Mechanism of Isotactic Polypropylene Formation with C_1-Symmetric Metallocene Catalysts

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Received September 29, 2005

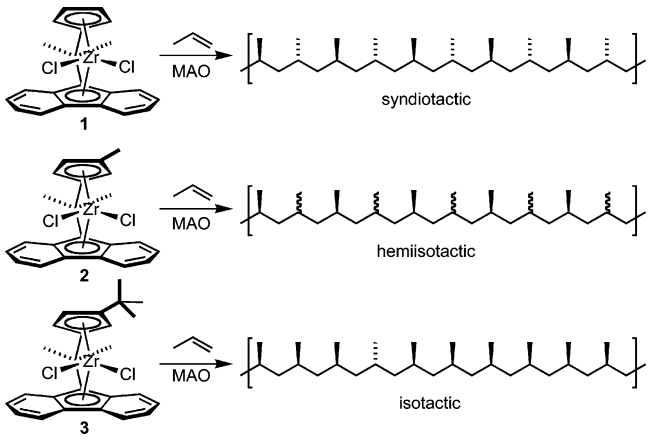
The mechanism for isotactic polypropylene formation by the C_1-symmetric catalyst system [Me_2C(3-*tert*-butyl-C_5H_3)($C_{13}H_8$)]$ZrCl_2$/MAO (MAO = methylaluminoxane, $C_{13}H_8$ = fluorenylidene) has been examined. Evidence supports an alternating mechanism, where both sites of the metallocene wedge are utilized for monomer insertion, rather than the previously proposed site epimerization (inversion at Zr) following each monomer insertion. As the polymerization temperature increases (0 to 60 °C) with lower concentrations of propylene, the site epimerization mechanism begins to compete, as evidenced by an increase in isotacticity. The alternating mechanism also accounts for polypropylene microstructures obtained with Me_2C(3-R-C_5H_3)(Oct)$ZrCl_2$/MAO, where Oct = octamethyloctahydrodibenzofluorenylidene and R = methyl, cyclohexyl, diphenylmethyl, and with Me_2C(3-*tert*-butyl-4-Me-C_5H_2)(Oct)$ZrCl_2$/MAO. For an Oct-containing catalyst system with R = 2-methyl-2-adamantyl, unprecedentedly high (for a fluorenyl-based metallocene catalyst) isotacticity ([*mmmm*] > 99%) is obtained; the polymer prepared at 0 °C has T_m = 167 °C and M_w = 370 000.

Introduction

Shortly following the report by Ewen, Razavi, et al.[1] demonstrating the MAO-cocatalyzed (MAO = methylaluminoxane) formation of syndiotactic polypropylene with C_s-symmetric fluorenyl-containing metallocenes of the type $Me_2C(C_5H_4)(C_{13}H_8)MCl_2$ (e.g., M = Zr, **1**), several authors prepared cyclopentadienyl-substituted variants of the parent metallocene. Incorporation of a substituent at the 3 position of the cyclopentadienyl ring effects desymmetrization of the metallocene to C_1 symmetry. As a consequence, the obtained polymers were no longer syndiotactic, but displayed alternative tacticities depending on the nature of the substituent (Scheme 1).

Ewen,[2] Spaleck,[3] and Razavi[4] have each reported on C_1-symmetric fluorenyl-containing metallocenes and their behavior in propylene polymerizations. The parent C_s-symmetric zirconocene **1** (Scheme 1) produces syndiotactic polypropylene via a Cossée−Arlman[5] type chain migratory insertion mechanism in which monomer insertions occur sequentially at alternating sites of the metallocene.[6] Similarly, the hemiisotactic polypropylene produced by **2** is best explained by the same Cossée−Arlman type mechanism in which one site is enantioselective and the other site is aselective.[7] In contrast, **3** produces isotactic polypropylene.[8] The mechanism of isotactic polypropylene formation with this C_1-symmetric metallocene is still a topic of debate.

Scheme 1



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(1) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.

(2) (a) 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. (b) Ewen, J. A. Eur. Pat. Appl. EP 423101, 1989. (c) Ewen, J. A. *Macromol. Symp.* **1995**, *89*, 181−196. (d) Ewen, J. A.; Elder, M. J. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, 1995; pp 99−109.

(3) (a) Dolle, V.; Rohrmann, J.; Winter, A.; Antberg, M.; Klein, R. Eur. Pat. Appl. EP 399347, 1991. (b) Antberg, M.; Dolle, V.; Klein, R.; Rohrmann, J.; Spaleck, W.; Winter, A. In *Studies in Surface Science and Catalysis (Catalytic Olefin Polymerization, Volume 56)*; Keii, T., Soga, K., Eds.; Kodansha: Tokyo, 1990; pp 501−515. (c) Spaleck, W.; Antberg, M.; Aulbach, M.; Bachmann, B.; Dolle, V.; Haftka, S.; Küber, F.; Rohrmann, J.; Winter, A. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, 1995; pp 83−97. (d) Spaleck, W.; Aulbach, M.; Bachmann, B.; Küber, F.; Winter, A. *Macromol. Symp.* **1995**, *89*, 237−247.

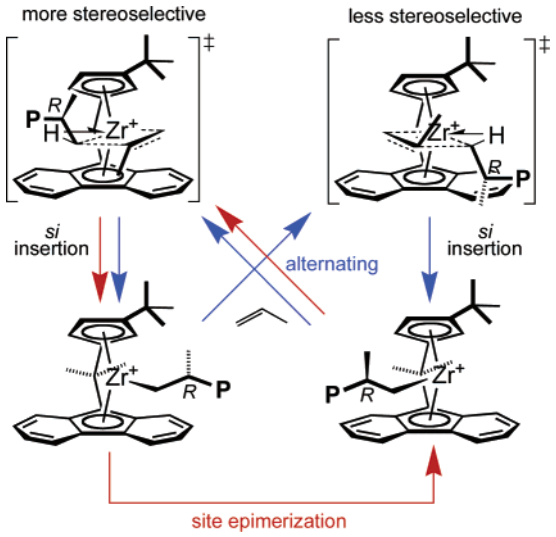
(4) (a) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1996**, *520*, 115−120. (b) Razavi, A.; Vereecke, D.; Peters, L.; Den Dauw, K.; Nafpliotis, L.; Atwood, J. L. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, 1995; pp 111−147. (c) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1995**, *497*, 105−111. (d) Razavi. A.; Peters, L.; Nafpliotis, L.; Vereecke, D.; Dendauw, K.; Atwood, J. L.; Thewald, U. *Macromol. Symp.* **1995**, *89*, 345−367.

(5) (a) Cossée, P. *J. Catal.* **1964**, *3*, 80−88. (b) Arlman, E. J. *J. Catal.* **1964**, *3*, 89−98. (c) Arlman, E. J.; Cossée, P. *J. Catal.* **1964**, *3*, 99−104.

(6) For a detailed mechanistic analysis employing C_s-symmetric metallocenes, see: Veghini, D.; Henling, L.; Burkhardt, T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573.

10.1021/om050841k CCC: $33.50
Publication on Web 06/16/2006

Scheme 2



Proposed Mechanisms for Isotactic Polypropylene Formation with C_1-Symmetric Metallocene Catalysts. There are two limiting mechanisms possible for the formation of isotactic polypropylene with C_1-symmetric metallocene catalysts.[9] These are the *site epimerization* mechanism and the *alternating* mechanism (Scheme 2).

The majority of published reports for isotactic polypropylene formation with metallocenes based on **3** invoke the site epimerization[10] mechanism (red pathway) to account for the observed isoselectivity.[2c,d,3c,4a,b,11] As shown in Scheme 2 for one enantiomer of racemic **3**, the growing polymer chain is on the left side of the metallocene wedge directed up and away from the benzo substituent of the fluorenyl ligand in the transition state for monomer insertion at the more stereoselective site. The methyl group of the incoming monomer is directed down in a *trans* arrangement from the growing polymer chain. Following migratory insertion, the growing polymer chain is located on the more crowded, right side of the metallocene wedge and moves away from the bulky *tert*-butyl substituent in a unimolecular site epimerization process that inverts stereochemistry at the metal center. These two consecutive processes regenerate the original coordination site for monomer insertion. Hence, only one transition structure is employed, one that uses olefin coordination from one side of the metallocene for monomer insertion, according to a strict site epimerization model. One of the primary explanations offered in support of the site epimerization mechanism is that the *tert*-butyl side of the metallocene is too sterically crowded to accommodate the growing polymer chain. Calculations by Morokuma[12] suggest that the bulky substituent forbids the growing chain from residing nearby, necessitating a site epimerization following every insertion. Calculations by Fink[13] and Corradini,[14] however, are more forgiving and allow the insertion with the polymer chain proximal to the *tert*-butyl group.[15]

Also shown in Scheme 2 is a second limiting mechanism, the alternating (blue pathway) mechanism. Following monomer insertion at the more stereoselective site, the second site becomes available for monomer coordination. In the transition state for insertion at the less stereoselective site, the growing polymer chain is directed competitively by both the *tert*-butyl group (down) and the benzo substituent (up). In order for the resulting polymer to be isotactic, the *tert*-butyl group must prevail, and the growing polymer chain is preferentially directed toward the benzo substituent. Insertion ensues with a *trans* arrangement between the polymer chain and the methyl group of the inserting monomer; this regenerates the original coordination site. In contrast to the site epimerization mechanism, the alternating mechanism employs two sites for monomer insertion, using olefin coordination at both sides of the metallocene wedge, as is currently accepted for the syndioselective (**1**) and hemiisoselective (**2**) relatives of isoselective **3**.

Despite widespread support for the site epimerization mechanism, there has been little convincing evidence presented in its defense. We sought to experimentally test which of the two mechanisms, or combination thereof, most accurately describes

(7) For reviews of homogeneous, metallocene-mediated Ziegler−Natta olefin polymerizations, see: (a) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170, and references therein. (b) Janiak, C. In *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A.; Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; pp 547−623. (c) Kaminsky, W., Ed. *Metalorganic Catalysts for Synthesis and Polymerization, Recent Results by Ziegler−Natta and Metallocene Investigations*; Springer: Berlin, 1999. (d) Marks, T. J.; Stevens, J. C., Eds. *Top. Catal.* **1999**, *7*, 1−208. (e) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205−1221. (f) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252. (g) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345. (h) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457−1470. (i) Scheirs, J., Kaminsky, W., Eds. *Metallocene-Based Polyolefins: Preparation, Properties and Technology*; John Wiley & Sons: New York, 2000. (j) Kaminsky, W.; Scholz, V.; Werner, R. *Macromol. Symp.* **2000**, *159*, 9−17. (k) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982−3998.

(8) (a) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. EP 537130, 1993. (b) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181−193.

(9) A comparison of mechanisms for isoselective propylene polymerization using C_1-symmetric metallocene precatalysts is given by: Busico, V.; Cipullo, R.; Talarico, G.; Segre, A. L.; Chadwick, J. C. *Macromolecules* **1997**, *30*, 4786−4790.

(10) The term "site epimerization mechanism" is used in preference to other terms found in the literature. The term "epimerization" (Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; p 1198) refers to the inversion of a single stereocenter when two or more are present and can be correctly applied to metallocene polymerizations when the stereochemistry of the metal is inverted while the stereocenters present on the polymer chain remain unchanged. (a) "Consecutive addition": Farina, M.; Terragni, A. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 791−798. (b) "Skipped insertion": ref 2a. (c) "Skipped-out insertions" and "chain migratory catalyst isomerization": ref 2c. (d) "Back-skip mechanism": ref 2d. (e) "Retention mechanism": Di Silvestro, G.; Sozzani, P.; Terragni, A. *Macromol. Chem. Phys.* **1996**, *197*, 3209−3228. (f) "Isomerization without monomer insertion": Fink, G.; Herfert, N. *Preprints of the International Symposium on Advances in Olefin, Cycloolefin, and Diolefin Polymerization*; Lyon, 1992; p 15. (g) "Site-to-site chain migration": ref 3c. (h) "Side-to-side swing" and "back swing": ref 4a. (i) "Chain stationary insertion mechanism": ref 4b. (j) "Hindered chain migratory insertion": Razavi, A.; Bellia, V.; De Brauwer, Y.; Hortmann, K.; Lambrecht, M.; Miserque, O.; Peters, L.; Van Belle, S. In *Metalorganic Catalysts for Synthesis and Polymerization, Recent Results by Ziegler−Natta and Metallocene Investigations*; Kaminsky, W., Ed.; Springer: Berlin, 1999; pp 236−247.

(11) Hefert, N.; Fink, G. *Makromol. Chem. Macromol. Symp.* **1993**, *66*, 157−178.

(12) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1996**, *15*, 766−777.

(13) (a) van der Leek, Y.; Angermund, K.; Reffke, M.; Kleinschmidt, R.; Goretzki, R.; Fink, G. *Chem. Eur. J.* **1997**, *3*, 585−591. (b) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Macromol. Rapid Commun.* **2000**, *21*, 91−97.

(14) Corradini, P.; Cavallo, L.; Guerra, G. In *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; John Wiley & Sons: New York, 2000; pp 3−36.

(15) Straightforward examples of propylene insertion into sterically encumbered sites do exist for C_2-symmetric metallocenes: (a) Resconi, L.; Piemontesi, F.; Camurati, I.; Sudmeijer, O.; Nifant'ev, I. E.; Ivchenko, P. V.; Kuz'mina, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 2308−2321. (b) Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S.; Mercandelli, P.; Sironi, A. *Organometallics* **2000**, *19*, 420−429. This paper is concerned with the competitive insertion at open and encumbered sites when *both* are present in the same catalyst.

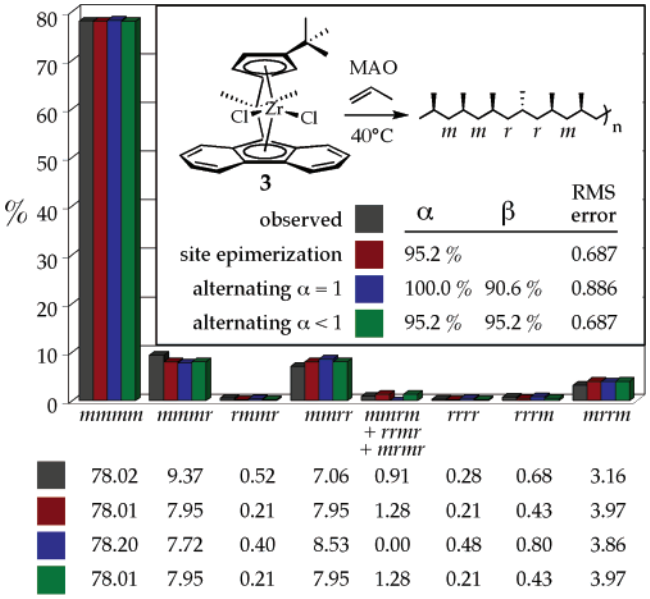


Figure 1. Statistical pentad analysis of a polypropylene sample (from ref 4a) made with **3**/MAO at 40 °C in liquid monomer.

the polymerization behavior of C_1-symmetric metallocene **3** and related catalysts.[16]

Results and Discussion

Expected Pentad Distributions. Polymer stereochemistry provides a permanent record of the stereochemical mechanism for monomer enchainment. Therefore, observed polymer tacticity can be compared to that predicted by each of the possible mechanisms. Figure 1 presents such a comparison. The pentad distribution reported for a polymer sample[4a] prepared with **3**/MAO in liquid monomer at 40 °C is subjected to three statistical models.

