Metallocene-Mediated Olefin Polymerization: The Effects of Distal Ligand Perturbations on Polymer Stereochemistry

Thesis by
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For Lynn, Mom, Dad, and Ed

Acknowledgments

While writing a three-hundred page dissertation is difficult, properly acknowledging everyone who has contributed to its production is arguably more challenging. I guess that is why this section is the final addition to my thesis. I am indebted to many people for assistance, advice, and encouragement that have made my graduate experience both enjoyable and productive.

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ABSTRACT: New group IV compounds containing a 9-dialkylaminofluorenide ligand have been prepared. Their properties and reactivity have been investigated. For example, single crystal X-ray analysis of the metallocene (9-(N,N-dimethylamino)fluorenyl)$_2$ZrCl$_2$ (**4**) reveals a bonding mode that includes a zirconium-nitrogen bond. In combination with methylaluminoxane (MAO), several aminofluorenide complexes afford atactic polypropylene.

A statistical model has been developed that quantifies the unidirectional site epimerization probability, ε, for singly- and doubly-bridged C_1- symmetric metallocene polymerization catalysts. The unidirectional site epimerization model allows deconvolution of the site sequence probability and the stereochemical probability for producing a given pentad.

Highly stereoregular syndiotactic polypropylene is obtained with the catalyst systems $Ph_2C(Oct)(C_5H_4)ZrCl_2$ / MAO (**8** / MAO) (Oct = octamethyloctahydrodibenzofluorenyl, $C_{29}H_{36}$) and $Me_2C(Oct)(C_5H_4)ZrCl_2$ / MAO (**12** / MAO). Melting temperatures as high as 153°C or 154°C are found for the thermally quenched polymers. Distal ligand perturbations are demonstrated to have a dramatic effect on polymer stereochemistry.

Polypropylenes that are isotactic-hemiisotactic or syndiotactic-hemiisotactic can be made with proper R substituent selection in the catalyst system $Me_2C(Flu)(3\text{-}R\text{-}C_5H_3)ZrCl_2$ / MAO or $Me_2C(Oct)(3\text{-}R\text{-}C_5H_3)ZrCl_2$ / MAO, where Flu = fluorenyl ($C_{13}H_8$). The prepared polymers have been subjected to a statistical model which suggests that the metallocenes have one highly selective site (99%) and one site of variable selectivity which is highly dependent on the nature of the R substituent and whether the metallocene contains the Flu or Oct ligand.

Control of the tacticity of isotactic-hemiisotactic polypropylene, as quantified by the parameter α, is achieved by proper R substituent selection in the catalyst system $R'_2C(3\text{-}R\text{-}C_5H_3)(C_{13}H_8)MCl_2$ / MAO. For R = 2-adamantyl, R' = Ph, and M = Zr or Hf, α is approximately 0.60 and the polypropylene obtained is elastomeric. Its properties are rationalized by the statistical existence of isotactic stereoblocks among an otherwise amorphous hemiisotactic medium.

For the C_1-symmetric polymerization catalyst $Me_2C(3\text{-}t\text{-butyl-}C_5H_3)(9\text{-}C_{13}H_8)ZrCl_2$ / MAO, evidence gathered here supports an alternating mechanism in which both sites of the metallocene wedge are utilized for monomer insertion. For an Oct-containing catalyst system with a cyclopentadienyl substituent of R = 2-methyl-2-adamantyl, unprecedentedly high isotacticity (>99% [mmmm]) is observed for a fluorenyl-based metallocene catalyst. Melting temperatures for such isotactic polymers can be as high as 167°C (T_p = 0°C).

Metallocene-Mediated Olefin Polymerization: The Effects of Distal Ligand Perturbations on Polymer Stereochemistry

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Introduction

Chapter 1 does not categorically fit within the subject matter described by the title of this thesis. Nonetheless, it is included as representative of some of the synthetic-organometallic contributions made early in my graduate career.

The remaining chapters are unified under a general theme that is summarized by the title: *Metallocene-Mediated Olefin Polymerization: The Effects of Distal Ligand Perturbations on Polymer Stereochemistry.* While the polymer tacticities explored vary considerably from chapter to chapter, their existence depends on modifications of the metallocene's ligand which are quite removed spatially from the catalytic metal center.

Chapter 2 describes a unidirectional site epimerization model and applies this model to polymers made: previously in the Bercaw group by Tim Herzog and Dario Veghini employing doubly-bridged metallocenes; and currently by employing novel singly-bridged metallocenes. Very preliminary results regarding this model were reported in a footnote in the paper by Veghini, et al. This chapter provides the complete results as well as their theoretical origin.

Chapter 3 focuses mainly on preparing highly syndiotactic polypropylene via perturbations of the metallocene's distal framework. The very high polymer melting temperatures constitute macroscopic observables that are a direct consequence of seemingly innocuous modifications; indeed, some might have predicted that modifications so distant from the metal itself would have little or no impact on polymer stereochemistry.

Chapter 4 discusses the synthesis of isotactic-hemiisotactic and syndiotactic-hemiisotactic polypropylenes—tacticities made possible by very subtle changes in the substituents of metallocene catalysts. A very broad spectrum of polymer properties is thereby achievable.

Chapter 5 is derivative of Chapter 4, and the two might have been combined. Instead, the elastomeric polypropylene obtained for certain types of isotactic-hemiisotactic polypropylene is described its own chapter. The polymer properties result from a scrupulous understanding of the impact slight ligand modifications have on both polymer stereochemistry and polymer molecular weight.

Chapter 6 aims to settle which of two debated mechanisms applies to certain C_1-symmetric metallocene polymerization catalysts. Much of the mechanistic elucidation was made possible by preparing distally perturbed variants of the parent metallocene. The effects were often large and led to the design of a highly modified, highly isospecific metallocene catalyst.

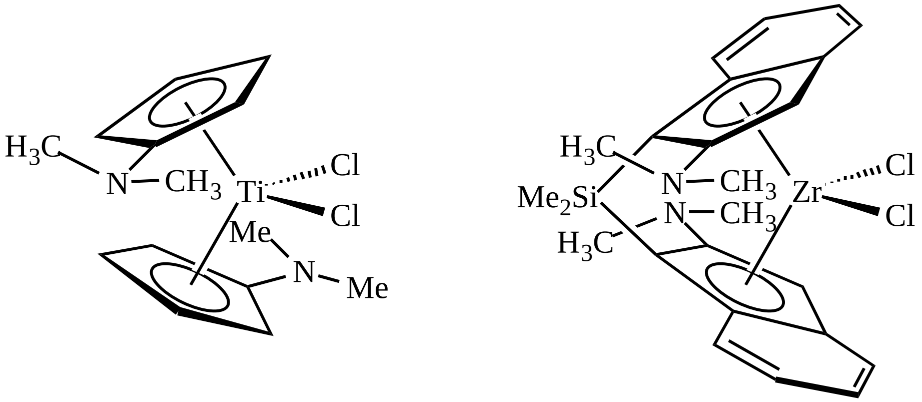
Chapter 1

Aminofluorenide Derivatives of Group IV Metallocenes

ABSTRACT: New group IV compounds containing a 9-(dialkylamino)fluorenide ligand have been prepared. Their properties and reactivity have been investigated. For example, single crystal X-ray analysis of the metallocene (9-(N,N-dimethylamino)fluorenyl)$_2$ZrCl$_2$ (**4**) reveals a bonding mode that includes a zirconium-nitrogen bond. The asymmetric unit contains two molecules of different hapticities; these are best described as η^4,η^4 and η^3, η^4. The barrier to rotation around the C-N bond of (9-(N,N-diisopropylamino)fluorenyl)(pentamethylcyclopentadienyl)ZrCl$_2$ (**9**) has been determined: $\Delta G^\ddagger$ (-25°C) = 11.1 kcal/mol. Unlike related aminoborollide complexes, aminofluorenide complexes resist quaternization by alkyl halides. Several aminofluorenide complexes have been tested for propylene polymerization behavior in the presence of methylaluminoxane (MAO); atactic polypropylene is obtained with very low activities. The syntheses of 9-(dialkylamino)fluorene compounds are described, as are the syntheses of group IV compounds via the corresponding 9-(dialkylamino)fluorenide lithium salts.

1.1 Introduction

Group IV metallocenes bearing amine groups directly appended to the cyclopentadienyl rings[1-4] have long been synthetic targets and have recently been shown to be of catalytic interest.[5] For example, (N,N-dimethylamino cyclopentadienyl)$_2$TiCl$_2$ (**1**)[2] and *rac*-Me$_2$Si(2-(N,N-dimethylamino)indenyl)$_2$ZrCl$_2$ (**2**)[5] can be prepared from the corresponding lithium salts and TiCl$_4$ or ZrCl$_4$. In conjunction with methylaluminoxane (MAO), **2** forms an active propylene polymerization catalyst.[5]

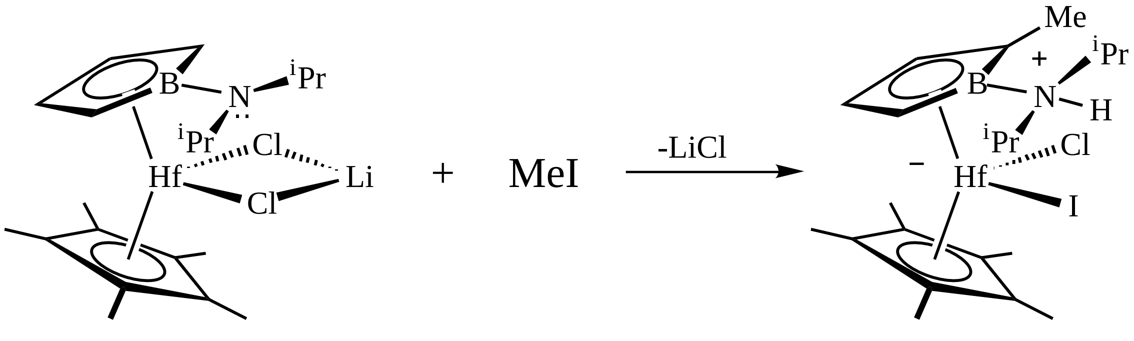


1 **2**

Figure 1. Previously reported aminocyclopentadienyl metallocenes.

Several group IV compounds containing the dianionic aminoborollide ligand have been prepared and characterized.[6] Compound **3** contains a diisopropylamino group directly bound to the boron atom of the borole ligand. Such amphoteric complexes show Lewis acidic and basic reactivity and effect heterolytic cleavage of various bonds. For example, **3** reacts with methyl iodide to give the zwitterionic compound shown in Figure 2.

We are interested in understanding the fundamental properties of fluorenide as an early transition metal ligand. Curiously, although (fluorenyl)$_2$ZrCl$_2$ thermally decomposes both in solution and in the solid state, its single crystal structure has been solved.[7] Moreover, it is essentially inactive towards the polymerization of propylene in the presence of MAO.[8] Various modifications of the fluorenyl ligand—including the placement of alkyl groups in the 9 and 1-8 benzo positions—afford stability to such metallocene dichloride complexes. It was proposed that placement of dialkylamino groups in the 9 positions of the fluorenyl moieties would not only provide a more robust compound, but would create one having interesting structural features, small molecule reactivity on account of its Lewis basic and acidic sites, and polymerization activity.



3

Figure 2. Aminoborollide-containing metallocenes often show Lewis acid / base reactivity.

1.2 Ligand Synthesis

The syntheses of several 9-(N,N-dialkylamino)fluorene compounds are known.[9, 10] Synthetic methods for aminofluorenes are much simpler and allow for greater substituent variation than those for aminocyclopentadiene and aminoindene compounds. The reasons are twofold: the availability of 9-bromofluorene, which is subject to nucleophilic attack by various amines; and, the thermal stability of the aminofluorene products (compare N,N-dimethylaminocyclopentadiene, which decomposes above -30°C[1]).

9-Bromofluorene is commercially available and readily reacts with non-hindered secondary amines to afford 9-(N,N-dialkylamino)fluorenes. A more general route was sought, however, that was amenable to the amination of benzo functionalized fluorenes, since several of these are available by other synthetic routes, including Friedel-Crafts acylations and alkylations. Hence, a general, two-pot synthesis of 9-(N,N-dimethylamino)fluorenyl lithium in gram quantities from inexpensive starting materials was devised (Figure 3). This bromination/amination sequence was successfully applied to fluorene, 1-methylfluorene, and 2,7-di-*tert*-butylfluorene.

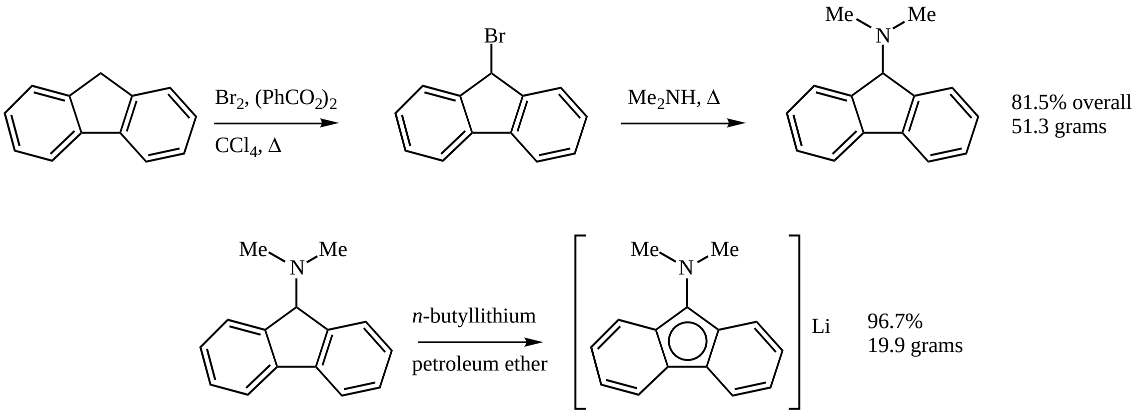
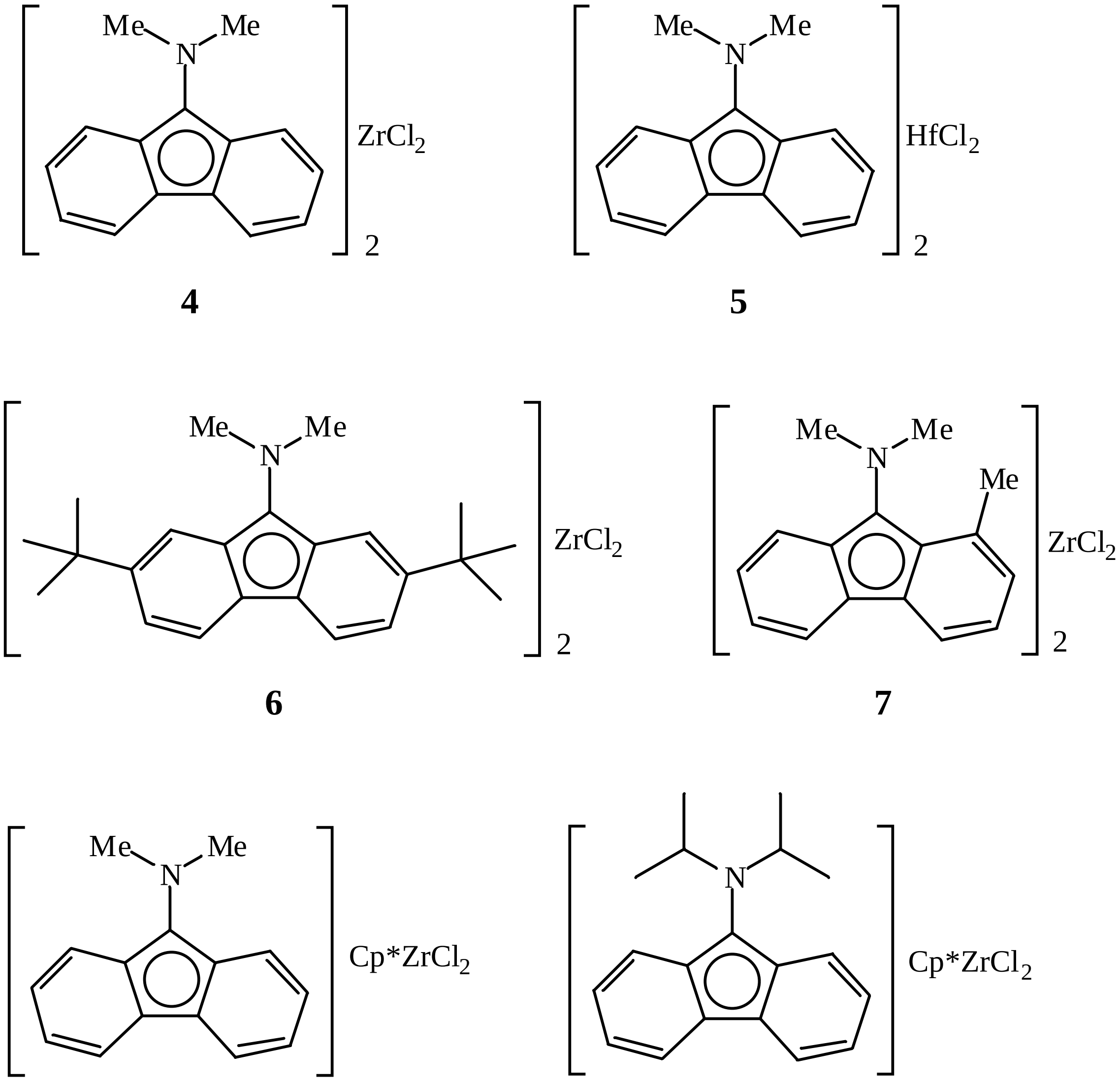


Figure 3. Two-pot synthesis of 9-(N,N-dimethylamino)fluorenyl lithium from fluorene.

1.3 Metallocene Synthesis

Reaction of two equivalents of the corresponding lithium salt with $ZrCl_4$ (or $HfCl_4$) in diethyl ether provided metallocenes **4 - 7**. Reaction of one equivalent of the corresponding lithium salt with Cp^*ZrCl_3 in diethyl ether provided mixed ring metallocenes **8** and **9** (Figure 4). Compound **7** was obtained as a 61:39 mixture of diastereomers. Attempts to prepare metallocenes bearing two dialkylaminofluorenide ligands with bulky alkyl groups (*e.g.*, 9-(N,N-diisopropylamino)fluorenide, 9-(N-piperidine)fluorenide, or 9-(N-methyl-N-phenyl)fluorenide) were unsuccessful and resulted in decomposition.



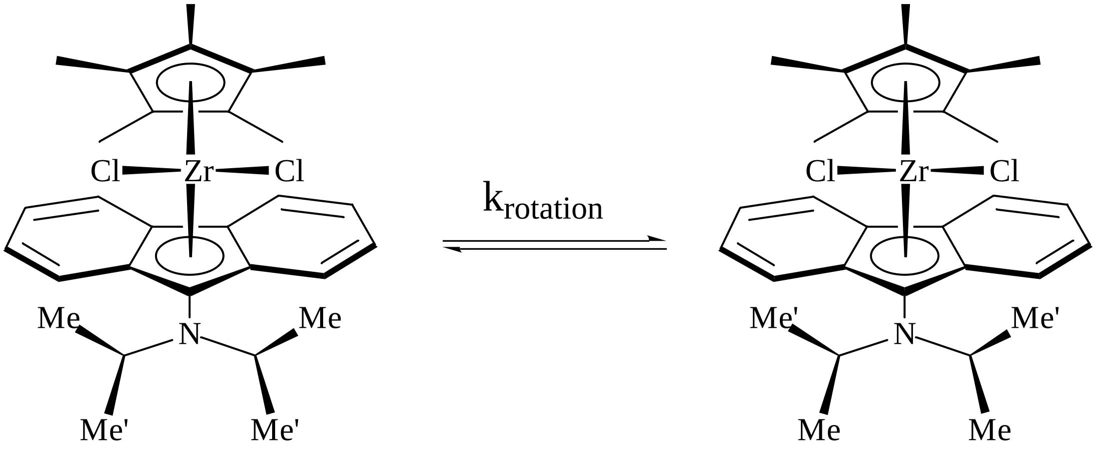
4 **5** **6** **7** **8** **9**

Figure 4. Metallocenes bearing two dialkylaminofluorenide ligands (**4** - **7**), and mixed ring metallocenes bearing one dialkylaminofluorenide ligand (**8** and **9**).

1.4 Metallocene Characterization

The metallocene dichlorides have been characterized by ^{1}H NMR. The solution ^{1}H NMR spectra of **4**, **5**, and **6** are consistent with structures of C_{2v} symmetry; **8** and **9** display C_s symmetry; and one diastereomer of **7** is consistent with C_2 symmetry, while the other is of C_s symmetry. In solution, all molecules undergo rapid fluxional rearrangements that equivalence the benzo moieties of the aminofluorenide ligands.

Compound **9** was subjected to variable temperature ^{1}H NMR in order to study the barrier to rotation around the C-N bond of the aminofluorenide ligand (Figure 5). At ambient and above temperatures, the methyl protons of the isopropyl groups are magnetically equivalent, due to fast rotation about the C-N bond. However, at cold temperatures, the rotation becomes slow, and the diastereotopic methyl protons resonate at different frequencies. The ^{1}H NMR (in toluene-d_8) was monitored between 65°C and -65°C at 5°C increments. At the high temperature limit, the methyl protons of the isopropyl groups give a doublet centered at 1.19 ppm. At the low temperature limit, two doublets, separated by 358 Hz, are seen: one at 0.79 ppm and the other at 1.69 ppm (Figure 6). The coalescence temperature is approximately -25°C. Therefore, $k_{rotation}$(-25°C) = 796 s^{-1}, and $\Delta G^{\ddagger}$ (-25°C) is calculated to be 11.1 kcal/mol.



9

Figure 5. Slow rotation around the C-N bond of metallocene **9** provides magnetically inequivalent methyl groups.

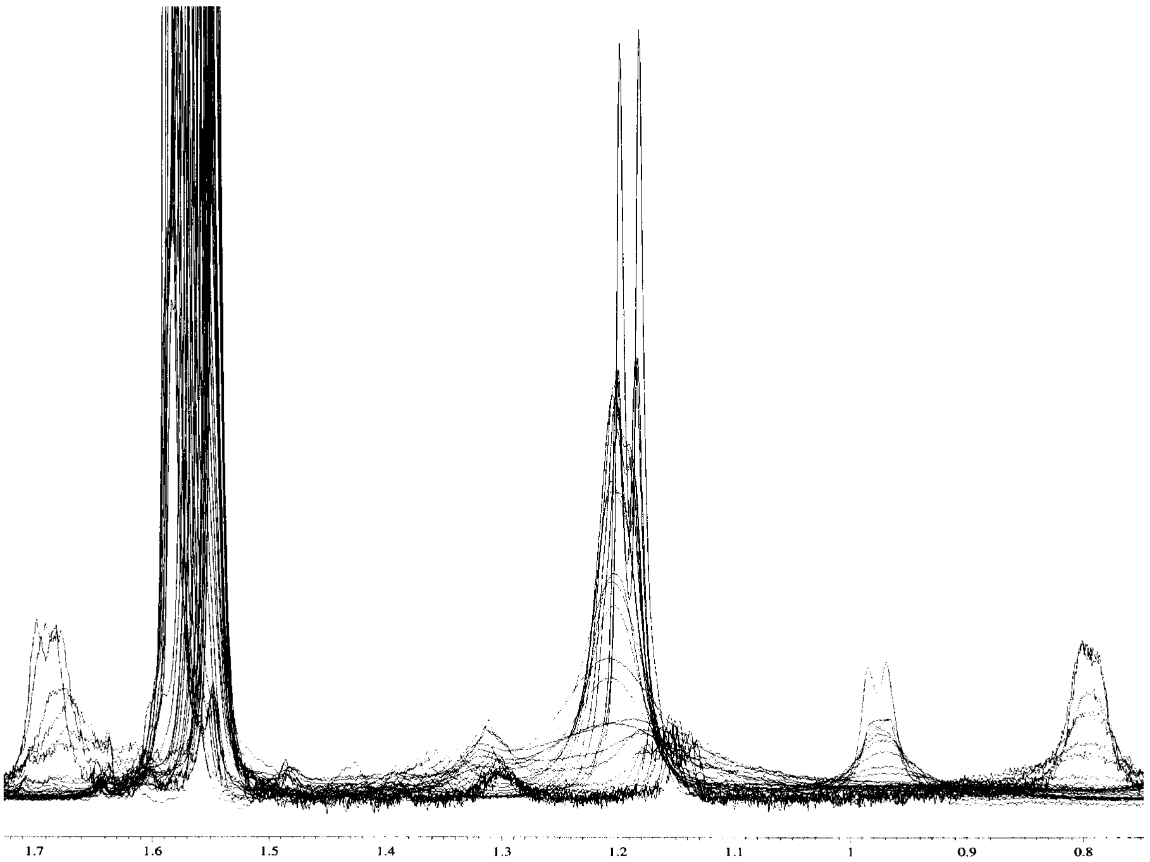


Figure 6. An overlay of the spectra from the variable temperature study of **9** is shown (toluene-d_8). The peak near 1.59 ppm is attributed to the protons of the Cp* ligand. The peaks near 0.98 and 1.31 ppm are attributed to impurities.

(9-(N,N-dimethylamino)fluorenyl)$_2$ZrCl$_2$ (**4**) has been characterized by X-ray crystallography.[11] In the solid state, a novel coordination geometry for the dimethylaminofluorenide ligand is observed. There are two different molecules in the asymmetric unit (Figure 7). One is best described as a bis η^4 aminofluorenyl complex, where, in addition to η^3 coordination to the fluorenide moiety, Zr is also bound to the lone pair of the amine nitrogen. The second molecule is best described as an η^4, η^3 mixed hapticity complex, in which zirconium is nonetheless bound to both nitrogen atoms. This coordination geometry contrasts that seen for N,N-dimethylaminocyclopentadienide[2], 2-(N, N-dimethylamino)indenide[4, 5], and N,N-diisopropylaminoborollide[6] for which there is essentially no metal-nitrogen bonding observed in the solid state. The solid state C-N bond lengths determined for **4** are 1.454(8) Å, 1.444(8), 1.436(8) and 1.448(8), whereas those determined for **1** and **2** are 1.347(5) and 1.354(7), respectively. While there is significant C-N double bond character in complexes **1** and **2**, such double bond character in **4** has been sacrificed to form a metal-nitrogen bond. This metal-nitrogen bond stabilizes the complex and the inability to form it may explain why dialkylaminofluorenide anions with bulky alkyl groups are considerably less competent as transition metal ligands.

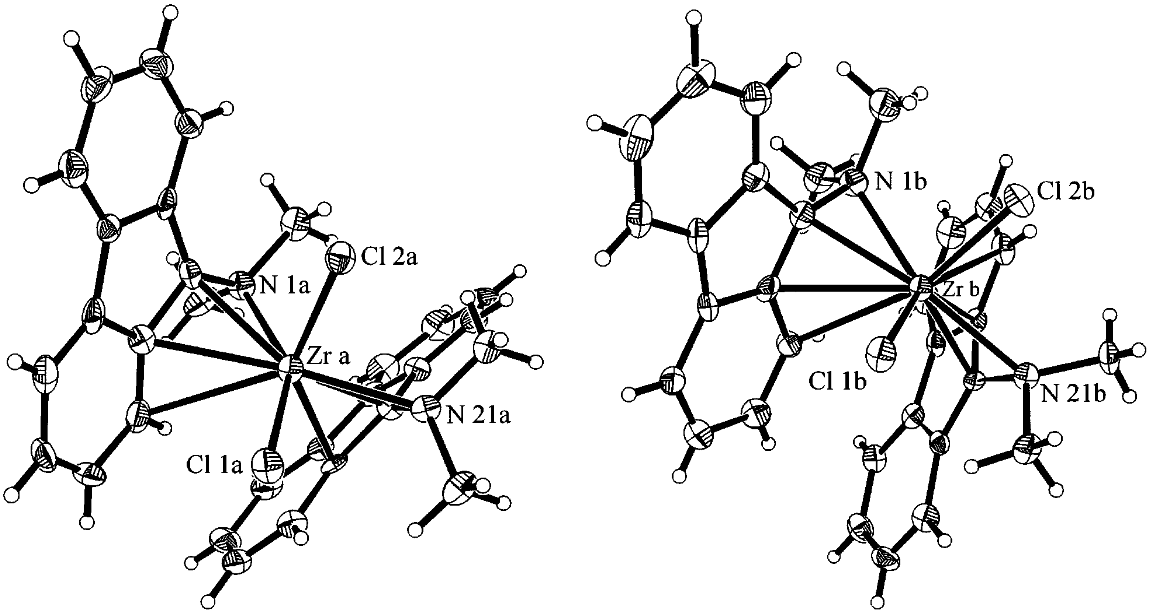


Figure 7. Single crystal X-ray structure of **4**, depicted with 50% probability ellipsoids. The molecule on the left is η^4, η^4, while the molecule on the right is η^4, η^3.

1.5 Electronic Spectroscopy

The UV-visible electronic spectra of the zirconium complex **4** and the hafnium complex **5** were obtained (in toluene, Figure 8). The deep red zirconium complex shows an absorption band at 420 nm (ε = 6400 $M^{-1}cm^{-1}$). The corresponding absorption band for the orange-yellow hafnium complex is blue shifted and lies at 402 nm (ε = 5800 $M^{-1}cm^{-1}$). This blue shift of the absorption band on going from zirconium to hafnium is consistent with a LMCT band arising from excitation of a Zr (IV) or Hf (IV) ground state d^0 complex, and discounts other ground state resonance forms such as Zr (II) or Hf (II), for which a MLCT band would presumably red shift.[6b]

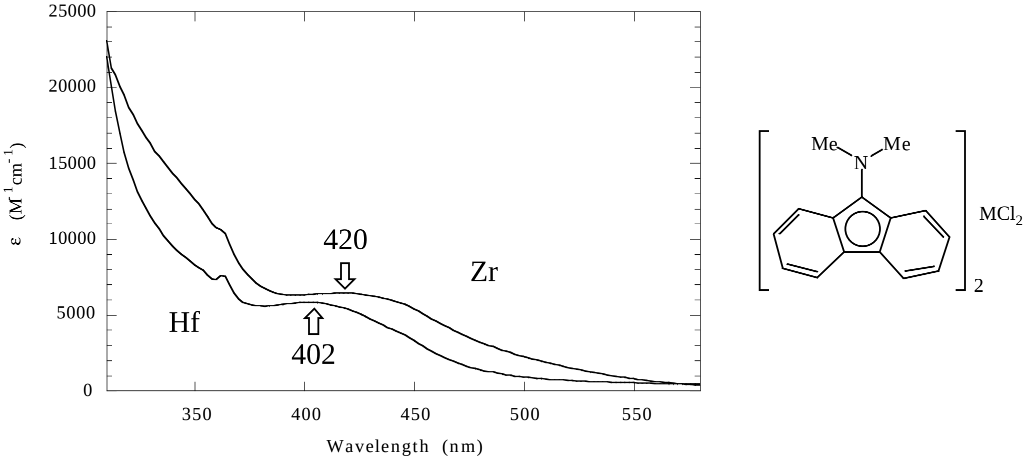


Figure 8. The hafnium compound is blue shifted relative to the zirconium compound.

1.6 Reactivity of Aminofluorenide Metallocenes

In contrast to the reactivity observed with group IV complexes containing the aminoborollide ligand (*e.g.*, **3**), zirconium and hafnium compounds containing a dialkylaminofluorenide ligand are relatively unreactive towards methyl iodide. Complexes **4**, **5**, and **8** show no reactivity toward an excess of methyl iodide over 24 hours at room temperature, as starting material persists (Figure 9). This reactivity difference is likely associated with the metal-nitrogen bond present in **4**, **5**, and **8**, but absent in **3**.

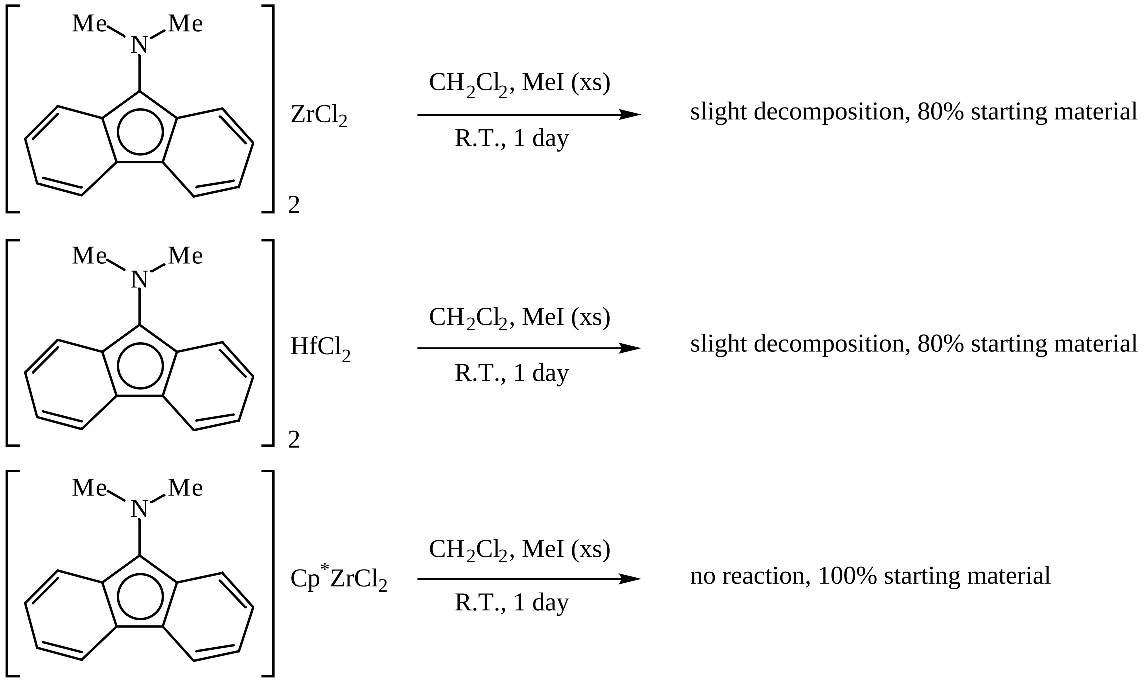


Figure 9. Attempted quaternization of the amine groups in **4**, **5**, and **8** proved unsuccessful.

1.7 Polymerization Results

Propylene polymerizations with **2**/MAO suffer from long induction periods (2-3 hours) and relatively low activity.[5] The metallocenes investigated here, combined with MAO, each polymerize propylene, but are likewise plagued with low activities (Table 1). Moreover, the integrity of the organometallic complex is in question since all complexes bleach upon exposure to MAO. The species responsible for polymerization has likely lost its dialkylaminofluorenide ligands. The polymerizations are generally irreproducible and afford but small quantities of amorphous, atactic polypropylene.

Table 1. Propylene polymerization results with **4**, **5**, **8**, and **9** / MAO.[a]

Metallocene (mg)	Propylene (mL)	MAO (equivalents)	Temperature (°C)	Time (hours)	Yield (grams)
4 (10)	25	500	20	16	2.00
4 (11)	25	500	0	2	0.02
5 (12)	25	500	20	16	0.02
8 (9)	25	500	20	7.5	0.03
9 (10)	25	500	20	7.5	0.02

[a] Propylene is condensed into a 3 oz. Lab Crest glass pressure reactor containing MAO at 0°C. A solution of metallocene in 2.0 mL toluene is injected via a septum. The reaction is vented, quenched with MeOH / HCl, and the polymers are precipitated with MeOH.

