 1 min. The reaction mixture was stirred at room temperature for 18 h before the solvent was removed, and 50 mL of petroleum ether was added by vacuum transfer. After the mixture was stirred, the solvent was decanted from the red oil and the oil dried in vacuo to provide the product in quantitative yield as a red-yellow powder.

Me_2C(3-(2-norbornyl)C_5H_3)($C_{13}H_8$)$ZrCl_2$ (6). In the glovebox, 2.44 g of Me_2C(3-(2-norbornyl)C_5H_3)($C_{13}H_8$)Li_2 (6.44 mmol) was combined with $ZrCl_4$ (1.50 g, 6.44 mmol) in a 100 mL round-bottom flask. This was equipped with a 180° needle valve, and 40 mL of petroleum ether was condensed in by vacuum transfer at −78 °C. The vessel was warmed slowly, and after 24 h of stirring, the solvent was removed. Then 30 mL of dichloromethane was added and removed, followed by addition and removal of 30 mL of diethyl ether. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of diethyl ether. The filtrate volume was reduced to 30 mL, and the precipitated product was collected on a swivel frit and dried in vacuo: 1.26 g of **5** (37.2%) in a 54:46 diastereomeric ratio. MS (LC-MS): *m*/*z* 526.6 (M$^+$). Spectroscopic data for the major diastereomer (54%) are as follows. ^{1}H NMR (C_6D_6): δ 1.01−1.35 (m, 8H, norbornyl *H*), 1.89−2.07 (m, 2H, norbornyl *H*), 1.82, 1.83 (s, 6 H, C(C*H*$_3$)$_2$), 3.20 (m, 1H, 2-*H* norbornyl), 5.42, 5.45, 6.09 (t, $^3J_{HH}$ = 3.3, 3.3, 2.9 Hz, 3H, Cp *H*), 7.00, 7.03, 7.35, 7.35 (t, $^3J_{HH}$ = 7.7, 7.7, 7.3, 7.3 Hz, 4H, Flu *H*), 7.45, 7.47, 7.84, 7.86 (d, $^3J_{HH}$ = 8.1, 8.8, 8.4, 8.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 23.52, 29.71, 34.05, 37.25, 40.13, 41.00, 43.61, (norbornyl *C*), 28.58, 28.66 (*C*H$_3$), 40.51 (CH$_3$*C*CH$_3$), 65.70, 79.12, 114.31, 122.59, 122.88, 123.15, 140.29 (Cp and Flu *C*H$_0$), 102.73, 103.79, 116.17 (Cp *C*H$_1$), 123.49, 123.58, 124.64, 124.74, 124.80, 124.84, 128.76, 128.84 (Flu *C*H$_1$). Spectroscopic data for the minor diastereomer (46%) are as follows. ^{1}H NMR (C_6D_6): δ 1.01−1.35 (m, 8H, norbornyl *H*), 1.89−2.07 (m, 2H, norbornyl *H*), 1.79, 1.83 (s, 6 H, C(C*H*$_3$)$_2$), 3.13 (m, 1H, 2-*H* norbornyl), 5.23, 5.54, 6.04 (t, $^3J_{HH}$ = 3.0, 2.9, 2.9 Hz, 3H, Cp *H*), 6.98, 7.03, 7.30, 7.30 (t, $^3J_{HH}$ = 7.7, 7.7, 7.7, 7.7 Hz, 4H, Flu *H*), 7.43, 7.45, 7.83, 7.84 (d, $^3J_{HH}$ = 8.4, 8.1, 8.4, 8.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 23.68, 29.80, 34.17, 36.97, 39.39, 41.53, 43.29, (norbornyl *C*), 28.58, 28.58 (*C*H$_3$), 40.55 (CH$_3$*C*CH$_3$), 65.65, 79.02, 113.27, 122.55, 122.88, 123.40, 138.57 (Cp and Flu *C*H$_0$), 102.31, 103.69,

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[26] (a) Senda, Y.; Ohno, A.; Ishiyama, J.; Imaizumi, S.; Kamiyama, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 613−616. (b) Kropp, P. J.; Adkins, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2709−2717.