The first is enantiomorphic site control,[17] which is predicted by the site epimerization mechanism, since it employs a single site with enantioselectivity α. The second is an alternating model that is generally applicable to a catalyst that regularly alternates insertions between a perfectly stereoselective site (α = 1) and a variably stereoselective site having a stereoselectivity equal to β. This model employs a single independent parameter. The third is an alternating model that is applicable to a catalyst that regularly alternates insertions between two variably stereoselective sites. The stereoselectivity of one site is α, and the stereoselectivity of the other site is β. This model employs two independent parameters. Both alternating models assume that no site epimerization is occurring. For a derivation of these alternating models, see the Supporting Information.[18,19]

Unfortunately, the RMS errors[20] provided by these fits are too similar to draw definitive conclusions concerning which mechanism, site epimerization or alternating, better predicts the microstructure of the polypropylene produced. The enantiomorphic site control model predicts that **3**/MAO is employing one site with a stereoselectivity of 95.2%. The alternating model with α = 1 predicts that **3**/MAO employs two sites, one with a stereoselectivity of 100.0% and the other with a stereoselectivity of 90.6%. The alternating model with α < 1 predicts that **3**/MAO employs two sites, each with a stereoselectivity of 95.2%. For this model the dependence of the RMS error on α and β is somewhat shallow; for α = 97.0% and β = 93.0%, the rms error = 0.749, not significantly different from 0.687. Related polymers subjected to these models have also provided inconclusive results.[21]

Effect of Polymerization Temperature and Monomer Concentration on Isotacticity. For the site epimerization mechanism (Scheme 2), it is predicted that an increase in polymerization temperature or a decrease in monomer concentration will not significantly alter the polymer stereochemistry, since this mechanism employs a single propagative transition state with a stereoselectivity relatively independent of these parameters. However, the polymer microstructure will be sensitive to changes in polymerization temperature and monomer concentration, if the alternating mechanism is the principal pathway and the site epimerization pathway is accessible. As the polymerization temperature increases or the monomer concentration decreases, unimolecular site epimerization will become increasingly likely, relative to bimolecular propagation. To the extent that this occurs, the more stereoselective site will be employed at the expense of the less stereoselective site. Therefore, if the alternating mechanism is operating and the site epimerization mechanism is accessible, one would anticipate increased isotacticity with an increase in polymerization temperature or a decrease in monomer concentration.

The literature reports that propylene polymerizations with **3**/MAO conducted in liquid monomer at varying polymerization temperatures[4] result in a shallow dependence of isotacticity on polymerization temperature, as shown in Table 1. However, for a similar series of experiments conducted in *dilute* monomer (10 vol % in toluene), a more pronounced increase in isotacticity is found with an increase in polymerization temperature. Furthermore, a comparison between those polymerizations conducted in liquid monomer and those conducted in 10% monomer shows that higher isotacticity prevails under dilute monomer conditions with Δ[*mmmm*] values of 4.7%, 10.8%, and 11.9% for polymerization temperatures of 20, 40, and 60 °C, respectively. Although there are fewer runs to compare, polymerization system **4**/MAO reveals similar trends, albeit with diminished magnitude (Table 1).

These results demonstrate that isotacticity *can* increase with increasing polymerization temperature and decreasing monomer concentration. The two-site alternating mechanism is likely

(16) Perturbations introduced by a *chain epimerization* mechanism are expected to be minimal and are neglected in the initial treatment presented here. (a) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329−9330. (b) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667−6676. (c) Janiak, C. In *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; p 596.

(17) (a) Farina, M. *Top. Stereochem.* **1987**, *17*, 1−111. (b) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355−6364.

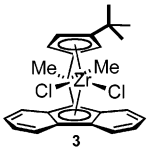
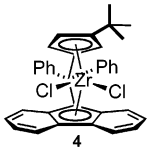
(18) Related models have been developed. (a) Reference 17a. (b) Farina, M.; Di Silvestro, G.; Sozzani, P. *Macromolecules* **1993**, *26*, 946−950. (c) Farina, M.; Terragni, A. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 791−798. (d) Farina, M.; Di Silvestro, G.; Terragni, A. *Macromol. Chem. Phys.* **1995**, *196*, 353−367. (e) Di Silvestro, G.; Sozzani, P.; Terragni, A. *Macromol. Chem. Phys.* **1996**, *197*, 3209−3228. (f) Reference 13a.

(19) A stochastic matrix method has been developed for C_1-symmetric metallocene catalysts: (a) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M. *Macromolecules* **1997**, *30*, 6251−6263. (b) Busico, V.; Cipullo, R. *Prog. Polym. Sci.* **2001**, *26*, 443−533. (c) Reference 7g. However, the models in the Supporting Information section avoid matrix methods and are readily applied with common software programs such as Microsoft Excel.

(20) The least-squares minimization was performed for the eight measured intensities (*mmrm*, *rrmr*, and *mrmr* were combined) according to RMS error = $((\sum(I_{obs} - I_{calc})^2)/8)^{0.5}$. *Cautionary note*: Comparisons of RMS errors and the resultant interpretations are always subject to the limitations inherent in the statistical model. To the extent that stereochemical behavior deviates from these idealized models, incorrect conclusions are increasingly possible. Additionally, errors as high 1−3% are typical for pentad distributions measured by ^{13}C NMR for the polymers reported here.

(21) This includes polypropylenes made with metallocenes **3**, **4**, **6**, **9**, **13**, **14**, and **16**.

Table 1. Dependence of Polymer Melting Temperature and *mmmm* Pentad Content on Polymerization Temperature and Monomer Concentration

 3			 4		
T_p (°C)	T_m (°C)	*mmmm* (%)	T_p (°C)	T_m (°C)	*mmmm* (%)
liquid monomer[a]			liquid monomer[c]		
20	133	79.2	0	119.6	74.1
40	129	78.0	20	118.2	77.0
60	127	77.5			
80	127	76.8			
10% monomer in toluene[b]			10% monomer in toluene[d]		
0	128.8	82.2	0	120.9	78.1
20	134.1	83.9	20	131.2	77.6
40	135.4	88.8			
60	128.4	89.4			

[a] See ref 4b. [b] Table 5, entries 1−4. [c] Table 5, entries 7, 8. [d] Table 5, entries 9, 10.

dominant, but can yield to the site epimerization mechanism under certain conditions. These results and interpretations are consistent with two reports: (1) that **3**/MAO provides polymers of increasing isotacticity as the monomer concentration is progressively decreased (T_p = 50 °C; for liquid monomer, 1.7 and 0.9 M, [*mmmm*] = 80%, 85%, and 87%, and T_m = 125, 129, and 134 °C, respectively)[22a] and (2) that **3**/MAO provides polymers of increasing isotacticity with increasing polymerization temperature for reactions conducted in toluene with a monomer pressure of 2.0 bar ([*mmmm*] = 83.5% at 10 °C and [*mmmm*] = 87.8% at 70 °C).[22b]

Steric Perturbation of the Fluorenyl Ligand. In addition to performing polymerizations under various reaction conditions, a powerful probative approach is steric modification of the parent metallocene. To this end, 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]fluorene[23] has been incorporated as a more sterically hindered ligand (Oct) into various C_1-symmetric metallocenes.[24]

Substitution of the fluorenyl (Flu) ligand with the Oct ligand is expected to result in increased stereoselectivity at the more stereoselective site (Scheme 3), because the Oct ligand is expected to be a better polymer chain directing substituent than the Flu ligand during the propagative transition state. However,

Scheme 3

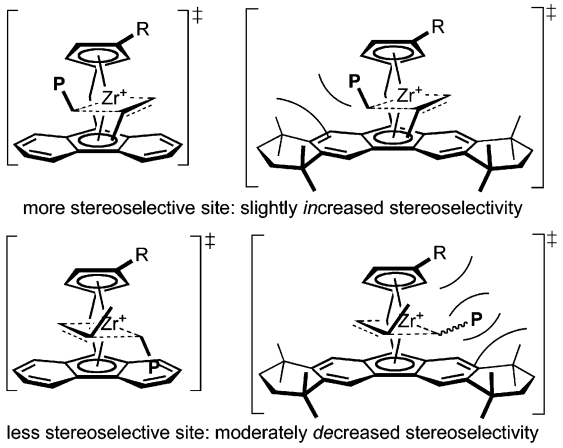
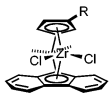
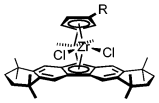


Table 2. Comparative Polymerizations between Fluorenyl-Containing and Oct-Containing Metallocenes for Various R Substituents (Table 5, entries 11−22)

								
R	compound	T_p (°C)	T_m[a] (°C)	[*mmmm*] (%)	compound	T_p (°C)	T_m[a] (°C)	[*mmmm*] (%)
methyl	**2**	0	am.	21.6	**7**	0	129.8	2.4
methyl	**2**	20	am.	18.3	**7**	20	116.8	2.4
cyclohexyl	**5**	0	am.	13.2	**8**	0	103.0	5.1
cyclohexyl	**5**	20	am.	14.5	**8**	20	am.	7.3
diphenylmethyl	**6**	0	136.6	86.1	**9**	0	124.7	74.4
diphenylmethyl	**6**	20	137.8	81.2	**9**	20	135.4	76.4

[a] am. = amorphous.

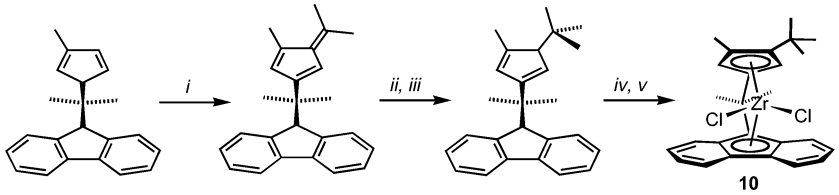
a substitution of the Flu ligand with the Oct ligand is expected to result in decreased stereoselectivity at the less stereoselective site (Scheme 3), because the Oct ligand is expected to compete more favorably with the opposing R substituent for directing the polymer chain during this propagative transition state. Moreover, a larger change in stereoselectivity at the less selective site might be anticipated. Therefore, if one observes *increased* isotacticity upon substitution of Flu with Oct, the site epimerization mechanism is likely operative, since it employs only the more stereoselective site. Conversely, if one observes *decreased* isotacticity upon substitution of Flu with Oct, the alternating mechanism is likely operative, since it employs both the more stereoselective site and the less stereoselective site.

Fluorenyl-containing metallocenes **2** (R = methyl), **5** (R = cyclohexyl), and **6** (R = diphenylmethyl) were examined, as were Oct-containing metallocenes **7** (R = methyl), **8** (R = cyclohexyl), and **9** (R = diphenylmethyl) (Table 2). In each case the isotacticity decreases substantially (Δ[*mmmm*] = 19.2%, 8.1%, and 11.7%, respectively for T_p = 0 °C) upon substitution of the Flu ligand with the Oct ligand. This is especially noteworthy for R = diphenylmethyl; the isoselectivity of **6** ([*mmmm*] = 81.2% at T_p = 20 °C) is greater than that of **3** (R = *tert*-butyl), whereas the isoselectivity of **9** ([*mmmm*] = 76.4% at T_p = 20 °C) is less than that of **3** ([*mmmm*] = 79.2% at T_p = 20 °C). The fact that the Oct-containing catalysts afford less isotactic polypropylene relative to the Flu analogues, regardless of R, implicates the alternating mechanism as the dominant mechanism.

(22) (a) Ewen, J. A.; Jones, R. L.; Elder, M. J. In *Metalorganic Catalysts for Synthesis and Polymerization, Recent Results by Ziegler−Natta and Metallocene Investigations*; Kaminsky, W., Ed.; Springer: Berlin, 1999; pp 150−169. (b) Kleinschmidt, R.; Reffke, M.; Fink, G. *Macromol. Rapid Commun.* **1999**, *20*, 284−288. (c) Increasing isotacticity with decreasing monomer concentration has also been identified in heterogeneous propylene polymerization systems (ref 9).

(23) (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.

Scheme 4



i: acetone, pyrrolidine; *ii*: excess methyllithium; *iii*: H_2O; *iv*: 2 *n*-BuLi; *v*: $ZrCl_4$

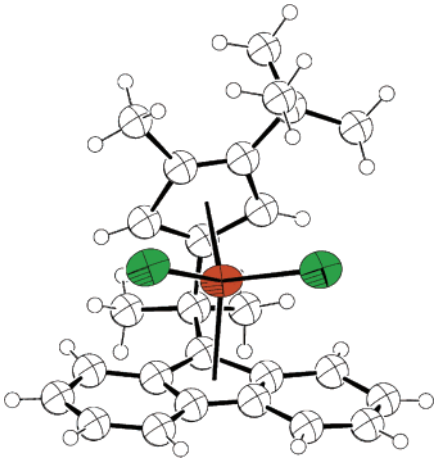


Figure 2. ORTEP drawing of the structure of Me_2C(3-*tert*-butyl-4-Me-C_5H_2)($C_{13}H_8$)$ZrCl_2$ (**10**) with 50% probability ellipsoids.

Steric Perturbation of the Cyclopentadienyl Ligand. To investigate the ability of the benzo substituent to direct the growing polymer chain at the more stereoselective site of **3**, a methyl substituent on the cyclopentadienyl ligand opposed to it was incorporated in zirconocene **10** (Scheme 4). Because the condensation of Me_2C(3-Me-C_5H_4)($C_{13}H_9$) with acetone occurs selectively at the four position of the cyclopentadienyl ring, away from the tertiary alkyl substituent, Me_2C(3-*tert*-butyl-4-Me-C_5H_2)($C_{13}H_8$)$ZrCl_2$ (**10**) was obtained as a single regioisomer. This structure was confirmed by an X-ray diffraction study (Figure 2).[25]

Table 3 presents the pentad distributions measured for polypropylenes obtained with **10**/MAO under a variety of polymerization conditions. The pentad distributions are moderately dependent on polymerization temperature and monomer concentration; the polymerization performed at 80 °C in 10% monomer produced polypropylene with the most dissimilar microstructure. As a representative example, the ^{13}C NMR of the methyl region for the polymer obtained in liquid monomer at 20 °C (Table 5, entry 24) is displayed in Figure 3.

The observed pentad distributions were subjected to a variety of statistical models. Table 4 shows this analysis for the polymer made with **10**/MAO at 20 °C in liquid monomer (Table 5, entry 24), and Figure 4 illustrates the corresponding statistical fits (see Supporting Information for details).[26] Chain end control and enantiomorphic site control are each single-site models. Between these two, the latter provides a better statistical fit. However, it poorly describes the pentad distribution and correctly predicts the intensity ordering of only four out of the nine resolved pentad peaks (#1, *mmmm*; #2, *mmrr*; #3, *mmmr*; and #8, *rmmr*). The alternating models are each two-site models. The alternating model with $\alpha = 1$ has only one independent parameter, but correctly predicts the intensity ordering of all seven allowed pentads. Not surprisingly, the alternating model with $\alpha < 1$, having two independent parameters, provides the best fit of all (although this is technically an unfair comparison).