1.8 Conclusions

Bromination of fluorene, followed by nucleophilic substitution by a secondary amine provides access to large quantities of a wide variety of 9-(N,N-dialkylamino)fluorenes. Several Group IV metallocene dichloride complexes containing the 9-(N,N-dialkylamino)fluorenide ligand have been prepared and characterized, including mixed ring metallocenes. The barrier to rotation about the carbon-nitrogen bond in (9-(N,N-diisopropylamino)fluorenyl)Cp*$ZrCl_2$ has been measured: $\Delta G^\ddagger$ (-25°C) = 11.1 kcal / mol. The complex (9-(N,N-dimethylamino)fluorenyl)$_2ZrCl_2$ has been characterized by X-ray crystallography. Novel modes of η^3 and η^4 binding, which include a zirconium-nitrogen bond, are observed in the solid state. The UV-visible electronic spectra of (9-(N,N-dimethylamino)fluorenyl)$_2HfCl_2$ shows an absorption band at 402 nm which is blue shifted relative to that of (9-(N,N-dimethylamino)fluorenyl)$_2ZrCl_2$, which is observed at 420 nm. The observed blue shift is consistent with a d^0 ground state. In contrast to the reactivity observed with Group IV complexes containing the aminoborollide ligand, zirconium and hafnium compounds containing a 9-(N,N-dialkylamino)fluorenide ligand are relatively unreactive towards methyl iodide. This emphasizes the reluctance of aminofluorenide complexes to disrupt the metal-nitrogen interaction. Group IV metallocenes bearing the 9-(N,N-dialkylamino)fluorenide ligand are active propylene polymerization catalysts in the presence of MAO, although such systems suffer from low overall catalytic activity and poor reproducibility.

1.9 Experimental Section

General Considerations. High vacuum line or standard Schlenk line techniques were employed in the synthesis and manipulation of all air sensitive compounds. Solvents were distilled from sodium, sodium benzophenone ketyl, or from calcium hydride. 9-bromofluorene is synthesized by the thermal bromination of fluorene[12] or by the reduction of 9-fluorenone by sodium borohydride followed by the reaction of the isolated 9-fluorenol with phosphorous tribromide.[13] 9-bromofluorene was also used as received from TCI America. Methylaluminoxane (Ethyl Corporation) is used as the dry solid obtained by removal of all volatiles from the toluene solution. Crystalline $LiCH_2Si(CH_3)_3$ (Aldrich, solution in pentane) is obtained by condensing the pentane solution. All other commercial materials were used as received: fluorene (Aldrich, 98%); n-butyllithium (Aldrich, 1.4 M in hexanes); dimethylamine (Aldrich, 40% in H_2O); $ZrCl_4$ (Aldrich, 99.5+%); $HfCl_4$ (Cerac, 99%); dibenzoylperoxide (Aldrich); Cp^*ZrCl_3 (Strem, 99%); and diisopropylamine (Aldrich, 99%). **Instrumentation.** 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 Spectometer. The GC was equipped with a column of dimensions 7.1 m x 0.1 µm having an HP-1 phase (Crosslinked Methyl Silicone Gum).

Preparation of 4.

9-(N,N-dimethylamino)fluorene. Bromine (17.5 mL, 340 mmol) in 200 mL of carbon tetrachloride was added dropwise via an addition funnel to a refluxing solution of fluorene (50.00 g, 300.8 mmol) and dibenzoylperoxide (3.00 g, 12.4 mmol) in 500 mL of carbon tetrachloride in a 2 L flask over a period of 8 hours. After 1 additional hour of refluxing, the pH neutral solution (which showed 95.9% conversion of fluorene to bromofluorene, by GC) was cooled and 100 mL of dimethylamine solution (40% in H_2O, 797 mmol) were syringed in. The sealed vessel was stirred at room temperature for 58 hours before H_2O/HCl (50 mL H_2O/50 mL concentrated aqueous HCl) were added gradually. The aqueous layer was isolated and the organic layer was extracted with H_2O/HCl (90 mL H_2O/10 mL concentrated aqueous HCl) and H_2O (2 x 100 mL). The aqueous layers were made basic with 100 mL of 10% aqueous NaOH. This was extracted with diethyl ether (1 x 200 mL and 2 x 100 mL) and the combined organic layers dried over $MgSO_4$ and pushed through a column of alumina, which was rinsed with another 150 mL ether. Rotavap removal of solvent gave a viscous yellow oil, which crystallized upon cooling. In vacuo drying afforded 51.30 grams (81.5%) of 9-(N,N-dimethylamino)fluorene. MS (GC-MS) m/z 209.3 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 6H, CH_3), 4.85 (s, 1H, 9-*H*-Flu), 7.29, 7.38 (t, $^3J_{HH}$ = 7.7, 7.3 Hz, 4H, Flu-*H*), 7.64, 7.70 (d, $^3J_{HH}$ = 7.7, 7.3 Hz, 4H, Flu-*H*). Elemental analysis calculated for $C_{15}H_{15}N_1$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.45, 85.57; H, 6.92, 6.76; N, 6.46, 6.39.

9-(N,N-dimethylamino)fluorenyl lithium. A large swivel frit apparatus is charged with 20.092 g 9-(N,N-dimethylamino)fluorene (96.00 mmol) before evacuation, backfilling with argon, and addition of 150 mL petroleum ether to dissolve the solid. 60.0 mL of 1.6 M *n*-butyllithium solution in hexanes (96.0 mmol) are added dropwise at room temperature over 15 minutes. The red precipitate was collected by filtration after 4 hours of stirring. In vacuo drying afforded 19.89 grams (96.7%) of the desired product as a red powder.

(9-(N,N-dimethylamino)fluorenyl)$_2$ZrCl$_2$ (4). A swivel frit apparatus is charged with 6.000 g 9-(N,N-dimethylamino)fluorenyl lithium (27.88 mmol) and 3.248 g sublimed $ZrCl_4$ (13.94 mmol). 60 mL of diethyl ether were condensed in at -78°C, and the cold bath subsequently removed. After 22 hours of stirring, solvent was removed and 60 mL methylene chloride were condensed in. The product was not fully soluble in this amount of solvent, but continuous extraction by refluxing for several hours left only the insoluble LiCl on the frit. The volume was reduced to 20 mL and the precipitate collected at 0°C. In vacuo drying gave 6.08 grams (75.3%) of the desired product. ^{1}H NMR (CD_2Cl_2): δ 2.97 (s, 12H, CH_3), 6.89 (d,

$^3J_{HH}$ = 7.7 Hz, 4H, Flu-*H*), 7.00 (t, $^3J_{HH}$ = 7.3 Hz, 4H, Flu-*H*), 7.17 (t, $^3J_{HH}$ = 7.4 Hz, 4H, Flu-*H*), 7.91 (d, $^3J_{HH}$ = 7.7 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 46.58 (CH_3), 115.28, 121.54, 122.82, 127.32 (Flu-CH_1), 132.66, 133.02 (Flu-C_0), 9-Flu-*C*, not determined.

Preparation of 5.

(9-(N,N-dimethylamino)fluorenyl)$_2$HfCl$_2$ (5). The procedure for **4** was employed except: 3.000 g 9-(N,N-dimethylamino)fluorenyl lithium (13.94 mmol) and 2.232 $HfCl_4$ (6.97 mmol) were used; the reaction duration was 9 hours; in vacuo drying gave 2.78 grams (59.9%) of the desired product. ^{1}H NMR (CD_2Cl_2): δ 3.03 (s, 12H, CH_3), 6.93 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Flu-*H*), 7.01 (t, $^3J_{HH}$ = 7.7 Hz, 4H, Flu-*H*), 7.09 (t, $^3J_{HH}$ = 7.0 Hz, 4H, Flu-*H*), 7.88 (d, $^3J_{HH}$ = 7.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 47.05 (CH_3), 118.15, 120.78, 122.85, 126.20 (Flu-CH_1), 133.91, 134.05 (Flu-C_0), 9-Flu-*C*, not determined.

Preparation of 6.

9-(N,N-dimethylamino)-2,7-di-*tert*-butylfluorene. Bromine (2.1 mL, 40.8 mmol) in 25 mL of carbon tetrachloride was added dropwise via an addition funnel to a refluxing solution of 2,7-di-*tert*-butylfluorene[14] (10.00 g, 35.91 mmol) and dibenzoylperoxide (0.36 g, 1.5 mmol) in 100 mL of carbon tetrachloride in a 500 mL flask over a period of 75 minutes. After 1 additional hour of refluxing, the pH neutral solution was cooled and 20 mL of dimethylamine solution (40% in H_2O, 147 mmol) were syringed in. The sealed vessel was stirred at 55°C for 24 hours before H_2O/HCl (50 mL H_2O/25 mL concentrated aqueous HCl) were added gradually. 400 mL H_2O and 200 mL hexane were added and the precipitate was collected by filtration and washed with 100 mL hexane (9.61 grams, 74.7%). The salt was combined with 200 mL H_2O, 50 mL of 10% aqueous NaOH, and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The organic layers were dried over $MgSO_4$, pushed through a column of alumina, which was rinsed with

150 mL diethyl ether, rotavapped and dried in vacuo to provide 8.48 g (73.5%) of product. MS (GC-MS) *m*/*z* 321.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.36 (s, 18H, $C(CH_3)_3$), 2.33 (s, 6H, N-$(CH_3)_2$), 4.81 (s, 1H, 9-Flu-*H*), 7.37, 7.56 (d, $^3J_{HH}$ = 8.0, 8.1 Hz, 4H, 3- and 4-Flu-*H*), 7.62 (s, 2H, 1-Flu-*H*). Elemental analysis calculated for $C_{23}H_{31}N_1$: C, 85.93; H, 9.72; N, 4.36. Found: C, 85.50; H, 9.67; N, 4.32.

(9-(N,N-dimethylamino)-2,7-di-*tert*-butylfluorenyl)$_2$ZrCl$_2$ (6). A swivel frit apparatus was charged with 9-(N,N-dimethylamino)-2,7-di-*tert*-butylfluorene (2.00 g, 6.22 mmol) and $LiCH_2Si(CH_3)_3$ (0.586 g, 6.22 mmol). Tetrahydrofuran (40 mL) was condensed in and the reaction was stirred at room temperature for 30 minutes before solvent was removed and $ZrCl_4$ (0.725 g, 3.11 mmol) was added. Diethyl ether (50 mL) was condensed in and the reaction was stirred at room temperature for 12 hours before it was filtered. The volume was reduced to 10 mL and 5 mL petroleum ether were condensed in. The chilled solution (-20°C) gave a precipitate, which was collected and dried in vacuo: 0.589 g (23.6%) of **6** as an orange powder. ^1H NMR (C_6D_6): δ 1.37 (s, 36H, $C(CH_3)_3$), 2.72 (s, 12H, CH_3), 7.16 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Flu-*H*), 7.35 (s, 4H, Flu-*H*), 7.61 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Flu-*H*).

Preparation of 7.

9-(N,N-dimethylamino)-1-methylfluorene. A solution of 1-methylfluorene (4.87 g, 27.0 mmol) and dibenzoylperoxide in carbon tetrachloride was brought to reflux before a solution of bromine (1.6 mL, 31 mmol) in 25 mL of carbon tetrachloride was added dropwise over 1 hour. After refluxing an additional 1.5 hours, the vessel was allowed to cool before dimethylamine (40% in H_2O, 20 mL, 146 mmol) was added. This was heated at 55°C for 50 hours and cooled. The reaction was stirred open overnight to remove excess dimethylamine and then gaseous HCl was bubbled through. The entire reaction was pumped to dryness via rotavap. Diethyl ether (200 mL) and hexane (100 mL) were added and the organic layer extracted with dilute aqueous HCl (2 x 100 mL). The aqueous layer, in turn, was extracted with diethyl ether (3 x 50 mL) before being made basic with aqueous NaOH. The aqueous layer was then extracted with diethyl ether (3 x 75 mL) and the organic layer dried over $MgSO_4$, pushed through a column of alumina, and rotavapped to provide the product as light yellow oil, which crystallized upon standing (3.66 g, 60.7%). MS (GC-MS) m/z 223.3 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 6H, N-(C*H*$_3$)$_2$) 2.52 (s, 3H, 1-Flu-C*H*$_3$), 4.85 (s, 1H, 9-Flu-*H*), 7.06, 7.48, 7.60, 7.68 (d, $^3J_{HH}$ = 7.3, 7.3, 7.3, 7.7 Hz, 4H, 2-, 4-, 5- and 8-Flu-*H*), 7.23, 7.26, 7.35 (t, $^3J_{HH}$ = 7.3, 7.7, 7.3 Hz, 3H, 3-, 6- and 7-Flu-*H*). Elemental analysis calculated for $C_{16}H_{17}N_1$: C, 86.06; H, 7.67; N, 6.27. Found: C, 84.61, 84.56; H, 7.16, 7.21; N, 6.24, 6.22.

(9-(N,N-dimethylamino)-1-methylfluorenyl)$_2$ZrCl$_2$ (7). The procedure for **6** was followed with: 9-(N,N-dimethylamino)-1-methylfluorene (1.00 g, 4.48 mmol), $LiCH_2Si(CH_3)_3$ (0.422 g, 4.48 mmol), and $ZrCl_4$ (0.522 g, 2.24 mmol). The first crop was collected from a saturated diethyl ether solution as a red solid: 0.080 g. A second crop was obtained (0.903 g) for a total yield of 72.4%. ^{1}H NMR (C_6D_6, 50°C): minor diastereomer (39%): δ 2.47 (s, 6H), 2.87 (s 12H), 6.69 (t, 2H), 6.91 (t, 2H), 7.05, (t, 2H), 7.28 (d, 2H), 7.43 (d, 2H), 7.50 (d, 2H), 7.54 (d, 2H); major diastereomer (61%): δ 2.58 (s, 6H), 2.87 (s 12H), 6.75 (t, 2H), 6.78 (t, 2H), 6.95, (t, 2H), 7.28 (d, 2H), 7.43 (d, 2H), 7.50 (d, 2H), 7.54 (d, 2H). Elemental analysis calculated for $C_{32}H_{32}N_2Zr_1Cl_2$: C, 63.35; H, 5.32; N, 4.62. Found: C, 58.59, 58.75; H, 5.61, 5.85; N, 4.38, 4.81.

Preparation of 8.

(9-(N,N-dimethylamino)fluorenyl)(pentamethylcyclopentadienyl)ZrCl$_2$ (8). A swivel frit apparatus was charged with 0.485 g 9-(N,N-dimethylamino)fluorenyl lithium (2.254 mmol) and 0.750 g Cp*ZrCl$_3$ (2.254 mmol). 30 mL diethyl ether were condensed in at -78°C and the reaction was allowed to warm slowly. After 9 hours, the reaction was filtered and the yellow solid extracted with refluxing diethyl ether. Condensation of the filtrate led to isolation of 0.729 g (64.0%) of **8** in two crops as a yellow crystalline solid. ^{1}H NMR (C_6D_6): δ 1.45 (s, 15H, Cp*-*H*), 2.98 (s, 6H, C*H*$_3$), 7.04 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.12 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.24 (d, $^3J_{HH}$

= 8.1 Hz, 2H), 7.73 (d, $^3J_{HH}$ = 7.7 Hz, 2H). Elemental analysis calculated for $C_{25}H_{29}N_1Zr_1Cl_2$: C, 59.39; H, 5.78; N, 2.77. Found: C, 58.82, 58.76, 58.73, 58.72; H, 5.91, 5.89, 6.00, 6.26; N, 2.86, 2.84, 2.96, 2.97.

Preparation of 9.

9-(N,N-diisopropylamino)fluorene. A flask was charged with 5.12 g 9-bromofluorene (20.9 mmol), 50 mL diisopropylamine, and 60 mL acetonitrile. The reaction was refluxed for 11 days and all volatiles were removed by rotary evaporation. A solution of 50 mL concentrated aqueous HCl / 150 mL water was added to the white solid. This was extracted with diethyl ether (2 x 50 mL). The remaining aqueous layer was made basic by addition of 200 mL 10% aqueous NaOH. This was extracted with diethyl ether (3 x 50 mL) and dried over $MgSO_4$. Filtration, rotary evaporation, and in vacuo drying gave 4.258 grams of product (76.8%). Recrystallization of the crude material from 50 mL EtOH gave the product as white crystals: 2.933 g (52.9%). MS (GC-MS) *m* / *z* 265.3 (M^+). ^{1}H NMR (C_6D_6): δ 1.09 (d, $^3J_{HH}$ = 6.2 Hz, 12H, C*H*$_3$), 2.90 (m (broad), 1H, C*H*Me$_2$), 4.96 (s, 1H, 9-*H*-Flu), 7.28, 7.35 (t, $^3J_{HH}$ = 7.3, 7.3 Hz, 4H, Flu-*H*), 7.60, 7.69 (d, $^3J_{HH}$ = 7.0, 7.7 Hz, 4H, Flu-*H*). Elemental analysis calculated for $C_{19}H_{23}N_1$: C, 85.99; H, 8.73; N, 5.28. Found: C, 85.48, 86.70; H, 8.21, 8.25; N, 5.11, 5.08.

(9-(N,N-diisopropylamino)fluorenyl)(pentamethylcyclopentadienyl)ZrCl$_2$ (9). A swivel frit apparatus was charged with 0.598 g 9-(N,N-diisopropylamino)fluorene (2.253 mmol) and 0.212 g $LiCH_2Si(CH_3)_3$ (2.251 mmol). 20 mL of tetrahydrofuran were condensed in at -78°C and the solution allowed to warm slowly. After 30 minutes, the solvent was removed and 0.750 g Cp^*ZrCl_3 (2.254 mmol) was added. 30 mL of diethyl ether were condensed in and the reaction stirred at room temperature for 12 hours. The solution was filtered and the orange material extracted with refluxing ether. The volume of the filtrate was reduced and the product **9** was collected in two crops (the second crop from CH_2Cl_2) as an orange crystalline solid: 0.758 g (59.9%). ^{1}H NMR (C_6D_6, 50°C): δ 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 12H, C*H*$_3$), 1.59 (s, 15H, Cp*-*H*), 2.04 (b, 2H,

Me_2CH), 6.87 (b, 2H), 6.99 (b, 2H), 7.70 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 8.01 (d, $^3J_{HH}$ = 8.4 Hz, 2H). Elemental analysis calculated for $C_{29}H_{37}N_1Zr_1Cl_2$: C, 62.01; H, 6.64; N, 2.49. Found: C, 57.37, 58.17, 61.40, 61.70; H, 6.21, 6.89, 6.99, 6.51; N, 2.21, 2.22, 2.62, 2.56.

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1.10 References and Notes

* Material in this chapter was presented, in part, by Miller, S. A.; Bercaw, J. E. 213th Amer. Chem. Soc. Nat. Meet., San Francisco 1997, INOR 196.

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11. (9-(N,N-dimethylamino)fluorenyl)$_2$ZrCl$_2$ (**4**, crystallized from dichloromethane) is monoclinic $P2_1/n$ (No. 14), a = 18.781(3) Å, b = 30.088(9) Å, c = 8.994(8) Å, β = 99.17(3)°, V = 5017(3) Å^3, Z = 8, T =160 K. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 100582. See Appendix A for X-ray crystallographic data of **4**.
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Chapter 2

Unidirectional Site-epimerization Model for the Polymerization of α-olefins

ABSTRACT: A statistical model has been developed that quantifies the unidirectional site epimerization probability, ε, for the C_1- symmetric metallocene polymerization catalysts: doubly-bridged *rac*-$(1,2\text{-SiMe}_2)_2\{\eta^5\text{-C}_5\text{H}_2\text{-4-(CHMe(CMe}_3))\}\{\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2\}\text{ZrCl}_2$ / MAO (**1** / MAO) and $(1,2\text{-SiMe}_2)_2\{\eta^5\text{-C}_5\text{H}_2\text{-4-(1}R\text{, 2}S\text{, 5}R\text{-menthyl)}\}\{\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2\}\text{ZrCl}_2$ / MAO (**2** / MAO); and singly-bridged $\text{Me}_2\text{C(3-adamantyl-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ / MAO (**3** / MAO) and $\text{Me}_2\text{Si(3-adamantyl-C}_5\text{H}_3)(\text{C}_{13}\text{H}_8)\text{ZrCl}_2$ / MAO (**4** / MAO). For **1** / MAO, a steep tacticity dependence on monomer concentration was found, as ε varied from 0.115 in neat monomer (syndiotactic, with [m] = 20.2%) to 0.908 in dilute, 0.5 M monomer (isotactic, with [m] = 88.5%). This polymerization system was calculated to have one site that is 99.2% enantioselective and a second site that is 83.5% enantioselective, but in the opposite sense. For **2** / MAO, ε varied from 0.177 in neat monomer ([m] = 25.9%) to 0.709 in dilute, 0.5 M monomer ([m] = 60.1%). This polymerization system was calculated to have one site that is 98.7% enantioselective and a second site that is 85.9% enantioselective, but in the opposite sense. For **3** / MAO, ε was relatively unresponsive to an increase in polymerization temperature for polymerizations run in 1.1 M propylene, as ε varied from 0.000 at T_p = 0°C ([m] = 60.1%) to 0.484 at T_p = 90°C ([m] = 71.6%). The model indicated that this polymerization system has one site that is 97.5% enantioselective and a second site that is 59.9% enantioselective. For **4** / MAO, ε was highly dependent on polymerization temperature for polymerizations run in 1.1 M propylene, as ε varied from 0.521 at T_p = 0°C ([m] = 79.3%) to 1.00 for $T_p \geq$ 20°C ([m] = 83.2% to 88.5%). The model indicated that this polymerization system has one site that is 92.1% enantioselective and a second site that is 80.6% enantioselective. Additionally, the unidirectional site epimerization model allows deconvolution of the site sequence probability and the stereochemical probability for producing a given pentad. The predicted distribution of site sequences as a function of ε is calculated.

2.1 Introduction

Metallocene polymerization catalysts are well appreciated for their steric tunability to produce poly(α-olefins) having a wide variety of stereochemical structures.[1] The interpretation of α-olefin polymer tacticities through stereochemical statistical models has long been the subject of intense research.[2] Despite their idealized nature and variable applicability to real polymerization systems, such models are indispensable tools for understanding the fundamental processes that occur at the transition metal during polymerization.

Here, we report our derivation of a unidirectional site epimerization model which we have applied to singly and doubly linked C_1-symmetric metallocene polymerization systems developed in our laboratories (Figure 1). While related models have been developed by Farina, Di Silvestro, et al.,[3] by Collins, et al.,[4] and by Randall, et al.,[5] our approach employs a two-part derivation which calculates the site sequence probabilities independently from the stereochemical probabilities. Additional insight into the polymerization mechanism is thus offered.

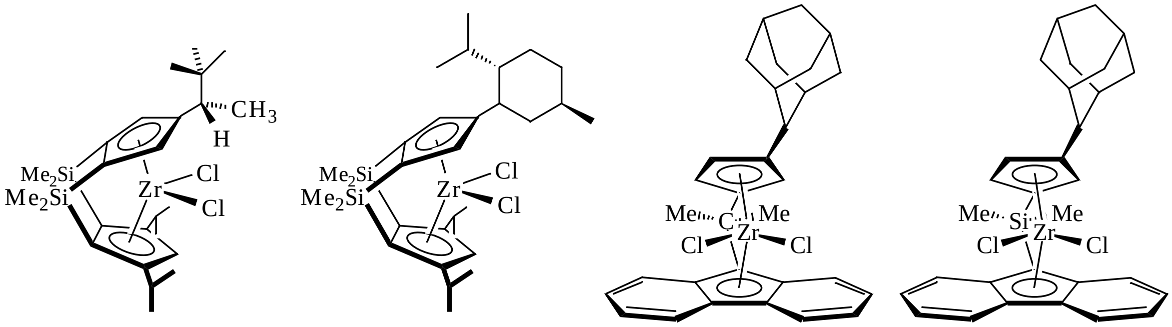

Figure 1. Singly- and doubly-bridged C_1-symmetric metallocene catalyst precursors **1-4**.

Monomer approach can occur at either one of two vacant sites of the active metallocene catalyst. The modified Rooney-Green mechanism[6] mandates alternating employment of these two sites for the bimolecular propagation steps. A unimolecular site epimerization process, however, can compete with the bimolecular insertion process and becomes stereochemically important when the two sites are not homotopic. As a result, the alternating mechanism yields to the site epimerization mechanism[7] to a degree which can be quantified.

2.2 Unidirectional Site Epimerization Model

Figure 2 depicts site A as the more stereoselective site and site B as the less stereoselective site. The alternating mechanism requires an ABABA or BABAB site employment for creation of a pentad. However, if the growing polymer chain is allowed to move away from the bulky R substituent—but not towards it—prior to monomer insertion, such a unidirectional site epimerization[8] permits eleven additional site sequences, as listed in Table 1.

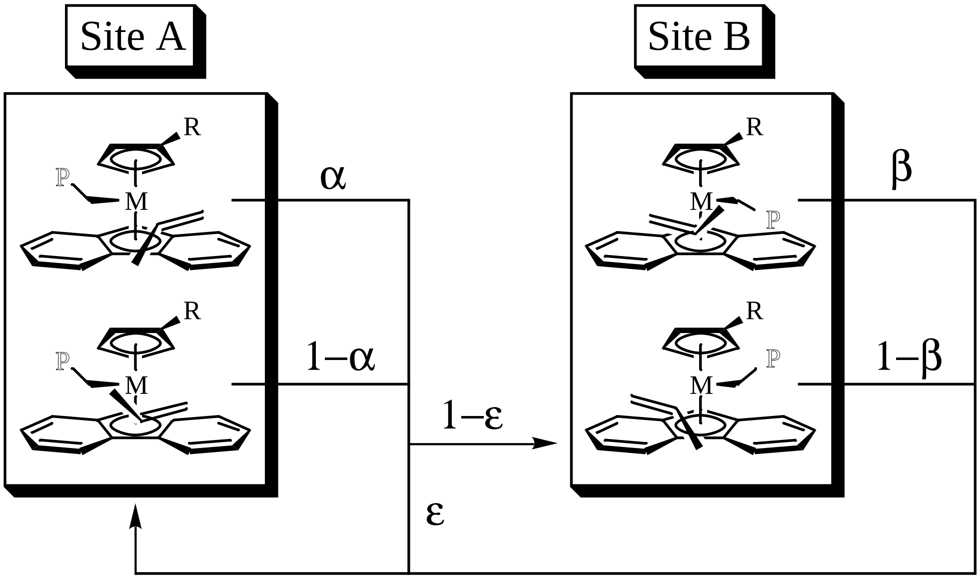

Figure 2. The unidirectional site epimerization model employs two stereochemical parameters (α and β) and the unidirectional site epimerization parameter (ε).

Table 1. Thirteen site sequences are possible with the unidirectional site epimerization model. The sequence probabilities vary as a function of epsilon(ε).

Epsilon		0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000
Sequence	# epim	Sequence Probabilities										
ABABA	0	0.500	0.426	0.356	0.288	0.225	0.167	0.114	0.069	0.033	0.009	0.000
BABAB	0	0.500	0.384	0.284	0.202	0.135	0.083	0.046	0.021	0.007	0.001	0.000
AABAB	1	0.000	0.043	0.071	0.086	0.090	0.083	0.069	0.048	0.027	0.008	0.000
ABAAB	1	0.000	0.043	0.071	0.086	0.090	0.083	0.069	0.048	0.027	0.008	0.000
BAABA	1	0.000	0.043	0.071	0.086	0.090	0.083	0.069	0.048	0.027	0.008	0.000
BABAA	1	0.000	0.043	0.071	0.086	0.090	0.083	0.069	0.048	0.027	0.008	0.000
AAABA	2	0.000	0.005	0.018	0.037	0.060	0.083	0.103	0.113	0.107	0.074	0.000
AABAA	2	0.000	0.005	0.018	0.037	0.060	0.083	0.103	0.113	0.107	0.074	0.000
ABAAA	2	0.000	0.005	0.018	0.037	0.060	0.083	0.103	0.113	0.107	0.074	0.000
BAAAB	2	0.000	0.004	0.014	0.026	0.036	0.042	0.041	0.034	0.021	0.007	0.000
AAAAB	3	0.000	0.000	0.004	0.011	0.024	0.042	0.062	0.079	0.085	0.066	0.000
BAAAA	3	0.000	0.000	0.004	0.011	0.024	0.042	0.062	0.079	0.085	0.066	0.000
AAAAA	4	0.000	0.000	0.001	0.005	0.016	0.042	0.093	0.185	0.341	0.596	1.000
Prob. site A		0.500	0.526	0.556	0.588	0.625	0.667	0.714	0.769	0.833	0.909	1.000
Prob. site B		0.500	0.474	0.444	0.412	0.375	0.333	0.286	0.231	0.167	0.091	0.000
Prob. 0 epim.		1.000	0.810	0.640	0.490	0.360	0.250	0.160	0.090	0.040	0.010	0.000
Prob. 1 epim.		0.000	0.171	0.284	0.346	0.360	0.333	0.274	0.194	0.107	0.033	0.000
Prob. 2 epim.		0.000	0.018	0.068	0.137	0.216	0.292	0.350	0.373	0.341	0.228	0.000
Prob. 3 epim.		0.000	0.001	0.007	0.022	0.048	0.083	0.123	0.158	0.171	0.133	0.000
Prob. 4 epim.		0.000	0.000	0.001	0.005	0.016	0.042	0.093	0.185	0.341	0.596	1.000

The probabilities of insertion at site A and site B can be calculated in terms of ε, the unidirectional site epimerization probability. Since each ε leads to insertion at site A and each (1-ε) leads to insertion at site B followed by insertion at site A, the *relative* amount of site A employment is ε + (1-ε) = 1, and the *relative* amount of site B employment is (1-ε). Therefore, the *absolute* probability that site A is employed is 1/(2-ε) and the *absolute* probability that site B is employed is (1-ε)/(2-ε). The probability of a given site sequence P_{XXXXX} (either AXXXX or BXXXX) is given by:

$$P_{AXXXX} = [1/(2-\varepsilon)]\,[(1-\varepsilon)^{(A,B)}]\,[(\varepsilon)^{(A,A)}]$$

$$P_{BXXXX} = [(1-\varepsilon)/(2-\varepsilon)]\,[(1-\varepsilon)^{(A,B)}]\,[(\varepsilon)^{(A,A)}]$$

where (A,A) is the integral number of times site A follows site A in a given sequence—which corresponds to a site epimerization—and (A,B) is the integral number of times site B follows site A in a given sequence. Recall from Figure 2 that site A always follows site B in this unidirectional model. These expressions are used to generate the probabilities shown in Table 1. Figure 3 graphically represents the probability that a given pentad will arise via a site sequence having 0, 1, 2, 3 or 4 site epimerizations, depending on the value of epsilon. For example, a system with $\varepsilon = 0.300$ will create a pentad with: zero site epimerizations 49.0% of the time; one site epimerization 34.6% of the time; two site epimerizations 13.7% of the time; three site epimerizations 2.2% of the time; and four site epimerizations 0.5% of the time. Note that for $\varepsilon = 0.644$, the probability that a pentad will form with zero site epimerizations is equal to the probability that it will form with four site epimerizations (Probability = 12.7%).

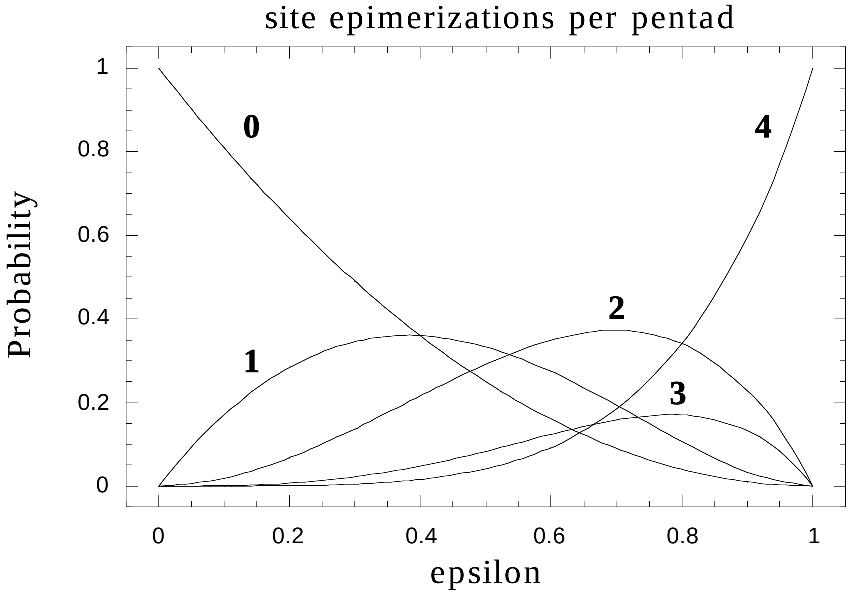

Figure 3. The probability that a pentad will be formed with 0, 1, 2, 3, or 4 site epimerizations varies as a function of ε.

In addition to the parameter ε, the unidirectional site epimerization model has two other independent parameters, α and β, which describe the enantioselectivity of site A and site B, respectively. These are defined such that a value of 1.0 for α and a value of 1.0 for β correspond to the same absolute sense of enantiofacial selectivity at each site. The parameters α and β will be included in calculating the intensity of a given pentad in proportion to the employment of site A and site B in its site sequence. A pentad's stereochemical probability P^*_{xxxx} will be given by the product of five terms:

$$P^*_{xxxx} = [(\alpha \text{ or } \beta)^a(1-(\alpha \text{ or } \beta))^b]\,[(\alpha \text{ or } \beta)^c(1-(\alpha \text{ or } \beta))^d]\,[(\alpha \text{ or } \beta)^e(1-(\alpha \text{ or } \beta))^f]$$
$$[(\alpha \text{ or } \beta)^g(1-(\alpha \text{ or } \beta))^h]\,[(\alpha \text{ or } \beta)^i(1-(\alpha \text{ or } \beta))^j]$$

where each term corresponds to one of the five sites employed. The choice between α and β is determined by the site sequence. For example, BAABA mandates $[\beta^a(1-\beta)^b]\ [\alpha^c(1-\alpha)^d]\ [\alpha^e(1-\alpha)^f]\ [\beta^g(1-\beta)^h]\ [\alpha^i(1-\alpha)^j]$. The values of the exponents a through j are either 1 or 0 and depend on the relative stereochemistry of the pentad xxxx. For example, the pentad rmmr will be described by

$$[(\alpha \text{ or } \beta)^1(1-(\alpha \text{ or } \beta))^0]\,[(\alpha \text{ or } \beta)^0(1-(\alpha \text{ or } \beta))^1]\,[(\alpha \text{ or } \beta)^0(1-(\alpha \text{ or } \beta))^1]$$
$$[(\alpha \text{ or } \beta)^0(1-(\alpha \text{ or } \beta))^1]\,[(\alpha \text{ or } \beta)^1(1-(\alpha \text{ or } \beta))^0]$$

or

$$[(\alpha \text{ or } \beta)^0(1-(\alpha \text{ or } \beta))^1]\,[(\alpha \text{ or } \beta)^1(1-(\alpha \text{ or } \beta))^0]\,[(\alpha \text{ or } \beta)^1(1-(\alpha \text{ or } \beta))^0]$$
$$[(\alpha \text{ or } \beta)^1(1-(\alpha \text{ or } \beta))^0]\,[(\alpha \text{ or } \beta)^0(1-(\alpha \text{ or } \beta))^1],$$

depending on the relative enantioselectivity of its first inserted monomer. Finally, the combination of the BAABA site sequence and the rmmr pentad will yield $P^*_{xxxx} = [\beta]\ [1-\alpha]\ [1-\alpha]\ [1-\beta]\ [\alpha]$ *or* $[1-\beta]\ [\alpha]\ [\alpha]\ [\beta]\ [1-\alpha]$. It can be seen that each probability will reduce to:

$$P^*_{xxxx} = (\alpha)^m(1-\alpha)^n(\beta)^p(1-\beta)^q$$

where m and n will sum to the number of times site A is employed and p and q will sum to the number of times site B is employed; and, m + n + p + q = 5. The rmmr pentad produced via the BAABA site sequence will have m = 1, n = 2, p = 1, q = 1 *or* m = 2, n =1, p = 1, q =1, depending on the relative enantioselectivity of the first inserted monomer.