117.44 (Cp *C*H$_1$), 123.37, 123.71, 124.64, 124.74, 124.80, 124.84, 128.84, 128.92 (Flu *C*H$_1$). Anal. Calcd for $C_{28}H_{28}ZrCl_2$: C, 63.86; H, 5.36. Found: C, 61.78, 61.58; H, 5.03, 5.23.

3-(2-Norbornyl)-6,6-diphenylfulvene. A 500 mL round-bottom flask was charged with a solution of norbornylcyclopentadiene (7.39 g, 46.1 mmol) and benzophenone (8.41 g, 46.2 mmol) in 100 mL of absolute ethanol. NaOMe (5.50 g, 102 mmol) was added, and the orange solution was stirred for 61 days before 100 mL of H_2O and 100 mL of diethyl ether were added. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide 14.88 g of red oily material. This was subjected to Kugelrohr distillation under high vacuum at 80−100 °C, leaving behind 9.30 g of red oil. This was Kugelrohred at 100−160 °C to afford 7.05 g of product as a viscous red oil (47.1%).

$Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)H_2$. In the glovebox, a 100 mL round-bottom flask was charged with 3-(2-norbornyl)-6,6-diphenylfulvene (7.05 g, 21.7 mmol) and fluorenyllithium diethyl ether adduct (5.35 g, 21.7 mmol). This flask was equipped with a 180° needle valve, and 60 mL of diethyl ether was condensed into the reaction vessel. After the mixture was stirred with intermittent heating by a warm water bath for 11 days, 20 mL of H_2O was slowly added. The precipitate that eventually formed was collected by suction filtration and dried in vacuo: yield 6.136 g (57.6%). MS (GC-MS): *m*/*z* 490.6 (M^+). Anal. Calcd for $C_{38}H_{34}$: C, 93.02; H, 6.98. Found: C, 78.93, 79.39; H, 5.27, 5.25.

$Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)Li_2$. A swivel frit was charged with $Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)H_2$ (6.136 g, 12.50 mmol) and evacuated before 60 mL of diethyl ether was condensed in. To the white slurry was added 17.0 mL of *n*-butyllithium in hexanes (1.6 M, 27.2 mmol) at room temperature over 3 min, giving a homogeneous solution, which began precipitation after 20 min. The reaction mixture was stirred at room temperature for 15 h, and the yellow precipitate was collected and dried in vacuo to give the product in quantitative yield.

$Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (7). In the glovebox, 3.24 g of $Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)Li_2$ (6.44 mmol) was combined with $ZrCl_4$ (1.50 g, 6.44 mmol) in a 100 mL round-bottom flask. This was equipped with a 180° needle valve, and 60 mL of petroleum ether was condensed in by vacuum transfer at −78 °C. The vessel was warmed slowly, and after 24 h of stirring, the solvent was removed. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of methylene chloride. The solvent was removed and the solid redissolved in 75 mL of toluene and 25 mL of methylene chloride. The obtained solution was filtered through a frit, all solvent was removed, and 40 mL of toluene was condensed in. The orange solid was broken up, stirred, collected on the frit, and dried in vacuo to afford the product **5** in a 64:36 diastereomeric ratio: yield 1.81 g (43.2%). MS (LC-MS): *m*/*z* 650.5 (M^+). Spectroscopic data for the major diastereomer (64%) are as follows. ^{1}H NMR (C_6D_6): δ 0.99−1.40 (m, 8H, norbornyl *H*), 1.83−2.09 (m, 2H, norbornyl *H*), 3.09 (m, 1H, 2-*H* norbornyl), 5.53, 5.71, 6.19 (t, $^3J_{HH}$ = 3.0, 2.9, 2.6 Hz, 3H, Cp *H*), 6.91−7.13 (m, 6H, phenyl *H*), 7.56, 7.56, 7.75, 7.75 (d, $^3J_{HH}$ = 8.1, 8.1, 7.7, 7.7 Hz, 4H, phenyl *H*), 6.49, 6.53, 7.89, 7.89 (d, $^3J_{HH}$ = 8.8, 8.8, 8.1, 8.1 Hz, 4H, Flu *H*), 6.78, 6.81, 7.31, 7.33 (t, $^3J_{HH}$ = 7.7, 7.7, 8.4, 8.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 23.91, 29.78, 34.42, 37.34, 40.19, 41.64, 43.41 (norbornyl *C*), 58.33 (Ph*C*Ph), 78.20, 109.96, 121.26, 121.61, 123.10, 123.30, 138.11, 145.00, 145.00 (Cp, phenyl, and Flu *C*H$_0$), 104.38, 105.22, 115.76 (Cp *C*H$_1$), 123.97, 123.97, 124.61, 124.69, 125.30, 125.30, 126.68, 126.73, 127.26, 127.31, 128.03, 128.11, 128.23, 129.05, 129.08, 129.17, 129.29, 129.36 (phenyl and Flu *C*H$_1$). Spectroscopic data for the minor diastereomer are as follows. ^{1}H NMR (C_6D_6): δ 0.99−1.40 (m, 8H, norbornyl *H*), 1.83−2.09 (m, 2H, norbornyl *H*), 3.19 (m, 1H, 2-*H* norbornyl), 5.66, 5.80, 6.11 (t, $^3J_{HH}$ = 2.9, 2.9, 2.6 Hz, 3H, Cp *H*), 6.91−7.13 (m, 6H, phenyl *H*), 7.58, 7.60, 7.79, 7.79 (d, $^3J_{HH}$ = 8.1, 8.1, 8.0, 8.0 Hz, 4H, phenyl *H*), 6.45, 6.58, 7.91, 7.91 (d, $^3J_{HH}$ = 8.8, 8.8, 8.1, 8.1 Hz, 4H, Flu *H*), 6.76, 6.78, 7.29, 7.33 (t, $^3J_{HH}$ = 7.7, 7.7, 8.4, 8.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 23.88, 29.66, 34.14, 37.02, 39.45, 40.93, 44.04 (norbornyl *C*), 58.33 (Ph*C*Ph), 78.43, 108.97, 121.37, 121.50, 123.00, 123.30, 139.95, 144.92, 145.20 (Cp, phenyl, and Flu *C*H$_0$), 103.63, 105.16, 116.84 (Cp *C*H$_1$), 123.67, 124.07, 124.61, 124.74, 125.13, 125.39, 126.57, 126.64, 127.26, 127.31, 128.09, 128.11, 128.18, 129.08, 129.17, 129.29, 129.36, 129.45 (phenyl and Flu *C*H$_1$). Anal. Calcd for $C_{38}H_{32}ZrCl_2$: C, 70.13; H, 4.96. Found: C, 71.10, 70.50; H, 4.71, 4.64.

6,6-(3,3,5,5-Tetramethylcyclohexylidene)fulvene. Hexane-washed sodium spheres (2.40 g, 104 mmol) were slowly added to 100 mL of absolute ethanol. The sodium had fully reacted before cyclopentadiene (6.0 mL, 72.6 mmol) and 3,3,5,5-tetramethylcyclohexanone (10.0 mL, 57.1 mmol) were added. After 30 h, the reaction mixture was poured into 200 mL of water and 100 mL of diethyl ether was added. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were extracted with water (3 × 50 mL), dried over $MgSO_4$, filtered, and rotavapped to produce the product in quantitative yield as a yellow oil. MS (GC-MS): *m*/*z* 202.3 (M^+). ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 12H, C*H*$_3$), 1.04 (s, 2H, C*H*$_2$), 2.39 (s, 4H, C*H*$_2$), 6.52, 6.52 (m, 4H, fulvene *H*).

1-(Cyclopentadienyl)-3,3,5,5-tetramethylcyclohexane. A 500 mL flask was charged with $LiAlH_4$ (2.50 g, 65.9 mmol) and 200 mL of tetrahydrofuran. An addition funnel containing 6,6-(3,3,5,5-tetramethylcyclohexylidene)fulvene (11.89 g, 58.8 mmol) dissolved in 50 mL of tetrahydrofuran was attached. The vessel was cooled to 0 °C before dropwise addition over 25 min. After 17 h of stirring at room temperature, the vessel was cooled to 0 °C and 20 mL of water was added dropwise. Then, aqueous NH_4Cl (100 mL) and water (200 mL) were added before the organic layer was isolated. A 15 mL amount of concentrated aqueous HCl was added to the aqueous layer, and it was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide 11.87 g of product (98.8%) as a light orange oil. MS (GC-MS): *m*/*z* 204.3 (M^+).