Table 3. Pentad and Dyad Distributions (%) Obtained for Polypropylenes from 10/MAO (Table 5, entries 23−29)

	neat C_3H_6		10% C_3H_6 in toluene				
T_p (°C) =	0	20	0	20	40	60	80
mmmm	26.9	30.0	28.5	31.3	32.4	27.1	18.0
mmmr	13.4	15.1	16.1	17.6	16.4	15.6	14.1
rmmr	4.8	3.1	2.9	2.2	3.2	3.3	3.6
mmrr	20.4	19.2	18.3	18.1	17.4	17.5	16.3
mmrm + *rrmr*	4.2	5.2	6.5	10.0	7.9	10.3	14.6
mrmr	0.2	1.2	2.3	2.3	2.8	4.5	7.5
rrrr	11.7	8.9	6.9	4.4	5.6	4.9	6.6
rrrm	10.8	8.7	9.2	5.8	5.6	7.4	9.1
mrrm	7.6	8.6	9.3	8.3	8.6	9.5	10.1
m	57.5	61.0	61.1	66.4	66.1	62.1	54.9
r	42.5	39.0	38.9	33.6	33.9	37.9	45.1

Figure 5 plots the RMS error of the statistical models as a function of polymerization conditions for entries 23−29 (Table 5).[27] In liquid propylene, the hemiisoselective alternating models provide the best fits. In dilute monomer, the alternating model with $\alpha < 1$ excels the enantiomorphic site control model up to 80 °C.

The statistical calculations are most consistent with the operation of a two-site, alternating mechanism for **10**/MAO in liquid monomer. The single-site models cannot adequately describe such polymers, which are essentially hemiisotactic with a slight bias toward isotactic. However, the statistical results indicate increased employment of the site epimerization mechanism by **10**/MAO as the monomer concentration is decreased and the polymerization temperature is increased.

The parameters α and β derived from the alternating model with $\alpha < 1$ (Table 4) are the stereoselectivities of the two sites and predict the stereochemical mechanism shown in Scheme 5. At the more stereoselective site, the growing polymer chain is preferentially directed away from the *tert*-butyl group and the enantiofacial selectivity is 94.5%, corresponding to $\Delta\Delta G^{\ddagger} = 1.66$ kcal/mol at 20 °C. At the less stereoselective site, benzo and methyl are comparable in their abilities to direct the growing

(24) For reports of the Oct ligand see: (a) Miller, S. A.; Bercaw, J. E. U.S. Patent 6,469,188, 2002. (b) Miller, S. A.; Bercaw, J. E. U.S. Patent 6,693,153, 2004. (c) Miller, S. A.; Bercaw, J. E. *Organometallics* **2004**, *23*, 1777−1789. (d) Irwin, L. J.; Reibenspies, J. H.; Miller, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 16716−16717. (e) Irwin, L. J.; Miller, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 9972−9973. (f) Irwin, L. J.; Reibenspies, J. H.; Miller, S. A. *Polyhedron* **2005**, *24*, 1314−1324.

(25) Crystals of **10** were grown from benzene/*n*-heptane and were triclinic $P\bar{1}$, $a = 9.286(3)$ Å, $b = 17.711(6)$ Å, $c = 17.903(6)$ Å, $\alpha = 61.037(14)°$, $\beta = 81.471(14)°$, $\gamma = 78.713(15)°$, $V = 2521.2(13)$ Å^3, $Z = 4$, $T = 98$ K. Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK) deposition number 137698.

(26) The least-squares minimization was performed for the nine measured intensities according to RMS error = $((\sum(I_{obs} - I_{calc})^2)/9)^{0.5}$.

(27) The statistical analyses for the remaining polymers are found in the Supporting Information.

Table 4. Statistical Pentad and Dyad (%) Comparison to Several Stereochemical Models for a Polypropylene Sample Made with 10/MAO at 20 °C in Liquid Monomer (Table 5, entry 24)

	observed	chain end control	enantiomorphic site control	alternating model $\alpha = 1$	alternating model $\alpha < 1$
mmmm	30.0	29.1	30.1	31.6	29.6
mmmr	15.1	21.0	16.7	14.6	15.3
rmmr	3.1	3.8	2.8	4.4	4.0
mmrr	19.2	7.6	16.7	23.5	21.0
mmrm + *rrmr*	5.2	23.8	11.3	0.0	4.7
mrmr	1.2	7.6	5.7	0.0	2.3
rrrr	8.9	0.5	2.8	9.7	7.4
rrrm	8.7	2.8	5.7	8.8	8.0
mrrm	8.6	3.8	8.3	7.3	7.6
m	61.0	73.4	66.4	62.4	62.9
r	39.0	26.6	33.6	37.6	37.1
σ		0.734			
α			0.786	1.000	0.945
σ				0.624	0.646
RMS error		8.73	3.53	2.44	1.02

Table 5. MAO-Cocatalyzed Propylene Polymerization Results with 3−16

entry	zirconocene (mg)/MAO[a]	T_p (°C)	toluene (mL)	C_3H_6 (mL)	time (min)	yield (g)	T_m[b] (°C)	[*mmmm*] (%)	M_w	M_w/M_n
1	**3** (2.0)	0	30.0	3	60	0.84	129	82.2		
2	**3** (2.0)	20	30.0	3	10	0.56	134	83.9		
3	**3** (2.0)	40	30.0	3	5	0.50	135	88.8		
4	**3** (2.0)	60	30.0	3	5	0.38	128	89.4		
5	**3** (2.0)	0	2.0	30	20	0.93	126	79.5		
6	**3** (2.0)	20	2.0	30	3	1.01	125	81.5		
7	**4** (2.0)	0	2.0	30	15	0.45	120	74.1	431 000	1.74
8	**4** (2.0)	20	2.0	30	5	1.77	118	77.0	252 000	1.88
9	**4** (1.0)	0	30.0	3	30	0.30	121	78.1		
10	**4** (1.0)	20	30.0	3	15	1.71	131	77.6		
11	**2** (1.0)	0	2.0	30	15	1.43	n.o.	21.6	80 000	1.81
12	**2** (1.0)	20	2.0	30	10	4.95	n.o.	18.3		
13	**5** (1.0)	0	2.0	30	10	0.71	n.o.	13.2		
14	**5** (1.0)	20	2.0	30	10	4.01	n.o.	14.5		
15	**6** (2.0)	0	2.0	30	20	0.32	137	86.1		
16	**6** (2.0)	20	2.0	30	20	0.47	138	81.2		
17	**7** (1.5)	0	2.0	30	15	0.37	130	2.4		
18	**7** (1.5)	20	2.0	30	5	0.86	117	2.4		
19	**8** (2.0)	0	2.0	30	20	0.36	103	5.1		
20	**8** (2.0)	20	2.0	30	20	5.53	n.o.	7.3		
21	**9** (2.7)	0	2.0	30	20	0.05	125	74.4		
22	**9** (2.7)	20	2.0	30	20	0.14	135	76.4		
23	**10** (1.0)	0	2.0	30	3	1.23	n.o.	26.9	653 000	1.87
24	**10** (0.5)	20	1.0	30	3	1.12	n.o.	30.0	397 000	2.31
25	**10** (1.0)	0	30.0	3	10	1.90	n.o.	28.5		
26	**10** (1.0)	20	30.0	3	10	1.82	n.o.	31.3		
27	**10** (1.0)	40	30.0	3	10	1.16	n.o.	32.4		
28	**10** (1.0)	60	30.0	3	10	0.47	n.o.	27.1		
29	**10** (1.0)	80	30.0	3	10	0.10	n.o.	18.0		
30	**11** (0.5)[c]	0	1.0	30	30	1.50	n.o.	28.4	134 000	3.15
31	**11** (0.5)[c]	20	1.0	30	10	1.08	n.o.	31.4	81 900	4.38
32	**12** (1.0)	0	2.0	30	15	0.18	109	60.2	360 000	1.75
33	**12** (1.0)	20	2.0	30	15	1.62	110	57.5	322 000	1.70
34	**13** (2.0)	0	2.0	30	5	0.16	129	78.6	76 700	1.81
35	**13** (2.0)	20	2.0	30	30	0.36	131	80.0	80 900	2.63
36	**14** (1.0)	0	2.0	30	10	0.41	158	>98	171 000	1.93
37	**14** (1.0)	20	2.0	30	10	0.83	154	>98	113 000	1.93
38	**14** (2.0)	0	2.0	55	60	3.88	160	>98	157 000	2.48
39	**14** (2.0)	20	2.0	55	10	2.13	156		124 000	1.90
40	**14** (2.0)	0	2.0	55	10	1.38	159		160 000	1.91
41	**14** (2.0)	0	30.0	3	180	0.87	158		102 000	1.82
42	**14** (2.0)	20	30.0	3	90	0.50	148		54 400	2.08
43	**15** (3.0)	0	2.0	30	120	0.03	n.o.			
44	**15** (3.0)	20	2.0	30	120	0.02	n.o.			
45	**16** (2.0)	0	2.0	30	20	0.29	167	>99	370 000	1.39
46	**16** (2.0)	20	2.0	30	20	0.70	163	>99	425 000	1.77

[a] MAO = 1000 equiv unless otherwise specified. [b] n.o. = melting temperature not observed. [c] 2000 equiv of MAO used.

polymer chain. However, benzo is slightly more directing and the enantiofacial selectivity is 64.6%, corresponding to $\Delta\Delta G^{\ddagger} = 0.35$ kcal/mol at 20 °C. Contrary to steric arguments[2c,4a,4b] that claim monomer insertion cannot occur while the growing polymer chain is proximal to the *tert*-butyl group of **3**/MAO, the catalyst system **10**/MAO readily inserts monomer at both sites of the metallocene despite the presence of a bulky *tert*-butyl group.

If indeed the alternating mechanism is operating for **3**/MAO, the two-parameter statistical model (Figure 1) suggests that the

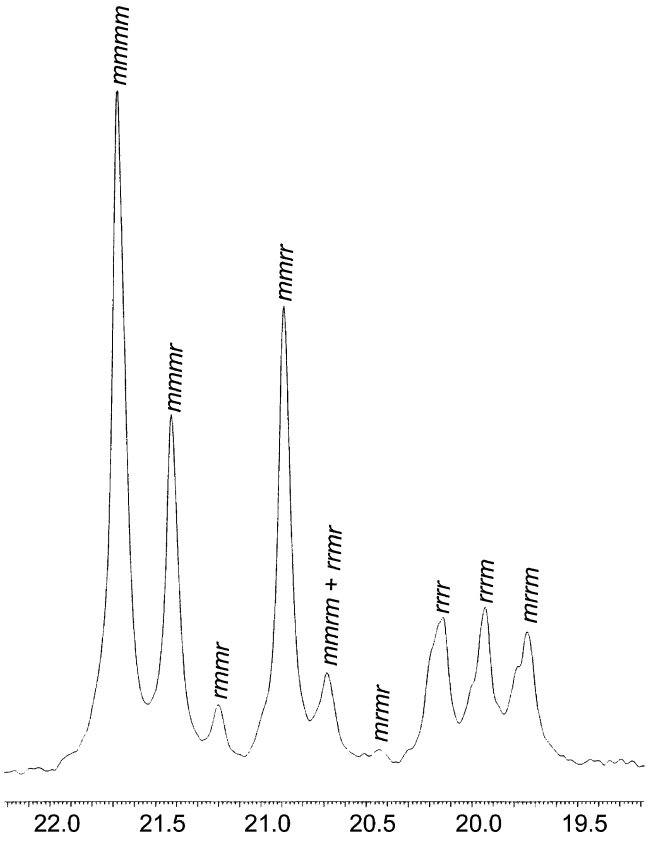


Figure 3. ^{13}C NMR of the methyl region for polypropylene obtained with **10**/MAO in liquid monomer at 20 °C (Table 5, entry 24).

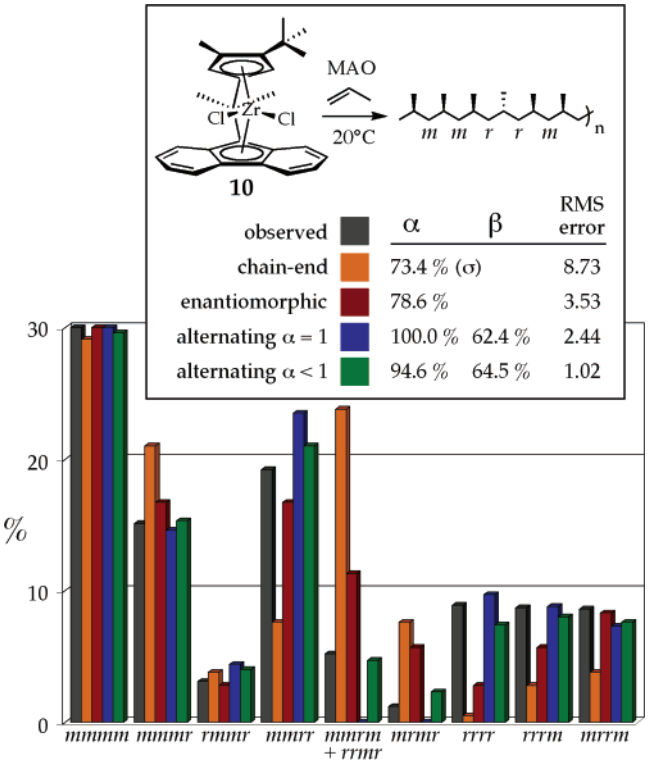


Figure 4. Statistical pentad analysis of a polypropylene sample made with **10**/MAO at 20 °C in liquid monomer (Table 5, entry 24).

coordination sites are operating with an average stereoselectivity of 95.2% (benzo > H; *tert*-butyl > benzo). This stereoselectivity should correspond to that of the more stereoselective site of

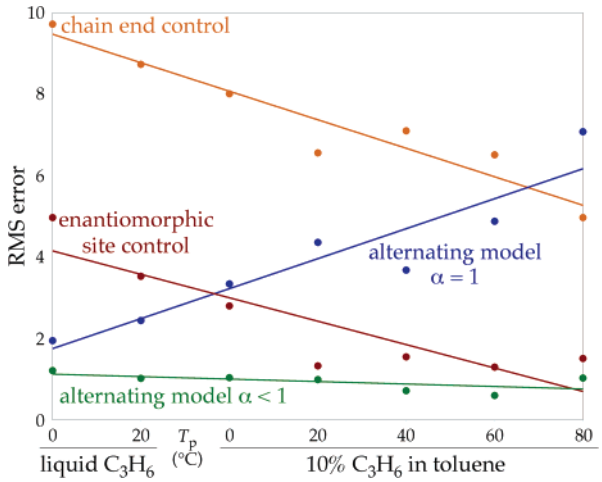
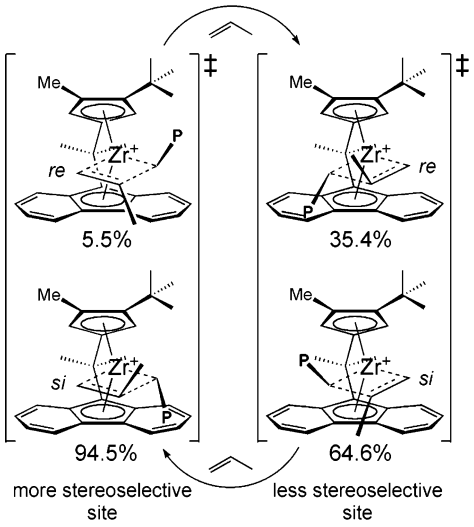


Figure 5. Dependence of the RMS error for a given statistical model on polymerization temperature and monomer concentration for polymerizations with **10**/MAO.