The usual degeneracies that apply to the unsymmetrical pentads present in many statistical models (*e.g.*, $P_{mmmr} = P_{rmmm}$) do not necessarily apply to the unidirectional site epimerization model and each of the 16 possible pentads must be considered separately. The complete set of probabilities will contain 13 (the number of site sequences possible) x 16 (the number of pentads possible) x 2 (the number of possible relative orientations of the pentad's first inserted monomer) = 416 terms, each of which is given by the product of the site sequence probability and the stereochemical probability:[9]

$$P_n = P_{XXXXX} . P^*_{xxxx}$$

The probability of a given pentad is then obtained by summing the 26 P_n terms that correspond to it. Table 2 provides the general probabilities for P_{XXXXX} and P^*_{xxxx}.

Table 2. The probability P_{XXXXX} depends on the site sequence employed. The probability P^*_{xxxx} depends on both the site sequence and pentad produced.

Sequence	P_{XXXXX} =	Pentad	$P^*_{xxxx} = [(\alpha \text{ or } \beta)^a(1-(\alpha \text{ or } \beta))^b]$ $[(\alpha \text{ or } \beta)^c(1-(\alpha \text{ or } \beta))^d]$ $[(\alpha \text{ or } \beta)^e(1-(\alpha \text{ or } \beta))^f]$ $[(\alpha \text{ or } \beta)^g(1-(\alpha \text{ or } \beta))^h]$ $[(\alpha \text{ or } \beta)^i(1-(\alpha \text{ or } \beta))^j]$		
			abcdefghij	or	abcdefghij
ABABA	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^2]\ [(\varepsilon)^0]$	mmmm	1010101010		0101010101
BABAB	$[(1-\varepsilon)/(2-\varepsilon)]\ [(1-\varepsilon)^2]\ [(\varepsilon)^0]$	mmmr	1010101001		0101010110
AABAB	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^2]\ [(\varepsilon)^1]$	rmmm	1001010101		0110101010
ABAAB	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^1]$	rmmr	1001010110		0110101001
BAABA	$[(1-\varepsilon)/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^1]$	mmrr	1010100110		0101011001
BABAA	$[(1-\varepsilon)/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^1]$	rrmm	1001101010		0110010101
AAABA	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^2]$	mrmm	1010010101		0101101010
AABAA	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^2]$	mmrm	1010100101		0101011010
ABAAA	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^2]$	rmrr	1001011001		0110100110
BAAAB	$[(1-\varepsilon)/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^2]$	rrmr	1001101001		0110010110
AAAAB	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^1]\ [(\varepsilon)^3]$	mrmr	1010010110		0101101001
BAAAA	$[(1-\varepsilon)/(2-\varepsilon)]\ [(1-\varepsilon)^0]\ [(\varepsilon)^3]$	rmrm	1001011010		0110100101
AAAAA	$[1/(2-\varepsilon)]\ [(1-\varepsilon)^0]\ [(\varepsilon)^4]$	rrrr	1001100110		0110011001
		rrrm	1001100101		0110011010
		mrrr	1010011001		0101100110
		mrrm	1010011010		0101100101

2.3 Application of the Unidirectional Site Epimerization Model to Doubly-bridged Metallocenes

We have previously reported propylene polymerization results obtained with C_1-symmetric, doubly-bridged metallocenes (**1** and **2**, Figure 1).[10] With *rac*-$(1,2\text{-SiMe}_2)_2\{\eta^5\text{-C}_5\text{H}_2\text{-4-(CHMe(CMe}_3))\}\{\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2\}\text{ZrCl}_2$ / MAO (**1**/MAO), a steep tacticity dependence on monomer concentration was found, as the system gradually changes from syndiotactic to isotactic with decreasing monomer concentration. In liquid propylene, relatively syndiotactic polypropylene is obtained having [r] = 79.8% for T_p = 20°C, while under dilute monomer conditions of 0.5 M propylene in toluene, isotactic polypropylene is obtained with [m] = 88.5% for T_p = 25°C. Table 3 tabulates the polymerization data obtained with **1**/MAO.

Table 3. Polymerization data for catalyst systems **1-4**/MAO.

Entry	Catalyst/MAO	$[C_3H_6]$ (M)[a]	T_p (°C)	[m] (%)	[r] (%)	T_m (°C)[b]
1	**1**	12.5	20	20.2	79.8	102
2	**1**	4.6	25	39.7	60.3	n.o.
3	**1**	3.4	25	50.5	49.5	n.d.
4	**1**	2.1	25	62.0	38.0	n.d.
5	**1**	0.8	25	86.7	13.3	108
6	**1**	0.5	25	87.8	12.2	n.d.
7	**2**	12.5	20	25.9	74.1	n.o.
8	**2**	4.6	25	24.8	75.2	n.o.
9	**2**	3.4	25	29.3	70.7	n.d.
10	**2**	2.1	25	44.6	55.4	106
11	**2**	0.8	25	53.0	47.0	80
12	**2**	0.5	25	60.1	39.9	n.d.
13	**3**	1.1	0	60.1	39.9	n.o.
14	**3**	1.1	20	59.8	40.2	n.o.
15	**3**	1.1	40	60.6	39.4	n.o.
16	**3**	1.1	60	62.1	37.9	n.o.
17	**3**	1.1	75	67.3	32.7	n.o.
18	**3**	1.1	90	71.6	28.4	n.o.
19	**4**	1.1	0	79.3	20.7	77
20	**4**	1.1	20	87.9	12.1	118
21	**4**	1.1	40	88.5	11.5	127
22	**4**	1.1	60	84.4	15.6	123
23	**4**	1.1	80	83.2	16.8	110

[a] 12.5 M $[C_3H_6]$ corresponds to liquid monomer. 1.1 M $[C_3H_6]$ corresponds to 3 mL propylene in 30 mL toluene. [b] n.d. = not determined; n.o. = no melting temperature observed by DSC.

A least squares fit[11] was performed on the pentad distribution for Entry 1 (liquid monomer, T_p = 20°C, see Table 4). This established the enantiofacial selectivity parameters and the calculated site epimerization parameter for this catalyst in liquid propylene at 20°C. α was determined to be 0.992 while β was determined to be 0.165. These numbers suggest that catalyst **1**/MAO has one highly enantioselective site (99.2%) and one moderately enantioselective site having the opposite facial selectivity (83.5%). The parameter ε was found to be 0.115, meaning that the less selective site (site B) is skipped 11.5% of the time because unimolecular site epimerization competes with bimolecular insertion at that site.

Table 4. Unidirectional site epimerization model applied to **1**/MAO.[a]

Entry	1 obs	1 calc	2 obs	2 calc	3 obs	3 calc	4 obs	4 calc	5 obs	5 calc	6 obs	6 calc
[mmmm]	1.3	2.1	9.9	7.1	17.7	15.4	29.3	28.6	65.5	65.5	65.6	65.2
[mmmr]	4.4	4.5	11.6	10.6	15.0	14.8	16.6	16.9	13.0	11.7	14.4	11.8
[rmmr]	4.0	4.8	3.7	4.2	3.3	3.6	3.2	2.5	0.9	0.5	0.5	0.5
[mmrr]	14.4	13.8	18.9	18.5	19.9	21.6	18.1	21.7	12.8	12.6	13.6	12.7
[mmrm] + [rrmr]	6.6	7.1	10.3	13.0	9.1	10.7	7.3	6.9	0.9	1.4	0.5	1.4
[mrmr]	0.0	0.3	0.0	0.5	0.0	0.5	0.5	0.5	0.9	0.2	0.5	0.2
[rrrr]	49.5	49.3	23.9	22.7	14.6	11.8	7.2	5.5	0.9	0.7	0.5	0.7
[rrrm]	17.5	15.4	16.2	15.7	12.0	11.5	8.8	6.9	0.9	1.2	0.5	1.2
[mrrm]	2.3	2.6	5.7	7.7	8.3	10.2	9.1	10.6	4.2	6.3	3.8	6.3
[m]	20.2	22.0	39.7	37.8	50.5	50.1	62.0	62.5	86.7	84.8	87.8	84.7
[r]	79.8	78.0	60.3	62.2	49.5	49.9	38.0	37.5	13.3	15.2	12.2	15.3
ε		0.115		0.407		0.578		0.717		0.909		0.908
% RMS		0.854		1.585		1.598		1.591		0.877		1.312

[a] The parameters α (0.992) and β (0.165) are determined by RMS minimization of Entry 1 and are maintained at these values for application to Entries 2-6.

As the monomer concentration is decreased, this unimolecular site epimerization is able to compete more effectively with bimolecular propagation. As the concentration decreases—12.5, 4.6, 3.4, 2.1, 0.8, 0.5 M—the site epimerization probability, ε, increases: 0.115, 0.407, 0.578, 0.717, 0.909, 0.908. At the lowest monomer concentration investigated, an insertion at site A is followed by a site epimerization 91% of the time, while successful insertion at site B occurs only 9% of the time.

For this analysis, we make the assumption that α and β are intrinsic to the system and do not vary significantly with concentration. Indeed, allowing α, β, and ε to vary independently provides satisfactorily similar results for those pentad distributions which contain significant amounts of eight or nine pentads (Entries 3-5). Without this assumption, the parameters obtained for Entries 6 and 7 can be varied considerably with only small changes in the RMS error. This arises because deviations in the parameter β become less important as ε becomes large. Table 4 provides the numerical results of the statistical fits, and Figure 4 compares the observed ^{13}C NMR pentad distributions with those calculated by the unidirectional site epimerization model.

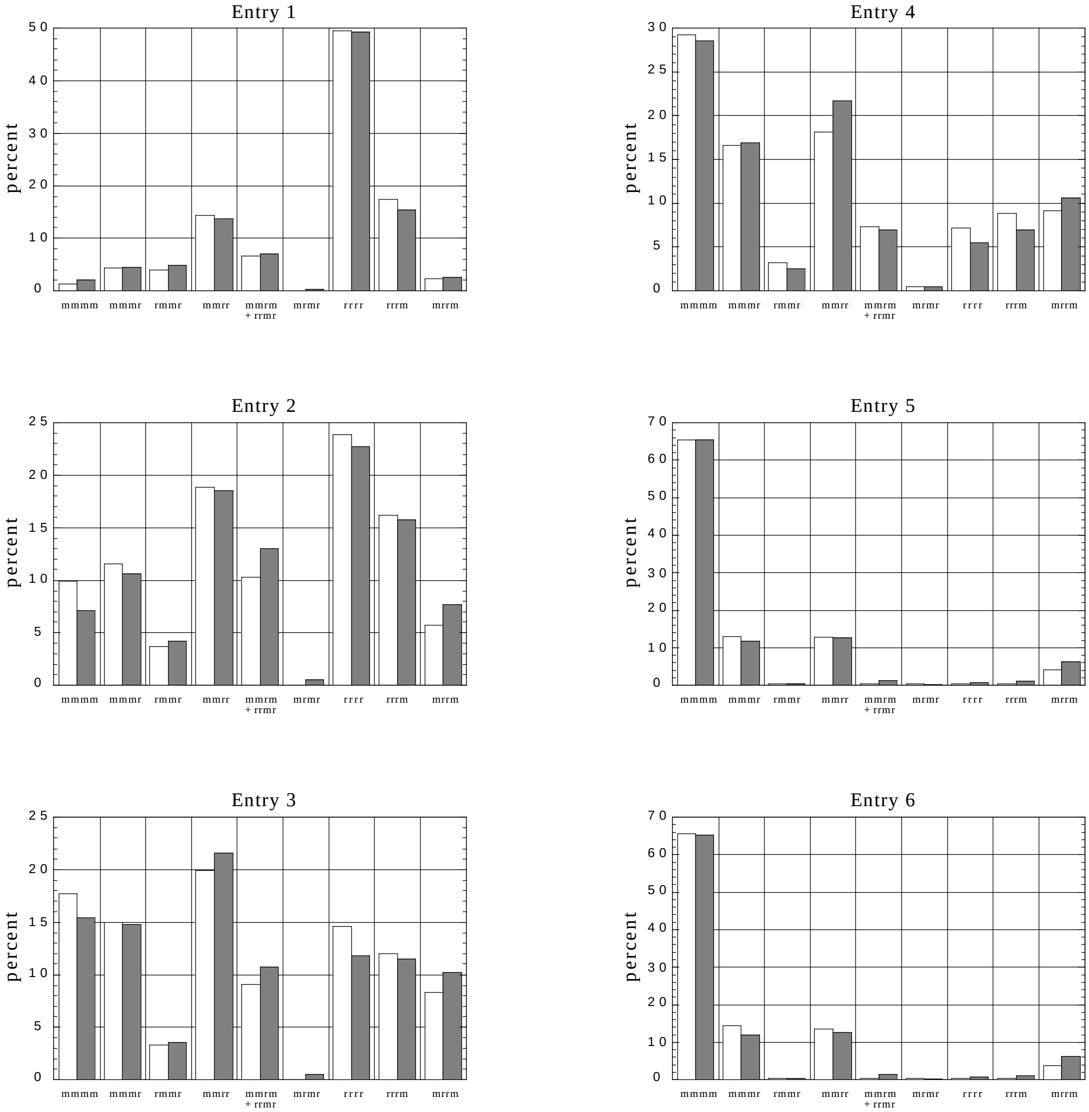

Figure 4. Observed (white) vs. calculated (shaded) pentad distributions for the unidirectional site epimerization model applied to **1**/MAO (see Table 4).

If the enantiofacial selectivity parameters α and β remain constant for **1**/MAO and epsilon is extrapolated to $\varepsilon = 0$ (no site epimerization), the model yields values of [r] = 82.9% and [rrrr] = 62.5%. This suggests that, even under ideal polymerization conditions, only modestly syndiotactic polypropylene could be obtained. Similarly, if epsilon is extrapolated to $\varepsilon = 1.0$ (all site epimerization), the model yields values of [m] = 98.3% and [mmmm] = 95.9%. In principle, highly isotactic polypropylene could be obtained with **1**/MAO. In practice, such conditions (low monomer concentration and high temperature) might effect low molecular weight polymers and chain epimerizations.[12]

If epsilon is interpolated until [r] = [m] = 50%, the model predicts ε = 0.577. This means **1**/MAO is more likely to site epimerize than not, and that site A is employed 70.2% of the time and site B is employed 29.8% of the time. Moreover, this catalyst system is unable to produce atactic polypropylene, as [rrrr] = 11.9% and [mmmm] = 15.3% for this polymer. The pentad distribution for this polymer is compared with that for perfectly atactic polypropylene ([rrrr] = [mmmm] = 6.25%) in Figure 5. One of the striking differences is that the calculated mrmr peak (0.5%) is almost absent. This is readily understood by analyzing the most likely ways to form the mrmr pentad, as depicted in Figure 6. Since the probability of employing a site sequence with two consecutive B sites is zero for the unidirectional site epimerization model, the only way to create the mrmr pentad is to misinsert at the more stereoselective site, which is 99.2% selective. Indeed, this pentad is virtually absent in every polymer analyzed.[13]

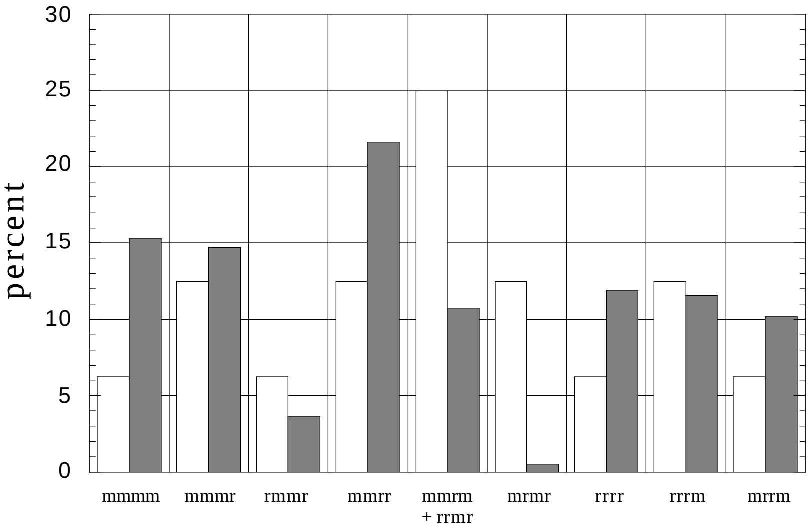

Figure 5. Comparison of perfectly atactic polypropylene (white) to that predicted for **1**/MAO with [m] = [r] = 50% (shaded).

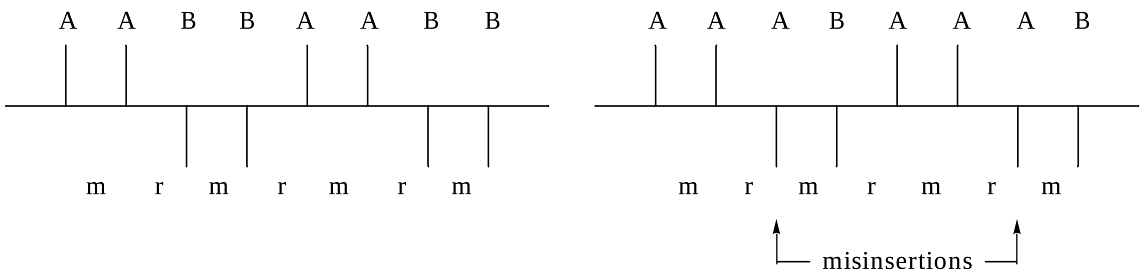

Figure 6. The mrmr pentad must be formed via misinsertions at the more stereoselective site, A.

An analysis with similar results can be performed on polypropylenes obtained from $(1,2\text{-SiMe}_2)_2\{\eta^5\text{-C}_5\text{H}_2\text{-4-(1}R\text{, 2}S\text{, 5}R\text{-menthyl)}\}\{\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2\}\text{ZrCl}_2$ / MAO (**2** / MAO) over a range of monomer concentrations (Entries 7-12). The least squares minimization of Entry 7 (Table 5) provides the following parameters: $\alpha = 0.987$; $\beta = 0.141$; $\varepsilon = 0.177$. With fixed values of α and β, the unidirectional site epimerization parameter increases with decreasing monomer concentration. As the concentration decreases—12.5, 4.6, 3.4, 2.1, 0.8, 0.5 M—the site epimerization probability, ε, increases: 0.177, 0.247, 0.289, 0.503, 0.630, 0.709. Figure 7 plots the unidirectional site epimerization parameter, ε, as a function of monomer concentration for **3** / MAO and **4** / MAO with a polymerization temperature of 25°C.

Table 5. Unidirectional site epimerization model applied to **2** / MAO.[a]

Entry	7 obs	7 calc	8 obs	8 calc	9 obs	9 calc	10 obs	10 calc	11 obs	11 calc	12 obs	12 calc
[mmmm]	3.3	2.0	1.6	2.8	4.3	3.4	11.5	9.6	18.6	17.7	26.3	25.6
[mmmr]	4.5	4.8	6.8	6.1	8.1	7.0	12.9	12.3	15.9	15.5	15.3	16.7
[rmmr]	6.0	4.3	2.6	4.2	3.9	4.2	4.4	4.1	2.6	3.5	3.8	2.8
[mmrr]	12.9	13.0	16.1	14.1	14.7	15.0	19.5	19.8	21.5	21.8	17.2	21.8
[mmrm] + [rrmr]	11.4	10.3	11.4	12.4	11.4	13.2	12.1	13.0	8.4	10.2	8.9	7.8
[mrmr]	0.0	0.5	0.0	0.5	0.0	0.6	0.0	0.7	1.8	0.7	3.0	0.7
[rrrr]	45.4	45.4	38.3	38.2	34.4	34.2	18.8	17.2	11.2	9.8	7.0	6.2
[rrrm]	13.7	16.4	19.3	17.1	17.2	17.2	13.3	14.2	11.8	10.4	8.5	7.7
[mrrm]	2.8	3.2	3.8	4.5	5.9	5.2	7.4	9.0	8.2	10.5	9.7	10.7
[m]	25.9	23.1	24.8	26.7	29.3	29.0	44.6	42.7	53.0	53.0	60.1	60.3
[r]	74.1	76.9	75.2	73.3	70.7	71.0	55.4	57.3	47.0	47.0	39.9	39.7
ε		.177		.247		.289		.503		.630		.709
% RMS		1.234		1.274		.835		1.150		1.311		1.918

[a] The parameters α (0.987) and β (0.141) are determined by RMS minimization of Entry 7 and are maintained at these values for application to Entries 8-12.

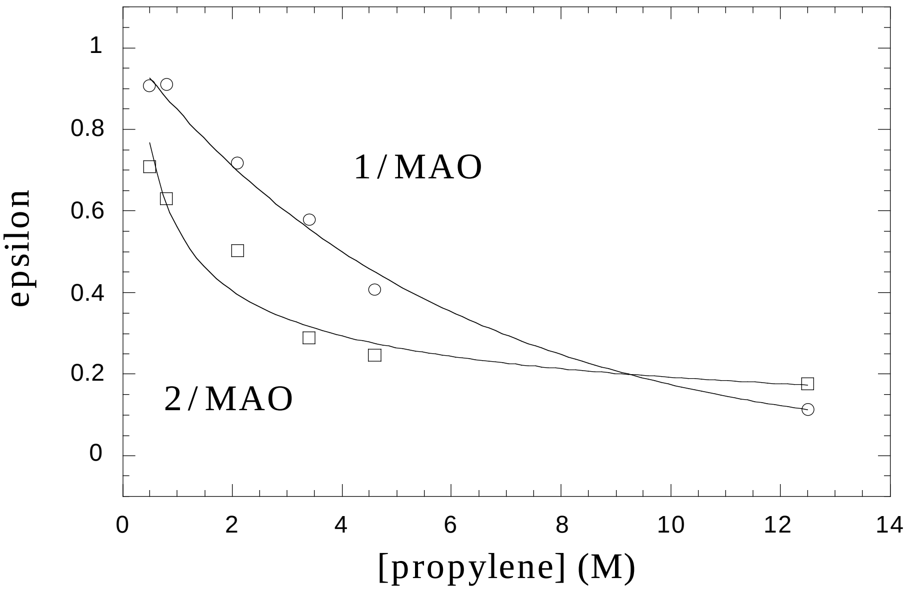

Figure 7. The parameter ε varies as a function of propylene concentration for **1**/MAO and **2**/MAO.

2.4 Application of the Unidirectional Site Epimerization Model to Singly-bridged Metallocenes

The singly-bridged metallocene catalyst $Me_2C(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$/MAO (**3**/MAO) has been subjected to a series of propylene polymerizations conducted at increasing polymerization temperatures. A least squares fit of the unidirectional site epimerization model to Entry 13 (1.1 M $[C_3H_6]$, T_p = 0°C) establishes the stereochemical parameters: $\alpha = 0.975$ and $\beta = 0.599$ (Table 6). This indicates that both sites of the metallocene prefer the same enantioface of the incoming monomer. With fixed values of α and β, conditions of dilute monomer (1.1 M), and increasing polymerization temperature—0, 20, 40, 60, 75, 90°C—the unidirectional site epimerization parameter, ε, increases: 0.000, 0.000, 0.069, 0.181, 0.353, 0.484. This system is relatively unresponsive to changes that increase the likelihood of unimolecular site epimerization over that of bimolecular propagation. For this system at 20°C, ε = 0.000, while for **1**/MAO and **2**/MAO under similar conditions (25°C, 0.8 M), ε = 0.909 and 0.630, respectively.

Table 6. Unidirectional site epimerization model applied to **3**/MAO.[a]

Entry	13 obs	13 calc	14 obs	14 calc	15 obs	15 calc	16 obs	16 calc	17 obs	17 calc	18 obs	18 calc
[mmmm]	26.4	26.8	26.0	26.8	27.2	28.0	28.4	30.4	34.2	35.4	40.1	40.6
[mmmr]	14.3	14.6	14.6	14.6	15.7	15.2	16.5	15.9	16.8	16.4	16.4	16.2
[rmmr]	6.5	4.8	5.9	4.8	4.5	4.1	3.7	3.3	2.9	2.3	3.0	1.8
[mmrr]	23.2	22.9	23.6	22.9	22.7	22.3	20.2	21.3	17.4	20.0	15.8	18.8
[mmrm] + [rrmr]	2.2	2.4	2.2	2.4	3.0	3.2	5.5	4.2	6.6	4.7	6.4	4.4
[mrmr]	0.6	1.2	0.6	1.2	0.6	1.2	1.2	1.2	2.7	1.1	2.1	1.0
[rrrr]	9.6	10.5	9.9	10.5	8.9	9.3	6.3	7.5	3.7	5.1	2.7	3.5
[rrrm]	9.0	9.6	9.1	9.6	8.2	9.0	7.7	8.1	5.8	6.3	4.8	4.9
[mrrm]	8.3	7.3	8.0	7.3	9.1	7.6	10.4	8.1	9.8	8.6	8.8	8.7
[m]	60.1	59.4	59.8	59.4	60.6	60.7	62.1	63.0	67.3	67.1	71.6	70.8
[r]	39.9	40.6	40.2	40.6	39.4	39.3	37.9	37.0	32.7	32.9	28.4	29.2
ε		0.000		0.000		0.069		0.181		0.353		0.484
% RMS		0.801		0.666		0.710		1.284		1.434		1.377

[a] The parameters α (0.975) and β (0.599) are determined by RMS minimization of Entry 13 and are maintained at these values for application to Entries 14-18.

The seemingly minor substitution of the isopropylidene bridge of **3** for the dimethylsilylene bridge of $Me_2Si(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**4**) results in drastically different polymerization behavior.[14] A least squares fit of the unidirectional model to Entry 19 (1.1 M $[C_3H_6]$, T_p = 0°C) provides the following parameters: α = 0.921, β = 0.806, and ε = 0.521 (Table 7). Although the amount of site epimerization for **3**/MAO under these conditions is negligible, **4**/MAO site epimerizes over half of the time. Moreover, an increase in the polymerization temperature to 20°C results in a system that is 100% prone to site epimerization. Therefore, Entries 20-23 are fit to the unimolecular site epimerization model with α as the only independent parameter, which is equivalent to enantiomorphic site control. Figure 8 plots the unidirectional site epimerization parameter, ε, as a function of polymerization temperature for **3**/MAO and **4**/MAO with a monomer concentration of 1.1 M.

Table 7. Unidirectional site epimerization model applied to **4**/MAO.[a]

Entry	19 obs	19 calc	20 obs	20 calc	21 obs	21 calc	22 obs	22 calc	23 obs	23 calc
[mmmm]	53.3	53.6	69.5	70.0	74.0	74.7	65.3	65.9	60.7	60.8
[mmmr]	12.4	14.3	10.0	10.4	6.5	9.0	10.4	11.5	12.8	12.7
[rmmr]	2.4	1.1	2.0	0.4	1.5	0.3	1.4	0.5	1.2	0.7
[mmrr]	12.7	14.5	8.9	10.4	9.3	9.0	9.0	11.5	11.4	12.7
[mmrm] + [rrmr]	7.0	4.0	2.3	1.6	2.3	1.1	4.0	2.2	4.2	2.9
[mrmr]	2.6	1.9	1.4	0.8	1.4	0.6	1.5	1.1	1.6	1.5
[rrrr]	1.1	1.2	0.5	0.4	0.9	0.3	1.2	0.5	0.8	0.7
[rrrm]	2.9	2.3	0.9	0.8	0.9	0.6	2.6	1.1	1.6	1.5
[mrrm]	5.5	7.2	4.3	5.2	3.2	4.5	4.6	5.7	5.8	6.4
[m]	79.3	79.2	87.9	87.2	88.5	89.3	84.4	85.3	83.2	82.8
[r]	20.7	20.8	12.1	12.8	11.5	10.7	15.6	14.7	16.8	17.2
ε		0.521		1.000		1.000		1.000		1.000
α		0.921		0.931		0.943		0.920		0.905
% RMS		1.551		0.857		1.163		1.332		0.673

[a] The parameters α (0.921) and β (0.806) are determined by RMS minimization of Entry 19. For Entries 20-23, ε is calculated to be 1.000 and the sole independent parameter, α, is determined by RMS minimization.

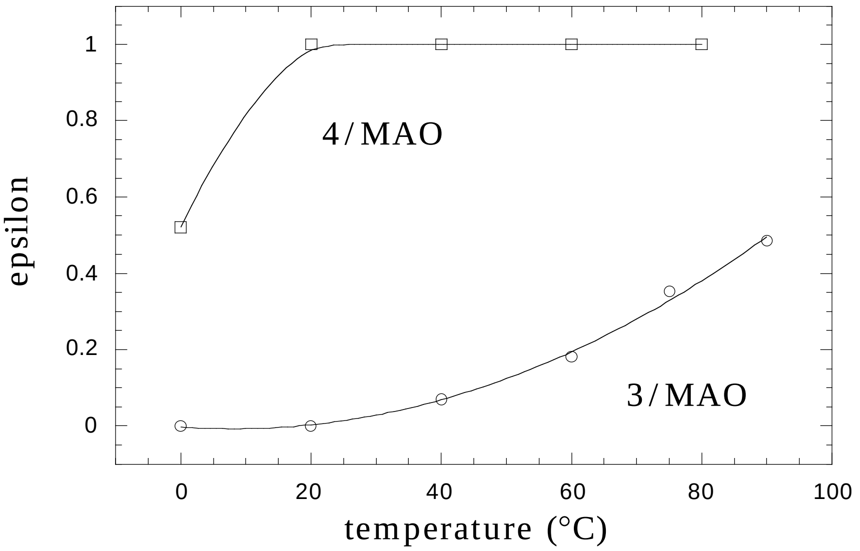

Figure 8. The parameter ε varies as a function of polymerization temperature for **3**/MAO and **4**/MAO.

2.5 Conclusions

A satisfactory statistical description of polymers obtained with **1-4**/MAO relies on the inclusion of the parameter ε, which quantifies the likelihood of unidirectional site epimerization, relative to propagation. Inclusion of this parameter—in addition to the stereochemical parameters, α and β—was necessary and sufficient, since no evidence for site epimerization in the opposite direction was identified. In general ε was found to increase with decreasing monomer concentration and increasing polymerization temperature, although the specific dependence is highly sensitive to the nature of the catalyst employed. More complex polymerization systems will require a bidirectional site epimerization model.[8] Such a model is currently under investigation for its application to systems that site epimerize in two directions.

2.6 Experimental Section

General Considerations. Unless otherwise noted, all reactions and procedures are carried out under an inert atmosphere of argon or nitrogen using standard glove box, Schlenk and high vacuum line techniques.[15] Solvents are dried according to standard procedures. The following reagents were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%); 2-adamantanone (99%); fluorene (98%); n-butyllithium (1.6 M in hexanes); and zirconium tetrachloride (99.5%). Dicyclopentadiene was obtained from Aldrich and cracked following standard procedures prior to use. Dichlorodimethylsilane was obtained from Aldrich and dried over calcium hydride prior to use. Syntheses of metallocenes **1** and **2** and their polymerization results have been reported.[10] **Instrumentation.** NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC-MS were acquired with a Hewlett Packard 5890 Series II Gas Chromatograph connected to a Hewlett Packard 5989A Mass Spectometer. The GC was equipped with a column of dimensions 7.1 m x 0.1 μm having an HP-1 phase (Crosslinked 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.

Preparation of 3.

adamantylfulvene. (Synthesis modified from reference 16) 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 hours before the yellow precipitate was collected by suction filtration, rinsed with a small volume of methanol and dried *in vacuo*. 25.71 grams (77.9%) of adamantylfulvene were isolated. MS (GC-MS) m/z 198.3 (M^+). ^1H 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-CH_1), 135.81, 167.38 (fulvene-CH_0). Elemental analysis calculated for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.20, 90.22; H, 8.39, 8.50.

2-adamantylcyclopentadiene. 6.00 grams (30.3 mmol) of adamantylfulvene were dissolved in 30 mL of tetrahydrofuran and this solution added over 30 minutes to at stirred slurry of $LiAlH_4$ (1.40 g, 0.0369 mol) at 0°C. After 5 hours 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 H_2O, 25 mL concentrated HCl, and 50 mL diethyl ether were added, the organic layer isolated, and the aqueous layer extracted with addition diethyl ether (3 x 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 methanol, 50 mL ethanol, 20 mL tetrahydrofuran, 36 mL acetone (0.49 mol) and 0.5 mL pyrrolidine (0.006 mol). After stirring for 48 hours, 5 mL of acetic acid were injected, followed by 200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 40 mL). The combined organic layers were extracted with H_2O (3 x 25 mL) and with 10% aqueous NaOH (3 x 25 mL), dried over $MgSO_4$, filtered and rotavapped. The obtained yellow solid was further purified by overnight Soxhlet extraction by 150 mL 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. Elemental analysis calculated for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 82.23, 82.23; H, 8.78, 8.82.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$. 10.5 mL 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 tetrahydrofuran. After stirring for 5 hours, a solution of 3-(2-adamantyl)-6,6-dimethylfulvene (4.00 g, 0.0166 mol) in 40 mL tetrahydrofuran was injected over 2 minutes. After stirring for 20 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer isolated, and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_4)(C_{13}H_8)H_2$ (6.77 g, 16.6 mmol) in 75 mL 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 hours, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield as an orange powder.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (3). 2.00 grams of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_4)(C_{13}H_8)Li_2$ (0.00478 mol) and 1.114 g $ZrCl_4$ (0.00478 mol) were combined in a swivel frit apparatus. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 14 hours if stirring. 40 mL of methylene chloride were 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 grams (55.5%) of **2** as an orange powder following collection at 0°C and *in vacuo* drying. MS (LC-MS) m/z 566.5 (M^+). ^1H NMR (C_6D_6): δ 1.36 - 2.04 (m, 14H, adamantyl-*H*), 1.84, 1.86 (s, 6 H, $C(CH_3)_2$), 3.32 (s, 1H, 2-*H*-adamantyl), 5.44, 5.48, 6.18 (m, 3H, Cp-*H*), 6.95, 7.03, 7.29, 7.34 (t, $^3J_{HH}$ = 7.7, 7.7, 8.0, 8.0 Hz, 4H, Flu-*H*), 7.41, 7.49, 7.84, 7.84 (d, $^3J_{HH}$ = 8.8, 9.1, 7.7, 7.7 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.58, 28.65 (C-(CH_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-CH_1), 123.41, 123.67, 124.61, 124.67, 124.76, 124.83, 128.81, 128.81 (Flu-CH_1), 139.93 (9-Flu-*C*),CH_0 not determined. Elemental analysis calculated 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.