3-(3,3,5,5-Tetramethylcyclohexyl)-6,6-dimethylfulvene. A 500 mL flask was charged with 1-(cyclopentadienyl)-3,3,5,5-tetramethylcyclohexane (11.87 g, 58.1 mmol), 100 mL of methanol, acetone (30 mL, 430 mmol), and pyrrolidine (1.0 mL, 12 mmol). After the mixture was stirred for 52 h, 5 mL of acetic acid was added, along with 200 mL of water and 100 mL of diethyl ether. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were extracted with H_2O (3 × 30 mL) and 10% aqueous NaOH (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, rotavapped, dried in vacuo, and pushed through a short column of alumina to provide the product in quantitative yield as a yellow oil. MS (GC-MS): *m*/*z* 244.4 (M^+).

$Me_2C(3\text{-}(3,3,5,5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)H_2$. A 250 mL flask was charged with fluorene (3.69 g, 22.2 mmol), evacuated, and back-filled with argon before 60 mL of tetrahydrofuran and 14.0 mL of *n*-butyllithium in hexanes (1.6 M, 22.4 mmol) were syringed in. The orange solution was stirred for 2 h before 3-(3,3,5,5-tetramethylcyclohexyl)-6,6-dimethylfulvene (5.42 g, 22.2 mmol) was syringed in. Following an additional 6 h, the stirred reaction mixture was quenched by addition of 60 mL of aqueous NH_4Cl. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give 8.75 g of product as a light yellow oil (96.1%).

$Me_2C(3\text{-}(3,3,5,5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)Li_2$. A round-bottom flask containing 8.75 g (21.3 mmol) of $Me_2C(3\text{-}(3,3,5,5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)H_2$ was attached to a swivel frit and evacuated before 75 mL of diethyl ether was condensed in. At 0 °C, 28.0 mL of *n*-butyllithium in hexanes (1.6 M, 44.8 mmol) was syringed in over 2 min. After the mixture was stirred for 15 h at room temperature, solvent was removed and 75 mL of petroleum ether was condensed in. Solvent was decanted from the viscous oil, and the remaining material was dried in vacuo, yielding 8.29 g (92.0%) of the product as a bright orange powder.

$Me_2C(\eta^5$-3-(3,3,5,5-tetramethylcyclohexyl)$C_5H_3)(\eta^5$-$C_{13}H_8)ZrCl_2$ (8). In the glovebox, 1.81 g of Me_2C(3-(3,3,5,5-tetramethylcyclohexyl)$C_5H_3)(C_{13}H_8)Li_2$ (4.29 mmol) was combined with $ZrCl_4$ (1.00 g, 4.29 mmol) in a 100 mL round-bottom flask. This was attached to a swivel frit and 50 mL of petroleum ether was condensed in by vacuum transfer at −78 °C. The vessel was warmed slowly, and after 15 h of stirring, the solvent was removed. A 40 mL portion of methylene chloride was condensed in; the solution was warmed and stirred before solvent removal. Then, 30 mL of diethyl ether was condensed in and the slurry was warmed and stirred. The obtained orange solid was extracted several times on the frit with refluxing diethyl ether before the filtrate was condensed to 20 mL. The precipitate was collected on the frit and dried in vacuo to afford the product **7**: yield 0.16 g (6.6%). Second and third crops were obtained: 0.13 and 0.23 g (21.2% for all three crops). MS (LC-MS): *m*/*z* 570.6 (M^+). ^1H NMR (CD_2Cl_2): δ 0.83, 0.83, 0.90, 0.99 (s, 12H, cyclohexyl−C*H*$_3$), 0.88−1.27 (m, 6H, cyclohexyl *H*), 2.33, 2.35 (s, 6 H, C(C*H*$_3$)$_2$), 2.69 (t, $^3J_{HH}$ = 12.4 Hz, 1H, 1-*H* cyclohexyl), 5.46, 5.69, 5.99 (t, $^3J_{HH}$ = 2.6, 3.3, 2.6 Hz, 3H, Cp *H*), 7.24, 7.26, 7.51, 7.53 (t, $^3J_{HH}$ = 7.7, 7.7, 7.7, 7.5 Hz, 4H, Flu *H*), 7.82, 7.86, 8.12, 8.12 (d, $^3J_{HH}$ = 8.8, 9.2, 8.4, 8.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 26.77, 27.23, 28.47, 28.52, 28.62, 28.67 (*C*H$_3$), 31.44 (1-cyclohexyl *C*), 32.05, 39.71, 40.50, 43.45, 49.00, 52.01 (cyclohexyl and Me*C*Me *C*H$_0$ and *C*H$_2$), 102.69, 102.74, 115.19 (Cp *C*H$_1$), 123.56, 123.58, 123.58, 124.62, 124.73, 124.73, 124.78, 124.80 (benzo *C*H$_1$), 141.29 (9-Flu *C*), *C*H$_0$ not determined. Anal. Calcd for $C_{31}H_{36}ZrCl_2$: C, 65.24; H, 6.36. Found: C, 60.96, 61.75; H, 5.53, 5.60.