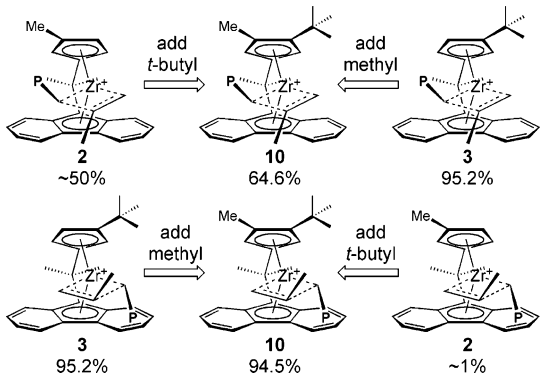
Scheme 5



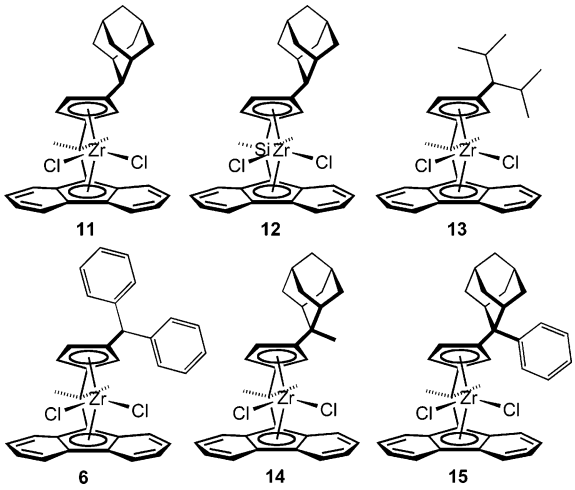
10/MAO (94.5%, *tert*-butyl > benzo) insofar as the methyl group of **10** has no effect on the stereochemistry of insertion at that site. Similarly, the stereoselectivity of the less stereoselective site of **10**/MAO (64.6%, benzo > methyl) should correspond to that of the less stereoselective site of the known hemiisoselective catalyst system $Me_2C(3\text{-}Me\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$/MAO (**2**/MAO)[2a,4b] (approximately 50%, benzo ≈ methyl) insofar the *tert*-butyl group of **10** has no effect on the stereoselectivity at that site. These stereoselectivity differences represent small energy differences, and their magnitudes are proportional to the steric perturbation: −1% for the addition of methyl to **3** and +15% for the addition of *tert*-butyl to **2** (left side of Scheme 6). The magnitude of the stereoselectivity difference is markedly larger when the steric perturbation occurs proximal to the growing polymer chain: −31% for the addition of methyl to **3** and +94% for the addition of *tert*-butyl to **2** (right side of Scheme 6).

Steric Perturbation of the 3-Cyclopentadienyl Substituent. Because **3**/MAO likely employs the alternating rather than site epimerization mechanism, steric perturbation of the 3-cyclopentadienyl substituent should have an effect on polymer stereochemistry much greater than previously thought. For this reason, the zirconocenes shown in Scheme 7 were prepared.

Scheme 6



Scheme 7



Each was subjected to MAO-cocatalyzed propylene polymerizations at 0 and 20 °C, as reported in entries 15, 16, and 30−44 of Table 5.

Catalyst system **11**/MAO employs the alternating mechanism[28] and affords essentially hemiisotactic polypropylene with [*mmmm*] = 28.4%. While 2-adamantyl is large, its steric effect is not as great as a tertiary alkyl substituent, and apparently it is far inferior to *tert*-butyl in its ability to direct the growing polymer chain during the transition state for monomer insertion. Zirconocene **12** is identical to **11** except that it bears a dimethylsilylene bridge. Such silicon-containing metallocenes often undergo site epimerization more readily than alkylidene analogues.[2d,3d,29] More rapid site epimerization for **12**/MAO relative to **11**/MAO is indeed apparent, as [*mmmm*] doubles to 60.2%, indicative that this metallocene employs the more stereoselective site to a greater degree.[30]

Zirconocenes **13** and **6** produce polypropylene with isotacticities ([*mmmm*] = 78.6%, 80.0% for **13** and 86.1%, 81.2% for **6**) comparable to those produced by the parent *tert*-butyl-substituted zirconocene **3** ([*mmmm*] = 79.5% and 81.5%), despite the fact that they contain *secondary* alkyl substituents on the cyclopentadienyl ring. Thus, it is not necessary to have a tertiary alkyl cyclopentadienyl substituent to obtain moderately isotactic polypropylene. Moreover, atoms beyond the α and *β* carbons of the substituent can greatly impact the polymer stereochemistry—despite their distal position relative to the metal center—as evidenced by the comparatively meager isotacticity reported for the isopropyl analogue Me_2C(3-isopropyl-C_5H_3)-($C_{13}H_8$)$ZrCl_2$/MAO: [*mmmm*] = 15.4% for T_p = 10 °C and [*mmmm*] = 44.0% for T_p = 70 °C (2.0 bar of propylene in toluene).[22b,31]

The second largest cyclopentadienyl substituent employed, 2-methyl-2-adamantyl,[32] is incorporated into metallocene **14**. This metallocene is capable of producing highly isotactic polypropylene ([*mmmm*] > 98%) with a melting temperature of 160 °C (Table 5, entry 38, T_p = 0 °C). The high isoselectivity can be explained by one of two limiting scenarios. First, the alternating mechanism is operating and the 2-methyl-2-adamantyl substituent is an exceedingly good polymer-directing substituent compared to benzo, rendering a catalyst with two highly stereoselective sites. Second, the steric demands of the 2-methyl-2-adamantyl substituent prohibit use of that site, and the alternating mechanism is no longer operating; the site epimerization mechanism is now dominant, and metallocene **14** employs only one highly stereoselective site for monomer insertion. In either case, it is difficult to rationalize the comparatively poor isoselectivity of **3**/MAO ([*mmmm*] = 79.5%) if one claims that **3**/MAO *always* operates by the site epimerization mechanism—further evidence supporting the alternating mechanism for **3**/MAO.

The largest cyclopentadienyl substituent employed, 2-phenyl-2-adamantyl, is incorporated into zirconocene **15**. **15**/MAO is essentially inactive for propylene polymerization. Apparently, the cyclopentadienyl substituent is so large that both the alternating and site epimerization mechanisms have effectively halted.[33]

Formation of Highly Isotactic Polypropylene with C_1-Symmetric Metallocene Catalysts. We sought to apply everything we have learned about isotactic polypropylene formation with C_1-symmetric zirconocene catalysts to design a zirconocene precatalyst capable of producing very highly isotactic polypropylene. Zirconocene dichloride precatalyst **16** is the result of this endeavor. Its structural features result from three important factors. First, the cyclopentadienyl substituent should be larger than *tert*-butyl, but not so large that it inhibits polymerization altogether. Therefore, the 2-methyl-2-adamantyl substituent has been incorporated into **16**. Second, factors that encourage site epimerization generally lead to polymers of

(28) (a) Miller, S. A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934−945. (b) Miller, S. A. *Macromolecules* **2004**, *37*, 3983−3995.

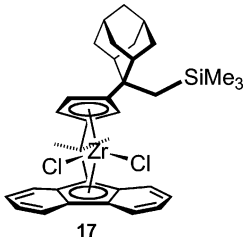
(29) Patsidis, K.; Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1996**, *509*, 63−71.

(30) Miller, S. A. Ph.D. Thesis, California Institute of Technology, 2000, Chapter 2.

(31) Yano, A.; Kaneko, T.; Sato, M.; Akimoto, A. *Macromol. Chem. Phys.* **1999**, *200*, 2127−2135.

(32) For previous examples of metallocenes bearing the 2-methyl-2-adamantyl substituent, see: Abrams, M. B.; Yoder, J. C.; Loeber, C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1389−1401.

(33) **15**/MAO is essentially inactive for *ethylene* polymerization as well (activity = 12 gP/(gZr·h) at 20 °C). To test the suggestion that this metallocene simply deactivates by aryl C−H activation, Me_2C(3-(2-(CH_2-$SiMe_3$)-2-adamantyl)-C_5H_3)($C_{13}H_8$)$ZrCl_2$ (**17**) was prepared and tested for its MAO-cocatalyzed propylene polymerization behavior.



17

The small amount of amorphous polypropylene (activity = 460 gP/(gZr·h) at 20 °C) that was obtained is attributed to impurities present in the metallocene (likely Me_2C(3-(2-adamantyl)-C_5H_3)($C_{13}H_8$)$ZrCl_2$ based on the synthetic procedure), and the lack of any isotactic polypropylene suggests that the aliphatic cyclopentadienyl substituent 2-(CH_2SiMe_3)-2-adamantyl effectively inhibits polymerization as well.

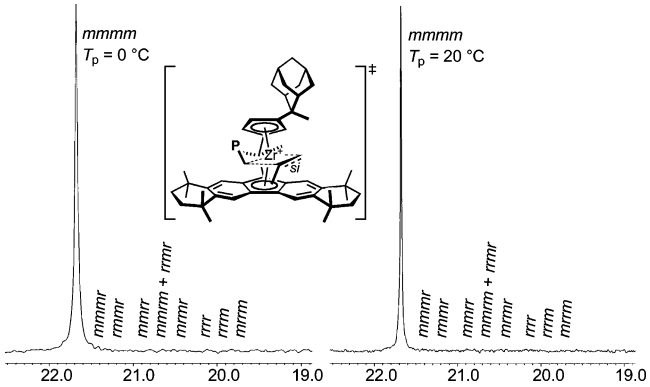
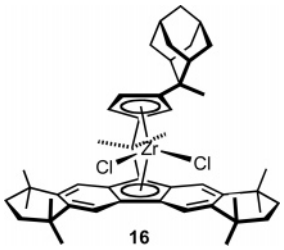


Figure 6. Highly isoselective polymerization catalyst **16**/MAO likely employs a single propagative transition state (shown), yielding isotactic polypropylene largely devoid of stereoerrors as determined by ^{13}C NMR spectroscopy (methyl region depicted).

higher isotacticity, since the more stereoselective site is used preferentially. This can be accomplished, in principle, by altering polymerization conditions[34] or by the inclusion of a dimethylsilylene bridge. For **16**, it is plausible that site epimerization predominates because of extreme steric crowding contributed by both the 2-methyl-2-adamantyl substituent and the opposing Oct ligand. Third, to the extent that the catalyst system utilizes a given site for monomer insertion, enhancement of the stereoselectivity at that site will lead to higher isotacticity. Since the Oct ligand is a better polymer-directing group than fluorenyl, incorporation of the Oct ligand in metallocene **16** is expected to lead to greater isoselectivity at the more stereoselective site.



16

The propylene polymerization results with **16**/MAO are given in entries 45 and 46 of Table 5. Highly isotactic polypropylenes are obtained, as stereoerrors are virtually absent by ^{13}C NMR analysis ([*mmmm*] > 99%, Figure 6). The polymers have high melting temperatures (167.0 and 162.7 °C, respectively) and large enthalpies of melt (92.0 and 87.5 J/g, respectively). Significantly, the highest previously reported melting temperature for an isotactic polypropylene made via *homogeneous* catalysis is 166 °C.[35] The high isoselectivity of **16**/MAO suggests that it employs a single propagative transition state for monomer insertion, as depicted in Figure 6.

Conclusions

Although a site epimerization mechanism for isotactic polypropylene formation with $Me_2C(3\text{-}tert\text{-butyl-}C_5H_3)(C_{13}H_8)ZrCl_2$/MAO (**3**/MAO) has been invoked, experimental evidence does not conclusively support it. The microstructure of this material is sufficiently isotactic that stereochemical analyses cannot conclusively differentiate between a single-site model employing enantiomorphic site control (site epimerization mechanism) and a two-site model having one highly stereoselective site and one moderately stereoselective site (alternating mechanism). Other approaches, therefore, were developed to interrogate the two possible mechanisms.

The following observations suggest that the alternating mechanism predominates, while the site epimerization mechanism can compete under certain conditions for **3**/MAO and other closely related C_1-symmetric zirconocenes/MAO. An increase in isotacticity is observed for polymerization conditions that favor unimolecular site epimerization over bimolecular propagation. Incorporation of the bulky Oct ligand in place of fluorenyl effects a decrease in isotacticity, a change consistent with a slight increase in stereoselectivity at one site and a substantial decrease in stereoselectivity at a second site. The model system $Me_2C(3\text{-}tert\text{-butyl-4-Me-}C_5H_2)(C_{13}H_8)ZrCl_2$/MAO (**10**/MAO) produces essentially hemiisotactic polypropylene, suggesting that both sites of the metallocene are readily employed for insertion, despite the presence of a bulky *tert*-butyl group. Finally, the use of a cyclopentadienyl substituent larger than the *tert*-butyl group results in increased isotacticity. The combination of these results implies operation of the alternating mechanism with **3**/MAO in which the two enantioselectivities are somewhat different but have an average of 95.2% at 40 °C.

Three key elements contributed to the design of a highly isoselective metallocene catalyst system, $Me_2C(3\text{-}(2\text{-Me-}2\text{-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})ZrCl_2$/MAO (**16**/MAO): incorporation of a cyclopentadienyl substituent larger than *tert*-butyl; considerable steric bulk on one side of the metallocene to encourage site epimerization; and exploitation of the enhanced ability of the octamethyloctahydrodibenzofluorenyl (Oct) ligand to direct the growing polymer chain away in the transition state for monomer insertion. This catalyst system is capable of producing highly isotactic polypropylene ([*mmmm*] > 99%, T_m up to 167 °C) and demonstrates how the correct understanding of the mechanism can lead to the rational design of improved catalysts.

Experimental Section

General Considerations and Instrumentation. Unless otherwise noted, all reactions and procedures are carried out under argon or nitrogen using standard glovebox, Schlenk, and high-vacuum line techniques.[36] Solvents are dried according to standard procedures. NMR spectra were recorded on a JEOL GX-400 (^1H, 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. The elemental analysis of air-sensitive metallocenes routinely provides numbers lower than those calculated. In some cases this can be attributed to residual LiCl, but it is more likely a systemic problem related to incomplete combustion.

Zirconocene Dichloride Syntheses. Preparation of 2 and 3. Metallocenes **2** and **3** were synthesized as described in the literature.[4a,c] For **3**: MS (LC-MS) *m*/*z* 488.6 (M^+). Anal. Calcd for $C_{25}H_{26}Zr_1Cl_2$: C, 61.46; H, 5.36. Found: C, 43.94; H, 4.31.