Preparation of 4.

fluorenyllithium. A Schlenk tube was charged with fluorene (31.81 g, 191.4 mmol), evacuated, backfilled with argon, and charged with 150 mL toluene. n-butyllithium solution (120.0 mL, 192 mmol, 1.6 M in hexanes) was syringed in and the reaction was stirred for 103 hours 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 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 hours, 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-fluorenyl)$_2$ (MS (GC-MS) *m/z* 388.4 (M^+)), as reported by reference 17, occurs to about 10% (GC), but apparently does not affect the synthesis of **4**.

2-adamantylcyclopentadienyllithium. Adamantylcyclopentadiene (10.78 g, 53.81 mmol) was added to a swivel frit and 75 mL diethyl ether were 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 minutes. After stirring for 15 hours 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).

$Me_2Si(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. A swivel frit was charged with 9-($ClMe_2Si$)-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 hours. Solvent was removed and 50 mL diethyl ether were 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 minutes at room temperature. Solvent was removed after stirring for 20 hours. 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).

$Me_2Si(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (4). 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) were 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 hours. The solid was placed in a cellulose extraction thimble and was extracted overnight with 150 mL 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 (**4**) was collected on the frit and dried in vacuo: 0.707 g (14.1%). MS (LC-MS) m/z 582.7 (M^+). ^1H NMR (CD_2Cl_2): δ 1.11, 1.13 (s, 6H, CH_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 ($Si\text{-}CH_3$), 27.92, 32.49, 32.66, 37.86, 38.55, 38.71, 44.23 (adamantyl-*C*), 111.31, 111.86, 120.23 (Cp-CH_1), 123.52, 124.03, 124.20, 124.82, 126.23, 126.31, 128.54, 128.62 (Flu-CH_1), CH_0 not determined. Elemental analysis calculated for $C_{30}H_{32}Si_1Zr_1Cl_2$: C, 61.83; H, 5.53. Found: C, 58.63; H, 4.94.

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 6110 drying system equipped with an OXYSORB™ column. Polymerizations were conducted in a graduated Lab Crest glass reaction vessel (3 oz. nominal volume) and were stirred with a magnetic stir bar. Monomer was condensed into the vessel (containing toluene and MAO) over several minutes at room temperature. The vessel was then equilibrated at the polymerization temperature with an ice or water bath for 10 minutes. A given reaction commenced upon injection of a toluene solution of the metallocene into the vessel with a 2.5 mL Hamilton syringe rated to 200 psi. 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. Toluene and methanol were removed from the obtained polymers by *in vacuo* drying.

Representative Polymerization Procedures.

Entry 13. In the glove box, a 3 oz. Lab Crest pressure reactor was charged with MAO (0.102 g, 1.76 mmol [Al], 2000 equivalents) and 28.0 mL toluene. Propylene (3 mL) was condensed in at room temperature and the vessel equilibrated at 0°C for 10 minutes. A solution of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ **3** (0.0005 g, 9×10^{-4} mmol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 30 minutes. The reaction was vented and quenched with methanol/HCl. 0.13 grams of polypropylene were obtained. Reaction durations and isolated yields were as follows: Entry 14, 10 minutes, 0.25 g; Entry 15, 10 minutes, 0.44 g; Entry 16, 10 minutes, 0.18 g; Entry 17, 30 minutes, 0.15 g; Entry 18, 60 minutes, 0.21g.

Entry 19. In the glove box, a 3 oz. Lab Crest pressure reactor was charged with MAO (0.100 g, 1.72 mmol [Al], 1000 equivalents) and 28.0 mL toluene. Propylene (3 mL) was condensed in at room temperature and the vessel equilibrated at 0°C for 10 minutes. A solution of $Me_2Si(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ **4** (0.0010 g, 1.7 x 10^{-3} mmol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice / water bath for 90 minutes. The reaction was vented and quenched with methanol / HCl. 1.10 grams of polypropylene were obtained. Reaction durations and isolated yields were as follows: Entry 20, 45 minutes, 1.07 g; Entry 21, 15 minutes, 1.38 g; Entry 22, 15 minutes, 1.54 g; Entry 23, 15 minutes, 1.86 g.

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 / minute) 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.[18] 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 seconds and a minimum of 1000 scans were used.

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2.7 References and Notes

* Preliminary results for the application of the unidirectional site epimerization model to **1** / MAO are reported in footnote 26 of reference 10b.

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c) Reference 1d, p. 565.

7. The term "site epimerization mechanism" is used in preference to other terms found in the literature: "consecutive addition" (Reference 3b);

"skipped insertion" (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); "back-skip mechanism" (Reference 14a); "retention mechanism" (Reference 3d); and "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.).

8. While substantially more complex, a bidirectional site epimerization model has been derived as well. This model employs four independent parameters and is considerably different from that devised by Farina and Di Silvestro (Reference 3). Its derivation and application will be presented in a forthcoming manuscript.
9. See Appendix G for a representation of the 416 possible pentads in the unidirectional site epimerization model.
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Chapter 3

Highly Stereoregular Syndiotactic Polypropylene Formation with Metallocene Catalysts Via Distal Ligand Perturbation

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

3.1 Introduction

The first highly efficient syndiotactic polypropylene polymerization system was reported by Ewen et al. in 1988.[1] The original design employed a fluorenyl containing metallocene precatalyst of the type $Me_2C(C_{13}H_8)(C_5H_4)MCl_2$ ($C_{13}H_8$ = fluorenyl) activated by methylaluminoxane (MAO). This system suffered from two kinds of stereoerrors that decreased the syndiotacticity of the produced polymer: enantiofacial misinsertions and site epimerizations. Figure 1 describes the general mechanism for syndiotactic polypropylene synthesis and shows the mechanistic steps responsible for stereoerror formation. Perfectly syndiotactic polypropylene (Figure 2) arises from a regularly alternating mechanism which employs sequentially opposite enantiofaces of the propylene monomer; the stereochemical designation “r” is used to describe the *racemo* relationship between two adjacent stereocenters.[2] Figure 2 also shows the stereochemical outcome of an enantiofacial misinsertion and of a site epimerization. The former results in an isolated mm triad—where “m” describes adjacent stereocenters having a *meso* relationship—while the latter results in an isolated m dyad.

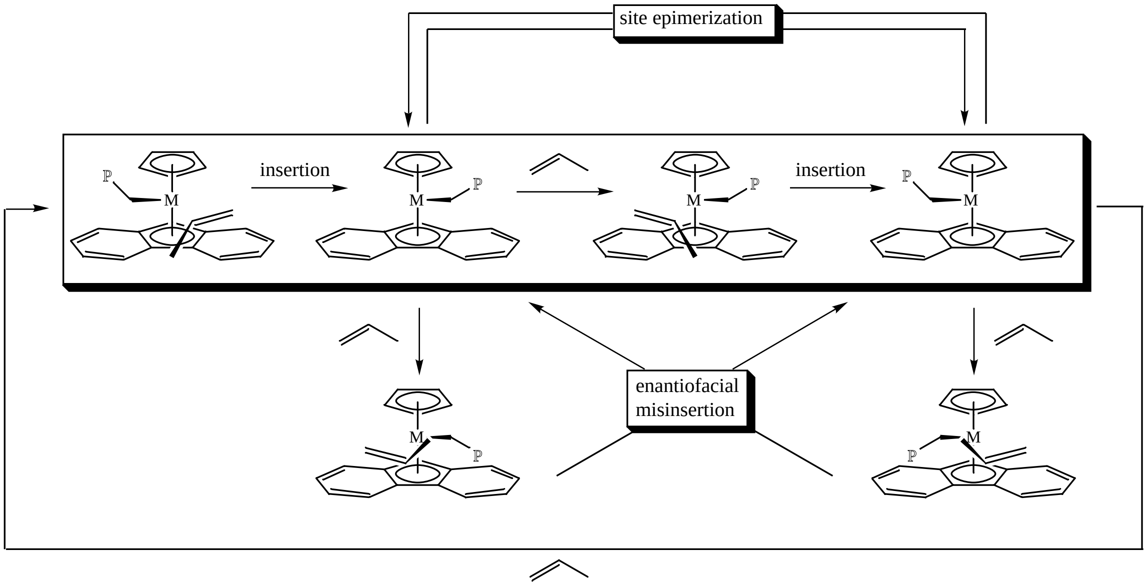


Figure 1. Two main types of stereoerrors occur in syndiospecific polymerization systems: site epimerizations and enantiofacial misinsertions.

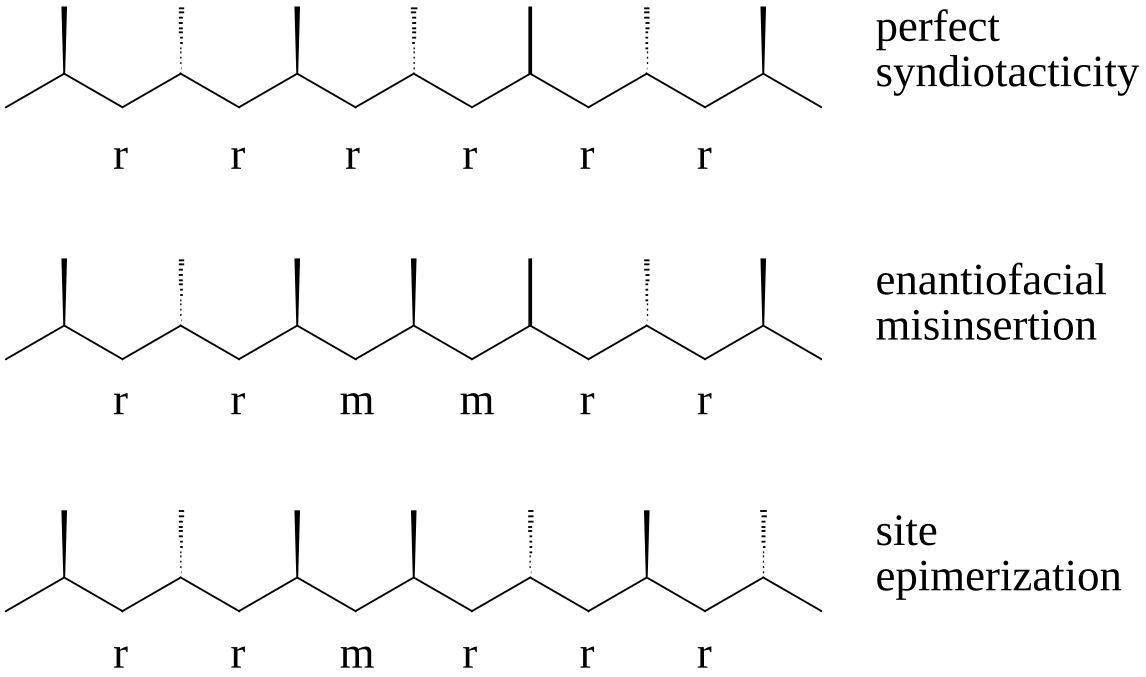


Figure 2. Stereochemical representation of perfectly syndiotactic polypropylene and syndiotactic polypropylene containing mistakes arising from enantiofacial misinsertion and site epimerization.

Since Ewen's initial discovery, several metallocene-based systems have been devised that excel the original with respect to syndiospecificity, activity, molecular weight, and polymer melting temperature (T_m).[3, 4] Ewen, Razavi, et al. developed the original singly-bridged metallocenes **1**, **2**.[1] Razavi et al. developed bridge-modified analogs **3**, and **4**.[5] Alt, Zenk, et al. and Ewen et al. have prepared several fluorenyl substituted metallocenes, including **5**.[6, 7] Bercaw, Herzog, et al. have developed doubly-bridged syndiospecific metallocenes; examples are given by **6** and **7**.[8] Table 1 presents representative data regarding polymers made by MAO cocatalyzed polymerizations. The doubly-bridged metallocenes produce the highest melting syndiotactic polypropylene known for metallocene-based systems. For a given ligand system, the hafnium analogs generally provide polymers of lower syndiotacticity.

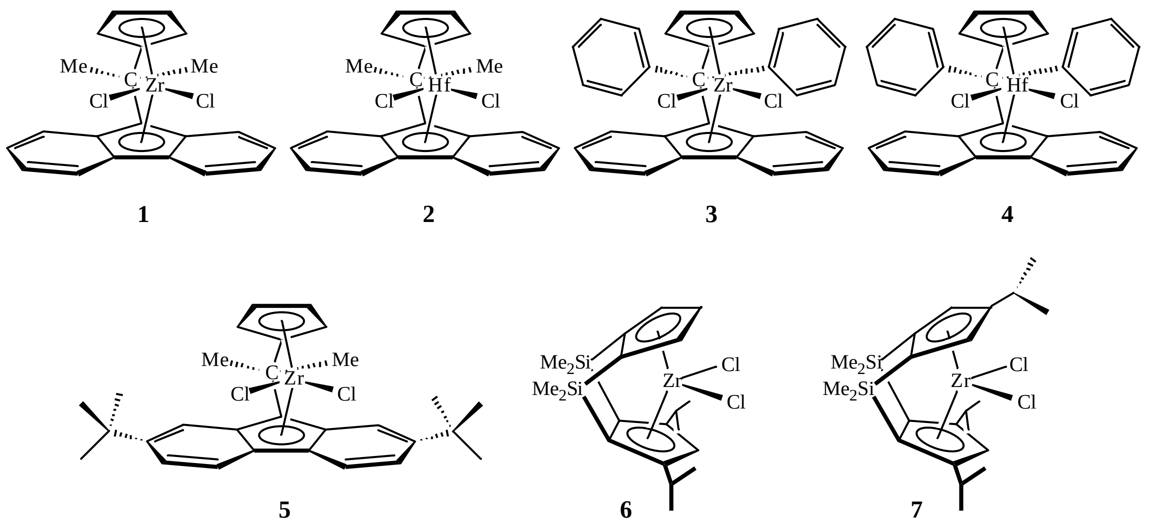


Figure 3. Known syndiospecific metallocene precatalysts **1**, **2**, **3**, **4**, **5**, **6**, and **7**.

Table 1. MAO cocatalyzed polymerization results with **1**, **2**, **3**, **4**, **5**, **6**, and **7**.

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

3.2 Metallocene Synthesis

According to the current understanding of propagative stereocontrol,[9] enantiofacial misinsertions occur in parent fluorenyl systems whenever the growing polymer chain is directed toward the fluorenyl ligand during the transition state for insertion. The three-dimensional nature of the isopropyl substituents of the doubly-bridged metallocenes **6** and **7** apparently disfavors the analogous transition state for misinsertion, as these provide polymers containing fewer enantiofacial misinsertions (rmmr typically <1%). Our initial goal was to prepare a fluorenyl-based metallocene with similar steric properties such that enantiofacial misinsertions were minimized.

Metallocene **5** bears added steric bulk in the form of two *tert*-butyl groups at the 2 and 7 positions of the fluorenyl ligand. However, only a modest increase in syndiospecificity is observed over that of the parent system. A simple steric analysis suggests that steric bulk placed at the 3 and 6 positions of the fluorenyl ligand might better approximate the steric situation present in the doubly bridged metallocenes. Therefore, the sterically expansive substituted fluorenes 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo [b, h] fluorene[10] (OctH) and 1,1,4,4-tetramethyl-1,2,3,4-tetrahydrobenzo [b] fluorene[11] (TetH) were prepared according to Figure 4.

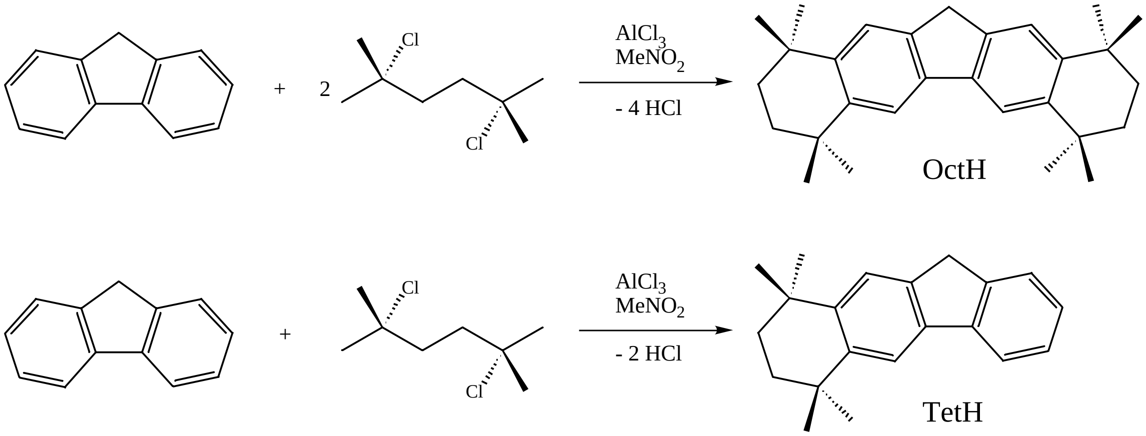


Figure 4. Synthesis of OctH and TetH via Friedel-Crafts cycloalkylation.

A vastly improved synthesis OctH has allowed the large scale (100 g) synthesis of this sterically loaded fluorene. Figure 4 shows the Friedel-Crafts double cycloalkylation of fluorene, which proceeds in high isolated yields (>95%). All starting materials are inexpensive and commercially available with the exception that 2,5-dichloro-2,5-dimethylhexane must be prepared in one facile step from the corresponding, inexpensive diol. TetH is prepared by the analogous single cycloalkylation and must be separated from residual fluorene and OctH, which forms competitively. Despite this and modest yields (43%), TetH can be prepared pure and on multigram scales (16 g). TetH bears tertiary substitution at the 2 and 3 positions while OctH bears tertiary substitution at the 2, 3, 6, and 7 positions.

Metallocenes incorporating the Oct and Tet ligands are prepared according to the exemplary syntheses shown in Figure 5. Crystals of the intermediate diprotio ligand $Ph_2C(OctH)(C_5H_5)$ were subjected to X-ray diffraction analysis.[12] This revealed the presence of four different molecules residing in the asymmetric unit. These varied because of alternate positioning of the sp^3 carbon in the cyclopentadienyl ring and because of different conformers possible for the 2,5-dimethylhexane-2,5-diyl substituent (Table 2). For example, Figure 6 shows the structure with the proximal (same side of the fluorene ring as 9-H) methyl groups near the 3 and 6 positions of fluorene occupying axial (left) and equatorial (right) positions. Synthesized metallocenes containing the Oct and Tet ligands are shown in Figure 7.

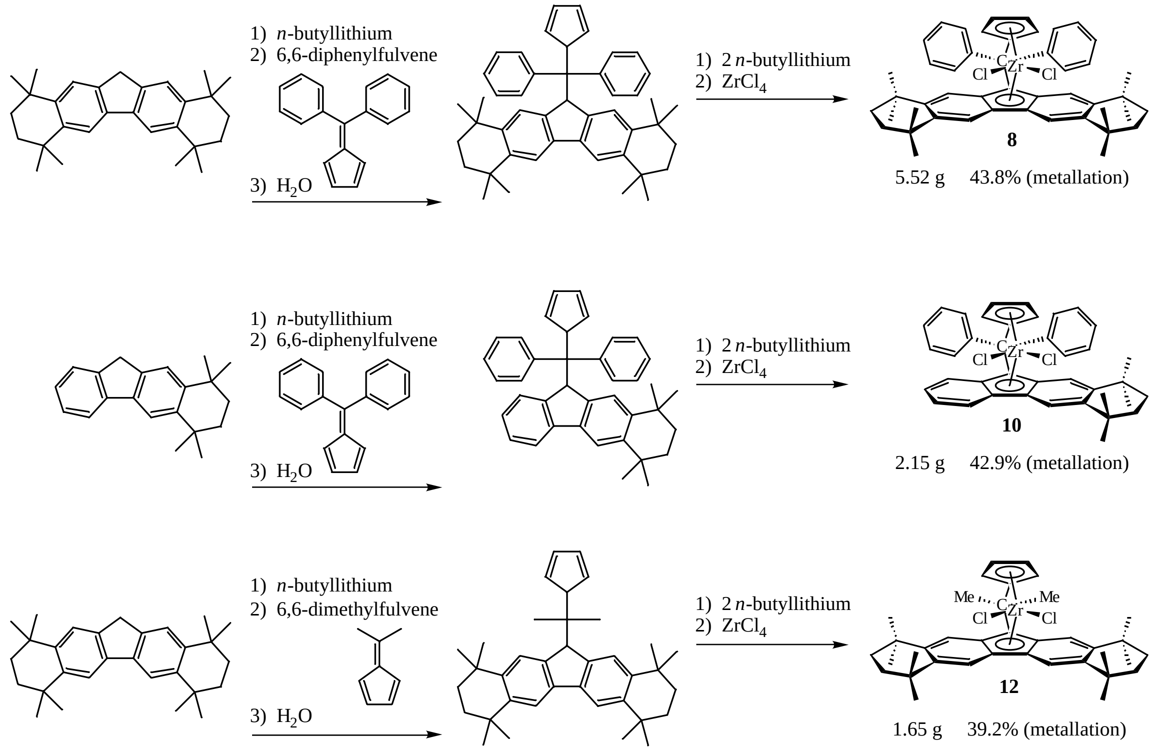


Figure 5. General synthetic route to **8**, **10**, and **12**.

Table 2. Description of four identified structures for $Ph_2C(OctH)(C_5H_5)$.

Molecule	position of Cp sp^3 carbon	position of left proximal methyl group	position of right proximal methyl group
A (Figure 6)	3	axial	equatorial
B	3	axial	axial
C	4	axial	equatorial
D	4	equatorial	axial

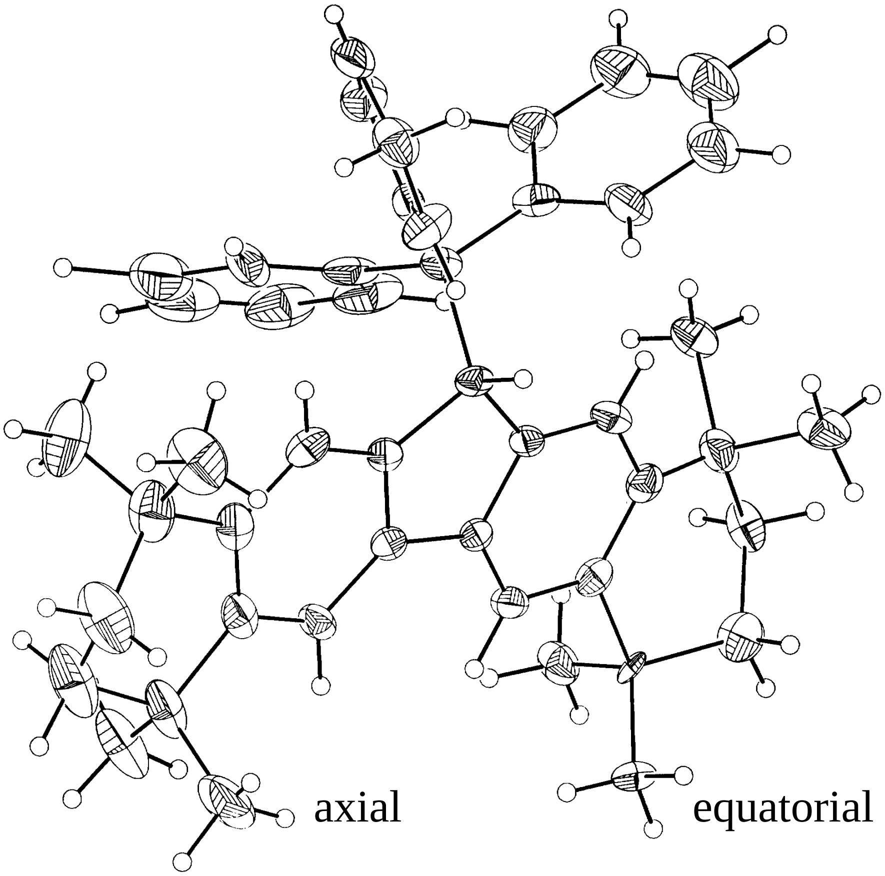


Figure 6. X-ray crystal structure of $Ph_2C(OctH)(C_5H_5)$. Thermal ellipsoids are shown with 50% probability.

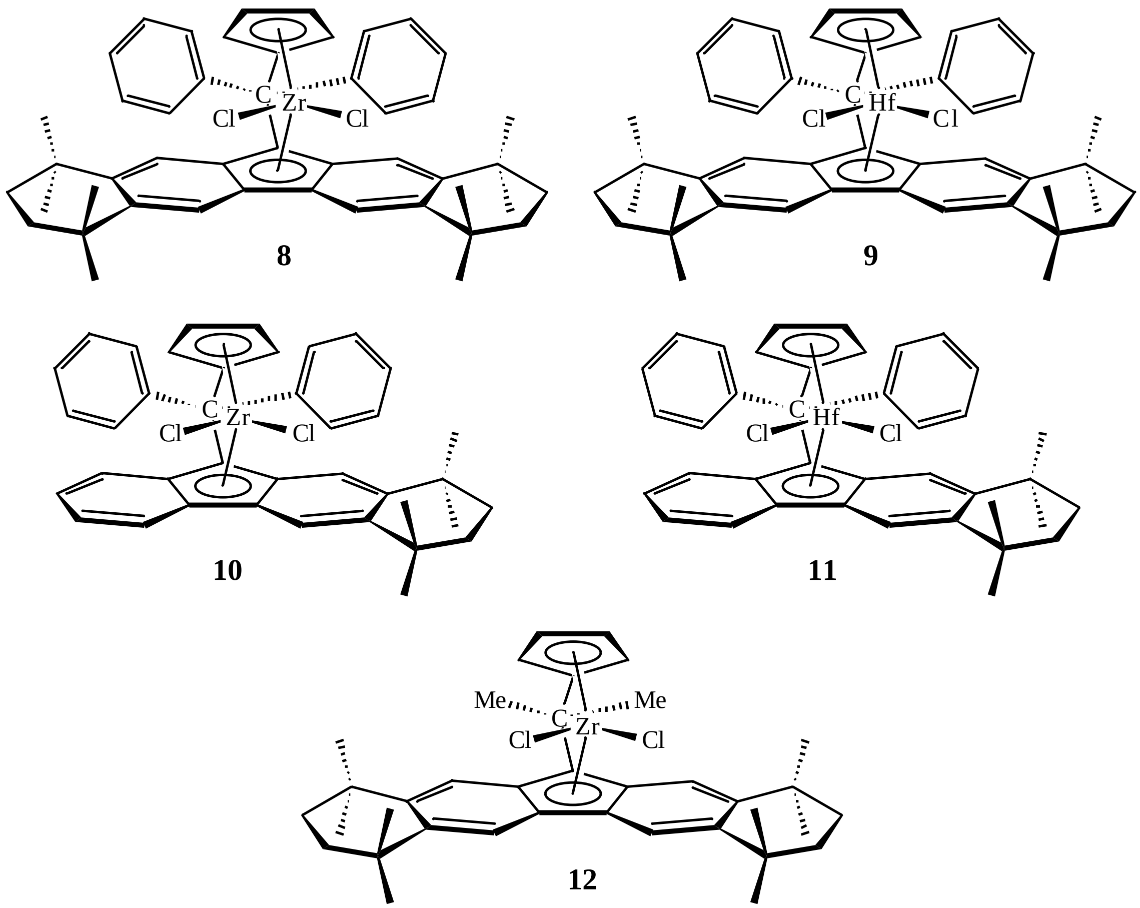


Figure 7. Oct and Tet containing metallocenes **8**, **9**, **10**, **11**, and **12**.

3.3 Metallocene Characterization

Metallocene complexes **8** - **12** have been characterized by ^{1}H NMR. Compounds **8**, **9**, and **12** display C_s symmetry in solution, consistent with rapid interconversion of the two chair-like conformers possible for the tetramethyltetrahydrobenzo substituents. Additionally, compounds **10** and **11**—present as a racemic mixture of enantiomers—display C_1 symmetry in solution. As seen for the parent fluorenyl complexes **3** and **4**,[5] rotation around the C-phenyl bond of **8** - **11** is slow on the NMR timescale.

The solid state crystal structures of metallocene complexes **8** and **10** have been determined by X-ray crystallography.[13, 14] Figure 8 shows the structure found for metallocene **8** and Figure 9 shows the structure found for metallocene **10**. These were each crystallized from dichloroethane and have empirical formulas of **8** · $(C_2H_4Cl_2)_{1.5}$ and **10** · $(C_2H_4Cl_2)_{1.5}$. In contrast to the several conformations found in the solid state for the diprotio ligand $Ph_2C(OctH)(C_5H_5)$, metallocenes **8** and **10** present only single conformations. The proximal methyl groups of **8** are described as axial/equatorial (Figure 8) and the proximal methyl group of **10** is described as axial (Figure 9).

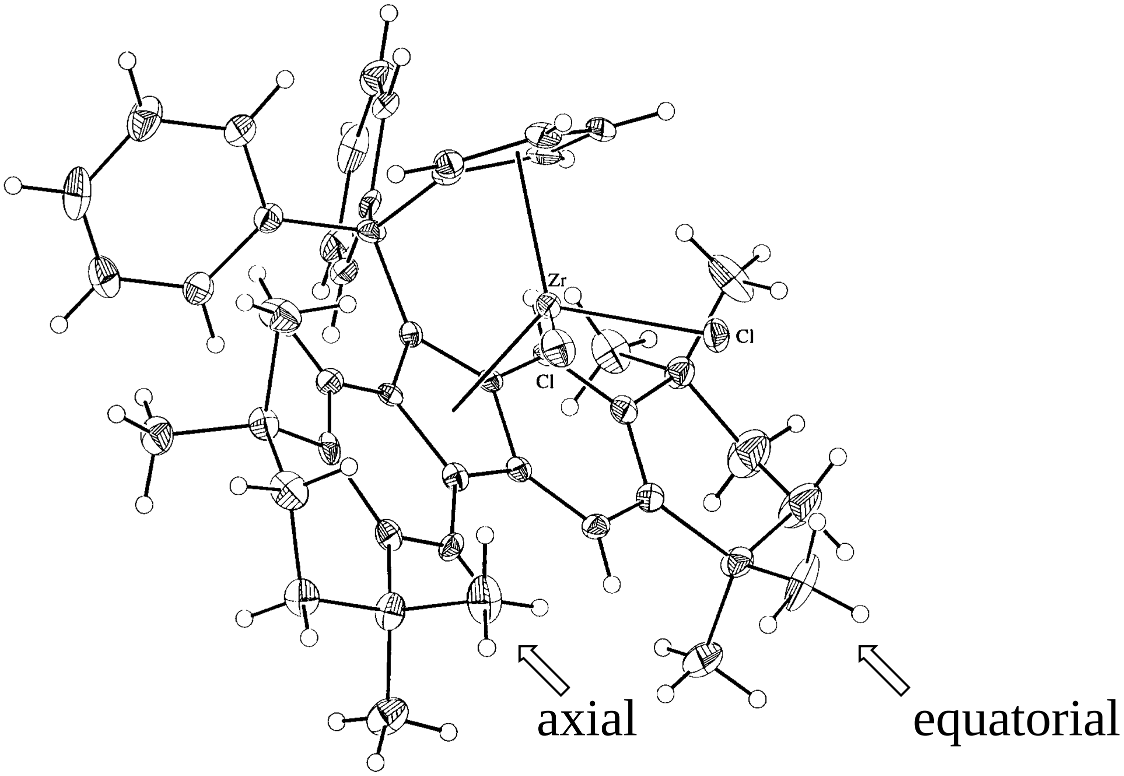


Figure 8. X-ray crystal structure of **8**. Thermal ellipsoids are shown with 50% probability.

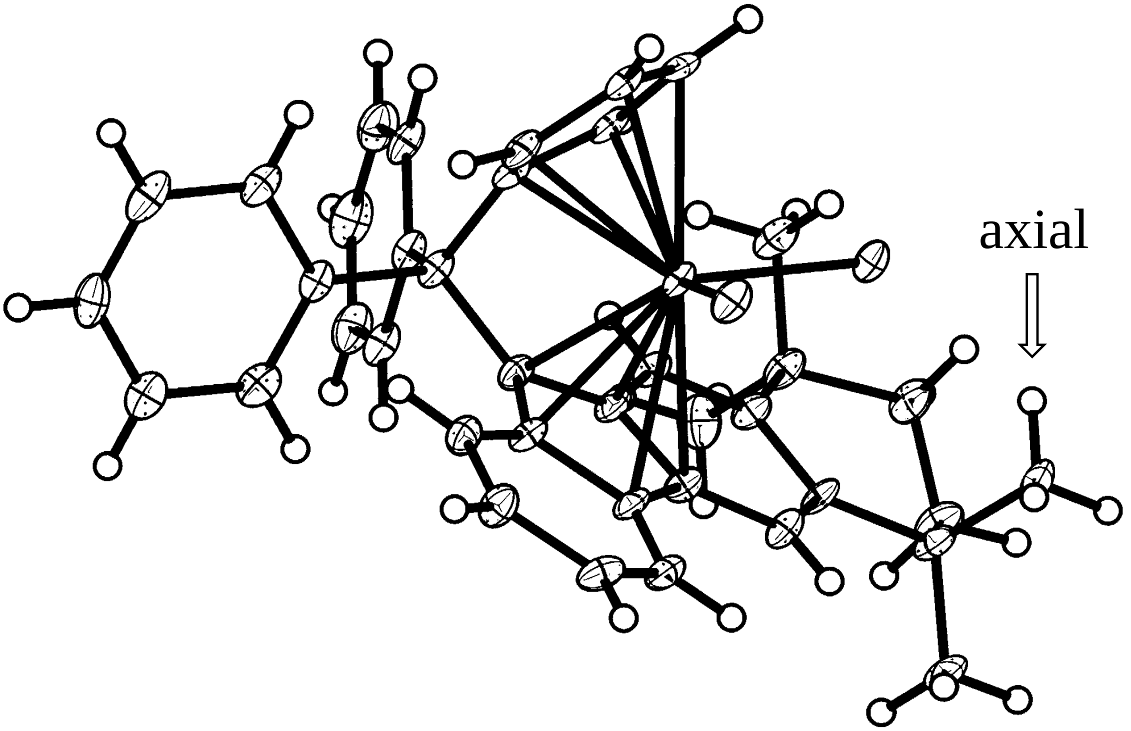
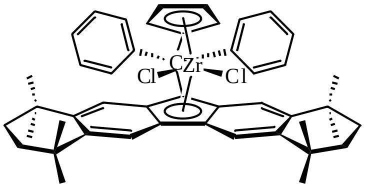
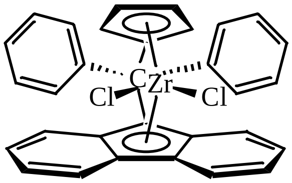


Figure 9. X-ray crystal structure of **10**. Thermal ellipsoids are shown with 50% probability.

3.4 UV/Visible Spectroscopic Analysis

The variety of color changes observed during polymerizations with fluorenyl-containing metallocenes prompted a UV/visible spectroscopic analysis. While addition of MAO (500 equivalents) to a toluene solution of $Ph_2C(C_{13}H_8)(C_5H_4)ZrCl_2$ (**13**) results in a small red shift of the absorption band (λ_{max} from 498 nm to 518 nm; $\Delta E = 775\ cm^{-1}$), an unprecedentedly large red shift is observed for the addition of MAO (500 equivalents) to a toluene solution of $Ph_2C(C_{29}H_{36})(C_5H_4)ZrCl_2$ (**8**) (λ_{max} from 520 nm to 586 nm; $\Delta E = 2166\ cm^{-1}$) (Table 3). Quite possibly, this effect could arise from the ability of the sterically demanding Oct ligand to disfavor associated ion pairs. Metallocene **10**, which contains the Tet ligand, undergoes MAO induced color transitions which are very similar to those observed with parent fluorenyl compound **13** (purple polymerization reactions), suggesting that the extensive substitution on *both* sides of metallocene **8** are requisite for observing drastic shifts in the LMCT band.