3,6,6-Trimethylfulvene. A 1 L flask was charged with 400 mL of methanol, methylcyclopentadiene (120.0 mL, 1.21 mol), acetone (200 mL, 2.72 mol), and pyrrolidine (40.0 mL, 0.464 mol). After the orange solution was stirred for 71 h, 50 mL of acetic acid was added, followed by 1200 mL of H_2O and 200 mL of diethyl ether. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (5 × 100 mL). The combined organic layers were extracted with H_2O (3 × 30 mL) and 10% aqueous NaOH (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, and rotavapped to give 158.8 g of a red-orange oil that was subjected to Kugelrohr distillation under high vacuum. The first 15 g of material that distilled at room temperature was discarded, and the product was obtained from the second fraction that was distilled at 50 °C: yield 136.58 g (94.0%).

Me_2C(3-methyl-$C_5H_3)(C_{13}H_8)H_2$. A 500 mL round-bottom flask was charged with fluorene (55.32 g, 332.8 mmol). This was equipped with a 180° needle valve, evacuated, and backfilled with argon before 240 mL of diethyl ether was added via syringe. A 210.0 mL portion of *n*-butyllithium in hexanes (1.6 M, 336.0 mmol) was syringed in at room temperature over 20 min. After the obtained yellow slurry was shaken and stirred for 1 h, 3,6,6-trimethylfulvene (40.00 g, 332.8 mmol) was syringed in over 25 min, providing a clear red solution. After this mixture was stirred for 17 h, the vessel was cooled to 0 °C and 60 mL of aqueous NH_4Cl solution was added. The slurry was filtered and the aqueous layer removed. The obtained solid was extracted from a cellulose extraction thimble with 500 mL of diethyl ether/hexanes for 2 days. The first crop was obtained by filtration of the cooled filtrate: 28.45 g following in vacuo drying (29.9%). The second and third crops were obtained by filtration of the chilled (−78 °C) filtrate and amounted to 11.86 and 1.08 g, respectively (43.4% for all three crops). MS (GC-MS): *m*/*z* 286.3 (M^+). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 90.99, 90.92; H, 7.21, 7.21.