(34) In addition to low monomer concentration and high polymerization temperatures, the addition of methylene chloride has been observed to increase the relative rate of the site epimerization process for **1**/MAO: Fink, G.; Herfert, N.; Montag, P. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, 1995; pp 159−179.

(35) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Rheingold, A. L.; Liable-Sands, L. M.; Sommer, R. D. *J. Am. Chem. Soc.* **2001**, *123*, 4763−4773.

(36) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization, Vol. 357*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington D.C., 1987; pp 79−98.

Fluorenyllithium/Diethyl Ether. A 500 mL flask was charged with fluorene (47.00 g, 282.8 mmol) and attached to a swivel frit before 200 mL of diethyl ether was condensed in. *n*-Butyllithium solution (180.0 mL, 288 mmol, 1.6 M in hexanes) was syringed in over 20 min at room temperature. After stirring for 18 h, the yellow precipitate was collected and dried in vacuo: 50.64 g (72.7% based on the mono diethyl ether adduct).

3-*tert*-Butyl-6,6-diphenylfulvene. An argon-filled 1 L Schlenk flask was charged with 6,6-dimethylfulvene (40.15 g, 378.2 mmol) and 180 mL of diethyl ether. At 0 °C, methyllithium/lithium bromide solution (420 mL, 630 mmol, 1.5 M in diethyl ether) was syringed in over 25 min. The reaction was stirred for 7 days before it was cooled to 0 °C, and 60 mL of aqueous NH_4Cl solution was slowly added, followed by 120 mL of water. 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 provide 38.41 g of *tert*-butylcyclopentadiene (83.1%). 15.00 g of this material was combined with 100 mL of ethanol and 22.37 g of benzophenone. The solids were dissolved before sodium methoxide (15.00 g, 278 mmol) was added. The reaction was stirred for 27 days before 500 mL of water and 200 mL of diethyl ether were added. 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 provide a red oil, which was subjected to Kugelrohr distillation. Under high vacuum, 16.56 g was removed and the next fraction was collected as product at 60 °C: 9.22 g of red, viscous oil (26.2%).

Ph_2C(3-*tert*-butyl-C_5H_3)($C_{13}H_8$)H_2. A 250 mL flask was charged with waxy 3-*tert*-butyl-6,6-diphenylfulvene (9.22 g, 32.2 mmol) and fluorenyllithium diethyl ether adduct (7.928 g, 32.19 mmol). Diethyl ether (75 mL) was condensed in, and the homogeneous reaction formed much precipitate after 16 days. After 20 days, 60 mL of aqueous NH_4Cl solution was slowly added, and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 × 30 mL), and the combined organic layers were dried over $MgSO_4$ and filtered. The product crystallized from solution at −78 °C, and the product was obtained as a white powder in two crops: 6.58 g (45.2%). MS (GC-MS): *m*/*z* 452.5 (M^+). Anal. Calcd for $C_{35}H_{32}$: C, 92.87; H, 7.13. Found: C, 91.37; H, 6.56.

Ph_2C(3-*tert*-butyl-C_5H_3)($C_{13}H_8$)Li_2. A swivel frit was charged with Ph_2C(3-*tert*-butyl-C_5H_3)($C_{13}H_8$)H_2 (6.359 g, 14.05 mmol), and 75 mL of diethyl ether. *n*-butyllithium solution (20.0 mL, 32.0 mmol, 1.6 M in hexanes) was syringed in over 2 min at room temperature. After 22 h, the orange precipitate was collected and dried in vacuo to provide the product in theoretical yield (6.53 g).

Ph_2C(3-*tert*-butyl-C_5H_3)($C_{13}H_8$)$ZrCl_2$ (4). A 100 mL flask was charged with Ph_2C(3-*tert*-butyl-C_5H_3)($C_{13}H_8$)Li_2 (3.987 g, 8.583 mmol) and $ZrCl_4$ (2.000, 8.583 mmol) and equipped with a 180° needle valve. Petroleum ether (60 mL) was condensed in at −78 °C and the cold bath removed. After 42 h, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL of methylene chloride overnight. The filtrate was attached to a swivel frit, filtered, and condensed to 10 mL. The precipitate was collected and dried in vacuo: 1.841 g and a second crop of 0.614 g (46.7% yield for both crops). MS (LC-MS): *m*/*z* 612.6 (M^+). ^{1}H NMR (CD_2Cl_2): δ 1.18 (s, 9H, C(C*H*$_3$)$_3$), 5.61, 5.77, 6.22 (m, 3H, Cp-*H*), 6.39, 6.43, 8.18, 8.18 (d, $^3J_{HH}$ = 8.8, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*), 6.96, 6.99, 7.85, 7.85 (t, $^3J_{HH}$ = 7.0, 7.7, 7.3, 7.3 Hz, 4H, Flu-*H*), 7.33, 7.33, 7.95, 7.99 (d, 4H, phenyl-*H*), 7.30, 7.53, 7.46, 7.48, 7.54, 7.57 (t, 6H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2, 40 °C): δ 29.90 (C(*C*H$_3$)$_3$), 33.20 (*C*(CH$_3$)$_3$), 101.33, 105.86, 115.11 (Cp-*C*H$_1$), 121.05, 121.51, 123.27, 124.00 (fluorenyl-*C*H$_0$), 123.60, 124.26, 124.46, 124.79, 125.40, 125.48, 126.63, 126.79, 127.19, 127.23, 127.94, 128.01, 129.03, 129.12, 129.12, 129.12, 129.26, 129.39 (benzo-*C*H$_1$ and Cp-*C*H$_1$), 145.03, 145.11 (ipso-*C*), 146.18 (9-fluorenyl-*C*), other *C*H$_0$, not determined. Anal. Calcd for $C_{35}H_{30}Zr_1Cl_2$: C, 68.61; H, 4.93. Found: C, 64.90; H, 4.56.

6,6-(Pentamethylene)fulvene. (Synthesis modified from ref 37.) Pyrrolidine (30.0 mL, 359 mmol) was slowly syringed into a solution of cyclohexanone (150.0 mL, 1447 mmol) and cyclopentadiene (100.0 mL, 1213 mmol) in 100 mL of methanol. The reaction was stirred for 96 h before 40 mL of acetic acid was added, followed by 300 mL of H_2O and 200 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, and rotavapped to give 158.8 g of a yellow oil, which was subjected to Kugelrohr distillation under high vacuum. The first 20 g of material that distilled at 50 °C was discarded, and the product was obtained from the second fraction that distilled at 80 °C: 110.13 g (61.1%).

Cyclohexylcyclopentadiene. 6,6-(Pentamethylene)fulvene (15.66 g, 107.1 mmol) was dissolved in 50 mL of tetrahydrofuran, and this solution was added over 12 min to a stirred slurry of $LiAlH_4$ (4.500 g, 118.6 mmol) in 100 mL of tetrahydrofuran at 0 °C. After 15 h of stirring at room temperature, the reaction was cooled to 0 °C and quenched by slow addition of 20 mL of saturated NH_4Cl solution. Then 300 mL of H_2O and 50 mL of diethyl ether were added; the organic layer was isolated, and the aqueous layer was extracted with additional diethyl ether (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give the product, 2-cyclohexylcyclopentadiene, in quantitative yield as a light yellow oil: 15.88 g.

3-Cyclohexyl-6,6-dimethylfulvene. To cyclohexylcyclopentadiene (15.88 g, 107.7 mmol) was added 100 mL of methanol, acetone (20.0 mL, 272 mmol), and pyrrolidine (1.0 mL, 12 mmol). After stirring for 21 h, 5 mL of acetic acid was injected, followed by 150 mL of H_2O and 100 mL of diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 × 50 mL). The combined organic layers were extracted with H_2O (3 × 30 mL) and with 10% aqueous NaOH (3 × 30 mL), dried over $MgSO_4$, filtered, and rotavapped. The product was obtained in quantitative yield (20.17 g) as a yellow liquid and further purified by passing the neat liquid through a short column of alumina.

Me_2C(3-cyclohexyl-C_5H_3)($C_{13}H_8$)H_2. A 15.5 mL portion of an *n*-butyllithium solution (24.8 mmol, 1.6 M in hexanes) was syringed into a solution of fluorene (4.047 g, 24.35 mmol) in 60 mL of tetrahydrofuran. After stirring for 45 min, 3-cyclohexyl-6,6-dimethylfulvene (4.58 g, 24.3 mmol) was injected via syringe. After stirring for 15 h, 60 mL of a saturated NH_4Cl solution was added, 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 give the product in quantitative yield (8.63 g) as a yellow oil.

Me_2C(3-cyclohexyl-C_5H_3)($C_{13}H_8$)Li_2. The dianion was prepared by treating a solution of Me_2C(3-cyclohexyl-C_5H_3)($C_{13}H_8$)H_2 (8.63 g, 24.3 mmol) in 50 mL of diethyl ether with 32.0 mL of *n*-butyllithium solution (51.2 mmol, 1.6 M in hexanes) at 0 °C. After stirring for 20 h, the solvent was removed by vacuum transfer, and 75 mL of petroleum ether was condensed in. The dilithio salt was isolated by filtration and in vacuo drying in quantitative yield as a red-orange powder.

Me_2C(3-cyclohexyl-C_5H_3)($C_{13}H_8$)$ZrCl_2$ (5). A 2.500 g portion of Me_2C(3-cyclohexyl-C_5H_3)($C_{13}H_8$)Li_2 (6.82 mmol) and 1.59 g of $ZrCl_4$ (6.82 mmol) were combined in a swivel frit apparatus. Then 30 mL of petroleum ether was condensed in at −78 °C. This was allowed to warm slowly to room temperature before solvent removal after 17 h of stirring. Methylene chloride (40 mL) 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. The volume was reduced to 20 mL, and two crops

(37) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849−1853.

were obtained for a total of 1.261 g (35.9%) of **5** as an orange powder following collection at 0 °C and in vacuo drying. MS (LC-MS): *m*/*z* 514.7 (M^+). ^{1}H NMR (C_6D_6): δ 0.87−1.26 (m, 10H, cyclohexyl-*H*), 1.81, 1.82 (s, 6H, C(CH_3)$_2$), 2.58 (m, 1H, 1-*H*-cyclohexyl), 5.27, 5.40, 6.05 (t, $^3J_{HH}$ = 2.6, 2.6, 2.6 Hz, 3H, Cp-*H*), 7.01, 7.03, 7.30, 7.35 (t, $^3J_{HH}$ = 7.0, 6.9, 8.4, 7.0 Hz, 4H, Flu-*H*), 7.45, 7.47, 7.83, 7.83 (d, $^3J_{HH}$ = 8.0, 8.1, 8.4, 8.4 Hz, 4H, Flu-*H*). Anal. Calcd for $C_{27}H_{28}Zr_1Cl_2$: C, 63.01; H, 5.48. Found: C, 57.74; H, 5.53.

6,6-Diphenylfulvene. (Synthesis modified from ref 38.) 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.

(Diphenylmethyl)cyclopentadiene. A 500 mL flask was charged with $LiAlH_4$ (4.50 g, 119 mmol) and 100 mL of tetrahydrofuran. An addition funnel containing 6,6-diphenylfulvene (20.00 g, 86.84 mmol) dissolved in 100 mL of tetrahydrofuran was attached. The vessel was cooled to 0 °C before dropwise addition over 45 min. After 22 h of stirring at room temperature, the vessel was cooled to 0 °C, and 60 mL of aqueous NH_4Cl solution was added dropwise. Then, 300 mL of water and 20 mL of concentrated aqueous HCl were added before the organic layer was isolated. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to provide the product in quantitative yield (20.17 g) as a light yellow oil.

3-(Diphenylmethyl)-6,6-dimethylfulvene. A 500 mL flask was charged with (diphenylmethyl)cyclopentadiene (10.00 g, 43.0 mmol), 50 mL of methanol, acetone (20.0 mL, 272 mmol), and pyrrolidine (5.0 mL, 60 mmol). After stirring for 67 h, the yellow precipitate was collected by suction filtration, was washed with 20 mL methanol, and was dried in vacuo: 8.24 g (70.3%).

$Me_2C(3\text{-}(diphenylmethyl)\text{-}C_5H_3)(C_{13}H_8)H_2$. A 250 mL flask was charged with fluorene (3.661 g, 22.03 mmol), evacuated, and backfilled with argon before 50 mL of tetrahydrofuran and 14.0 mL of *n*-butyllithium solution (22.4 mmol, 1.6 M in hexanes) were syringed in. The orange solution was stirred for 1 h before a solution of 3-(diphenylmethyl)-6,6-dimethylfulvene (6.00 g, 22.03 mmol) in 15 mL of tetrahydrofuran was syringed in. Following an additional 16 h, the stirred reaction was quenched by slow 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, and rotavapped to give the product in quantitative yield (9.66 g) as a light yellow oil.

$Me_2C(3\text{-}(diphenylmethyl)\text{-}C_5H_3)(C_{13}H_8)Li_2$. A round-bottom flask containing 9.66 g (22.0 mmol) of $Me_2C(3\text{-}(diphenylmethyl)\text{-}C_5H_3)(C_{13}H_8)H_2$ 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 solution (44.8 mmol, 1.6 M in hexanes) was syringed in over 2 min. After stirring for 18 h at room temperature, the red precipitate was collected and dried in vacuo to provide the product in quantitative yield (9.92 g).

$Me_2C(3\text{-}(diphenylmethyl)\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (6). In the glovebox, 1.933 g of $Me_2C(3\text{-}(diphenylmethyl)\text{-}C_5H_3)(C_{13}H_8)Li_2$ (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 allowed to warm slowly, and after 24 h of stirring, solvent was removed. Methylene chloride (50 mL) was condensed in; the solution was warmed and stirred before solvent removal. The solid was extracted for 64 h in a cellulose extraction thimble with 150 mL of methylene chloride. The filtrate volume was reduced to 50 mL, and the precipitated product was collected on a swivel frit and dried in vacuo: 1.520 g of **6** (59.2%). MS (LC-MS): *m*/*z* 598.5 (M^+). ^{1}H NMR (C_6D_6): δ 1.59, 1.76 (s, 6H, (CH_3)$_2$C-Flu-Cp), 5.24, 5.39, 5.77 (m, 3H, Cp-*H*), 5.92 (s, 1H, C*H*Ph$_2$), 6.90, 6.94, 7.29, 7.33 (t, $^3J_{HH}$ = 7.0, 7.3, 7.7, 7.7 Hz, 4H, Flu-*H*), 6.96−7.15 (m, 10H, phenyl-*H*), 7.39, 7.42, 7.82, 7.85 (d, $^3J_{HH}$ = 8.8, 8.0, 8.4, 8.4 Hz, 4H, Flu-*H*). Anal. Calcd for $C_{34}H_{28}Zr_1Cl_2$: C, 68.21; H, 4.71. Found: C, 52.61; H, 3.82.

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 of 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 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, CH_3), 1.90 (s, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 32.59 (*C*H$_3$), 41.21 (*C*H$_2$), 70.13 (*C*H$_0$). Anal. 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, CH_3), 1.77 (apparent s, 8H, CH_2), 3.82 (s, 2H, CH_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. Calcd for $C_{29}H_{38}$: C, 90.09; H, 9.91. Found: C, 89.07, 89.16; H, 8.94, 8.85.