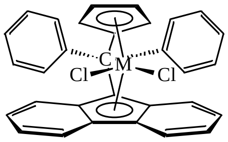
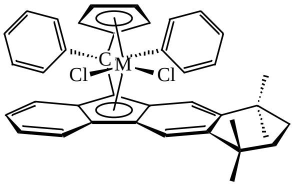
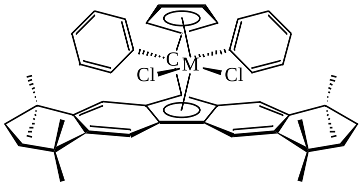
Table 3. Color change as a function of time for **8** and **13** following addition of MAO.

	 **8**		 **13**	
Time (minutes)	λ_{max}	Color	λ_{max}	Color
0 (no MAO)	520	pink	498	orange
5	612	green	512	purple
10	608	green	514	purple
60	586	blue	514	purple
120	586	blue	516	purple
180	586	blue	518	purple
1080	586	blue	518	purple

To the extent that the red shift is proportional to counterion dissociation, one might expect catalyst activity to correlate with the magnitude of the red shift. This phenomenon has been reported with the indenyl-containing complex *rac*-$C_2H_4(1\text{-}C_9H_6)_2ZrCl_2$ following the addition of varying amounts of MAO.[15] The observed red-shift of the absorption band is attributed to the formation of an increasing proportion of the dissociated to associated zirconocenium species $[C_2H_4(1\text{-}C_9H_6)_2ZrX]^+$ $[MAOCl]^-$. The polymerization activity was shown to be proportional to the observed red-shift.

The same correlation between propylene polymerization activity and the observed red shift is also found for the Flu-, Tet-, and Oct-containing metallocene series. Table 4 shows that Oct-containing metallocenes **8** and **9** are the most active (1000 equivalents MAO, units = kg polymer/(mol M·hour)), despite being the most sterically crowded.

Table 4. Activity comparisons for Flu-, Tet-, and Oct-containing metallocene catalyst systems.[a]

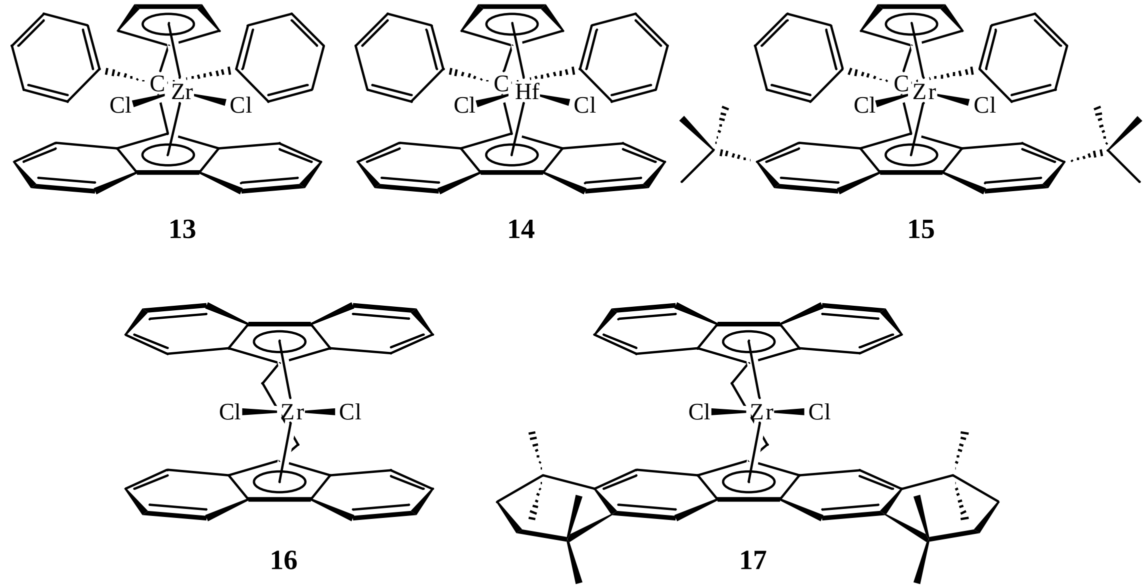
						
T_p (°C)	Zr (**13**)	Hf (**14**)	Zr (**10**)	Hf (**11**)	Zr (**8**)	Hf (**9**)
0	1000	70	540	69	1700	280
20	3800	600	6400	960	7800	1700

[a] Activity measured in units of kg polymer/(mol M·hour).

Although it is rare for d^0 complexes to emit,[16] several fluorenyl-containing complexes studied gave emission spectra; for example, irradiation of $Ph_2C(Oct)(C_5H_4)ZrCl_2$ (**8**, λ_{max} = 520) causes emission with a maximum near 590 nm. Although the lifetime of the zirconium species is apparently very short, the fluorescence lifetime for $Ph_2C(Oct)(C_5H_4)HfCl_2$ (**9**, λ_{max} = 492) was determined (in methylcyclohexane): τ = 155 ns (λ_{EM} = 610 nm).[17]

3.5 Polymerization Results

The five metallocene precatalysts shown in Figure 7 were subjected to MAO-cocatalyzed polymerizations of propylene. In addition to these metallocene precatalysts, those shown in Figure 10 were also prepared and tested, primarily for obtaining comparative data. Metallocenes **13**, **14**[5] and **16**[18] have been reported while **15** is the diphenylmethylidene-bridged variant of the isopropylidene-bridged compound **5**.[7] Metallocene **17** is a C_s-symmetric Oct-containing analog of **16**. The polymerization results are summarized in Table 5. Figure 11 depicts the ^{13}C NMR of the methyl region for two polymers made by metallocene **8**/MAO (Entry 1 and Entry 2). These two syndiotactic polypropylenes are largely devoid of stereoerrors.[19]



13 **14** **15**

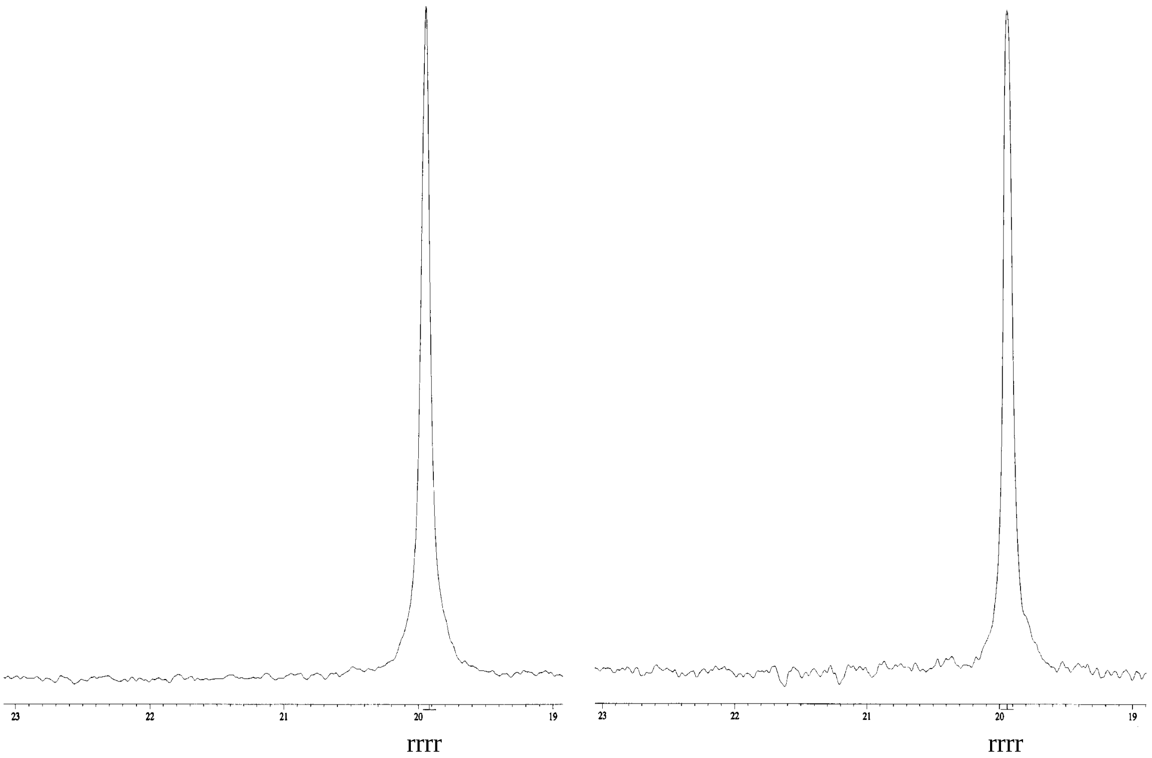
16 **17**

Figure 10. Fluorenyl-containing metallocenes **13**, **14**, **15**, **16**, and **17**.

Table 5. MAO-cocatalyzed polymerization results with **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, and **17**.

Entry	Metallocene (mg)	MAO (equiv.)	T_p (°C)	Toluene (mL)	C_3H_6 (mL)	Time (min.)	Yield (g)	Activity (gP / (gmet·h))	T_m [a] (°C)	[r] (%)	M_w	M_w / M_n
1	**8** (0.5)	2000	0	1.0	30	10	0.48	5700	153	>99	961,000	2.12
2	**8** (0.5)	2000	20	1.0	30	10	1.16	14000	148	>98	843,000	1.75
3	**8** (2.0)	1000	0	2.0	30	10	0.82	2500	149			
4	**8** (2.0)	1000	20	2.0	30	10	1.44	4300	146			
5	**8** (2.0)	1000	0	30.0	3	20	1.44	2200	146	>98		
6	**8** (2.0)	1000	20	30.0	3	5	1.68	10000	140			
7	**9** (3.0)	1000	0	2.0	30	15	0.25	330	111	88.6		
8	**9** (3.0)	1000	20	2.0	30	10	0.98	2000	88	89.8		
9	**10** (2.0)	1000	0	2.0	30	10	0.27	800	140	>98		
10	**10** (2.0)	1000	20	2.0	30	5	1.60	9600	137			
11	**11** (3.0)	1000	0	2.0	30	60	0.27	90	141	92.2		
12	**11** (3.0)	1000	20	2.0	30	20	1.27	1300	120	89.7		
13	**12** (0.5)	2000	0	1.0	30	10	0.26	3100	151	>98		
14	**12** (0.5)	2000	20	1.0	30	10	0.26	3100	147			
15[b]	**12** (2.0)	1000	0	2.0	30	10	1.16	3500	154	97.5	535,000	2.00
16	**12** (2.0)	1000	20	2.0	30	10	4.79	14000	153		310,000	2.03
17	**13** (1.0)	1000	0	2.0	30	10	0.31	1900	142			
18	**13** (1.0)	1000	20	2.0	30	10	1.13	6800	136			
19	**14** (3.0)	1000	0	2.0	30	30	0.16	110	124			
20	**14** (3.0)	1000	20	2.0	30	15	0.70	940	119			
21	**15** (2.0)	1000	0	2.0	30	5	1.12	6700	144			
22	**15** (2.0)	1000	20	2.0	30	3	2.24	22000	139			
23	**16** (0.5)	2000	0	1.0	30	5	3.00	72000	n.o.	50.2		
24	**16** (0.5)	2000	20	1.0	30	5	5.09	120000	n.o.	50.5		
25	**17** (0.5)	2000	0	1.0	30	5	1.09	26000	n.o.	81.3		
26	**17** (0.5)	2000	20	1.0	30	5	2.85	68000	n.o.	74.1		

[a] n.o. = not observed. [b] See Reference 19.



Entry 1 Entry 2

Figure 11. ^{13}C NMR spectrum of the methyl region for polypropylenes made by **8**/MAO (Entry 1 and Entry 2).

Since the thermal history of a syndiotactic polypropylene sample can often impact its melting behavior, polymer melting temperature for several polymers was monitored as a function of thermal history, as described in Table 6.[20] Generally, the first melting temperature is significantly higher than that obtained during subsequent scans. Those values measured during the second, third, and fourth scans correspond to the melting temperature of the thermally quenched polymer, and are quite similar. Annealing processes can often lead to unusually high melting temperatures,[21] as shown for Entry 3 following annealing for 16 hours at 145°C. The highest melting thermally quenched polymer reported here is that produced by metallocene **12**/MAO, which is capable of producing syndiotactic polypropylene with a melting temperature of 154.3°C (Entry 15).

Table 6. Polymer melting temperatures depend on the thermal history of the sample.

Entry		1st	2nd	3rd	4th		5th	6th	7th	8th
2	T_m (°C)	160.6	148.0	148.0	148.0					
	H_m (J/g)	83.2	38.2	36.1	37.2					
3	T_m	165.1	148.9	148.9	148.9	anneal	168.6	148.7	148.7	148.7
	H_m	80.2	48.2	47.0	47.6	145°C	65.7	48.2	47.0	48.0
4	T_m	157.3	146.1	146.1	146.1					
	H_m	73.6	43.1	44.3	44.9					
15	T_m	159.9	154.3	154.3	154.3					
	H_m	78.8	52.1	53.2	52.9					
16	T_m	156.6	153.1	153.4	153.4					
	H_m	81.1	47.2	47.9	48.1					
17	T_m	148.7	141.6	141.6	141.6					
	H_m	61.0	37.9	37.9	37.6					

3.6 Discussion

3.6.1 Theoretical Framework

Computational studies by Rappe et al.[22] have provided a framework for understanding some distal ligand perturbations. A phenomenon called the "agoraphilic" effect has been invoked to explain why some seemingly innocuous steric perturbations often greatly alter the stereochemical steps of propylene enchainment. Preliminary theoretical models have been developed that qualitatively explain why the Oct ligand in propylene polymerization systems of the type $R_2C(Oct)(C_5H_4)ZrCl_2$/MAO can simultaneously prevent enantiofacial misinsertions and discourage site epimerization, relative to the parent fluorenyl-containing (Flu) systems.[23]

Using Lennard-Jones potentials for the van der Waals interactions of the growing polymer chain with the ancillary ligand, one can rationalize the relative lack of enantiofacial misinsertions as follows. While the transition state for misinsertion is discouraged because of unfavorable interactions between the growing polymer chain and the benzo substituent of the Flu ligand, the transition state for misinsertion with the Oct analog is even more disfavored because of extreme steric repulsion between the growing polymer chain and the tetramethyltetrahydrobenzo substituent of the Oct ligand. Since the barrier to misinsertion is higher for the Oct system, it will compensate by employing the transition state for correct enantiofacial insertion (Figure 12).

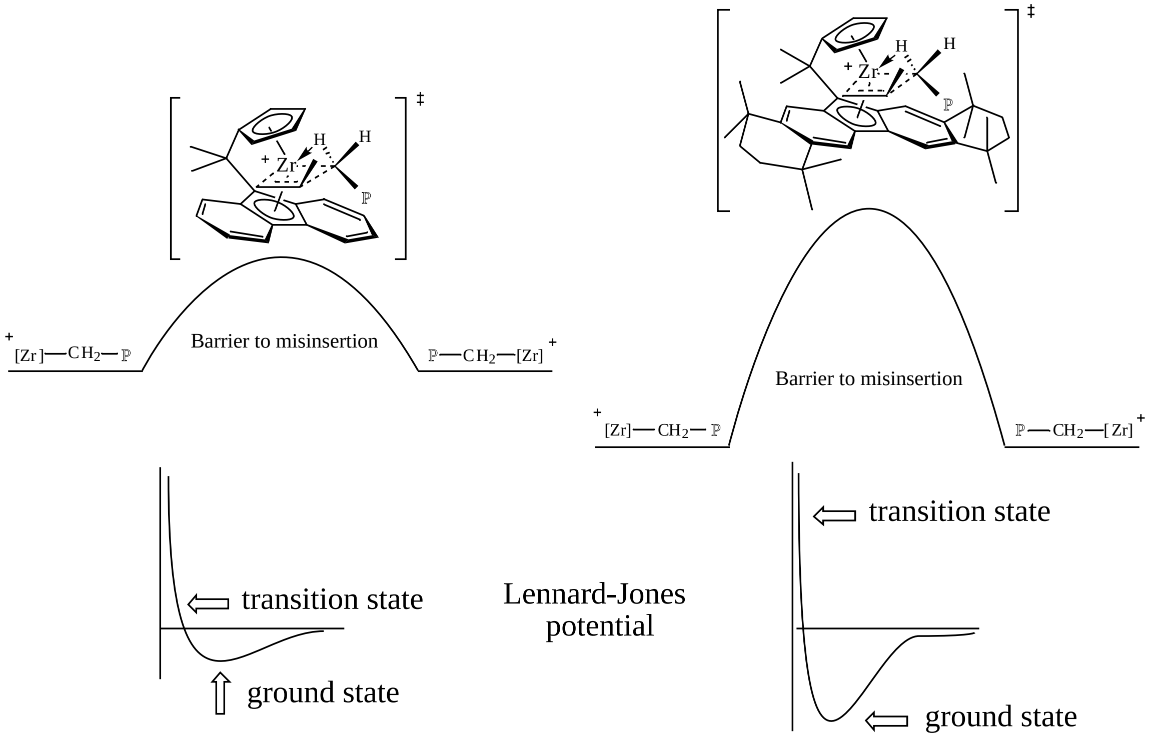


Figure 12. The transition state for enantiofacial misinsertion is more disfavored for Oct-containing metallocenes than for fluorenyl-containing metallocenes.

Similarly, one can use Lennard-Jones potentials to rationalize the relative lack of site epimerizations found in the Oct-containing systems. While there is an attractive ground state interaction between the growing polymer chain and the benzo substituent of the fluorenyl ligand, the attractive interaction between the growing polymer chain and the tetramethyltetrahydrobenzo substituent of the Oct ligand is even greater, because of increased interactions between the aliphatic growing polymer chain and the extensive aliphatic portion of the Oct ligand (Figure 13). The ground state stabilization for the Oct system translates into a site epimerization barrier that is larger than that of the Flu system.

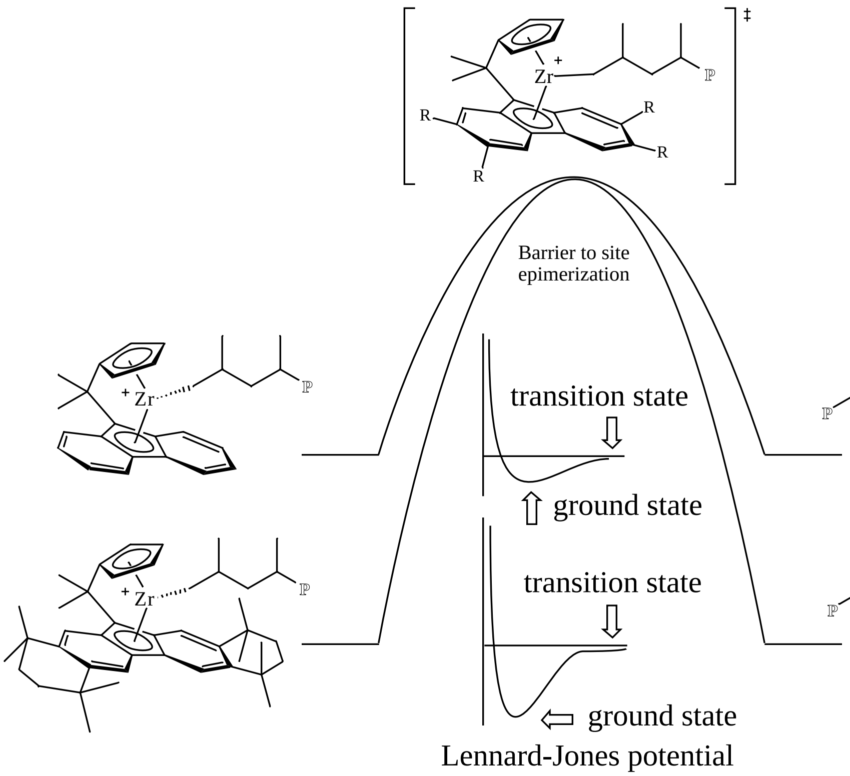
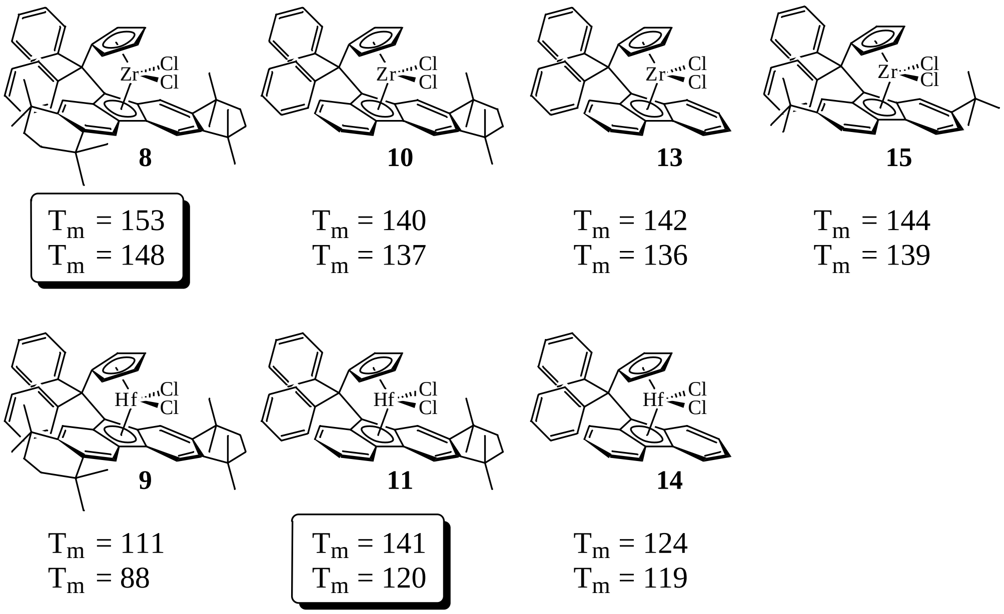


Figure 13. A ground state attractive interaction between the growing polymer chain and the Oct ligand increases the barrier to site epimerization relative to the that of the fluorenyl-containing system.

3.6.2 Oct vs. Tet vs. Flu

Figure 14 displays the melting temperature for syndiotactic polypropylenes obtained with metallocenes (/MAO; 1000 equivalents; neat propylene; T_p = 0°C and 20°C) having various distal fluorenyl substituents. In agreement with the theoretical framework presented, the syndiospecificity of the Oct-containing metallocene **8** excels that of **10**, **13**, and **15**. An inspection of the X-ray crystal structures of **8** and **10** looking down the zirconium-centroid axis (Figure 15) reveals a surprisingly close arrangement of the chloride ligands with the “distal” 2,5-dimethyl-2,5-hexane-diyl substituents. Notwithstanding the shorter zirconium-α-carbon bond present in the active polymerization species, it is easy to picture steric interactions between the distal substituents and the β and γ carbons of the growing polymer chain. For the hafnium analogs, it is the Tet-containing catalyst system (**11**/MAO) that produces the highest melting polymer (Figure 14).



	8	10	13	15
T_p = 0°	T_m = 153	T_m = 140	T_m = 142	T_m = 144
T_p = 20°	T_m = 148	T_m = 137	T_m = 136	T_m = 139

	9	11	14
T_p = 0°	T_m = 111	T_m = 141	T_m = 124
T_p = 20°	T_m = 88	T_m = 120	T_m = 119

Figure 14. Polymer melting temperature depends on distal fluorenyl substitution.

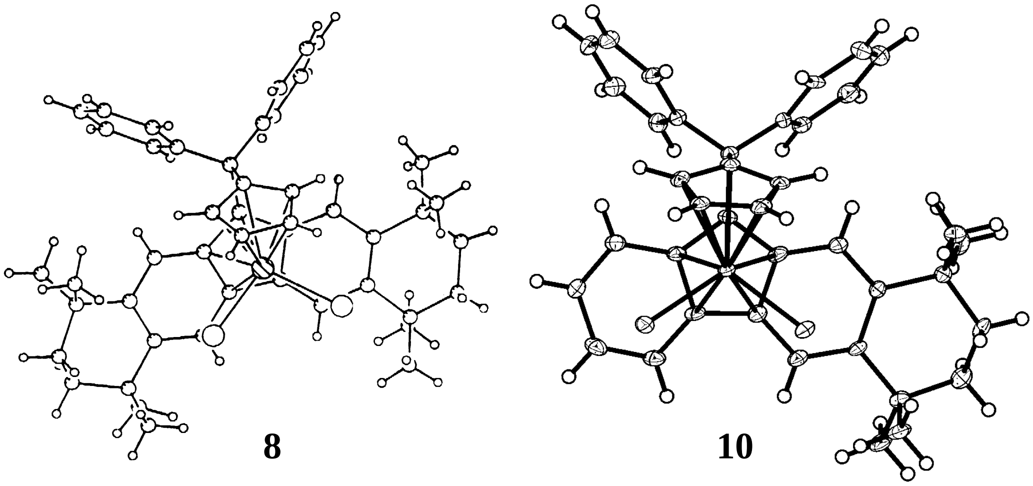


Figure 15. Alternative perspectives of **8** and **10**.

As shown in Figure 16, an isolated enantiofacial misinsertion will produce pentads of the type rrrm, rrmm, and rmmr in a 2:2:1 ratio. A single, isolated site epimerization will lead to pentads rrrm and rrmr in a 2:2 ratio. Assuming that stereoerrors are isolated (separated by 4 or more correctly inserted monomer units) one can calculate the relative likelihood of enantiofacial misinsertion vs. site epimerization. If the relative probability of enantiofacial misinsertion is defined as $P_{e.m.}$ and the relative probability of site epimerization is defined as $P_{s.e.}$, then the following relationships can be written, where I_{xxxx} is the measured intensity for the xxxx pentad:

$$I_{rrrm} = 2\ P_{e.m.} + 2\ P_{s.e.}$$
$$I_{rmmr} = 1\ P_{e.m.}$$
$$I_{mmrr} = 2\ P_{e.m.}$$
$$I_{rmrr} = 2\ P_{s.e.}$$

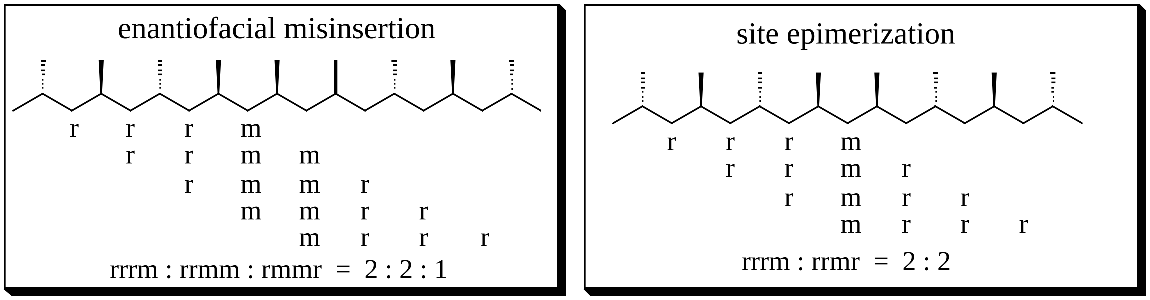


Figure 16. An enantiofacial misinsertion provides rrrm, rrmm, and rmmr pentads, while site epimerization provides rrrm and rrmr pentads.

A least squares calculation was performed on the relevant pentad intensities for Entries 7, 8, 11, and 12, which are polymers made with Oct-containing (**9**, Entries 7 and 8) and Tet-containing (**11**, Entries 11 and 12) hafnocenes. The same calculation was performed for Entry 15, which is a polymer made with an Oct-containing zirconocene (**12**). The results are summarized in Table 7. For catalyst systems **9**/MAO and **11**/MAO, an increase in polymerization temperature results in an increase in $P_{s.e.}$ since the unimolecular site epimerization process is favored to a greater degree than the bimolecular propagation step. However, the Tet-containing metallocene **11** is less likely to site epimerize than the Oct-containing analog **9**. This result is contrary to that observed for the zirconocene series, and may be a consequence of subtle factors not fully appreciated in the theoretical framework presented above. An additional apparent discrepancy is that **9** allows a considerable fraction of enantiofacial misinsertions while the isosteric zirconium analog **12** practically forbids them. This again may be the result of subtle changes upon metal substitution. An alternative explanation is that the hafnium catalyst allows chain epimerizations,[25] producing mm stereoerrors, which are the same stereochemical defects produced by isolated enantiofacial misinsertions.

Table 7. Least squares determination of the relative probabilities of enantiofacial misinsertion ($P_{e.m.}$) and site epimerization ($P_{s.e.}$).

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

3.6.3 Distal Desymmetrization

In the above catalytic systems that incorporate the Oct or Tet ligands, the distal ligand perturbation has been applied to a parent metallocene of C_s symmetry. An alternative approach is to apply the steric perturbation to a C_{2v}-symmetric metallocene. To this end, C_{2v}-symmetric metallocene **16**[18] was desymmetrized to the C_s-symmetric metallocene **17** by incorporation of one Oct ligand.[26] The polymerization results are reported in Table 5 in Entries 23 and 24 (**16**) and in Entries 25 and 26 (**17**); the pentad distributions are reported in Table 8. It is immediately apparent that the distal ligand perturbations have a pronounced effect on polymer stereochemistry. Whereas the polymers made from **16** are atactic with rrrr pentad fractions of approximately 6%, this pentad constitutes well over 40% of the polymers made from **17**. A stereochemical analysis of the pentad distributions[27] suggests that the latter polymers are made primarily via syndiospecific enantiomorphic site control (Table 9), and not by chain end control, although a competing site epimerization process likely contributes to a non-ideal statistical fit.

Table 8. Polypropylene pentad distributions from Entries 23, 24, 25, and 26.

Entry	23	24	25	26
metallocene	**16**	**16**	**17**	**17**
T_p (°C)	0	20	0	20
Pentad (%)				
mmmm	4.8	5.9	1.4	2.7
mmmr	11.2	10.5	2.3	3.9
rmmr	8.8	7.1	4.9	5.9
mmrr	12.2	13.7	11.8	12.2
mrmm + rmrr	24.3	23.9	4.7	9.4
mrmr	13.6	14.4	3.7	5.3
rrrr	6.3	6.6	49.1	41.9
rrrm	13.3	11.4	16.0	15.2
mrrm	5.5	6.5	6.1	3.5
r	50.1	50.5	81.3	74.1
m	49.9	49.5	18.7	25.9

Table 9. Statistical fits of polymers from Entries 25 and 26 to the chain end control model and the syndiospecific enantiomorphic site control model.

Entry	25			26		
metallocene	**17**			**17**		
T_p (°C)	0			20		
Pentad (%)	observed	chain end control	site control	observed	chain end control	site control
mmmm	1.4	0.1	1.5	2.7	0.1	1.8
mmmr	2.3	0.6	3.1	3.9	1.1	3.7
rmmr	4.9	1.7	7.8	5.9	2.4	8.0
mmrr	11.8	3.3	15.6	12.2	4.7	16.1
mrmm + rmrr	4.7	19.1	6.1	9.4	21.3	7.4
mrmr	3.7	3.3	3.1	5.3	4.7	3.7
rrrr	49.1	51.7	45.8	41.9	43.2	41.3
rrrm	16.0	18.5	15.6	15.2	20.2	16.1
mrrm	6.1	1.7	1.5	3.5	2.4	1.8
r	81.3	84.8	75.3	74.1	81.1	72.9
m	18.7	15.2	24.7	25.9	18.9	27.1
σ		0.152			0.189	
α			0.855			0.838
RMS error		6.03	2.52		5.29	1.87

3.7 Conclusions

For the series of syndiospecific polymerization catalysts of the type $R_2C(Flu')(C_5H_4)ZrCl_2$/MAO, it was found that the catalyst system with Flu' = octamethyloctahydrodibenzofluorenyl (Oct) provided polypropylene of significantly higher syndiotacticity over metallocenes containing other substituted fluorenyl ligands, including parent fluorenyl, tetramethyltetrahydrobenzofluorenyl (Tet), and 2,7-di-*tert*-butylfluorenyl. For the Oct-containing zirconocenes, melting temperatures as high as 153°C (**8**, R = Ph) or 154°C (**12**, R = Me) were measured for the thermally quenched polymer. These results underscore the importance of bulky substituents in the 3 and 6 positions of the fluorenyl ligand.

It is suggested that non-bonded repulsive interactions in the propagative transition state greatly disfavor enantiofacial misinsertions for Oct-containing metallocenes. At the same time, ground state attractive interactions possible between the growing polymer chain and the Oct ligand increase the barrier to site epimerization. These combined effects result in the highest syndiospecificity observed for a fluorenyl-based metallocene polymerization catalyst.

Despite the added steric bulk, the activities of Oct-containing metallocenes generally excel lesser substituted catalyst systems. Evidence that this might be related to ion-pairing effects is found in an unprecedentedly large red shift of the LMCT band upon exposure of $Ph_2C(Oct)(C_5H_4)ZrCl_2$ (**8**) to MAO ($\Delta E = 2166$ cm^{-1}).

For the hafnocenes, it is found that $Ph_2C(Tet)(C_5H_4)HfCl_2$/MAO (**11**/MAO) displays the highest syndiospecificity, surpassing both the fluorenyl and Oct analogs. This results from the unexpected and diminished propensity of the Tet-containing catalyst to perform site epimerizations. That this is contrary to the theoretical framework presented and contrary to the results obtained from the zirconocenes warrants further investigation, perhaps by molecular modeling studies.

Finally, the impact that the Oct ligand can have on the stereochemistry of the resulting polypropylene was further demonstrated by its inclusion in the metallocene $C_2H_4(Oct)(Flu)ZrCl_2$ (**17**). While the parent catalyst $C_2H_4(Flu)_2ZrCl_2$/MAO (**16**/MAO) produces essentially atactic polypropylene (rrrr = 6.3%), the distal substituents of $C_2H_4(Oct)(Flu)ZrCl_2$/MAO (**17**/MAO) effect an rrrr pentad content of 49.1%. Indeed, substituents seemingly too distant from the metal center can dramatically perturb polymer stereochemistry.

3.8 Experimental Section

General Considerations. Unless otherwise noted, all reactions and procedures are carried out under an inert atmosphere of argon or nitrogen using standard glove box, Schlenk and high vacuum line techniques.[28] Solvents are dried according to standard procedures. The following were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%); fluorene (98%); n-butyllithium (1.6 M in hexanes); zirconium tetrachloride (99.5%); aluminum chloride (99.99%); 2,5-dimethyl-2,5-hexanediol (99%); benzophenone (99%); and nitromethane (96%). Dicyclopentadiene was obtained from Aldrich and cracked following standard procedures prior to use. Crystalline $LiCH_2Si(CH_3)_3$ (Aldrich, solution in pentane) is obtained by condensing the pentane solution. 1,2-dibromoethane (Aldrich) was dried over calcium hydride and isolated by vacuum transfer. Hafnium tetrachloride (99%) was obtained from Cerac and used as received. **Instrumentation.** NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC-MS were acquired with a Hewlett Packard 5890 Series II Gas Chromatograph connected to a Hewlett Packard 5989A Mass Spectometer. The GC was equipped with a column of dimensions 7.1 m x 0.1 μm having an HP-1 phase (Crosslinked Methyl Silicone Gum). LC-MS were acquired with a Hewlett Packard 1090 Series II Liquid Chromatograph with a toluene phase (solvent dried over sodium / benzophenone). The LC was connected to a Hewlett Packard 59980B Particle Beam Interface, and this was connected to a Hewlett Packard 5989A Mass Spectrometer.