2,6,6-trimethyl-4-(C(methyl)$_2$(9-fluorenyl))fulvene. An 11.86 g amount of Me_2C(3-Me-$C_5H_3)(C_{13}H_8)H_2$ (41.41 mmol) was combined with 200 mL of acetone (2720 mmol) and 15.0 mL of pyrrolidine (180 mmol). After the mixture was stirred for 30 min, a homogeneous solution was obtained and stirring was ceased. The product slowly crystallized, and after 30 days the yellow crystals were collected by filtration. These were combined with 100 mL of methanol, and the mixture was brought to a boil for 4 h and stirred overnight as the vessel was cooled. Collection by suction filtration, rinsing with 25 mL of methanol, and in vacuo drying afforded 8.15 g of the desired product (60.3%). MS (GC-MS): *m*/*z* 326.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.02, 1.02 (s, 6H, C(C*H*$_3$)$_2$Flu), 2.16, 2.25, 2.53 (s, 9H, 2,6,6-C*H*$_3$ fulvene), 4.13 (s, 1H, 9-*H* Flu), 5.96, 6.54 (s, 2H, 3,5-*H* fulvene), 7.15, 7.31 (t, $^3J_{HH}$ = 7.4, 7.4 Hz, 4H, Flu *H*), 7.28, 7.70 (s, $^3J_{HH}$ = 7.3, 7.7 Hz, 4H, Flu *H*). ^{13}C NMR ($CDCl_3$): δ 19.04, 22.46, 24.53, 24.53, 25.18 (*C*H$_3$), 39.38 (*C*H$_0$), 55.66 (9-Flu *C*H$_1$), 114.78, 130.54 (fulvene *C*H$_1$), 119.30, 119.30, 126.07, 126.07, 126.52, 126.52, 126.92, 126.93 (Flu *C*H$_1$), 132.75, 133.98, 140.86, 151.75 (fulvene *C*H$_0$), 142.04, 142.04, 145.54, 145.54 (Flu *C*H$_0$). Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 90.83, 91.12; H, 7.33, 7.26.

Me_2C(3-*t*-Bu-4-Me-$C_5H_2)(C_{13}H_8)H_2$. A 250 mL round-bottom flask was charged with 5.087 g of 2,6,6-trimethyl-4-(C(methyl)$_2$(9-fluorenyl))fulvene (15.58 mmol). This flask was evacuated before 100 mL diethyl ether was condensed in. A 75.0 mL portion of methyllithium in diethyl ether (1.4 M, 105 mmol) was added by syringe, giving an orange homogeneous solution after 1 h. After 1 month of stirring, a small amount of orange precipitate was found. The amount slowly increased, and after 47 days total, the orange slurry was cooled to 0 °C and slowly quenched with 60 mL of H_2O. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the product in quantitative yield (5.34 g) as a light yellow oil, which slowly began to crystallize.

Me_2C(3-*t*-Bu-4-Me-$C_5H_2)(C_{13}H_8)Li_2$. A round-bottom flask containing 5.34 g (15.6 mmol) of Me_2C(3-*t*-Bu-4-Me-$C_5H_2)(C_{13}H_8)H_2$ was attached to a swivel frit and evacuated before 75 mL of diethyl ether was condensed in. At 0 °C, 22.0 mL of *n*-butyllithium in hexanes (1.6 M, 32.5 mmol) was syringed in over 1 min. After the mixture was stirred for 15 h at room temperature, an orange precipitate was collected and dried in vacuo: yield 5.37 g (97.3%).

$Me_2C(\eta^5$-3-*t*-Bu-4-Me-$C_5H_2)(\eta^5$-$C_{13}H_8)ZrCl_2$ (9). In the glovebox, 2.28 g of Me_2C(3-*t*-Bu-4-Me-$C_5H_2)(C_{13}H_8)Li_2$ (6.44 mmol) was combined with $ZrCl_4$ (1.50 g, 6.44 mmol) in a 100 mL round-bottom flask. This flask was equipped with a 180° needle valve, and 50 mL of petroleum ether was condensed in by vacuum transfer at −78 °C. The vessel was warmed slowly, and after 23 h of stirring, the solvent was removed. A 30 mL portion of methylene chloride was condensed in, the solution was warmed and stirred before solvent removal, 30 mL of diethyl ether was condensed in, and the slurry was warmed and stirred before solvent removal. The obtained solid was extracted overnight in a cellulose extraction thimble with 150 mL of methylene chloride. The obtained solution was filtered through a frit, all solvent was removed, and 50 mL of diethyl ether was condensed in. The pink solid was broken up, stirred, collected on the frit, and dried in vacuo to afford the product **9**: 1.60 g (49.5%). MS (LC-MS): *m*/*z* 502.3 (M^+). ^1H NMR (C_6D_6): δ 1.25 (s, 9H, C(C*H*$_3$)$_3$), 1.82, 1.85 (s, 6 H, C(C*H*$_3$)$_2$), 2.09 (s, 3H, Cp C*H*$_3$), 5.20, 5.50 (d, $^3J_{HH}$ = 3.6, 3.6 Hz, 3H, Cp *H*), 6.98, 6.98, 7.31, 7.31 (t, $^3J_{HH}$ = 7.0, 7.0, 7.3, 7.3 Hz, 4H, Flu *H*), 7.41, 7.47, 7.82, 7.85 (d, $^3J_{HH}$ = 8.4, 8.4, 8.0, 8.4 Hz, 4H, Flu *H*). ^{13}C NMR (CD_2Cl_2): δ 16.08, 28.24, 28.75 (*C*H$_3$), 29.17 (C(*C*H$_3$)$_3$), 33.52, 39.85 (*C*H$_0$), 78.40, 110.49, 121.76, 123.65, 123.79, 128.00, 140.84 (Cp and Flu *C*H$_0$), 102.93, 108.11 (Cp *C*H$_1$), 123.42, 123.64, 124.45, 124.55, 124.68, 124.96, 128.33, 128.80 (Flu *C*H$_1$). Anal. Calcd for $C_{26}H_{28}ZrCl_2$: C, 62.13; H, 5.61. Found: C, 60.88, 60.89; H, 4.90, 4.94.