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 stirring the orange solution 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, which 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 distilled at 50 °C: 136.58 g (94.0%).

$Me_2C(3\text{-}methyl\text{-}C_5H_3)(C_{29}H_{36})H_2$. A 13.5 mL portion of an *n*-butyllithium solution (21.6 mmol, 1.6 M in hexanes) was syringed into a solution of octamethyloctahydrodibenzofluorene (8.00 g, 20.7 mmol) in 90 mL of tetrahydrofuran. After stirring for 90 min, 3,6,6-trimethylfulvene (2.487 g, 20.7 mmol) was injected via syringe into the red solution. After stirring for 22 h, 60 mL of a saturated NH_4-

(38) Alper, H.; Laycock, D. E. *Synthesis* **1980**, *10*, 799.

Cl solution was added, 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 give the product in quantitative yield (10.49 g) as a light yellow oil.

Me_2C(3-methyl-C_5H_3)($C_{29}H_{36}$)Li_2. The dianion was prepared by treating a solution of Me_2C(3-methyl-C_5H_3)($C_{29}H_{36}$)H_2 (10.49 g, 20.7 mmol) in 75 mL of diethyl ether with 27.0 mL of *n*-butyllithium solution (43.2 mmol, 1.6 M in hexanes) at 0 °C. After stirring for 17 h, the precipitate was isolated by filtration and in vacuo drying to provide the dianion as a yellow powder: 8.707 g (81.1%).

Me_2C(3-methyl-C_5H_3)($C_{29}H_{36}$)$ZrCl_2$ (7). Me_2C(3-methyl-C_5H_3)-($C_{29}H_{36}$)Li_2 (3.34 g, 6.44 mmol) and 1.50 g of $ZrCl_4$ (6.44 mmol) were combined in a swivel frit apparatus. Then 50 mL of petroleum ether was condensed in at −78 °C. This was allowed to warm slowly to room temperature before solvent removal after 18 h of stirring. Methylene chloride (20 mL) was condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted from a cellulose extraction thimble overnight with 150 mL of diethyl ether. The volume of the filtrate was reduced to 25 mL, and the precipitate was collected at 0 °C. A total of 1.051 g (24.5%) of **7** as an orange-pink powder was obtained following in vacuo drying. MS (LC-MS): *m*/*z* 666.6 (M^+). ^{1}H NMR (C_6D_6): δ 1.20, 1.31, 1.31, 1.31, 1.31, 1.32, 1.50, 1.53 (s, 24H, Oct-C*H*$_3$), 1.65 (m, 8H, Oct-C*H*$_2$), 1.93 (s, 3H, Cp-C*H*$_3$), 2.03, 2.06 (s, 6H, (C*H*$_3$)$_2$C-Oct-Cp), 5.21, 5.50, 5.89 (t, $^3J_{HH}$ = 2.6, 2.9, 2.6 Hz, 3H, Cp-*H*), 7.56, 7.70, 8.29, 8.30 (s, 4H, Oct-*H*). Anal. Calcd for $C_{38}H_{48}Zr_1Cl_2$: C, 68.44; H, 7.25. Found: C, 62.90; H, 6.97.

Me_2C(3-cyclohexyl-C_5H_3)($C_{29}H_{36}$)H_2. An *n*-butyllithium solution (11.0 mL, 17.6 mmol, 1.6 M in hexanes) was syringed into a solution of octamethyloctahydrodibenzofluorene (6.603 g, 17.08 mmol) in 60 mL of tetrahydrofuran. After stirring for 50 min, 3-cyclohexyl-6,6-dimethylfulvene (3.216 g, 17.08 mmol) was injected via syringe into the red slurry. After stirring for 18 h, 60 mL of a saturated NH_4Cl solution was added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give the product in quantitative yield (9.82 g) as a light yellow wax.

Me_2C(3-cyclohexyl-C_5H_3)($C_{29}H_{36}$)Li_2. The dianion was prepared by treating a solution of Me_2C(3-cyclohexyl-C_5H_3)($C_{29}H_{36}$)H_2 (9.82 g, 17.1 mmol) in 75 mL of diethyl ether with 22.0 mL of *n*-butyllithium solution (35.2 mmol, 1.6 M in hexanes) at 0 °C. After stirring for 18 h, the precipitate was isolated by filtration and in vacuo drying to provide the dianion as an orange powder: 6.446 g (64.3%).

Me_2C(3-cyclohexyl-C_5H_3)($C_{29}H_{36}$)$ZrCl_2$ (8). Me_2C(3-cyclohexyl-C_5H_3)($C_{29}H_{36}$)Li_2 (2.518 g, 4.29 mmol) and 1.00 g of $ZrCl_4$ (4.29 mmol) were combined in a swivel frit apparatus. Then 30 mL of petroleum ether was condensed in at −78 °C. This was allowed to warm slowly to room temperature before solvent removal after 18 h of stirring. Methylene chloride (40 mL) was condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted from a cellulose extraction thimble overnight with 150 mL of diethyl ether. The volume of the filtrate was reduced to 50 mL, and the precipitate was collected at 0 °C. A total of 1.846 g (58.5%) of **8** as an orange powder was obtained following in vacuo drying. MS (LC-MS): *m*/*z* 734.8 (M^+). ^{1}H NMR (C_6D_6): δ 0.99−1.25 (m, 10H, cyclohexyl-*H*), 1.28, 1.30, 1.30, 1.31, 1.32, 1.33, 1.51, 1.51 (s, 24H, Oct-C*H*$_3$), 1.63 (m, 8H, Oct-C*H*$_2$), 2.08, 2.09 (s, 6H, (C*H*$_3$)$_2$C-Oct-Cp), 2.61 (m, 1H, 1-cyclohexyl-*H*), 5.44, 5.60, 6.07 (t, $^3J_{HH}$ = 2.9, 2.9, 2.6 Hz, 3H, Cp-*H*), 7.65, 7.71, 8.29, 8.30 (s, 4H, Oct-*H*). Anal. Calcd for $C_{43}H_{56}Zr_1Cl_2$: C, 70.26; H, 7.68. Found: C, 67.53; H, 7.76.

Me_2C(3-(diphenylmethyl)-C_5H_3)($C_{29}H_{36}$)H_2. A 250 mL flask was charged with octamethyloctahydrodibenzofluorene (2.988 g, 7.729 mmol), evacuated, and backfilled with argon before 60 mL of tetrahydrofuran and 5.2 mL of *n*-butyllithium solution (8.3 mmol, 1.6 M in hexanes) were syringed in. The orange solution was stirred for 4 h before a solution of 3-(diphenylmethyl)-6,6-dimethylfulvene (2.105 g, 7.728 mmol) in 25 mL of tetrahydrofuran was syringed in. Following an additional 30 h, the stirred reaction was quenched by slow 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 the product in quantitative yield (5.093 g) as a light yellow oil.

Me_2C(3-(diphenylmethyl)-C_5H_3)($C_{29}H_{36}$)Li_2. A round-bottom flask containing 5.093 g (7.728 mmol) of Me_2C(3-(diphenylmethyl)-C_5H_3)($C_{29}H_{36}$)H_2 was attached to a swivel frit and evacuated before 50 mL of diethyl ether was condensed in. At 0 °C, 10.4 mL of *n*-butyllithium solution (16.6 mmol, 1.6 M in hexanes) was syringed in over 2 min. After stirring for 26 h at room temperature, 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 (5.185 g) as an orange powder.

Me_2C(3-(diphenylmethyl)-C_5H_3)($C_{29}H_{36}$)$ZrCl_2$ (9). In the glovebox, 2.879 g of Me_2C(3-(diphenylmethyl)-C_5H_3)($C_{29}H_{36}$)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 allowed to warm slowly, and after 17 h of stirring, solvent was removed. Then 20 mL of methylene chloride was condensed in; the solution was warmed and stirred before solvent removal. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of diethyl ether. The filtrate volume was reduced to 40 mL, and the precipitated product was collected on a swivel frit and dried in vacuo: 0.793 g of **9** (22.6%). MS (LC-MS): *m*/*z* 818.8 (M^+). ^{1}H NMR (C_6D_6): δ 1.08, 1.20, 1.23, 1.29, 1.30, 1.30, 1.51, 1.58 (s, 24H, Oct-C*H*$_3$), 1.63 (m, 8H, Oct-C*H*$_2$), 1.90, 2.04 (s, 6H, (C*H*$_3$)$_2$C-Oct-Cp), 5.31, 5.55, 5.79 (t, $^3J_{HH}$ = 2.9, 3.0, 2.6 Hz, 3H, Cp-*H*), 5.86 (s, 1H, C*H*Ph$_2$), 6.91−7.15 (m, 10H, phenyl-*H*), 7.46, 6.65, 8.29, 8.31 (s, 4H, Oct-*H*). Anal. Calcd for $C_{50}H_{56}Zr_1Cl_2$: C, 73.32; H, 6.89. Found: C, 65.09; H, 6.86.

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. Then 210.0 mL of *n*-butyllithium in hexanes (1.6 M, 336.0 mmol) was syringed in at room temperature over 20 min. After shaking and stirring the obtained yellow slurry 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 stirring 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 massed 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. Me_2C(3-methyl-C_5H_3)($C_{13}H_8$)H_2 (11.86 g, 41.41 mmol) was combined with 200 mL of acetone (2720 mmol) and 15.0 mL of pyrrolidine (180 mmol). After stirring 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, brought to a boil for 4 h, and stirred overnight as the vessel 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^+). ^{1}H NMR ($CDCl_3$): δ 1.02, 1.02 (s, 6H, C(CH_3)$_2$Flu), 2.16, 2.25, 2.53 (s, 9H, 2,6,6-CH_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$_2$C(3-*tert*-butyl-4-methyl-C$_5$H$_2$)(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 was evacuated before 100 mL of diethyl ether was condensed in. Then 75.0 mL of methyllithium in diethyl ether (1.4 M, 105 mmol) was added by syringe, giving an orange, homogeneous solution after 1 h. After one 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$_2$C(3-*tert*-butyl-4-Me-C$_5$H$_2$)(C$_{13}$H$_8$)Li$_2$. A round-bottom flask containing 5.34 g (15.6 mmol) of Me$_2$C(3-*tert*-butyl-4-methyl-C$_5$H$_2$)(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 stirring for 15 h at room temperature, the orange precipitate was collected and dried in vacuo: 5.37 g (97.3%).

Me$_2$C(3-*tert*-butyl-4-Me-C$_5$H$_2$)(C$_{13}$H$_8$)ZrCl$_2$ (10). In the glovebox, 2.28 g of Me$_2$C(3-*tert*-butyl-4-methyl-C$_5$H$_2$)(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 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 allowed to warm slowly and after 23 h of stirring, solvent was removed. Methylene chloride (30 mL) was condensed in; the solution was warmed and stirred before solvent removal; 30 mL of diethyl ether was condensed in; 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 **10**: 1.60 g (49.5%). MS (LC-MS): *m*/*z* 502.3 (M^+). ^{1}H NMR (CD_2Cl_2): δ 1.16 (s, 9H, C(C*H*$_3$)$_3$), 2.07 (s, 3H, Cp-C*H*$_3$), 2.30, 2.32 (s, 6H, C(C*H*$_3$)$_2$), 5.43, 5.52 (d, $^3J_{HH}$ = 3.7, 3.7 Hz, 3H, Cp-*H*), 7.22, 7.23, 7.50, 7.53 (t, $^3J_{HH}$ = 7.3, 7.3, 8.4, 8.4 Hz, 4H, Flu-*H*), 7.79, 7.82, 8.10, 8.12 (d, $^3J_{HH}$ = 9.2, 9.2, 8.4, 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 $C_{26}H_{28}Zr_1Cl_2$: C, 62.13; H, 5.61. Found: C, 60.88, 60.89; H, 4.90, 4.94.

6,6-Adamantylidene-fulvene. (Synthesis modified from ref 32.) 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 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. Then 25.71 g (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. 6,6-Adamantylidenefulvene (6.00 g, 30.3 mmol) 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 was cooled to 0 °C and quenched by slow addition of 20 mL of saturated NH_4Cl solution. Then 300 mL of H_2O, 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 stirring for 48 h, 5 mL of acetic acid was injected, followed by 200 mL of H_2O 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_2O (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 with 150 mL of methanol. The precipitate in the filtrate was isolated by filtration at 0 °C and in vacuo drying: 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 stirring 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 stirring for 20 h, 60 mL of a saturated NH_4Cl 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$_4$)(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 stirring 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(3-(2-adamantyl)-C$_5$H$_3$)(C$_{13}$H$_8$)ZrCl$_2$ (11). A 2.00 g sample of Me$_2$C(3-(2-adamantyl)C$_5$H$_4$)(C$_{13}$H$_8$)Li$_2$ (0.00478 mol) and 1.114 g of $ZrCl_4$ (0.00478 mol) were combined in a swivel frit apparatus. Then 40 mL of petroleum ether was condensed in at −78 °C. This was allowed to warm slowly to room temperature before solvent removal after 14 h of stirring. Methylene chloride (40 mL) 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 **11** 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_6D_6): δ 1.84, 1.86 (s, 6H, C*H*$_3$), 1.36−2.04 (m, 14H, adamantyl-*H*), 3.32 (s, 1H, 2-adamantyl-*H*), 5.44, 5.48, 6.18 (m, 3H, Cp-*H*), 6.95, 7.03, 7.29, 7.34 (t, 4H, Flu-*H*), 7.41, 7.49, 7.84, 7.84 (d, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_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 $C_{31}H_{32}Zr_1Cl_2$: C, 65.70; H, 5.69. Found: C, 63.46, 61.93; H, 5.57, 5.42.

Fluorenyllithium. A Schlenk tube was charged with fluorene (31.81 g, 191.4 mmol), evacuated, backfilled with argon, and charged with 150 mL of toluene. *n*-Butyllithium solution (120.0 mL, 192 mmol, 1.6 M in hexanes) was syringed in, and the reaction was stirred for 103 h before the yellow slurry was cannulated onto a frit and the precipitate collected and dried in vacuo: 28.95 g (87.9%).

9-(ClMe$_2$Si)-fluorene. A swivel frit was charged with fluorenyllithium (7.00 g, 40.66 mmol) and 80 mL of petroleum ether. The vessel was cooled to −78 °C, and $SiMe_2Cl_2$ (10.0 mL, 82.44 mmol) was syringed in. The cold bath remained as the vessel was allowed to warm very slowly. After 48 h, the reaction was filtered and the solvent was removed from the filtrate to provide the product as an off-white powder: 8.10 g (77.0%). MS (GC-MS): *m*/*z* 258.3 (M^+). Competing formation of $Me_2Si(9\text{-fluorenyl})_2$ (MS (GC-MS) *m*/*z* 388.4 (M^+)), as reported by ref 39, occurs to about 10% (GC), but apparently does not affect the synthesis of **12**.