Metallocene Syntheses.

Preparation of 8.

6,6-diphenylfulvene. (Synthesis modified from reference 29) 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 ethanol. The solid was refluxed in 200 mL methanol for 1 hour. Upon cooling the solid was collected, rinsed with 75 mL methanol, and dried in vacuo for 48 hours to provide the product as an orange powder: 136.18 g (86.2%). MS (GC-MS) m/z 230.3 (M^+). Elemental analysis calculated for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 92.60, 92.59; H, 5.37, 5.19.

2,5-dichloro-2,5-dimethylhexane. A 2 liter argon purged vessel was charged with 2,5-dimethyl-2,5-hexanediol (200.00 g, 1.368 mol) and concentrated aqueous hydrochloric acid (1.00 L, 12.2 mol HCl) was poured in. The white slurry was shaken and stirred for 17 hours. The white solid was collected by suction filtration and rinsed with 500 mL water. The solid was dissolved in 1.00 L 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 minutes) dried in vacuo to provide the product: 237.96 g (95.0%). ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 12H, $\mathrm{C}H_3$), 1.90 (s, 4H, $\mathrm{C}H_2$). ^{13}C NMR ($CDCl_3$): δ 32.59 ($C\mathrm{H}_3$), 41.21 ($C\mathrm{H}_2$), 70.13 ($C\mathrm{H}_0$). Elemental analysis calculated 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 liter 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 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 nitromethane. The solution was added over 10 minutes and the purple reaction was stirred for 20 hours before it was slowly poured into 700 mL of ice water. The precipitate was collected by filtration and refluxed in 500 mL ethanol for 2 hours. Upon cooling, the solid was collected by filtration and this was refluxed in 300 mL hexanes for 2 hours. After cooling, the solid was collected by filtration and dried in vacuo, giving the product as a white powder: 62.53 grams (74.7%). MS (GC-MS) m/z 386.5 (M^+). ^{1}H NMR ($Cl_2DCCDCl_2$): δ 1.38, 1.43 (s, 24H, $\mathrm{C}H_3$), 1.77 (apparent s, 8H, $\mathrm{C}H\text{-}_2$), 3.82 (s, 2H, $\mathrm{C}H_2$), 7.49, 7.71 (s, 4H, Flu-H). ^{13}C NMR ($Cl_2DCCDCl_2$): δ 32.37, 32.53 ($C\mathrm{H}_3$), 34.68, 34.71 ($C\mathrm{H}_0$), 35.50, 35.55 ($C\mathrm{H}_2$), 36.47 ($C\mathrm{H}_2$), 117.48, 123.31($C\mathrm{H}_1$), 139.20, 140.80, 143.50, 143.66 ($C\mathrm{H}_0$). Elemental analysis calculated for $C_{29}H_{38}$: C, 90.09; H, 9.91. Found: C, 89.07, 89.16; H, 8.94, 8.85.

Alternative preparation of octamethyloctahydrodibenzofluorene. An argon-purged 2 liter vessel was charged with fluorene (45.30 grams, 0.2725 mol), 2,5-

dichloro-2,5-dimethylhexane (100.00 grams, 0.5461 mol) and nitromethane (800 mL). The solids were dissolved by gentle heating. A solution of $AlCl_3$ (44.65 grams, 0.335 mol) in 60 mL nitromethane was syringed in over 6 minutes. During the addition, much HCl is evolved through an oil bubbler and precipitate is rapidly formed. After stirring for 18 hours, the steel blue reaction is filtered and the solid collected on filter paper. 300 mL water is slowly added to the filtrate and the formed precipitate is collected by suction filtration. The combined precipitates were added slowly to 400 mL water. 200 mL hexanes were added to this and the slurry stirred over night to quench the aluminum chloride. The water layer was removed and the solvent removed from the remaining slurry by rotary evaporation. The solid was extracted over a period of 3 days with 300 mL diethyl ether from a cellulose extraction thimble. Diethyl ether was removed by rotary evaporation and the remaining solid boiled in 100 mL hexanes, cooled, filtered and washed with 50 mL hexanes. *In vacuo* drying afforded 87.75 grams of octamethyloctahydrodibenzofluorene as a white powder (83.3%). MS (GC-MS) m/z 386.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.32, 1.38 (s, 24H, CH_3), 1.72 (apparent s, 8H, $CH\text{-}_2$), 3.77 (s, 2H, CH_2), 7.43, 7.66 (s, 4H, Flu-*H*).

$Ph_2C(C_5H_4)(C_{29}H_{36})H_2$. A 300 mL flask was charged with octamethyloctahydrodibenzofluorene (12.00 g, 31.04 mmol), equipped with a 180° needle valve, evacuated and charged with diethyl ether (120 mL) by vacuum transfer. At 0°C, n-butyllithium (21.0 mL, 33.6 mmol, 1.6 M in hexanes) were syringed in over 3 minutes, giving much yellow precipitate. After 21 hours, the solvent was removed and 6,6-diphenylfulvene (7.148 g, 31.04 mmol) was added. Diethyl ether (150 mL) was condensed in and the reaction stirred at room temperature for five days before 60 mL aqueous NH_4Cl were added slowly at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (4 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped to provide the crude product in quantitative yield (19.15 g). The material can be recrystallized from ethanol. MS (GC-MS) m/z 616.8 (M^+). Major isomer (76%): ^1H NMR ($Cl_2DCCDCl_2$, 100°C): δ 1.02, 1.22, 1.33, 1.36 (s, 24H, CH_3), 1.71 (m, 8H, CH_2), 3.00 (s, 2H, Cp-CH_2), 5.54 (s, 1H, 9-Oct-*H*), 6.24, 6.24, 6.28 (m, 3H, Cp-CH_1), 7.11 - 7.18 (m, 10H, phenyl-*H*), 7.35, 7.35 (s, 4H, Oct-*H*). ^{13}C NMR ($Cl_2DCCDCl_2$, 100°C): δ 32.00, 32.03, 32.12, 32.39 (*C*H_3), 34.37, 34.50 (*C*H_0), 35.74, 35.85 (*C*H_2), 40.85 (Cp-*C*H_2), 53.16 (9-Oct-*C*H_1), 60.08 (*C*(Oct)(Cp)(Ph)$_2$), 116.14, 125.40, 125.82 (Cp-*C*H_1), 127.04, 130.18 (Oct-*C*H_1), 126.76, 128.84, 130.31, 131.08, 135.93 (phenyl-*C*H_1), 140.04, 142.34, 142.38, 143.59 (Oct-*C*H_0), other *C*H_0 not determined. Minor isomer (24%): ^{1}H NMR ($Cl_2DCCDCl_2$, 100°C): δ 1.08, 1.25, 1.33, 1.36 (s, 24H, CH_3), 1.72 (m, 8H, CH_2), 2.94 (s, 2H, Cp-CH_2), 5.49 (s, 1H, 9-Oct-*H*), 6.36, 6.49, 6.58 (m, 3H, Cp-CH_1), 7.11 - 7.18 (m, 10H, phenyl-*H*), 7.29, 7.29 (s, 4H, Oct-*H*). Elemental analysis calculated for $C_{47}H_{52}$: C, 91.50; H, 8.50. Found: C, 90.36, 90.47; H, 7.72, 7.76.

$Ph_2C(C_5H_4)(C_{29}H_{36})ZrCl_2$ (8). A 250 mL flask was charged with $Ph_2C(C_5H_4)(C_{29}H_{36})H_2$ (10.00 g, 16.21 mmol) and $LiCH_2Si(CH_3)_3$ (3.053 g, 32.42 mmol) and equipped with a 180° needle valve. Diethyl ether (75 mL) was condensed in at -78°C and the cold bath removed. Upon warming, 25 mL of tetrahydrofuran were condensed in. After 45 hours, solvent was removed and $ZrCl_4$ (3.78 g, 16.2 mmol) was added. Petroleum ether (75 mL) was condensed in at -78°C and the cold bath was removed. After 47 hours, solvent was removed and the pink material was extracted in a cellulose extraction thimble with 200 mL diethyl ether for 2 days. The volume was reduced to 100 mL and the precipitate was collected and dried in vacuo: 5.03 g (39.9%). Two additional crops were obtained for a total mass of 5.519 g (43.8%). MS (LC-MS) *m* / *z* 776.8 (M^+). ^{1}H NMR (C_6D_6): δ 1.01, 1.07, 1.35, 1.51 (s, 24H, Oct-CH_3), 1.61 (m, 8H, Oct-CH_2), 5.68, 6.21 (s, 4H, Cp-*H*), 6.42, 8.42 (s, 4H, Oct-*H*), 6.97, 7.08, 7.12 (t, $^3J_{HH}$ = 7.0, 7.3, 8.1 Hz, 6H, phenyl-*H*), 7.70, 7.74 (d, $^3J_{HH}$ = 7.7, 7.7 Hz, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 30.97, 31.75, 32.42, 33.50 (*C*H_3), 34.56, 34.80, 34.83, 35.05 (*C*H_0 and *C*H_2), 57.92 (Ph*C*Ph), 74.25, 108.78, 119.78, 121.09, 144.90, 146.12, 146.81 (Cp-, phenyl-, and Oct-*C*H_0), 102.05, 117.83 (Cp-*C*H_1), 121.61, 122.18, 126.71, 127.17, 129.01, 129.10, 129.46 (phenyl- and Oct-*C*H_1). Elemental analysis calculated for $C_{47}H_{50}Zr_1Cl_2$: C, 72.65; H, 6.49. Found: C, 69.93; H, 6.10.

Preparation of 9.

$Ph_2C(C_5H_4)(C_{29}H_{36})HfCl_2$ (9). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{29}H_{36})H_2$ (3.500 g, 5.637 mmol) and $LiCH_2Si(CH_3)_3$ (1.100 g, 11.68 mmol) and equipped with a 180° needle valve. Diethyl ether (50 mL) was condensed in at -78°C and the cold bath removed. Upon warming, 5 mL of tetrahydrofuran were condensed in. After 45 hours, solvent was removed and $HfCl_4$ (2.00 g, 6.244 mmol) was added. Petroleum ether (50 mL) was condensed in at -78°C and the cold bath was removed. After 43 hours, solvent was removed and the yellow material was extracted in a cellulose extraction thimble with 150 mL diethyl ether overnight. The volume was reduced to 50 mL and the precipitate was collected and dried in vacuo: 0.975 g (19.9%). MS (LC-MS) *m*/*z* 864.5 (M^+). ^1H NMR (C_6D_6): δ 1.02, 1.08, 1.35, 1.51 (s, 24H, Oct-CH_3), 1.61 (m, 8H, Oct-CH_2), 5.65, 6.16 (t, $^3J_{HH}$ = 2.6, 2.7, 4H, Cp-*H*), 6.47, 8.40 (s, 4H, Oct-*H*), 6.98, 7.08, 7.13 (t, $^3J_{HH}$ = 7.4, 7.6, 9.0 Hz, 6H, phenyl-*H*), 7.70, 7.77 (d, $^3J_{HH}$ = 7.8, 7.9Hz, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 31.13, 31.81, 32.47, 33.64 (CH_3), 34.59, 34.78, 34.78, 35.07 (CH_0 and CH_2), 57.73 (Ph*C*Ph), 74.03, 111.64, 118.78, 119.55, 145.18, 145.55, 146.54 (Cp-, phenyl-, and Oct-CH_0), 99.66, 116.96 (Cp-CH_1), 121.23, 121.93, 126.72, 127.15, 128.97, 129.10, 129.49 (phenyl- and Oct-CH_1). Elemental analysis calculated for $C_{47}H_{50}Hf_1Cl_2$: C, 65.31; H, 5.83. Found: C, 63.53; H, 5.33.

Preparation of 10.

tetrahydrotetramethylbenzofluorene. A 2 liter argon purged vessel was charged with fluorene (200.0 g, 1203 mmol), 2,5-dichloro-2,5-dimethylhexane (25.00 g, 136.5 mmol) and 1000 mL of nitromethane. The solids were dissolved by heating to 60°C, and when the vessel had cooled to 50°C, a solution of $AlCl_3$ (25.00 g, 187.5 mmol) in nitromethane (40 mL) was syringed in over 2 minutes, giving a dark green homogeneous solution. After 15 minutes, 60 mL water were syringed in very slowly, followed by addition of 100 mL water. The formed precipitate (>99% fluorene by GC) was removed by filtration. The filtrate (77.5:22.5 ratio of FluH:TetH) was extracted with hexane (7 x 100 mL). Solvent was removed by rotavap from the combined hexane extracts, giving 64.7 grams of FluH and TetH. This material was subjected to Kugelrohr distillation under high vacuum. Several fractions were removed at 100°C until 22.54 grams of material remained. This material was dissolved in 300 mL boiling ethanol, hot filtered, and slowly cooled. The pure product was obtained by collection of the precipitate and in vacuo drying: 16.06 g (42.5%). Essentially pure fluorene was recovered from several of the removed fractions and by Kugelrohr distillation of the original filtrate: 133.7 g, 75.4% of the theoretically recoverable amount of 177.3 g. MS (GC-MS) m/z 276.3 (M^+). ^1H NMR ($CDCl_3$): δ 1.38, 1.42 (s, 12H, CH_3), 1.78 (apparent s, 4H, CH_2), 3.88 (s, 2H, CH_2), 7.29 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Flu-*H*), 7.38 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Flu-*H*), 7.53 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Flu-*H*), 7.54 (s, 1H, Flu-*H*), 7.78 (s, 1H, Flu-*H*), 7.80 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Flu-*H*). ^{13}C NMR ($CDCl_3$): δ 32.27, 32.40 (CH_3), 34.66, 34.73 (CH_0), 35.40, 35.40 (CH_2), 36.69 (CH_2), 117.67, 119.65, 123.05, 125.03, 126.33, 126.65 (CH_1), 139.47, 140.65, 141.98, 143.54, 143.68, 143.90 (CH_0). Elemental analysis calculated for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.51, 90.17; H, 7.99, 7.65.

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

mL, 30.4 mmol, 1.6 M in hexanes) was syringed into the white slurry over 3 minutes at room temperature. The reaction was stirred for 22 hours before the orange solid was collected by filtration and dried *in vacuo*: 7.21 g (quantitative yield).

$Ph_2C(C_5H_4)(C_{21}H_{22})ZrCl_2$ (10). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{21}H_{22})Li_2$ (3.895 g, 7.51 mmol) and $ZrCl_4$ (1.750 g, 7.51 mmol) and equipped with a 180° needle valve. Petroleum ether (60 mL) was condensed in at -78°C and the cold bath was removed. The reaction was allowed to warm slowly, and after 18 hours the solvent was removed. The solid was placed in a cellulose extraction thimble and extracted with 150 mL methylene chloride overnight. The filtrate was switched onto a swivel frit and solvent was removed. 200 mL toluene were condensed in and the solution filtered. The filtrate was reduced in volume to 40 mL and the pink precipitate was collected and dried *in vacuo*: 2.149 g (42.9%). MS (LC-MS) m/z 666.6 (M^+). ^1H NMR (CD_2Cl_2): δ 0.83, 0.94, 1.40, 1.46 (s, 12H, CH_3), 1.61, 1.68 (m, 4H, CH_2), 5.66, 5.71 (q, $^3J_{HH}$ = 2.6, 2.9 Hz, 2H, Cp-*H*), 6.31, 6.31 (t, $^3J_{HH}$ = 2.6, 2.6 Hz, 2H, Cp-*H*), 6.24, 8.15 (s, 2H, Tet-*H*), 6.39, 8.16 (d, $^3J_{HH}$ = 8.8, 8.8 Hz, 1H, Tet-*H*), 6.96, 7.23 (t, $^3J_{HH}$ = 7.7, 7.3 Hz, 2H, Tet-*H*), 7.33, 7.49 (m, 6H, phenyl-*H*). 7.86, 7.88, 7.93, 7.96 (d, $^3J_{HH}$ = 8.8, 7.7, 6.6, 6.6, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 30.95, 31.75, 32.41, 33.53 (CH_3), 34.53, 34.53, 34.86, 34.95 (CH_0 and CH_2), 102.90, 103.13, 117.88, 118.67 (Cp-CH_1), 121.58, 122.17, 123.98, 124.63, 125.01, 126.60, 126.77, 127.22, 127.29, 127.93, 128.18, 129.07, 129.10, 129.18, 129.21, 129.49 (Tet-CH_1 and phenyl-CH_1), 144.76, 145.02, 146.62, 147.35 (Tet-CH_0 and phenyl-CH_0), remaining CH_0 not determined. Elemental analysis calculated for $C_{39}H_{36}Zr_1Cl_2$: C, 70.25; H, 5.44. Found: C, 71.46; H, 5.55.

Preparation of 11.

$Ph_2C(C_5H_4)(C_{21}H_{22})HfCl_2$ (11). A swivel frit was charged with $Ph_2C(C_5H_4)(C_{21}H_{22})Li_2$ (1.40 g, 2.70 mmol) and $HfCl_4$ (1.000 g, 3.12 mmol). Petroleum ether (60 mL) was condensed in at -78°C and the cold bath was removed. The reaction was allowed to warm slowly and after 40 hours, the solvent was removed. 100 mL diethyl ether were added by vacuum transfer and the solution was filtered. The filtrate was condensed to 25 mL and the product precipitated very slowly. The yellow solid was collected and dried *in vacuo*: 0.518 g (25.4%). MS (LC-MS) *m / z* 754.7 (M^+). ^1H NMR (CD_2Cl_2): δ 0.84, 0.95, 1.39, 1.45 (s, 12H, CH_3), 1.61, 1.68 (m, 4H, CH_2), 5.61, 5.67 (q, $^3J_{HH}$ = 2.6, 2.6 Hz, 2H, Cp-*H*), 6.25, 6.25 (t, $^3J_{HH}$ = 2.9, 2.9 Hz, 2H, Cp-*H*), 6.28, 8.12 (s, 2H, Tet-*H*), 6.43, 8.13 (d, $^3J_{HH}$ = 8.8, 8.0 Hz, 2H, Tet-*H*), 6.93, 7.32 (t, $^3J_{HH}$ = 8.8, 6.0 Hz, 2H, Tet-*H*), 7.33, 7.47 (m, 6H, phenyl-*H*), 7.85, 7.87, 7.95, 7.96 (d, $^3J_{HH}$ = 7.7, 8.8, 6.6, 7.0 Hz, 4H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 31.07, 31.80, 32.43, 33.62 (CH_3), 34.56, 34.78, 34.81, 34.96 (CH_0 and CH_2), 100.48, 100.70, 116.91, 117.72 (Cp-CH_1), 118.71, 119.83, 120.52, 121.41 (Tet-CH_0), 121.25, 121.92, 123.70, 124.49, 124.56, 126.60, 126.78, 127.18, 127.25, 127.68, 128.99, 128.99, 129.07, 129.16, 129.22, 129.51 (Tet-CH_1 and phenyl-CH_1), 145.03, 145.28, 146.09, 147.06 (Tet-CH_0 and phenyl-CH_0), remaining CH_0 not determined. Elemental analysis calculated for $C_{39}H_{36}Hf_1Cl_2$: C, 62.12; H, 4.81. Found: C, 61.11; H, 5.02.

Preparation of 12.

6,6-dimethylfulvene. (Synthesis modified from reference 30) A 2 L vessel was charged with methanol (875 mL), cyclopentadiene (101.0 g, 1528 mmol), and acetone (230 mL). Pyrrolidine (13.5 mL, 112 mmol) was syringed in over 10 minutes. The reaction was stirred for 18 hours before an aqueous acetic acid solution (50 mL acetic acid / 200 mL water) was added over 2 minutes. Diethyl ether (500 mL) and water (1000 mL) were added and the organic layer isolated. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were extracted with water (5 x 150 mL). The ether layer was dried over $MgSO_4$, filtered and rotavapped at 40°C for 2 hours. This provided ether-free fulvene (156.81 g, 96.7%). This material was further cleaned by pushing the neat liquid through a short column of alumina: 111.2 g (68.5%).

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

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

$Me_2C(C_5H_4)(C_{29}H_{36})ZrCl_2$ (12). In the glove box, a swivel frit apparatus was charged with $Me_2C(C_5H_4)(C_{29}H_{36})Li_2$ (3.246 g, 6.436 mmol) and zirconium tetrachloride (1.500 g, 6.437 mmol). 50 mL of petroleum ether were condensed in and the reaction stirred at room temperature for 51 hours before solvent removal. 20 mL dichloromethane were condensed in, stirred, and removed. Then, 30 mL diethyl ether were condensed in, stirred, and removed. In the glove box, the solid was transferred to a cellulose extraction thimble and this was extracted overnight with 100 mL diethyl ether. The obtained slurry was transferred back to the swivel frit and the volume reduced to 30 mL. The orange precipitate (**12**) was collected on the frit and dried *in vacuo*: 1.649 g (39.2%). MS (LC-MS) *m/z* 653.7 (M^+). ^1H NMR (CD_2Cl_2): δ 1.23, 1.38, 1.39, 1.49 (s, 24H, Oct-CH_3), 1.73 (m, 8H, Oct-CH_2), 2.32 (s, 6H, $(CH_3)_2$C-Oct-Cp), 5.57, 6.20 (t, $^3J_{HH}$ = 2.6, 2.2 Hz, 4H, Cp-*H*), 7.63, 8.04 (s, 4H, Oct-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.60, 31.88, 32.22, 32.37, 33.50 (CH_3), 34.78, 34.86, 35.03, 35.11 (CH_0 and CH_2), 40.06 (Me*C*Me), 75.23, 112.89, 121.05, 121.50, 145.68, 147.68 (Cp- and Oct-CH_0), 100.45, 118.44 (Cp-CH_1), 120.63, 122.06 (Oct-CH_1). Elemental analysis calculated for $C_{37}H_{46}Zr_1Cl_2$: C, 68.07; H, 7.10. Found: C, 60.14; H, 6.45.

Preparation of 13 and 14. The syntheses of **13** and **14** were accomplished as follows by slight modification of the literature procedure.[5a]

Preparation of 13.

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

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

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

Preparation of 14.

$Ph_2C(C_5H_4)(C_{13}H_8)HfCl_2$ (14). A 100 mL flask was charged with $Ph_2C(C_5H_4)(C_{13}H_8)Li_2$ (2.55 g, 6.24 mmol) and $HfCl_4$ (2.000 g, 6.24 mmol) and equipped with a 180° needle valve. Petroleum ether (60 mL) was condensed in at -78°C and the cold bath removed. After 21 hours, solvent was removed from the yellow slurry and the solid was extracted in a cellulose thimble with 150 mL methylene chloride for 2 days. The filtrate was switched onto a swivel frit and gravity filtered. The volume of the filtrate was reduced to 40 mL and the precipitate was collected and dried *in vacuo*: 1.15 g (28.5%). MS (LC-MS) m/z 644.7 (M^+). ^1H NMR (CD_2Cl_2): δ 5.75, 6.30 (t, $^3J_{HH}$ = 3.0, 2.6 Hz, 4H, Cp-*H*), 6.46, 8.16 (d, $^3J_{HH}$ = 8.8, 8.4 Hz, 4H, Flu-*H*), 6.97, 7.31, 7.35 (t, $^3J_{HH}$ = 7.0, 7.4, 7.4 Hz, 6H, phenyl-*H*), 7.45, 7.52 (t, $^3J_{HH}$ = 7.7, 7.4 Hz, 4H, Flu-*H*), 7.86, 7.94 (d, $^3J_{HH}$ = 7.4, 8.1 Hz, 4H, phenyl-*H*). Elemental analysis calculated for $C_{31}H_{22}Hf_1Cl_2$: C, 57.82; H, 3.44. Found: C, 53.97; H, 3.23.

Preparation of 15.

$Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)H_2. A 250 mL flask was charged with 2,7-di-*tert*-butylfluorene[31] (10.00 g, 35.91 mmol) and equipped with a 180° needle valve. The flask was evacuated and 125 mL diethyl ether were condensed in before n-butyllithium solution (23.0 mL, 36.8 mmol, 1.6 M in hexanes) were syringed in over 3 minutes at room temperature. After 3.5 hours, solvent was removed and 6,6-diphenylfulvene (8.271 g, 35.91 mmol) were added. Diethyl ether (100 mL) were condensed in and the reaction was stirred for 26 days. Water (60 mL) was slowly added and the white precipitate which slowly formed was collected by suction filtration. 13.11 grams (71.8%) of white powder were isolated after drying *in vacuo* at 80°C for several hours. MS (GC-MS) *m/z* 508.6 (M^+). Elemental analysis calculated for $C_{39}H_{40}$: C, 92.08; H, 7.92. Found: C, 89.42; H, 7.07.

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

$Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)$ZrCl_2$ (15). A 100 mL flask was charged with $Ph_2C(C_5H_4)$(2,7-di-*tert*-butylfluorenyl)Li_2 (3.351 g, 6.437 mmol) and $ZrCl_4$ (1.500 g, 6.437 mmol). Petroleum ether (60 mL) was condensed in at -78°C and the cold bath was removed. The reaction was allowed to warm slowly, and after 23 hours the solvent was removed. The solid was placed in a cellulose extraction thimble and extracted with 150 mL methylene chloride overnight. The filtrate was switched onto a swivel frit, filtered, and condensed to 10 mL. The orange precipitate was collected and dried *in vacuo*: 1.271 g (29.5%). MS (LC-MS) *m/z* 668.5 (M^+). ^1H NMR (CD_2Cl_2): δ 1.04 (s, 18H, $C(CH_3)_3$), 5.69, 6.34 (t, $^3J_{HH}$ = 2.6, 3.7 Hz, 4H, Cp-*H*), 6.34, (s, 2H, Flu-*H*), 7.62, 8.05 (d, $^3J_{HH}$ = 8.8, 8.8 Hz, 4H, Flu-*H*), 7.89, 7.98 (d, $^3J_{HH}$ = 8.1, 8.1 Hz, 4H, phenyl-*H*), 7.31, 7.38, 7.48 (t, $^3J_{HH}$ = 7.3, 7.3, 7.7

Hz, 6H, phenyl-*H*). ^{13}C NMR (CD_2Cl_2): δ 30.36 (C(CH$_3$)$_3$), 34.98 (C(CH$_3$)$_3$), 58.28 (*C*(Cp)(Flu)(Ph)$_2$), 77.82, 110.21, 120.82, 121.63, 144.86, 150.76 (Flu-*C*H$_0$, phenyl-*C*H$_0$, and Cp-*C*H$_0$), 102.86, 118.39, 119.94, 123.95, 124.66, 126.65, 127.26, 129.07, 129.14, 129.47 (Flu-*C*H$_1$ and phenyl-*C*H$_1$). Elemental analysis calculated for $C_{39}H_{38}Zr_1Cl_2$: C, 70.03; H, 5.73. Found: C, 67.36; H, 5.13.

Preparation of 16. Metallocene **16** was synthesized as reported in the literature.[18] MS (LC-MS) *m* / *z* 518.5 (M^+). Elemental analysis calculated for $C_{28}H_{20}Zr_1Cl_2$: C, 64.85; H, 3.89. Found: C, 62.92; H, 3.62.

Preparation of 17.

2-(9-fluorenyl)-bromoethane. A 500 mL Schlenk flask was charged with fluorene (50.00 g, 300.8 mmol), evacuated, backfilled with argon, and charged with 180 mL tetrahydrofuran via syringe. At 0°C, n-butyllithium solution (200.0 mL, 320 mmol, 1.6 M in hexanes) was syringed in over 20 minutes. After 1 hour this fluorenyllithium solution was cannulated over 60 minutes into a 1 L flask containing 1,2-dibromoethane (180 mL, 2090 mmol) and 180 mL petroleum ether. After stirring for 29 hours, all volatiles were removed by vacuum transfer. Then, 300 mL of water and 400 mL of methylene chloride were added. The organic layer was isolated and the aqueous layer was extracted with methylene chloride (3 x 50 mL). The organic layers were dried over $MgSO_4$, filtered, and rotavapped. The resulting orange oil was stirred in 100 mL boiling hexanes; this was cooled and filtered. Solvent was removed from the filtrate and the resulting oil was subjected to Kugelrohr distillation under high vacuum at 80°C to remove 1 mL of material. The second crop, collected at 110°C, was dissolved in 100 mL hexanes; the solution was pushed through a column of alumina, rotavapped, and dried *in vacuo* to provide 50.55 g (61.5%) of the product as an oil which crystallized upon standing. MS (GC-MS) *m* / *z* 272.2 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.49, 3.29 (m, 4H, C*H*$_2$), 4.16 (m, 1H, 9-Flu-*H*), 7.32, 7.38, 7.51, 7.75 (m, 8H, Flu-*H*). Elemental analysis calculated for $C_{15}H_{13}Br_1$: C, 65.95; H, 4.80. Found: C, 67.35; H, 4.46.

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

1,2-ethano($C_{29}H_{36}$)($C_{13}H_8$)$ZrCl_2$ (17). A 100 mL flask was charged with 1,2-ethano($C_{29}H_{36}$)($C_{13}H_8$)H_2 (3.000 g, 5.182 mmol), evacuated, and charged with 50 mL diethyl ether. n-butyllithium (7.0 mL, 11.2 mmol, 1.6 M in hexanes) was syringed in over 3 minutes. After 43 hours, solvent was removed from the yellow slurry and $ZrCl_4$ (1.300 g, 5.58 mmol) was added. Petroleum ether was condensed in at -78°C and the reaction was allowed to warm slowly. After 29 hours, solvent was removed, 50 mL diethyl ether were condensed in, and this was stirred an additional 40 hours. Solvent was removed and the pink-red solid was extracted from a cellulose extraction thimble overnight with 150 mL diethyl ether. The volume of the filtrate was reduced to 30 mL and the precipitate was collected on a frit and dried in vacuo: 0.779 grams (20.3%). MS (LC-MS) *m/z* 738.7 (M^+). ^1H NMR (C_6D_6): δ 1.20, 1.36, 1.37, 1.39 (s, 24H, Oct-C*H*$_3$), 1.60 (m, 8H, Oct-C*H*$_2$), 3.93 (m, 4H, ethano-*H*), 6.98, 7.09 (t, $^3J_{HH}$ = 8.4, 8.4 Hz, 4H, Flu-*H*), 7.50, 7.54 (d, $^3J_{HH}$ = 9.2, 8.4 Hz, 4H, Flu-*H*), 7.52, 7.89 (s, 4H, Oct-*H*). ^{13}C NMR (CD_2Cl_2): δ 29.68, 30.00 (CH_2-CH_2), 31.61, 32.35, 32.57, 33.87 (CH_3), 34.87, 34.97, 35.00, 35.07 (CH_0 and CH_2), 102.10, 105.40, 120.88, 121.28, 126.55, 127.35, 145.74, 146.91 (Flu- and Oct-CH_0), 119.59, 121.97, 122.49, 124.39, 124.49, 127.84 (Flu- and Oct-CH_1). Elemental analysis calculated for $C_{44}H_{48}Zr_1Cl_2$: C, 71.51; H, 6.55. Found: C, 69.50; H, 6.07.

Propylene Polymerization Procedures. CAUTION: All polymerization procedures should be performed behind a blast shield. All polymerization reactions were prepared in nitrogen filled gloveboxes. Methylaluminoxane (MAO) was purchased as a toluene solution from Albemarle Corporation and used as the dry powder obtained by in vacuo removal of all volatiles. Toluene was dried over sodium and distilled. Propylene from Scott Specialty Gases (>99.5%) was used following drying through a Matheson 6110 drying system equipped with an OXYSORB^{TM} column. Polymerizations were conducted in a 3 oz. Lab Crest glass reaction vessel and were stirred with a magnetic stir bar. Monomer was condensed into the vessel over several minutes at 0°C. The vessel was then equilibrated at either 0°C or at 20°C with an ice or water bath for 10 minutes. A given reaction commenced upon injection of a toluene solution of the metallocene into the vessel with a 2.5 mL Hamilton syringe rated to 200 psi. Temperature maintenance was monitored by an affixed pressure gauge. Polymerization reactions were vented and quenched with a small volume of methanol/concentrated HCl (12:1) and the polymers were separated from hydrolyzed aluminoxanes by precipitation from methanol, followed by filtration. Residual amounts of toluene and methanol were removed from the obtained polymers by in vacuo drying.

Representative Polymerization Procedures.

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

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

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

Entry 14. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.089 g, 1.53 x 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of $Me_2C(Oct)(C_5H_4)ZrCl_2$ (**12**, 0.0005 g, 7.7 x 10^{-7} mol) in toluene (1.0 mL) was injected and the reaction stirred in a 20°C water bath for 10 minutes. 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 / minute) 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.[32] 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 seconds and a minimum of 1000 scans were used.

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3.9 References and Notes

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19. The polymer described by Entry 15 has been analyzed by L. Resconi at Montell Polyolefins (see Reference 4b). The pentad distribution was determined by ^{13}C NMR (120°C in $C_2D_2Cl_4$): mmmm = 0.0%; mmmr = 0.0%; rmmr = 0.6%; mmrr = 1.2%; mmrm + rrmr = 2.7%; mrmr = 0.1%; rrrr = 91.7%; rrrm = 3.8%; mrrm = 0.0%. The intrinsic viscosity in tetrahydronaphthalene was determined at 135°C: 4.21 dL/g. This corresponds to a viscosimetric molecular weight (M_n) of 730,000. DSC measurements were identical to those reported in Table 5 (T_m = 154.3°C).

It was suggested that these polypropylenes are too syndiotactic to obtain reliable tacticity information. Therefore, polymer melting temperature is often taken as an alternative measure of syndiotacticity for the polymers reported herein.

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

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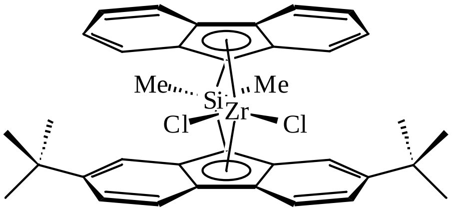
analog **17** provides polymers with rr triad contents of 71.2% and 60.6% (Table 8, Entries 25 and 26). These results highlight the importance of substitution at the 3 and 6 positions of fluorenyl for effecting a significant change in polymer stereochemistry.