Propylene Polymerization Procedures. *Caution! All polymerization procedures should be performed behind a blast shield.* The polymerization reaction apparatus was prepared in nitrogen-filled gloveboxes. Methylaluminoxane (MAO) was purchased as a toluene solution from Albemarle Corp. 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 6110 drying system equipped with an OXYSORB column. Polymerizations were conducted in Lab Crest glass reaction vessels (12 oz for propylene volumes greater than 60 mL or 3 oz for propylene volumes less than 60 mL), and mixtures were stirred with a magnetic stir bar. Monomer was condensed into the vessel over several minutes at 0 °C. The vessel was then equilibrated at either 0 or 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 reaction mixtures 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. Toluene and methanol were removed from the obtained polymers by in vacuo drying.

Representative Polymerization Procedures. Entry 8. In the glovebox, a 12 oz Lab Crest pressure reactor was charged with MAO (1.260 g, 21.7 mmol of [Al]). Propylene (350 mL) was condensed in at 0 °C over 2 h. A solution of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (**4**; 0.015 g, 0.022 mmol) in toluene (2.0 mL) was injected and the reaction mixture stirred in a 0 °C ice/water bath for 90 min. The reaction mixture was vented and quenched with methanol/HCl.

Entry 15. In the glovebox, a 3 oz Lab Crest pressure reactor was charged with MAO (1.118 g, 19.3 mmol of [Al]). Propylene (55 mL) was condensed in at 0 °C over 20 min. The vessel was then equilibrated at 20 °C for 10 min with a water bath. A solution of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)HfCl_2$ (**5**; 0.015 g, 0.019 mmol) in toluene (2.0 mL) was injected and the reaction mixture stirred in a 20 °C water bath for 60 min. The reaction mixture was vented and quenched with methanol/HCl.

Polymer Characterization. Polymer melting temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC 7). Typically four or five scans (from 50 to 200 °C at 10 °C/min) were required to find similar melting temperatures among the last two or three scans. Certain melting temperatures (entries in Table 2: 8−12, 15, 18, 19, and 24) were determined by BP-Amoco with a scan rate of 20 °C/min. Polymer molecular weights were determined by BP-Amoco and by ExxonMobil.

Mechanical properties were determined by BP-Amoco (entries 8 and 9) and by ExxonMobil (entries 5, 15, 18, and 24). BP-Amoco used the standard protocol, and the test specimens were compression-molded according to ASTM D1708. For mechanical testing, the crosshead separation rate was 50.8 cm/min. For the detailed mechanical testing protocol employed by ExxonMobil, see the Supporting Information.

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.[27] 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: Text giving the derivation of the isotactic block length distribution for isotactic−hemiisotactic polypropylene, details of the structure determination for **4**, including listings of final atomic coordinates, thermal parameters, and selected bond distances and angles, text giving the protocol for mechanical testing of polymers (entries 5, 15, 18, and 24), and figures and tables giving calculated isotactic block length distributions for entries 1, 3−5, 8−12, 15, 16, 18, 19, 20, and 22−24 (N_n for $n = 1-65$ and $\sum(N_n)$ for $n \geq 21$). This material is available free of charge via the Internet at http://pubs.acs.org.

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