2-Adamantylcyclopentadienyllithium. Adamantylcyclopentadiene (10.78 g, 53.81 mmol) was added to a swivel frit, and 75 mL of diethyl ether was added by vacuum transfer. At 0 °C, *n*-butyllithium solution (34.0 mL, 54.4 mmol, 1.6 M in hexanes) was syringed in over 5 min. After stirring for 15 h at room temperature, the white solid was collected on the frit and dried in vacuo. The product was isolated in quantitative yield (11.10 g).

Me$_2$Si(3-(2-adamantyl)-C$_5$H$_3$)(C$_{13}$H$_8$)Li$_2$. A swivel frit was charged with 9-(ClMe$_2$Si)-fluorene (5.500 g, 21.25 mmol) and adamantylcyclopentadienyllithium (4.383 g, 21.25 mmol). Tetrahydrofuran (40 mL) was condensed in and the reaction stirred at room temperature for 19 h. Solvent was removed, and 50 mL of diethyl ether was condensed in. Filtration and washing removed LiCl. To the filtrate was added *n*-butyllithium solution (28.0 mL, 44.8 mmol, 1.6 M in hexanes) over 5 min at room temperature. Solvent was removed after stirring for 20 h. Petroleum ether (50 mL) was condensed in, and the material was broken up by stirring and shaking. Solvent was decanted, and the red solid was dried in vacuo to provide the product in quantitative yield (9.23 g).

Me$_2$Si(3-(2-adamantyl)-C$_5$H$_3$)(C$_{13}$H$_8$)ZrCl$_2$ (12). A 100 mL flask was charged with $Me_2Si(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (3.73 g, 8.58 mmol) and $ZrCl_4$ (2.00 g, 8.58 mmol) and equipped with a 180° needle valve. Petroleum ether (50 mL) was condensed in at −78 °C, and the cold bath was removed. This was allowed to warm slowly with stirring, and solvent was removed after 19 h. The solid was placed in a cellulose extraction thimble and was extracted overnight with 150 mL of methylene chloride in a Soxhlet extractor. The filtrate was filtered on a swivel frit, and the volume was reduced to 30 mL. The yellow-orange precipitate was collected on the frit and dried in vacuo: 0.707 g (14.1%). MS (LC-MS): *m*/*z* 582.7 (M^+). ^{1}H NMR (CD_2Cl_2): δ 1.11, 1.13 (s, 6H, C*H*$_3$), 1.48−1.99 (m, 14H, adamantyl-*H*), 3.03 (s, 1H, 2-adamantyl-*H*), 5.49, 5.75, 6.34 (m, 3H, Cp-*H*), 7.27, 7.27, 7.58, 7.60 (t, 4H, Flu-*H*), 7.51, 7.59, 8.11, 8.11 (d, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2, 35 °C): δ −1.12, −1.05 (Si-*C*H$_3$), 27.92, 32.49, 32.66, 37.86, 38.55, 38.71, 44.23 (adamantyl-*C*), 111.31, 111.86, 120.23 (Cp-*C*H$_1$), 123.52, 124.03, 124.20, 124.82, 126.23, 126.31, 128.54, 128.62 (Flu-*C*H$_1$), *C*H$_0$ not determined. Anal. Calcd for $C_{30}H_{32}Si_1Zr_1Cl_2$: C, 61.83; H, 5.53. Found: C, 58.63; H, 4.94.

6,6-Diisopropylfulvene. A 500 mL round-bottom flask was charged with 150 mL of 2,4-dimethyl-3-pentanone (1060 mmol), 60.0 mL of cyclopentadiene (728 mmol), and 44.00 g of sodium methoxide (815 mmol). The deep red slurry was placed on a mechanical shaker for 12 days. Then 300 mL of aqueous NH_4Cl and 200 mL of diethyl ether were added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (5 × 50 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and rotavapped. Under high vacuum, unreacted ketone was removed by Kugelrohr distillation at 40 °C. Crude (95%) 6,6-diisopropylfulvene was obtained from the next Kugelrohr fraction at 60−80 °C; the orange oil massed 31.30 g (17.7%). ^{1}H NMR ($CDCl_3$): δ 1.28 (d, $^3J_{HH}$ = 7.0 Hz, 12H, C*H*$_3$), 3.11, (septet, $^3J_{HH}$ = 7.0 Hz, 2H, *i*-Pr-*H*), 6.46, 6.64 (m, 4H, fulvene-*H*).

2,4-Dimethyl-3-pentylcyclopentadiene. A 500 mL Schlenk flask was charged with 4.00 g of $LiAlH_4$ (105 mmol) and 150 mL of diethyl ether. An attached addition funnel was charged with 9.38 g of 6,6-diisopropylfulvene (57.8 mmol) and 50 mL of diethyl ether. The fulvene solution was added at 0 °C over 15 min and rinsed down with an additional 50 mL of diethyl ether. The cold bath was removed and the reaction was stirred for 48 h before it was cooled to 0 °C, and 50 mL of H_2O was added dropwise via a metered addition funnel. The ether layer was isolated, and the remaining white solid was extracted with diethyl ether (3 × 50 mL). The combined organic layers were filtered and rotavapped to yield 8.13 g of product (85.6%) as a light yellow oil.

3-(2,4-Dimethyl-3-pentyl)-6,6-dimethylfulvene. To 2,4-dimethyl-3-pentylcyclopentadiene (8.13 g, 49.5 mmol) were added 50 mL of methanol, 30 mL of acetone (409 mmol), and 10.0 mL of pyrrolidine (120 mmol). After stirring for 10 days, 15 mL of acetic acid was injected, followed by 300 mL of H_2O and 100 mL of diethyl ether. The organic layer was isolated, and the aqueous layer extracted with diethyl ether (3 × 50 mL). The combined organic layers were extracted with H_2O (3 × 30 mL) and with 10% aqueous NaOH (3 × 30 mL), dried over $MgSO_4$, filtered, and rotavapped. This material was subjected to Kugelrohr distillation under high vacuum. Then 3 mL was distilled at room temperature and discarded. Product was obtained from the next fraction, obtained at 80 °C: 9.39 g (92.9%) of an orange oil.

Me$_2$C(3-(2,4-dimethyl-3-pentyl)-C$_5$H$_3$)(C$_{13}$H$_8$)H$_2$. A 250 mL flask was charged with fluorenyllithium diethyl ether adduct (6.026 g, 24.47 mmol). Diethyl ether (60 mL) was condensed in, and 3-(2,4-dimethyl-3-pentyl)-6,6-dimethylfulvene (5.00 g, 24.5 mmol) was injected. After 6 days, 60 mL of aqueous NH_4Cl solution was slowly added 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 provide the product in quantitative yield (9.07 g) as a light yellow oil.

Me$_2$C(3-(2,4-dimethyl-3-pentyl)-C$_5$H$_3$)(C$_{13}$H$_8$)Li$_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2,4\text{-dimethyl-3-pentyl})\text{-}C_5H_3)(C_{13}H_8)H_2$ (9.07 g, 24.5 mmol) in 50 mL of diethyl ether with 33.0 mL of *n*-butyllithium solution (52.8 mmol, 1.6 M in hexanes) at 0 °C. After stirring for 25 h, the solvent was removed by vacuum transfer, and 75 mL of petroleum ether was condensed in. A red-orange powder was isolated in quantitative yield (9.36 g) by filtration and in vacuo drying.

Me$_2$C(3-(2,4-dimethyl-3-pentyl)-C$_5$H$_3$)(C$_{13}$H$_8$)ZrCl$_2$ (13). $Me_2C(3\text{-}(2,4\text{-dimethyl-3-pentyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (4.103 g, 10.73 mmol) and 2.500 g of $ZrCl_4$ (10.73 mmol) were combined in a 100 mL round-bottom flask, equipped with a 180° needle valve. Then 40 mL of petroleum ether was condensed in at −78 °C. This was allowed to warm slowly to room temperature before solvent removal after 26 h of stirring. Then 30 mL of methylene chloride was condensed in and removed in order to quench unreacted ligand. The orange solid was extracted in a cellulose extraction thimble for 48 h with 150 mL of diethyl ether. The filtrate volume was reduced to 75 mL, and 0.491 g (8.6%) of **13** as an orange powder was obtained following collection at 0 °C and in vacuo drying. MS (LC-MS): *m*/*z* 530.7 (M^+). ^{1}H NMR (C_6D_6): δ 0.58, 0.90, 0.93, 1.01 (d, $^3J_{HH}$ = 7.0, 7.0, 7.0, 7.0 Hz, 12H, C*H*$_3$), 1.84, 1.86 (s, 6H, C(C*H*$_3$)$_2$), 2.25, 2.25 (m, 2H, C*H*(CH$_3$)$_2$), 2.57 (t, $^3J_{HH}$ =

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2.4 Hz, 1H, 3-*H*-pentyl), 5.36, 5.53, 6.21 (t, $^3J_{HH}$ = 2.6, 3.3, 2.6 Hz, 3H, Cp-*H*), 6.98, 7.01, 7.29, 7.33 (t, $^3J_{HH}$ = 7.0, 7.0, 7.0, 7.0 Hz, 4H, Flu-*H*), 7.47, 7.47, 7.82. 7.82 (d, $^3J_{HH}$ = 8.8, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*). Anal. Calcd for $C_{28}H_{32}Zr_1Cl_2$: C, 63.37; H, 6.08. Found: C, 56.61; H, 5.56.

6,6-Adamantylidenefulvene. (Synthesis modified from ref 32.) 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 stirring 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^+).

3-(2-Methyl-2-adamantyl)-6,6-dimethylfulvene. A 500 mL flask was charged with 6,6-adamantylidenefulvene (18.00 g, 90.77 mmol), equipped with a 180° needle valve, and charged with 120 mL of diethyl ether. At 0 °C, methyllithium lithium bromide solution (150.0 mL, 225 mmol, 1.5 M in diethyl ether) was syringed in over 10 min. Dimethoxyethane (10 mL) was syringed in and the reaction was stirred at room temperature for 8 days when 60 mL of aqueous NH_4Cl solution was slowly added at 0 °C. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to provide 19.46 g of (2-methyl-2-adamantyl)cyclopentadiene as a light yellow oil (theoretical yield). To this were added 30 mL of acetone (409 mmol), 100 mL of methanol, and 10 mL of pyrrolidine (120 mmol). After stirring for 96 h, the yellow precipitate was collected by filtration, rinsed with 50 mL of methanol, and dried in vacuo to provide the product: 20.36 g (88.2%). MS (GC-MS): *m*/*z* 254.5 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.22, 2.17, 2.17 (s, 9H, C*H*$_3$), 1.56−2.04 (m, 14H, adamantyl-*H*), 6.17, 6.52, 6.54 (m, 3H, fulvene-*H*). ^{13}C NMR ($CDCl_3$): δ 22.88, 22.97, 27.92, 28.03 (*C*H$_1$), 27.92, 35.17, 35.17 (*C*H$_3$), 32.98, 32.98, 34.59, 34.59, 39.08 (*C*H$_2$), 41.47 (*C*H$_0$), 113.36, 121.04, 130.38 (fulvene-*C*H$_1$), 142.41, 146.12, 156.16 (fulvene-*C*H$_0$). Anal. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.57; H, 10.04.

Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)Li_2. A 250 mL flask was charged with 3-(2-methyl-2-adamantyl)-6,6-dimethylfulvene (8.000 g, 31.45 mmol) and fluorenyllithium diethyl ether adduct (7.744 g, 31.45 mmol). Diethyl ether (75 mL) was condensed in, and the reaction was stirred at room temperature for 4 days before 60 mL of aqueous NH_4Cl was slowly added at 0 °C. 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 Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)H_2 in theoretical yield (13.23 g). The flask was attached to a swivel frit and charged with 50 mL of diethyl ether before *n*-butyllithium solution (42.0 mL, 67.2 mmol, 1.6 M in hexanes) was syringed in over 4 min at 0 °C. After 23 h, solvent was removed and 75 mL of petroleum ether was added by vacuum transfer. The red solid was broken up, stirred, collected on the frit, and dried in vacuo: 15.85 g (18.26 g theoretical yield for the *bis* diethyl ether adduct).

Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)$ZrCl_2$ (14). A 100 mL flask was charged with Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)Li_2 (4.640 g, 10.73 mmol) and $ZrCl_4$ (2.500, 10.73 mmol) and equipped with a 180° needle valve. Petroleum ether (50 mL) was condensed in at −78 °C and the cold bath removed. After 70 h, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL of methylene chloride overnight. The filtrate was attached to a swivel frit, filtered, and condensed to 40 mL. The precipitate was collected and dried in vacuo: 3.246 g (52.1%). MS (LC-MS): *m*/*z* 580.5 (M^+). ^{1}H NMR (C_6D_6): δ 1.32−2.62 (m, 14H, adamantyl-*H*), 1.73, 1.85, 1.89 (s, 9H, C*H*$_3$), 5.73, 5.83, 6.14 (t, $^3J_{HH}$ = 3.3, 2.9, 3.3 Hz, 3H, Cp-*H*), 6.98, 7.02, 7.28, 7.34 (t, $^3J_{HH}$ = 7.0, 7.7, 7.0, 7.7 Hz, 4H, Flu-*H*), 7.46, 7.54, 7.76, 8.87 (d, $^3J_{HH}$ = 9.2, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 26.69, 27.47, 27.77, 28.99, 33.25, 33.76, 34.84, 39.36, 40.18 (adamantyl-*C*), 28.28, 29.11, (*C*H$_3$), 41.68 (2-*C*-adamantyl), 42.07 (2-*C*H$_3$-adamantyl), 102.54, 105.28, 120.28 (Cp-*C*H$_1$), 123.81, 124.17, 124.36, 124.46, 124.51, 125.25, 127.94, 129.10 (benzo-*C*H$_1$), 112.14, 120.68, 123.68, 125.72, 127.82, 129.55, 139.05, 145.94 (*C*H$_0$). Anal. Calcd for $C_{32}H_{34}Zr_1Cl_2$: C, 66.18; H, 5.90. Found: C, 57.60; H, 5.23.

(2-Phenyl-2-adamantyl)cyclopentadiene. A 300 mL flask was charged with 6,6-adamantylidenefulvene (10.00 g, 50.43 mmol), and 75 mL of diethyl ether was condensed in. At −78 °C 60.0 mL of phenyllithium solution (108 mmol, 1.8 M in cyclohexane/diethyl ether) was injected and the cold bath removed. After 89 h, the vessel was cooled to 0 °C, and 60 mL of aqueous NH_4Cl solution was slowly added. The ether 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 give the product in quantitative yield (13.94 g) as a tan-colored solid.

3-(2-Phenyl-2-adamantyl)-6,6-dimethylfulvene. To (2-phenyl-2-adamantyl)cyclopentadiene (13.94 g, 50.4 mmol) were added 100 mL of methanol, 50 mL of acetone (680 mmol), and 10.0 mL of pyrrolidine (120 mmol). After stirring for 4 days, 100 mL of methanol was added, and the yellow precipitate was collected by suction filtration. The product was washed with 100 mL of methanol and dried in vacuo: 14.76 g (92.5%). MS (GC-MS): *m*/*z* 316.5 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.63−2.22, 2.94 (m, 14H, adamantyl-*H*), 2.06, 2.10, (s, 6H, C*H*$_3$), 6.19 (s, 1H, 2-*H*-fulvene), 6.38, 7.48 (d, $^3J_{HH}$ = 5.5, 4.8 Hz, 2H, 4,5-*H*-fulvene), 7.05 (t, $^3J_{HH}$ = 7.0 Hz, 1H, 4-*H*-phenyl), 7.24, (t, $^3J_{HH}$ = 8.0 Hz, 2H, 3,5-*H*-phenyl), 7.40 (d, $^3J_{HH}$ = 7.7 Hz, 2H, 2,6-*H*-phenyl). Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 90.66; H, 8.56.