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Chapter 4

Synthesis of Isotactic-hemiisotactic and Syndiotactic-hemiisotactic Polypropylene

ABSTRACT: Isotactic-hemiisotactic polypropylene has a tacticity in which every other stereocenter is of the same configuration and the intervening stereocenters are not random, but tend to align with their neighbors. Similarly, syndiotactic-hemiisotactic polypropylene has a tacticity in which every other stereocenter is of the same configuration and the intervening stereocenters tend to be opposite their neighbors. Polypropylenes of these tacticities can be made with proper R substituent selection in the catalyst system $Me_2C(Flu)(3\text{-}R\text{-}C_5H_3)ZrCl_2$ / MAO or $Me_2C(Oct)(3\text{-}R\text{-}C_5H_3)ZrCl_2$ / MAO, where Flu = fluorenyl ($C_{13}H_8$) and Oct = octamethyloctahydrodibenzofluorenyl ($C_{29}H_{36}$). Several metallocenes with varying R substituents have been synthesized and their corresponding polymers analyzed by a statistical model which evaluates the stereoselectivity of each of the metallocene's two sites. This model suggests that the metallocenes have one highly selective site (99%) and one site of variable selectivity which is highly dependent on the nature of the R substituent and whether the metallocene contains the Flu or Oct ligand. The properties of the obtained polymers depend on the substitution pattern of the metallocene employed. For example, $Me_2C(Flu)(3\text{-}(3,3,5,5\text{-tetramethylcyclohexyl})\text{-}C_5H_3)ZrCl_2$ / MAO provides isotactic-hemiisotactic polypropylene having a melting temperature (98°C) higher than that predicted by its stereochemistry (m = 75.3%, mmmm = 49.3%). Its properties are rationalized by the presence of isotactic stereoblocks statistically longer than provided by enantiomorphic site control. The primary mistake process displayed by these catalysts is that of a unidirectional site epimerization, in which the chain migrates away from the R substituent in a unimolecular process prior to monomer insertion.

4.1 Introduction

Metallocene-mediated propylene polymerization is a fascinating process which has been exploited to prepare polypropylenes of many different tacticities. The careful design of variously substituted metallocenes has lead to polypropylenes that are atactic, isotactic, syndiotactic, hemiisotactic, and stereoblock isotactic-atactic, to mention just a few.[1] Fluorenyl-containing metallocenes are particularly capable of producing a wide variety of polymer tacticities depending on the exact nature of incorporated substituents. For example, **1**/MAO (Figure 1) is selective for the synthesis of syndiotactic polypropylene;[2] **2**/MAO is selective for the synthesis of hemiisotactic polypropylene;[3] and **3**/MAO is selective for the synthesis of isotactic polypropylene.[4]

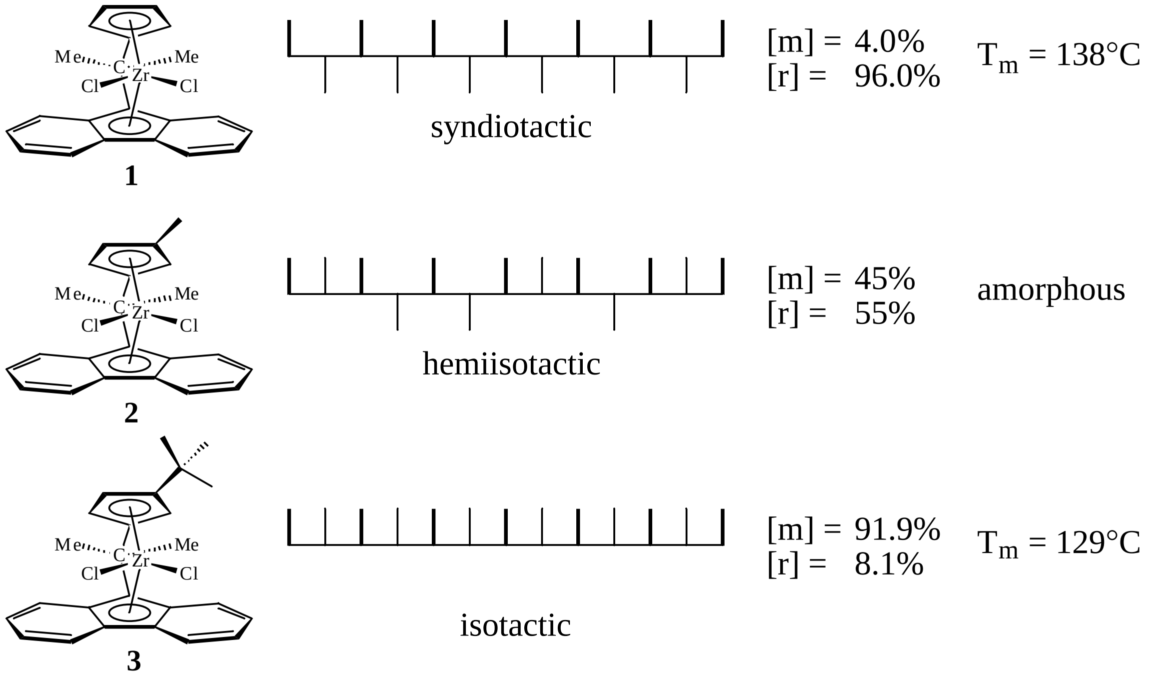


Figure 1. The MAO-cocatalyzed polymerization of propylene with **1** (T_p = 50°C), **2** (T_p = 65°C), and **3** (T_p = 40°C) provides syndiotactic, hemiisotactic, and isotactic polypropylene.

A common feature of each of the polymers from **1**, **2**, and **3** is that alternating stereocenters have the same relative stereochemistry (indicated by bold methyl groups).[5] It is the relative stereochemistry of the *intervening* stereocenters that determines the tacticity of the polymer. According to the generalized two site, alternating mechanism for polypropylene formation (Figure 2) syndiotactic polymer prevails when the two sites are of opposite enantioselectivity (α =0). When the two sites are of the same enantioselectivity (α = 1), then isotactic polypropylene obtains. For values of α near 0.5, hemiisotactic[6] polypropylene is formed since the intervening stereocenters are stereorandom.

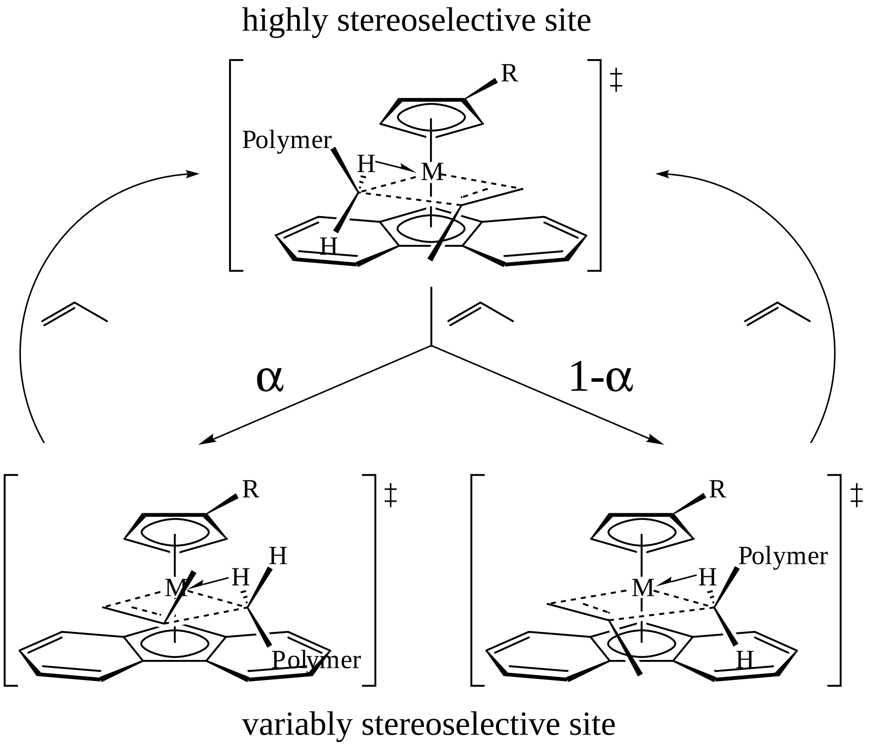


Figure 2. Generalized two-site, alternating mechanism for the formation of syndiotactic, hemiisotactic, and isotactic polypropylene.

We desired to control the “randomness” of the intervening stereocenters by modification of the ligand framework. A thorough understanding of the factors that influence α should result in increased control of the stereospecificity for monomer insertion at the variably stereoselective site, and may effect a wide variety of polymer tacticities—all based on the hemiisotactic regime.

4.2 Metallocene Design and Synthesis

The stereoselectivity for monomer insertion is indirectly controlled by the metallocene ligands. Computational studies and detailed mechanistic work[7] support the α-agostic transition state structure depicted in Figure 2. For polypropylene polymerization the choice between which of the two α-hydrogens occupies the agostic position is determined by the relative abilities of the metallocene substituents to direct the growing polymer chain.[8] The stereoselectivity is then determined by placement of the monomer methyl group *trans* to the growing polymer chain in the propagative transition state.[9] For hemiisotactic polypropylene prepared with **2**/MAO, methyl and benzo are comparable in their ability to direct the growing polymer chain in the transition state for insertion at the variably stereoselective site. The methyl group and the benzo substituent of fluorenyl are just two possible substituents for the target metallocenes represented in Figure 3. By varying the cyclopentadienyl substituent R and employing either fluorenyl or 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo [b, h] fluorenyl[10] (Oct), the stereoselectivity at the variably stereoselective site can be modulated.

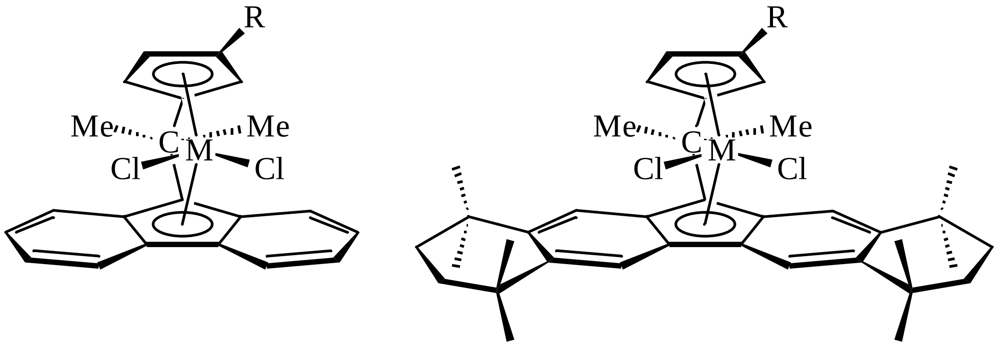


Figure 3. Target metallocenes incorporating various R substituents and either the fluorenyl or octamethyloctahydrodibenzofluorenyl ligand.

The generalized synthetic scheme for the preparation of the target metallocenes is shown in Figure 4. The nature of R, R', and R'' will determine the cyclopentadienyl substituent on the resultant metallocene. To obtain a secondary substituent, R’’ may be hydride, as in $LiAlH_4$. Typical metallation yields are in the range of 25% to 60% and typical isolated quantities vary from 0.5 grams to 2 grams.

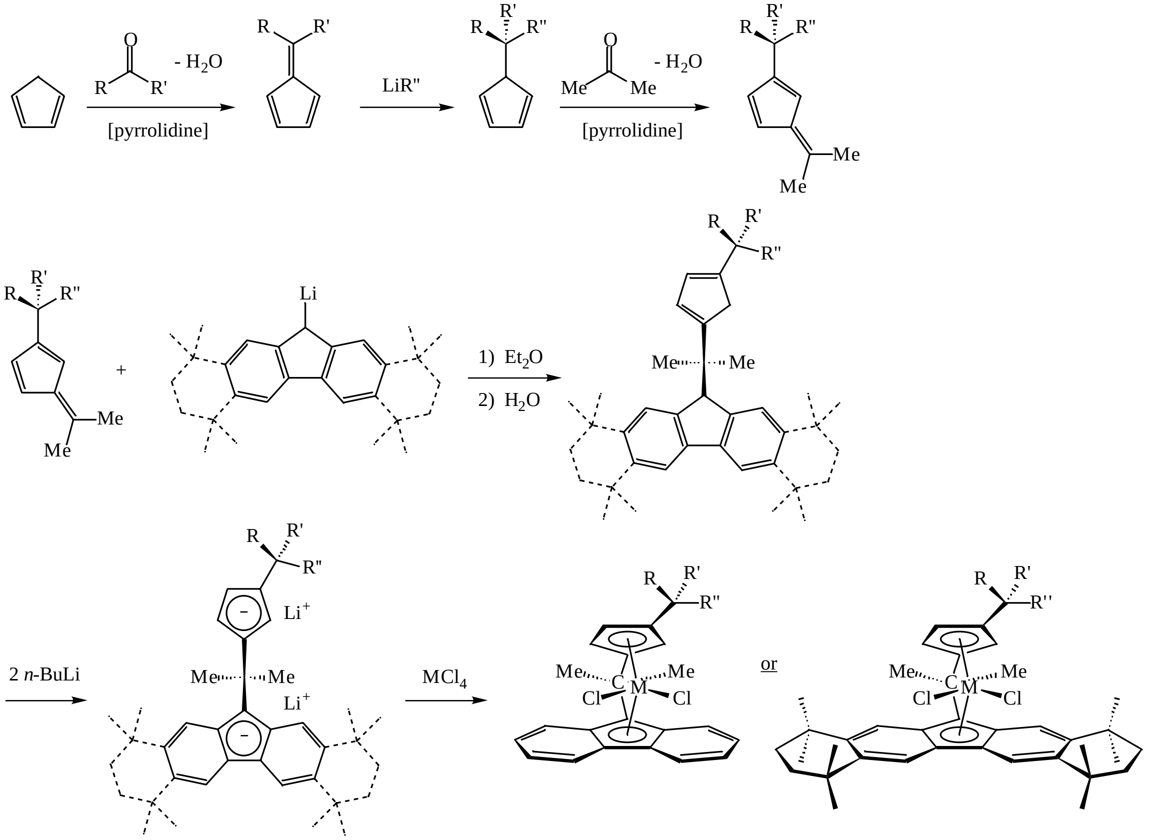
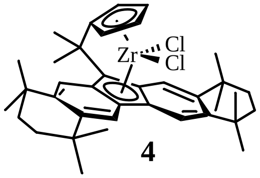
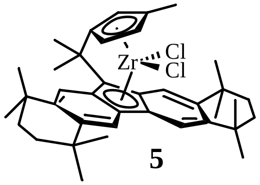
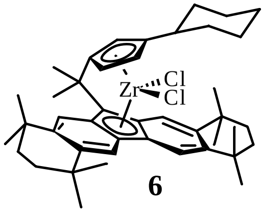
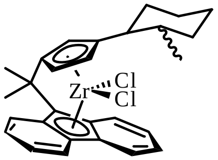
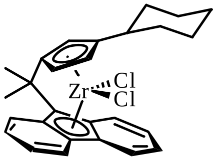
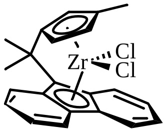


Figure 4. Generalized synthetic scheme for the preparation of target metallocenes.

4.3 Synthesis of Isotactic-hemiisotactic and Syndiotactic-hemiisotactic Polypropylene

Isotactic-hemiisotactic polypropylene has a tacticity in which the intervening stereocenters are not random, but tend to align with their neighbors (Figure 2, $\alpha > 0.5$). Syndiotactic-hemiisotactic polypropylene has a tacticity in which the intervening stereocenters tend to be opposite their neighbors (Figure 2, $\alpha < 0.5$). Several metallocenes were prepared and subjected to propylene polymerization at 0°C with 1000 equivalents of MAO to provide examples of isotactic-hemiisotactic and syndiotactic-hemiisotactic polypropylenes, as compiled in Figure 5.

	 **4**	 **5**	 **6**	 **7**	 **8**	 **2**
[mmmm]	0.0	2.4	5.1	13.1	13.2	21.6
[rrrr]	91.7	69.8	52.6	23.2	23.5	23.1
[m]	2.5	14.6	22.0	40.0	41.7	50.4
[r]	97.5	85.4	78.0	60.0	58.3	49.6
T_m (°C)	154	130	103	none	none	none

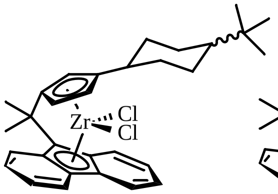
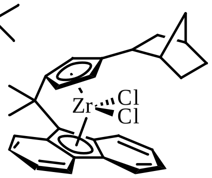
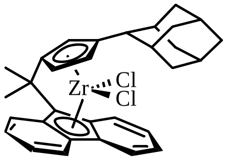
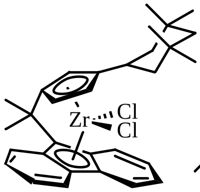
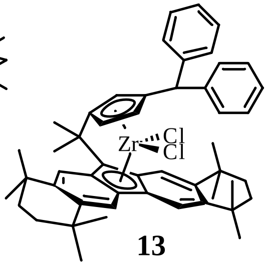
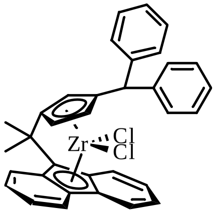
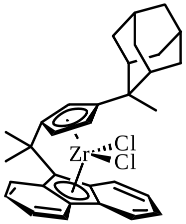
	 **9**	 **10**	 **11**	 **12**	 **13**	 **14**	 **15**
[mmmm]	24.2	27.5	28.4	49.3	74.4	86.1	>98
[rrrr]	15.9	13.6	7.9	3.5	0.0	0.0	0.0
[m]	54.7	57.6	62.3	75.3	89.2	94.7	>99
[r]	45.3	42.4	37.7	24.7	10.8	5.3	<1
T_m (°C)	none	none	none	98	125	137	159

Figure 5. Results of polymerizations performed in liquid propylene at 0°C with 1000 equivalents of MAO.

The metallocenes **2** and **4** - **15** are ordered according to the increasing fraction of m dyad present in their respective polymers. There is a qualitative correlation between the dyad content and the relative size of the polymer directing substituents. Metallocene **4** incorporates the smallest cyclopentadienyl substituent, hydrogen, and the larger of the two fluorenyl ligands, the Oct ligand. Predictably, this metallocene provides highly syndiotactic polypropylene with an α value near zero.[11] As the size of the R substituent increases for **5** and **6**, an increase in the m dyad content is observed, as predicted by the increased ability of methyl and cyclohexyl to direct the growing polymer chain during monomer insertion. Metallocenes **4**, **5**, and **6** provide polymers with sufficient r dyad content that melting temperatures are observed; these are proportional to the fraction of r dyads present and range from 154°C to 103°C.

Metallocenes **7** through **11** all contain cyclohexyl or substituted cyclohexyl substituents and produce amorphous polypropylenes with m dyad contents that range from 40.0% to 62.3%. Since **7** - **11** all contain the fluorenyl ligand, the substituents are ordered in their ability to direct the growing polymer chain—2-adamantyl being the most directing of this group. Note that substituents seemingly far from the metal center can have a significant impact on polymer stereochemistry. The parent, methyl-substituted metallocene, **2**, falls in the middle of this group and produces a polymer with 50.4% m dyads.

As the steric bulk of the cyclopentadienyl substituent is further increased, polymers with increasing m dyad contents are obtained. Although **12**, **13**, and **14** only contain secondary alkyl substituents, each produces polymer of sufficiently high isotacticity to display a melting temperature (98°C through 137°C) . A comparison of the polymers from **13** and **14** is consistent with the premise that diphenylmethyl is a good polymer directing substituent, but competes less favorably with the Oct ligand than with the benzo substituent of fluorenyl. With the tertiary 2-methyl-2-adamantyl substituent (**15**), highly isotactic polypropylene with a melting temperature of 159°C is produced; this is consistent with the mechanism in Figure 2 having an α value near unity.

4.4 Statistical Analysis of Isotactic-hemiisotactic and Syndiotactic-hemiisotactic Polypropylene

A statistical model has been developed to describe the entire range of tacticities obtained with the metallocenes in Figure 5.[12] For a hemiisotactic regime, every other stereocenter is of the same stereochemistry and the intervening stereocenters are of variable stereochemistry. Therefore, as in the hemiisotactic polymer shown in Figure 6, a given polymer can be represented by a string of mm and rr triads. This disallows the pentads containing isolated m and r dyads: mmrm, rrmr and mrmr. For a given triad, if the probability of obtaining an mm triad is defined as α, then the probability of obtaining an rr triad is $1-\alpha$.

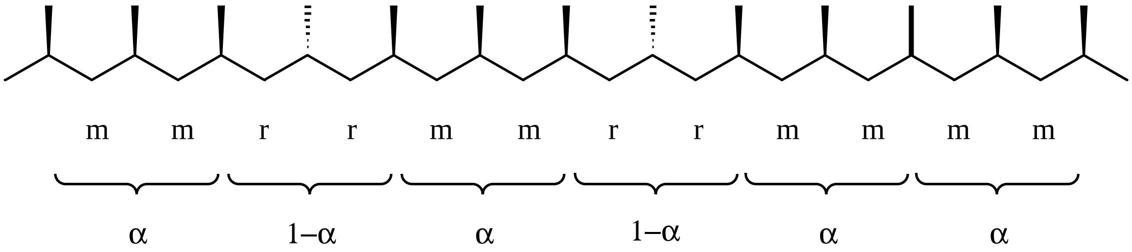


Figure 6. Perfectly hemiisotactic polypropylene contains only mm and rr triads.

The foregoing model assumes perfect enantioselectivity at the more stereoselective site. This model is not rigorously applicable to the polymers made with **2** and **4** - **15**, since each contains a finite amount of the forbidden pentads, mmrm, rrmr, and mrmr.[13] To the extent that the enantioselectivity at the more stereoselective site is not perfect, stereodefective mr and rm triads will replace those that are mm and rr.[14] As shown in Figure 7, an isolated enantiofacial misinsertion will give rise to two new triads; these will be mr or rm (Figure 8). For a given triad, the probability of obtaining an mm triad is defined as α, the probability of obtaining an rr triad is β, the probability of obtaining an mr triad is γ, and the probability of obtaining an rm triad is also γ; hence, $\alpha + \beta + \gamma + \gamma = 1$.

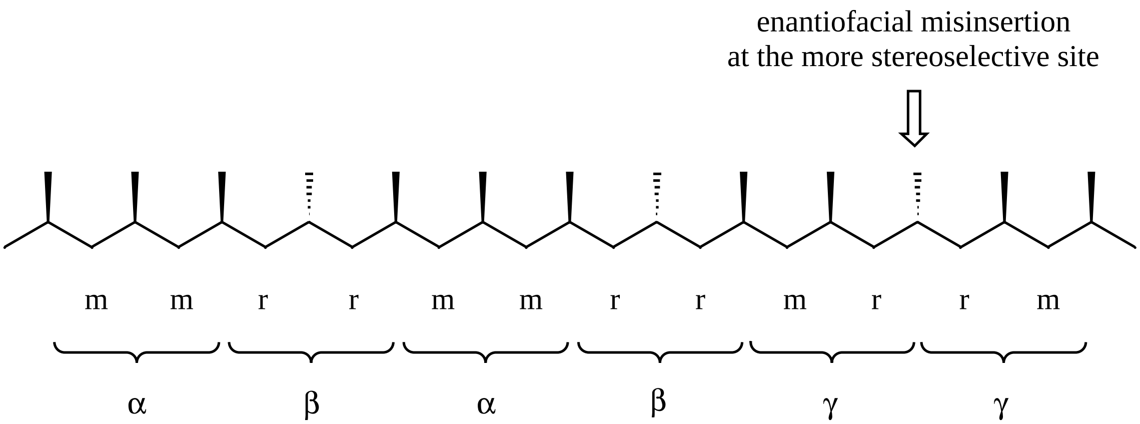


Figure 7. Enantiofacial misinsertion at the more stereoselective site will produce two stereodefective triads (mr and rm) each with probability γ.

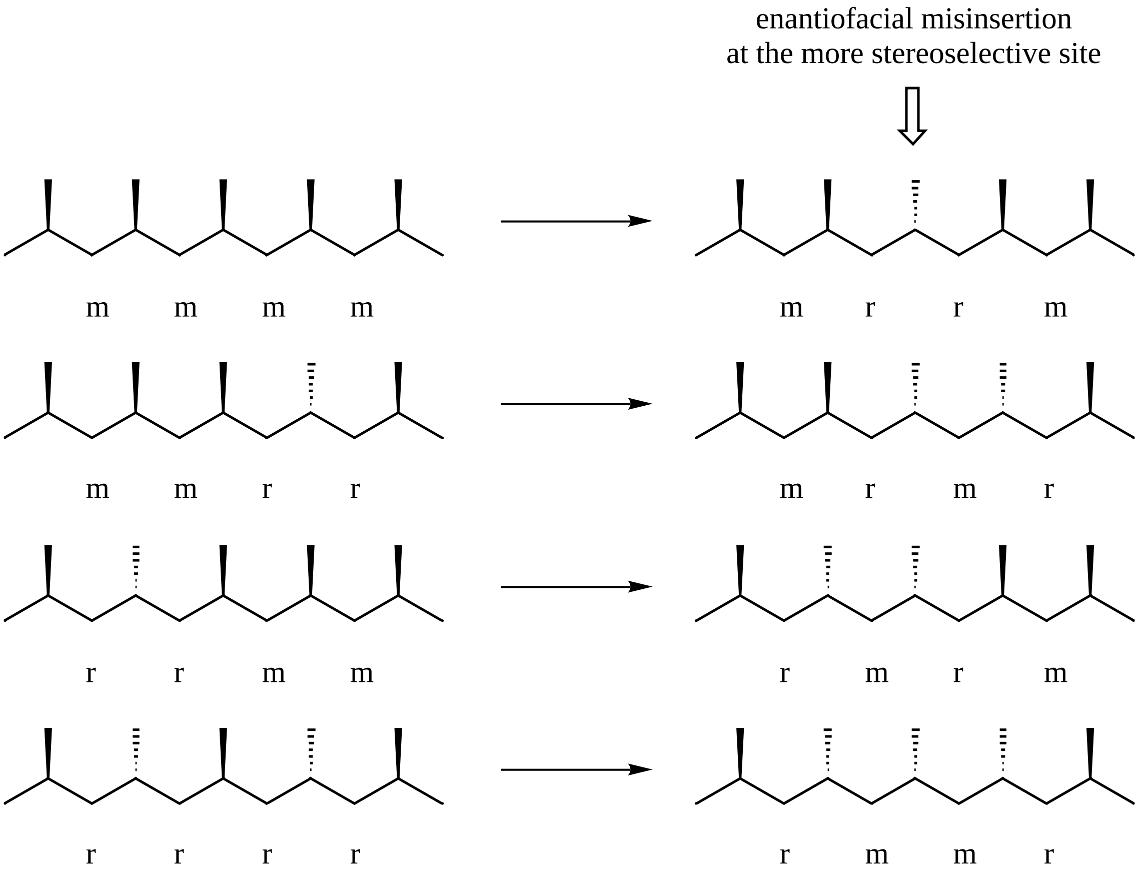


Figure 8. An isolated enantiofacial misinsertion at the more stereoselective site will give rise to mr and rm triads.

In calculating the predicted pentad intensities based on the parameters α, β and γ, one must account for the possibility that a pentad may span two or three triads. Accordingly, the pentad probabilities will contain second order terms spanning two triads as in [(xx)(xx)], and third order terms spanning three triads as in (x[x)(xx)(x]x). The resulting probabilities are shown in Figure 9, as are the probabilities for the specific case when $\gamma = 0$.

	pentad	P_{xxxx}	P_{xxxx} $(\gamma = 0)$
$P_{mm} = \alpha$	mmmm	$[\alpha^2 + (\gamma+\alpha)(\alpha)(\gamma+\alpha)]\ (0.5)$	$[\alpha^2 + (\alpha)(\alpha)(\alpha)]\ (0.5)$
$P_{rr} = \beta$	mmmr	$[\alpha\gamma + (\gamma+\alpha)(\alpha)(\gamma+\beta)]$	$[(\alpha)(\alpha)(\beta)]$
$P_{mr} = \gamma$	rmmr	$[\gamma^2 + (\gamma+\beta)(\alpha)(\gamma+\beta)]\ (0.5)$	$[(\beta)(\alpha)(\beta)]\ (0.5)$
$P_{rm} = \gamma$	mmrr	$[\alpha\beta + (\gamma+\alpha)(\gamma)(\gamma+\beta)]$	$[\alpha\beta]$
	mrmm	$[\gamma\alpha + (\gamma+\alpha)(\gamma)(\gamma+\alpha)]$	0
	rmrr	$[\gamma\beta + (\gamma+\beta)(\gamma)(\gamma+\beta)]$	0
	mrmr	$[\gamma^2 + (\gamma+\alpha)(\gamma)(\gamma+\beta)]$	0
$\alpha + \beta + 2\gamma = 1$	rrrr	$[\beta^2 + (\gamma+\beta)(\beta)(\gamma+\beta)]\ (0.5)$	$[\beta^2 + (\beta)(\beta)(\beta)]\ (0.5)$
	rrrm	$[\beta\gamma + (\gamma+\beta)(\beta)(\gamma+\alpha)]$	$[(\beta)(\beta)(\alpha)]$
	mrrm	$[\gamma^2 + (\gamma+\alpha)(\beta)(\gamma+\alpha)]\ (0.5)$	$[(\alpha)(\beta)(\alpha)]\ (0.5)$

Figure 9. Pentad probabilities in the hemiisotactic triad model.

As a representative example, the polymer made from the 2-adamantyl substituted metallocene (**11**/MAO) is subjected to the hemiisotactic triad model, the chain end control model, and the enantiomorphic site control model; the results are reported in Table 1. The chain end control model and the enantiomorphic site control model—each single parameter models—do not adequately describe the polymer formed.[15] However, the triad model with $\gamma = 0$, which also has one independent parameter, does provide an acceptable fit to the observed pentad distribution. The fit is slightly improved by allowing γ to exceed zero, using the triad model which employs two independent parameters.

Each of the polymers prepared at 0°C with **2**, and **4** - **15** have been subjected to the two parameter triad model. Table 2 compares the observed and calculated pentad distributions for these thirteen polymers. Some fit the model very well, but the calculated RMS errors are all acceptable. The parameter α corresponds well with the m dyad content of the polymers. The calculated enantioselectivity at the variably stereoselective site is a quantitative measure of the ability of the two substituents to direct the growing polymer chain during monomer insertion. This enantioselectivity is given by 1-β, and increases along the series as the size of the cyclopentadienyl substituent *relative* to the size of the opposing substituent (either benzo of fluorenyl or tetramethyltetrahydrobenzo of Oct) increases.

Table 1. Statistical analysis of a polymer made with **11**/MAO.

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $\gamma = 0$	triad model $\gamma > 0$
mmmm	28.4	26.4	31.9	30.2	29.8
mmmr	15.5	20.9	16.7	14.5	14.8
rmmr	5.3	4.1	2.6	4.6	4.5
mmrr	24.7	8.2	16.7	23.8	23.1
mrmm + rmrr	0.8	24.1	10.6	0.0	1.1
mrmr	0.4	8.2	5.3	0.0	0.2
rrrr	7.9	0.6	2.6	10.5	10.0
rrrm	7.4	3.3	5.3	9.2	9.3
mrrm	9.5	4.1	8.3	7.3	7.1
m	62.3	71.7	67.5	61.2	61.4
r	37.7	28.3	32.5	38.8	38.6
α		0.717	0.795	0.612	0.606
β				0.388	0.379
γ				0.000	0.007
RMS error		10.59	5.15	1.53	1.45

Table 2. Comparison of the observed pentad distribution and the pentad distribution calculated with the hemiisotactic triad mode having $\gamma > 0$.

Pentad (%)	**4** Obs.	**4** Calc.	**5** Obs.	**5** Calc.	**6** Obs.	**6** Calc.	**7** Obs.	**7** Calc.	**8** Obs.	**8** Calc.	**2** Obs.	**2** Calc.
mmmm	0.0	0.0	2.4	0.6	5.1	1.9	13.1	12.1	13.2	12.9	21.6	17.9
mmmr	0.0	0.0	2.4	1.2	3.4	3.5	10.0	11.3	9.6	11.0	10.9	12.2
rmmr	0.6	0.6	4.4	3.9	4.1	5.6	4.9	6.5	6.7	6.7	6.0	6.4
mmrr	1.2	1.2	6.9	8.7	13.0	14.0	19.3	22.3	22.3	23.5	21.8	25.0
mrmm + rmrr	2.7	2.7	2.9	3.4	5.0	5.0	4.3	4.7	1.6	2.2	1.3	0.0
mrmr	0.1	0.1	0.8	0.2	0.9	0.6	0.3	0.9	0.5	0.4	0.6	0.0
rrrr	91.7	91.7	69.8	70.8	52.6	52.8	23.2	22.4	23.5	23.8	23.1	19.6
rrrm	3.8	3.8	8.1	10.6	13.2	14.9	14.5	14.8	15.3	14.3	10.3	12.7
mrrm	0.0	0.0	2.2	0.6	2.8	1.7	10.4	5.1	7.3	5.2	4.4	6.1
m	2.5	2.6	14.6	11.8	22.0	20.8	40.0	43.8	41.7	43.6	50.4	49.0
r	97.5	97.4	85.4	88.2	78.0	79.2	60.0	56.2	58.3	56.4	49.6	51.0
α		0.012		0.099		0.177		0.405		0.421		0.490
β		0.960		0.863		0.761		0.530		0.549		0.510
γ		0.014		0.019		0.031		0.032		0.015		0.000
RMS error		0.035		1.450		1.397		2.167		1.000		2.327

Table 2. Continued.

Pentad (%)	**9** Obs.	**9** Calc.	**10** Obs.	**10** Calc.	**11** Obs.	**11** Calc.	**12** Obs.	**12** Calc.	**13** Obs.	**13** Calc.	**14** Obs.	**14** Calc.	**15** Obs.	**15** Calc.
mmmm	24.2	22.7	27.5	26.8	28.4	29.8	49.3	49.7	74.4	74.2	86.1	86.0	98	97.8
mmmr	11.8	14.0	12.9	14.6	15.5	14.8	13.2	14.7	10.2	9.0	5.8	5.2	0	1.0
rmmr	6.6	5.4	5.1	4.9	5.3	4.5	3.2	2.1	0.0	0.6	0.0	0.2	0	0.0
mmrr	20.6	23.8	21.3	23.5	24.7	23.1	15.5	16.7	9.3	9.8	5.5	5.5	0	0.5
mrmm + rmrr	2.3	2.0	2.0	1.5	0.8	1.1	2.6	2.7	0.0	0.3	0.0	0.1	0	0.5
mrmr	1.3	0.3	1.1	0.3	0.4	0.2	1.0	0.3	0.0	0.0	0.0	0.0	0	0.0
rrrr	15.9	13.8	13.6	11.5	7.9	10.0	3.5	3.0	0.0	0.7	0.0	0.2	0	0.0
rrrm	10.5	11.3	8.8	10.1	7.4	9.3	4.3	4.3	0.0	1.1	0.0	0.3	0	0.0
mrrm	6.9	6.6	7.8	7.0	9.5	7.1	7.3	6.4	6.1	4.4	2.6	2.6	0	0.2
m	54.7	55.2	57.6	58.8	62.3	61.4	75.3	76.4	89.2	88.8	94.7	94.1	99	99.3
r	45.3	44.8	42.4	41.2	37.7	38.6	24.7	23.6	10.8	11.2	5.3	5.9	1	0.8
α		0.539		0.579		0.606		0.747		0.886		0.941		0.990
β		0.435		0.402		0.379		0.220		0.111		0.058		0.005
γ		0.013		0.010		0.007		0.017		0.002		0.000		0.003
RMS error		1.663		1.335		1.450		0.850		0.884		0.229		0.419

4.5 Mechanism for the Formation of Isotactic-hemiisotactic and Syndiotactic-hemiisotactic Polypropylene

The parameters derived from the triad model with $\gamma > 0$ are related to the stereoselectivities of the two sites and predict the mechanism shown in Figure 10 for catalyst **11**/MAO. At the more stereoselective site, the growing polymer chain is preferentially directed away from the benzo substituent of the fluorenyl ligand and the enantiofacial selectivity is 99.3% (= 1 - γ). At the less stereoselective site, benzo and 2-adamantyl are comparable in their abilities to direct the growing polymer chain. However, 2-adamantyl is slightly more directing and the enantiofacial selectivity is 62.1% (= 1 - β). The statistical fits of the thirteen polymers are all consistent with the operation of a regularly alternating, two site mechanism having one highly stereoselective site and one site with a stereoselectivity that is markedly sensitive to the nature of the metallocene's substituents.