Me_2C(3-(2-phenyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)H_2. A 300 mL flask was charged with fluorenyllithium diethyl ether adduct (3.113 g, 12.64 mmol) and 3-(2-phenyl-2-adamantyl)-6,6-dimethylfulvene (4.000 g, 12.64 mmol). Diethyl ether (60 mL) was condensed in, and the reaction was stirred for 42 h before 60 mL of aqueous NH_4Cl solution was slowly added 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 provide the product in quantitative yield (6.10 g) as a light yellow oil.

Me_2C(3-(2-phenyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)Li_2. The dianion was prepared by treating a solution of Me_2C(3-(2-phenyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)H_2 (6.10 g, 12.6 mmol) in 50 mL of diethyl ether with 17.0 mL of *n*-butyllithium solution (27.2 mmol, 1.6 M in hexanes) at 0 °C. After stirring for 21 h, the solvent was removed and 50 mL of petroleum ether was condensed in. The product was isolated in quantitative yield (6.25 g) after filtration and in vacuo drying.

Me_2C(3-(2-phenyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)$ZrCl_2$ (15). A 100 mL flask was charged with Me_2C(3-(2-phenyl-2-adamantyl)-C_5H_3)($C_{13}H_8$)Li_2 (2.653 g, 5.364 mmol) and $ZrCl_4$ (1.250, 5.364 mmol) and equipped with a 180° needle valve. Petroleum ether (50 mL) was condensed in at −78 °C and the cold bath removed. After 22 h, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL of methylene chloride overnight. The filtrate was attached to a swivel frit and filtered. The solvent was removed, and 30 mL of diethyl ether was condensed in. The yellow-orange solid was collected and dried in vacuo: 1.993 g (57.8%). MS (LC-MS): *m*/*z* 642.6 (M^+). ^{1}H NMR (C_6D_6): δ 1.36−3.13 (m, 14H, adamantyl-*H*), 1.77, 1.83 (s, 6H, C(C*H*$_3$)$_2$), 5.49, 5.66, 5.98 (t, $^3J_{HH}$ = 3.3, 2.9, 2.9 Hz, 3H, Cp-*H*), 6.92, 6.99, 7.25, 7.30 (t, $^3J_{HH}$ = 7.0, 8.0, 7.7, 8.4 Hz, 4H, Flu-*H*), 7.03, 7.18 (t, $^3J_{HH}$ = 7.3, 7.0 Hz, 3H, phenyl-*H*), 7.38 (d, $^3J_{HH}$ = 8.8 Hz, 2H, phenyl-*H*), 7.40, 7.66, 7.73, 7.76 (d, $^3J_{HH}$ = 9.6, 7.3, 8.4, 8.0 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.17, 28.94 (C-(*C*H$_3$)$_2$), 26.43, 27.86, 32.27, 33.11, 34.25, 34.53, 37.85,

39.06, 40.03, 50.04 (adamantyl-*C*), 102.62, 105.10, 121.50 (Cp-*C*H_1), 123.63, 123.89, 124.26, 124.50, 124.56, 125.04, 125.48, 127.42, 127.42, 127.87, 128.00, 128.84, 129.62 (phenyl- and Flu-*C*H_1), 143.61, 144.27 (ipso-*C* and 9-Flu-*C*), *C*H_0 not determined. Anal. Calcd for $C_{37}H_{36}Zr_1Cl_2$: C, 69.13; H, 5.64. Found: C, 67.61; H, 5.39.

Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{29}H_{36}$)Li_2. A 250 mL flask was charged with octamethyloctahydrodibenzofluorene (6.079 g, 15.72 mmol), equipped with a 180° needle valve, and charged with 75 mL of diethyl ether before *n*-butyllithium solution (10.5 mL, 16.8 mmol, 1.6 M in hexanes) was syringed into the white slurry over 10 min. After 20 h, solvent was removed from the yellow slurry, and 3-(2-methyl-2-adamantyl)-6,6-dimethylfulvene (4.000 g, 15.72 mmol) was added. Diethyl ether (75 mL) was condensed in, and the reaction, which became homogeneous upon warming, was stirred for 13 days before 60 mL of water was slowly syringed in at 0 °C. 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, rotavapped, and dried in vacuo to provide Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)-($C_{29}H_{36}$)H_2 in theoretical yield (11.21 g). This flask was attached to a swivel frit, evacuated, and charged with diethyl ether (75 mL) by vacuum transfer. At room temperature, *n*-butyllithium solution (21.0 mL, 16.8 mmol, 1.6 M in hexanes) was syringed in over 8 min. After 15 h, solvent was removed, and 50 mL of petroleum ether was condensed in. The product slowly precipitated over 2 h and was collected and dried in vacuo: 3.525 g (34.3%).

Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{29}H_{36}$)$ZrCl_2$ (16). A swivel frit apparatus was charged with Me_2C(3-(2-methyl-2-adamantyl)-C_5H_3)($C_{29}H_{36}$)Li_2 (3.525 g, 5.399 mmol) and $ZrCl_4$ (1.258 g, 5.398 mmol). Petroleum ether (60 mL) was condensed in at −78 °C, and the cold bath remained as the reaction was allowed to warm very slowly. After 20 h, the reaction was filtered and all solvent was removed from the filtrate. A red powder was obtained following lyophilization from 30 mL of benzene. Hexamethyldisiloxane (30 mL) was condensed in, and the red slurry was stirred for 4 h before the product was collected by filtration and dried in vacuo: 0.614 g (14.2%). MS (LC-MS): *m*/*z* 800.9 (M^+). ^{1}H NMR (CD_2Cl_2): δ 1.20, 1.22, 1.34, 1.36, 1.36, 1.38, 1.39, 1.39 (s, 24H, Oct-CH_3), 1.32, 1.70 (m, 14H, adamantyl-*H*), 1.48 (s, 3H, 2-CH_3-adamantyl), 1.72 (m, 8H, Oct-CH_2), 2.29, 2.31 (s, 6H, (CH_3)$_2$C), 5.66 (m, 2H, Cp-*H*), 6.09 (t, $^3J_{HH}$ = 2.6 Hz, 1H, Cp-*H*), 7.60, 7.63, 7.98, 8.02 (s, 4H, Oct-*H*). ^{13}C NMR (CD_2Cl_2): δ 26.08, 27.55, 27.55, 27.55, 27.78, 27.78, 28.63, 28.86 (Oct-*C*H_3), 31.85, 32.37 (C(*C*H_3)$_2$), 31.81, 32.27, 33.24, 33.54 (adamantyl-*C*H_1), 33.49, 33.86, 34.13, 34.34, 34.45, 34.92, 35.09, 35.23, 35.29, 38.95, 38.99, 39.26, 39.57 (adamantyl and Oct*C*H_2 and *C*H_0), 41.68 (2-*C*-adamantyl), 42.46 (2-*C*H_3-2-adamantyl), 74.50 (*C*(CH_3)$_2$), 101.17, 102.23, 116.91 (Cp-*C*H_1), 120.51, 120.91, 121.70, 121.84 (benzo-*C*H_1), 139.44 (9-fluorenyl-*C*), 109.97, 119.60, 122.35, 122.42, 143.91, 145.32, 145.39, 145.74, 146.84, 147.48 (Cp and Oct *C*H_0). Anal. Calcd for $C_{48}H_{62}Zr_1Cl_2$: C, 71.96; H, 7.80. Found: C, 71.62; H, 7.37.

(2-(CH_2SiMe_3)-2-adamantyl)cyclopentadiene. A 250 mL flask was charged with 6,6-adamantylidenefulvene (8.000 g, 40.34 mmol) and $LiCH_2SiMe_3$ (8.000 g, 84.96 mmol). Then 100 mL of diethyl ether was condensed in, and the reaction was stirred at room temperature for 16 h when the vessel was cooled to 0 °C and 60 mL of aqueous NH_4Cl solution was slowly added. The organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to provide the product in quantitative yield (11.56 g).

3-(2-(CH_2SiMe_3)-2-adamantyl)-6,6-dimethylfulvene. To (2-(CH_2SiMe_3)-2-adamantyl)cyclopentadiene (11.56 g, 40.3 mmol) were added 100 mL of acetone (1360 mmol) and 10.0 mL of pyrrolidine (120 mmol). After stirring for 4 days, 10 mL of acetic acid was injected, followed by 200 mL of H_2O and 200 mL of diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 × 50 mL). The combined organic layers were extracted with H_2O (4 × 25 mL), dried over $MgSO_4$, filtered, and rotavapped. This material was subjected to Kugelrohr distillation under high vacuum. Then 10.8 g was distilled at 60 °C and discarded. Product was obtained from the next fraction, obtained at 120−140 °C: 10.54 g (80.0%) of a yellow oil.

Me_2C($C_{13}H_8$)(3-(2-(CH_2SiMe_3)-2-adamantyl)-C_5H_3)H_2. A 250 mL flask was charged with fluorenyllithium diethyl ether adduct (5.482 g, 22.26 mmol) and 3-(2-(CH_2SiMe_3)-2-adamantyl)-6,6-dimethylfulvene (7.270 g, 22.26 mmol). Diethyl ether (100 mL) was condensed in, and the reaction was stirred for 16 h before 60 mL of aqueous NH_4Cl solution was slowly added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (3 × 30 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the product in quantitative yield (10.97 g) as a waxy solid.

Me_2C($C_{13}H_8$)(3-(2-(CH_2SiMe_3)-2-adamantyl)-C_5H_3)Li_2. The dianion was prepared by treating a solution of Me_2C($C_{13}H_8$)(3-(2-(CH_2SiMe_3)-2-adamantyl)-C_5H_3)H_2 (10.97 g, 22.26 mmol) in 50 mL of diethyl ether with 30.0 mL of *n*-butyllithium solution (48.0 mmol, 1.6 M in hexanes) at 0 °C. After stirring for 23 h, the solvent was removed and 75 mL of petroleum ether was condensed in. The product was isolated by decanting the solvent and drying the residue in vacuo: 8.013 g (71.3%).

Me_2C(3-(2-(CH_2SiMe_3)-2-adamantyl)-C_5H_3)($C_{13}H_8$)$ZrCl_2$ (17). A 100 mL flask was charged with Me_2C($C_{13}H_8$)(3-(2-(CH_2SiMe_3)-2-adamantyl)-C_5H_3)Li_2 (4.331 g, 8.582 mmol) and $ZrCl_4$ (2.000, 8.583 mmol) and equipped with a 180° needle valve. Petroleum ether (50 mL) was condensed in at −78 °C and the cold bath removed. After 22 h, solvent was removed. This was attached to a swivel frit, 70 mL of toluene was condensed in, and the solution was filtered. The filtrate was condensed to 10 mL, and the precipitate was collected and dried in vacuo: 0.543 g (9.7%). MS (LC-MS): *m*/*z* 652.6 (M^+). ^{1}H NMR (C_6D_6): δ −0.03 (s, 9H, Si-(CH_3)$_3$), 1.36, 1.37 (s, 2H, C*H*$_2$Si(CH_3)$_3$), 1.36−2.15 (m, 14H, adamantyl-*H*), 2.33, 2.35 (s, 6H, CH_3), 5.66, 5.88, 6.30 (t, $^3J_{HH}$ = 2.9, 3.3, 2.6 Hz, 3H, Cp-*H*), 7.23, 7.25, 7.52, 7.52 (m, 4H, Flu-*H*), 7.82, 7.89, 8.07, 8.10 (d, $^3J_{HH}$ = 8.8, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 1.51 (Si-*C*H_3), 27.44, 27.64 (*C*H_3), 28.22, 29.12, 31.24, 34.19, 34.27, 34.30, 34.52, 36.14, 37.76, 39.62 (adamantyl-*C*), 103.07, 104.52, 120.20 (Cp-*C*H_1), 123.68, 124.14, 124.36, 124.69, 124.77, 125.33, 128.19, 129.01 (Flu-*C*H_1), *C*H_0 not determined. Anal. Calcd for $C_{35}H_{42}Si_1Zr_1Cl_2$: C, 64.38; H, 6.48. Found: C, 57.53; H, 5.51.

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 (Andrews Glass Co.) and 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 gastight 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. Polymerization reactions are further described in Table 5.

Representative Polymerization Procedures. Entry 36. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.100 g, 1.72×10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of **14** (0.001 g, 1.7×10^{-6} mol) in toluene (2.0 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 37. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.100 g, 1.72×10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of **14** (0.001 g, 1.7×10^{-6} mol) in toluene (2.0 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 38. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44×10^{-3} mol [Al]). Propylene (60 mL) was condensed in at 0 °C. A solution of **14** (0.002 g, 3.4×10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0 °C ice/water bath for 60 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 39. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44×10^{-3} mol [Al]). Propylene (55 mL) was condensed in at 0 °C. A solution of **14** (0.002 g, 3.4×10^{-6} mol) in toluene (2.0 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 40. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44×10^{-3} mol [Al]). Propylene (55 mL) was condensed in at 0 °C. A solution of **14** (0.002 g, 3.4×10^{-6} mol) in toluene (2.0 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 41. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44×10^{-3} mol [Al]) and 28.0 mL of toluene. Propylene (3 mL) was condensed in. A solution of **14** (0.002 g, 3.4×10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0 °C ice/water bath for 180 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 42. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44×10^{-3} mol [Al]) and 28.0 mL of toluene. Propylene (3 mL) was condensed in. A solution of **14** (0.002 g, 3.4×10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 20 °C water bath for 90 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 45. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.145 g, 2.50×10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of **16** (0.002 g, 2.5×10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0 °C ice/water bath for 20 min. The reaction was vented and quenched with dilute HCl/methanol.

Entry 46. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.145 g, 2.50×10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0 °C. A solution of **16** (0.002 g, 2.5×10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 20 °C water bath for 20 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.[40] Spectra were acquired at 124 °C with tetrachloroethane-d_2 as solvent. A 90 degree pulse was employed with broadband decoupling. A delay time of 3 s and a minimum of 1000 scans were used.

Acknowledgment. This work has been supported by US-DOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER13431), Exxon Chemicals America, and the National Science Foundation (Grant No. CHE-0131180). A DOD National Defense Science and Engineering Fellowship awarded to S.M. is also acknowledged. The authors thank Dr. Michael Day and Mr. Lawrence Henling for obtaining the X-ray crystal structure, as well as Dr. Terry Burkhardt at ExxonMobil and Dr. Andreas Ernst at BP-Amoco for assistance in obtaining molecular weight data.

Supporting Information Available: Derivation of the alternating models and complete statistical analysis for polypropylenes made by **10**/MAO (entries 23−29). Details of the X-ray structure determination for **10**, including selected bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050841K

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