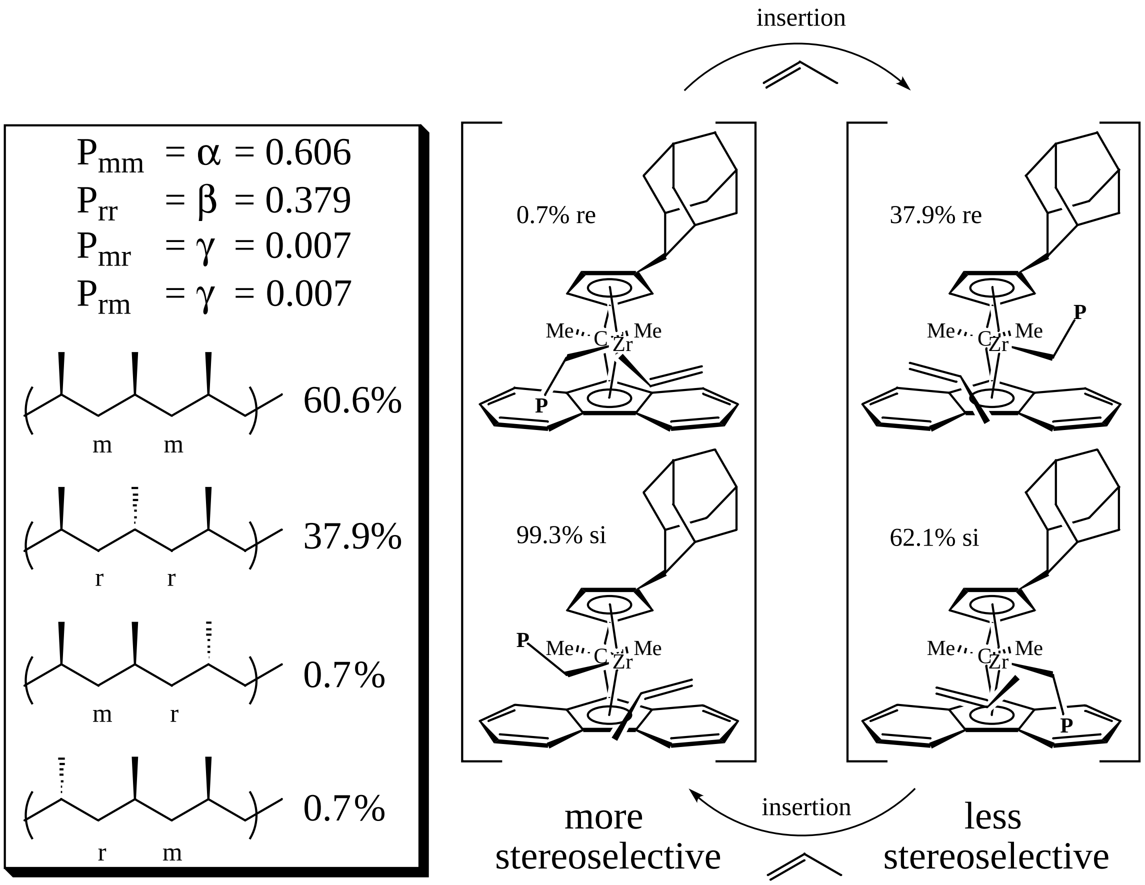


Figure 10. **11**/MAO produces polypropylene via a two site mechanism.

4.6 Stereoerror Formation in the Synthesis of Isotactic-hemiisotactic and Syndiotactic-hemiisotactic Polypropylene

Stereoerrors in the formation of hemiisotactic polypropylene can arise via three possible scenarios. The first (Figure 11) is an enantiofacial misinsertion at the more stereoselective site. The second is a site epimerization process (site epimerization mistake I) in which the growing polymer chain migrates away from the cyclopentadienyl R substituent in a unimolecular process prior to bimolecular monomer insertion. This event will skip the insertion at the variably stereoselective site. The third is a site epimerization process (site epimerization mistake II) in which the growing polymer chain migrates toward the cyclopentadienyl R substituent prior to monomer insertion. This event will skip the insertion at the highly stereoselective site.

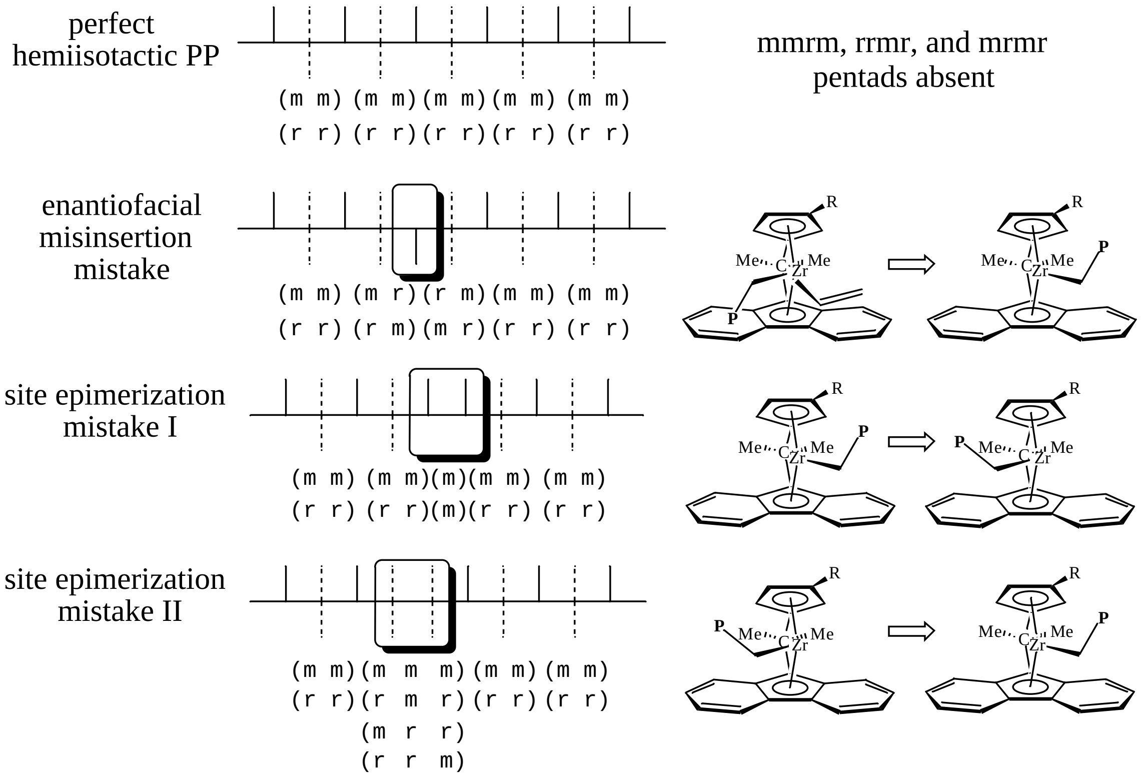
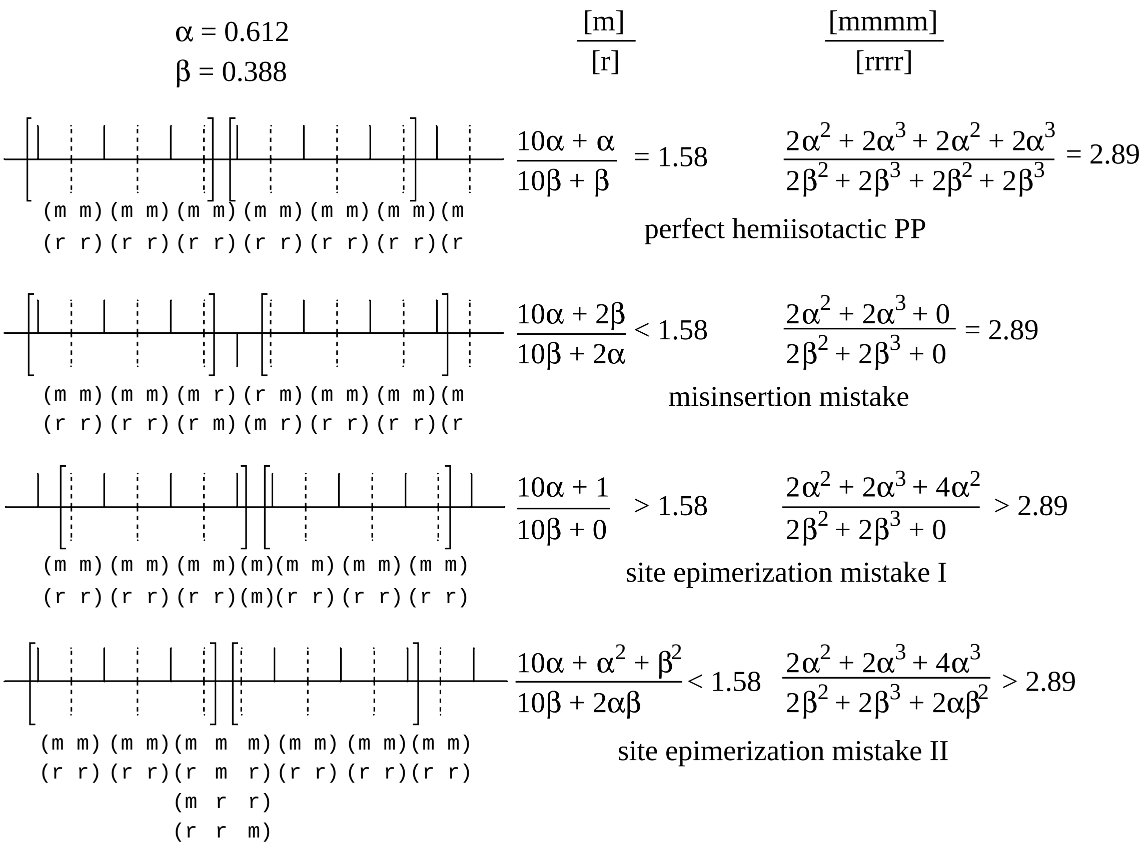


Figure 11. Stereoerrors in hemiisotactic polypropylene arise via enantiofacial misinsertion or via one of two site epimerization processes.

The occurrence of each of these stereoerrors will affect the pentad distribution differently. Figure 12 describes the effect an isolated stereoerror is predicted to have on the quotient [m]/[r] and the quotient [mmmm]/[rrrr].[16] For perfect hemiisotactic polypropylene made with **11**/MAO, α = 0.612 and β =0.388 (Table 1, triad model with γ = 0). In the absence of any stereoerrors, the predicted value for [m]/[r] is 1.58 and the predicted value for [mmmm]/[rrrr] is 2.89. If an enantiofacial misinsertion occurs, the value for [m]/[r] is expected to decrease, while the value for [mmmm]/[rrrr] is expected to remain unperturbed. Site epimerization mistake I is expected to increase the values of both [m]/[r] and [mmmm]/[rrrr]. Site epimerization mistake II is expected to decrease the quotient [m]/[r], but is expected to increase the quotient [mmmm]/[rrrr].



$\alpha = 0.612$
$\beta = 0.388$

$\frac{[m]}{[r]}$ $\frac{[mmmm]}{[rrrr]}$

$$\frac{10\alpha + \alpha}{10\beta + \beta} = 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 2\alpha^2 + 2\alpha^3}{2\beta^2 + 2\beta^3 + 2\beta^2 + 2\beta^3} = 2.89$$

perfect hemiisotactic PP

$$\frac{10\alpha + 2\beta}{10\beta + 2\alpha} < 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 0}{2\beta^2 + 2\beta^3 + 0} = 2.89$$

misinsertion mistake

$$\frac{10\alpha + 1}{10\beta + 0} > 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 4\alpha^2}{2\beta^2 + 2\beta^3 + 0} > 2.89$$

site epimerization mistake I

$$\frac{10\alpha + \alpha^2 + \beta^2}{10\beta + 2\alpha\beta} < 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 4\alpha^3}{2\beta^2 + 2\beta^3 + 2\alpha\beta^2} > 2.89$$

site epimerization mistake II

Figure 12. The predicted effect of stereoerrors on the quotient [m]/[r] and the quotient [mmmm]/[rrrr].

A series of polymerizations with hemiisotactic catalyst **11**/MAO were performed in dilute monomer (10% propylene in toluene, 2000 equivalents MAO) and at increasing polymerization temperatures (Table 3). The fraction of stereomistakes, as represented by the "forbidden" pentads mmrm + rrmr + mrmr, increased steadily with polymerization temperature from 2.8% to 8.5%. As the fraction of stereomistakes increased, the quotient [m]/[r] *and* the quotient [mmmm]/[rrrr] likewise increased. This observation is consistent with site epimerization mistake I being the dominant type of stereoerror for dilute polymerizations at increasing polymerization temperatures. If enantiofacial misinsertions were primarily responsible for the increase in stereoerrors, one would expect [m]/[r] to decrease and [mmmm]/[rrrr] to remain unperturbed. If site epimerization mistake II were the principal mechanism for stereoerror formation, one would expect [m]/[r] to decrease and [mmmm]/[rrrr] to increase.

Site epimerization mistake I is the intuitively more obvious site epimerization, since the growing polymer chain is allowed to migrate *away* from the bulky R substituent prior to monomer insertion.[17, 18]

Table 3. The quotient [m]/[r] and the quotient [mmmm]/[rrrr] increase with an increasing fraction of stereomistakes for **11**/MAO in 10% propylene.

Entry	T_p(°C)	[mmrm]+ [rrmr]+ [mrmr] (%)	[m] (%)	[r] (%)	[m]/[r]	[mmmm] (%)	[rrrr] (%)	[mmmm]/ [rrrr]
1	0	2.8	60.1	39.9	1.51	26.4	9.6	2.75
2	20	2.9	59.8	38.2	1.57	26.0	9.9	2.63
3	40	3.7	60.6	39.4	1.54	27.2	8.9	3.06
4	60	6.8	62.1	37.9	1.64	28.4	6.3	4.51
5	75	9.3	67.3	32.7	2.06	34.2	3.7	9.24
6	90	8.5	71.6	28.4	2.52	40.1	2.7	14.9

4.7 Isotactic Block Length Distribution for Isotactic-hemiisotactic Polypropylene

For an isotactic polymer produced under enantiomorphic site control, the stereoerrors are randomly distributed as depicted in Figure 13. However, the "stereoerrors" formed under an isotactic-hemiisotactic regime are not randomly distributed; they can occur only at every other monomer insertion. One can calculate the expected block length distributions for these two different regimes.

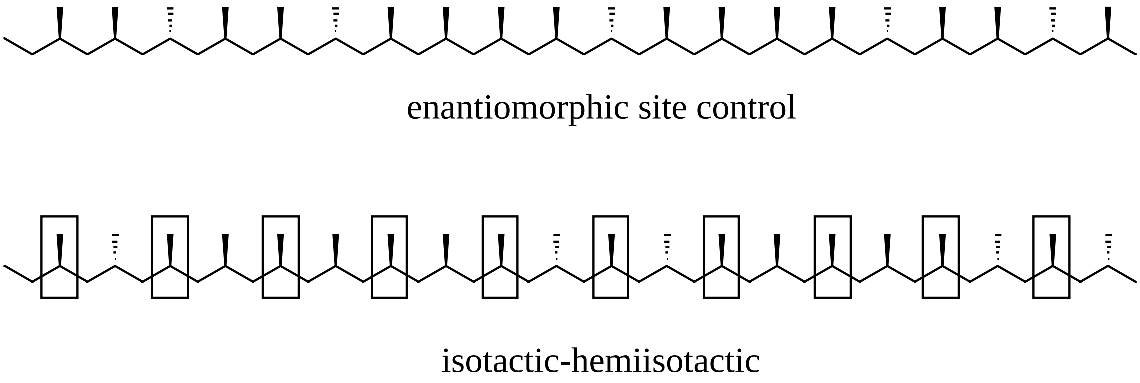


Figure 13. Stereoerrors are randomly distributed in enantiomorphic site control but occur only at every other insertion for isotactic-hemiisotactic polypropylene.

For the enantiomorphic site control model with a stereoselectivity parameter of α, the number of isotactic blocks having length n present in a polymer with number average molecular weight M_n is given by:[19]

$$N_n = [(1-\alpha)(\alpha)^{(n)}(1-\alpha)] \cdot [M_n / 42]$$

The isotactic block length distribution for hemiisotactic polypropylene can be derived to obtain the following dependence on the parameters α, β, γ, and M_n.[20]

$$N_{n(odd)} = [(\gamma + \beta)(\alpha)^{((n-1)/2)}(\beta + \gamma) + (\gamma)(\alpha)^{((n-3)/2)}(\gamma)] \cdot [M_n / 42]$$

and

$$N_{n(even)} = [2(\gamma + \beta)(\alpha)^{((n-2)/2)}(\gamma)] \cdot [M_n / 42]$$

Note that blocks of even length will be less abundant than comparable blocks of odd length; this is true for reasonably small values of γ. It is readily shown that the syndiotactic block length distribution is obtained following exchange of the parameters α and β in the these equations.[21]

Some of the best examples of isotactic-hemiisotactic polypropylene are obtained from **12**/MAO and its hafnium analog **16**/MAO ($Me_2C(C_{13}H_8)$(3-(3,3,5,5-tetramethylcyclohexyl)-$C_5H_3)HfCl_2$/MAO). These provide polymers with α parameters of approximately 0.75, which is halfway between that expected for perfect hemiisotactic polypropylene (α = 0.5) and isotactic polypropylene (α = 1.0). Representative pentad distributions are given in Table 4.

Table 5 compares the pentad distribution obtained with **16**/MAO at 0°C with those predicted by chain end control, enantiomorphic site control, and the hemiisotactic triad models having one or two independent parameters. Clearly, chain end control is not an adequate model for describing this polymer. Enantiomorphic site control, however, predicts a pentad distribution similar to that observed. Slightly better fits are obtained with the hemiisotactic triad models.

Table 4. Pentad distributions obtained with **12**/MAO and its hafnium analog, **16**/MAO.

Pentad (%) T_p (°C)	**12** (Zr) 0	**12** (Zr) 20	**16** (Hf) 0	**16** (Hf) 20
mmmm	49.3	47.9	43.8	45.6
mmmr	13.2	14.3	12.8	15.3
rmmr	3.2	2.8	4.2	2.6
mmrr	15.5	16.8	13.4	14.5
mrmm + rmrr	2.6	2.0	4.9	4.7
mrmr	1.0	1.2	2.7	1.4
rrrr	3.5	4.0	8.4	5.7
rrrm	4.3	4.1	4.6	3.1
mrrm	7.3	6.9	5.2	6.9
m	75.3	75.0	71.3	73.9
r	24.7	25.0	28.7	26.1
T_m (°C)	98	91	76	74

Table 5. Statistical analysis of a polymer made with **16**/MAO at 0°C.

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $\gamma = 0$	triad model $\gamma > 0$
mmmm	49.3	52.9	49.9	50.3	49.7
mmmr	13.2	18.2	14.9	13.9	14.7
rmmr	3.2	1.6	1.3	2.2	2.1
mmrr	15.5	3.1	14.9	18.4	16.7
mrmm + rmrr	2.6	18.8	5.1	0.0	2.7
mrmr	1.0	3.1	2.6	0.0	0.3
rrrr	3.5	0.0	1.3	3.7	3.0
rrrm	4.3	0.5	2.6	4.5	4.3
mrrm	7.3	1.6	7.5	7.0	6.4
m	75.3	85.3	77.4	75.7	76.4
r	24.7	14.7	22.6	24.3	23.6
α		0.853	0.870	0.757	0.747
β				0.243	0.220
γ				0.000	0.017
RMS error		7.598	1.636	1.429	0.850

Despite the seemingly similar pentad distributions predicted by the enantiomorphic site control model and the hemiisotactic triad model, the isotactic block length distributions calculated for each of these models are quite different. Comparing the isotactic block length distributions for these polymers provides the data in Table 6 ($\gamma = 0$). Consider a polymer with $M_n = 100{,}000$. A polymer produced under enantiomorphic site control with $\alpha = 0.870$ ([m] = 77.4%) will contain only 18 blocks of length 20 or greater. Contrast this with a hemiisotactic polymer having $\alpha = 0.757$ ([m] = 75.7%); it will contain 33 blocks of length 20 or greater, despite having a slightly lower m dyad content.

It is clear that for similar m dyad contents, the hemiisotactic polymer will contain many more isotactic blocks capable of participating in crystallite formation. Perhaps this condition contributes to the finding of relatively high melting temperatures (98°C and 91°C for **12**) for polymers with modest mmmm pentad contents (49.3% and 47.9% for **12**). Figure 14 compares the polymers made by **12** and **16** with other low melting polypropylenes made via enantiomorphic site control with C_2-symmetric metallocenes / MAO.[22]

The peculiar isotactic block length distribution for isotactic-hemiisotactic polymers has been exploited to prepare elastomeric polypropylene based on the hemiisotactic regime. With an α parameter near 0.6 and reasonably high molecular weights, the statistical presence of isotactic blocks presumably allows for crystallite formation among an otherwise amorphous hemiisotactic phase. A detailed analysis of this type of polymer and its preparation are reported elsewhere.[23]

Table 6. Isotactic block length distributions for polymers made via enantiomorphic site control (α = 0.870) and via the hemiisotactic model (α = 0.757).

M_n	100,000	100,000	200,000	200,000	1,000,000	1,000,000
α enantio.	0.870		0.870		0.870	
α hemiiso.		0.757		0.757		0.757
n	N_n	N_n	N_n	N_n	N_n	N_n
1	35.01	140.59	70.01	281.19	350.07	1405.93
2	30.46		60.91		304.56	
3	26.50	106.43	52.99	212.86	264.97	1064.29
4	23.05		46.10		230.52	
5	20.06	80.57	40.11	161.13	200.56	805.67
6	17.45		34.90		174.48	
7	15.18	60.99	30.36	121.98	151.80	609.89
8	13.21		26.41		132.07	
9	11.49	46.17	22.98	92.34	114.90	461.69
10	10.00		19.99		99.96	
11	8.70	34.95	17.39	69.90	86.97	349.50
12	7.57		15.13		75.66	
13	6.58	26.46	13.16	52.91	65.82	264.57
14	5.73		11.45		57.27	
15	4.98	20.03	9.96	40.06	49.82	200.28
16	4.33		8.67		43.35	
17	3.77	15.16	7.54	30.32	37.71	151.61
18	3.28		6.56		32.81	
19	2.85	11.48	5.71	22.95	28.54	114.77
20	2.48		4.97		24.83	
21	2.16	8.69	4.32	17.38	21.60	86.88
22	1.88		3.76		18.80	
23	1.64	6.58	3.27	13.15	16.35	65.77
24	1.42		2.85		14.23	
25	1.24	4.98	2.48	9.96	12.38	49.79
26	1.08		2.15		10.77	
27	0.94	3.77	1.87	7.54	9.37	37.69
28	0.82		1.63		8.15	
29	0.71	2.85	1.42	5.71	7.09	28.53
30	0.62		1.23		6.17	
31	0.54	2.16	1.07	4.32	5.37	21.60
32	0.47		0.93		4.67	
33	0.41	1.63	0.81	3.27	4.06	16.35
34	0.35		0.71		3.53	
35	0.31	1.24	0.61	2.48	3.07	12.38
36	0.27		0.54		2.68	
37	0.23	0.94	0.47	1.87	2.33	9.37
38	0.20		0.40		2.02	
39	0.18	0.71	0.35	1.42	1.76	7.09
40	0.15		0.31		1.53	
Sum N_n for $n \geq 21$	18.08	33.54	36.15	67.09	180.76	335.44

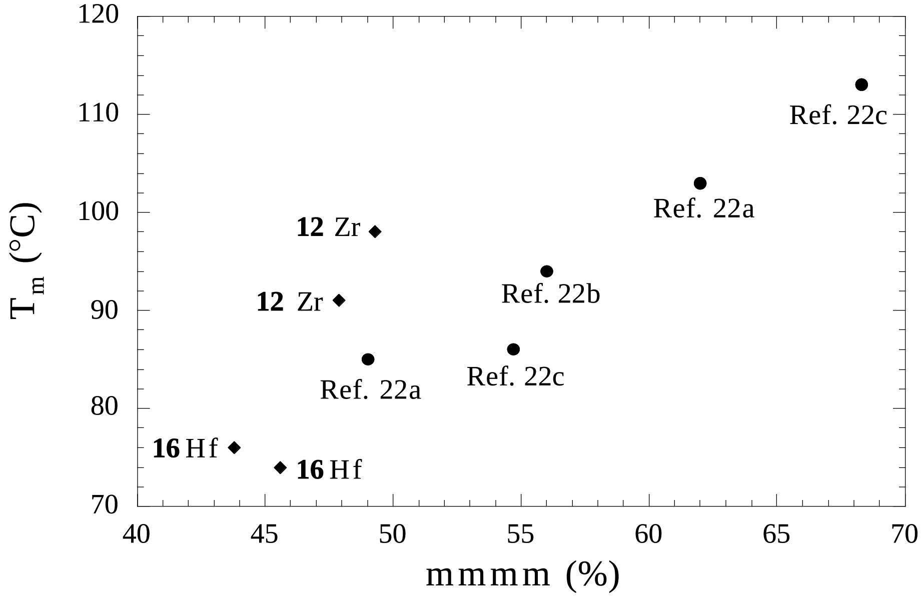


Figure 14. Polymer melting temperature vs. mmmm pentad content for low melting isotactic polypropylenes.

4.8 Conclusions

The incremental steric modification of the parent hemiisospecific metallocene catalyst system $Me_2C(C_{13}H_8)(3\text{-methyl-}C_5H_3)ZrCl_2$/MAO has afforded an array of catalyst systems capable of polymerizing propylene to a spectrum of hemiisotactic regimes. By employing metallocenes of the type $Me_2C(C_{13}H_8)(3\text{-R-}C_5H_3)ZrCl_2$ and $Me_2C(Oct)(3\text{-R-}C_5H_3)ZrCl_2$, with carefully selected R substituents, one can control the stereoselectivity at the metallocene's variably stereoselective site. Thus, polymer tacticities of isotactic-hemiisotactic ($\alpha > 0.5$) and syndiotactic-hemiisotactic ($\alpha < 0.5$) have been prepared.

The pentad distributions measured for the polypropylenes were subjected to a hemiisotactic statistical model which allows sequential mm, rr, mr, and rm triads. The results are consistent with a two site polymerization mechanism having minimal contributions from site epimerization processes (liquid monomer, T_p = 0°C). One site of the metallocene is highly stereoselective (typically 98 - 99%) and the second site has a stereoselectivity that is highly dependent on the nature of the R substituent and whether the metallocene contains the fluorenyl or the octamethyloctahydrodibenzofluorenyl (Oct) ligand.

For polymerizations performed in dilute monomer at increasing polymerization temperatures, the dominant type of stereoerror found for hemiisotactic polymerizations is that which results from a site epimerization in which the growing polymer chain migrates away from the R substituent on the cyclopentadienyl ring prior to monomer insertion.

The isotactic block length distribution for hemiisotactic polypropylene has been derived and compared to that expected under enantiomorphic site control. The distributions are dramatically different. For example, with hemiisotactic polymers, isotactic blocks of even length are essentially forbidden. For polymers of comparable m dyad content, the hemiisotactic polymer will contain far more crystallizable isotactic sequences than will a polymer formed via enantiomorphic site control. Depending on the parameter α, this condition can lead to interesting physical properties of the polymer, including increased melting temperatures and elastomeric properties.

4.9 Experimental Section

General Considerations. Unless otherwise noted, all reactions and procedures are carried out under an inert atmosphere of argon or nitrogen using standard glove box, Schlenk and high vacuum line techniques.[24] Solvents are dried according to standard procedures. The following were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%); fluorene (98%); n-butyllithium (1.6 M in hexanes); zirconium tetrachloride (99.5%); norcamphor (98%); 2-methylcyclohexanone (99%); 4-*t*-butylcyclohexanone (98%); 2-adamantanone (99%); and 3, 3, 5, 5-tetramethylcyclohexanone (98%); aluminum chloride (99.99%); 2,5-dimethyl-2,5-hexanediol (99%); benzophenone (99%); and nitromethane (96%). Dicyclopentadiene and di(methylcyclopentadiene) were obtained from Aldrich and cracked following standard procedures prior to use. **Instrumentation.** NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78

MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC-MS were acquired with a Hewlett Packard 5890 Series II Gas Chromatograph connected to a Hewlett Packard 5989A Mass Spectometer. The GC was equipped with a column of dimensions 7.1 m x 0.1 μm having an HP-1 phase (Crosslinked Methyl Silicone Gum). LC-MS were acquired with a Hewlett Packard 1090 Series II Liquid Chromatograph with a toluene phase (solvent dried over sodium/benzophenone). The LC was connected to a Hewlett Packard 59980B Particle Beam Interface, and this was connected to a Hewlett Packard 5989A Mass Spectrometer.

Metallocene Syntheses

Preparation of 2. The synthesis of **2** was performed as described in the literature.[3b]

Preparation of 4.

6,6-dimethylfulvene. (Synthesis modified from reference 25) A 2 L vessel was charged with methanol (875 mL), cyclopentadiene (101.0 g, 1528 mmol), and acetone (230 mL). Pyrrolidine (13.5 mL, 112 mmol) was syringed in over 10 minutes. The reaction was stirred for 18 hours before an aqueous acetic acid solution (50 mL acetic acid/200 mL water) was added over 2 minutes. Diethyl ether (500 mL) and water (1000 mL) were added and the organic layer isolated. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were extracted with water (5 x 150 mL). The ether layer was dried over $MgSO_4$, filtered and rotavapped at 40°C for 2 hours. This provided ether-free fulvene (156.81 g, 96.7%). This material was further cleaned by pushing the neat liquid through a short column of alumina: 111.2 g (68.5%).

2,5-dichloro-2,5-dimethylhexane. A 2 liter argon purged vessel was charged with 2,5-dimethyl-2,5-hexanediol (200.00 g, 1.368 mol) and concentrated aqueous hydrochloric acid (1.00 L, 12.2 mol HCl) was poured in. The white slurry was shaken and stirred for 17 hours. The white solid was collected by suction filtration and rinsed with 500 mL water. The solid was dissolved in 1.00 L 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 minutes) dried *in vacuo* to provide the product: 237.96 g (95.0%). ^1H NMR ($CDCl_3$): δ 1.55 (s, 12H, CH_3), 1.90 (s, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 32.59 (CH_3), 41.21 (CH_2), 70.13 (CH_0). Elemental analysis calculated 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 liter 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 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 nitromethane. The solution was added over 10 minutes and the purple reaction was stirred for 20 hours before it was slowly poured into 700 mL of ice water. The precipitate was collected by filtration and refluxed in 500 mL ethanol for 2 hours. Upon cooling, the solid was collected by filtration and this was refluxed in 300 mL hexanes for 2 hours. After cooling, the solid was collected by filtration and dried *in vacuo*, giving the product as a white powder: 62.53 grams (74.7%). MS (GC-MS) m/z 386.5 (M^+). ^1H NMR ($Cl_2DCCDCl_2$): δ 1.38, 1.43 (s, 24H, CH_3), 1.77 (apparent s, 8H, $CH\text{-}_2$), 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 (CH_3), 34.68, 34.71 (CH_0), 35.50, 35.55 (CH_2), 36.47 (CH_2), 117.48, 123.31(CH_1), 139.20, 140.80, 143.50, 143.66 (CH_0). Elemental analysis calculated for $C_{29}H_{38}$: C, 90.09; H, 9.91. Found: C, 89.07, 89.16; H, 8.94, 8.85.

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

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

$Me_2C(C_5H_4)(C_{29}H_{36})ZrCl_2$ (4). In the glove box, a swivel frit apparatus was charged with $Me_2C(C_5H_4)(C_{29}H_{36})Li_2$ (3.246 g, 6.436 mmol) and zirconium tetrachloride (1.500 g, 6.437 mmol). 50 mL of petroleum ether were condensed in and the reaction stirred at room temperature for 51 hours before solvent removal. 20 mL dichloromethane were condensed in, stirred, and removed. Then, 30 mL diethyl ether were condensed in, stirred, and removed. In the glove box, the solid was transferred to a cellulose extraction thimble and this was extracted overnight with 100 mL diethyl ether. The obtained slurry was transferred back to the swivel frit and the volume reduced to 30 mL. The orange precipitate (**4**) was collected on the frit and dried *in vacuo*: 1.649 g (39.2%). MS (LC-MS) m/z 653.7 (M^+). ^1H NMR (C_6D_6): δ 1.28, 1.30, 1.30, 1.52 (s, 24H, Oct-CH_3), 1.65 (m, 8H, Oct-CH_2), 2.02 (s, 6H, $(CH_3)_2$C-Oct-Cp), 5.51, 6.12 (m, 4H, Cp-*H*), 7.64, 8.28 (s, 4H, Oct-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.60, 31.88, 32.22, 32.37, 33.50 (CH_3), 34.78, 34.86, 35.03, 35.11 (CH_0 and CH_2), 40.06 (Me*C*Me), 75.23, 112.89, 121.05, 121.50, 145.68, 147.68 (Cp- and Oct-CH_0), 100.45, 118.44 (Cp-CH_1), 120.63, 122.06 (Oct-CH_1). Elemental analysis calculated for $C_{37}H_{46}Zr_1Cl_2$: C, 68.07; H, 7.10. Found: C, 60.14; H, 6.45.

Preparation of 5.

3, 6, 6-trimethylfulvene. A 1 liter flask was charged with 400 mL 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 hours, 50 mL of acetic acid were added, followed by 1200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (5 x 100 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and rotavapped to give 158.8 grams of a red-orange oil that was subjected to Kugelrohr distillation under high vacuum. The first 15 grams 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 grams (94.0%).

$Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})H_2$. 13.5 mL of an n-butyllithium solution (21.6 mmol, 1.6 M in hexanes) were syringed into a solution of octamethyloctahydrodibenzofluorene (8.00 g, 20.7 mmol) in 90 mL tetrahydrofuran. After stirring for 90 minutes, 3,6,6-trimethylfulvene (2.487 g, 20.7 mmol) was injected via syringe into the red solution. After stirring for 22 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})H_2$ (10.49 g, 20.7 mmol) in 75 mL 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 hours, the precipitate was isolated by filtration and *in vacuo* drying to provide the dianion as a yellow powder: 8.707 g (81.1%).

$Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (5). 3.34 grams of $Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})Li_2$ (6.44 mmol) and 1.50 g $ZrCl_4$ (6.44 mmol) were combined in a swivel frit apparatus. 50 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 18 hours of stirring. 20 mL of methylene chloride were 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 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 grams (24.5%) of **5** as an orange-pink powder was obtained following *in vacuo* drying. MS (LC-MS) m/z 666.6 (M^+). ^1H NMR (C_6D_6): δ 1.20, 1.31, 1.31, 1.31, 1.31, 1.32, 1.50, 1.53 (s, 24H, Oct-CH_3), 1.65 (m, 8H, Oct-CH_2), 1.93 (s, 3H, Cp-CH_3), 2.03, 2.06 (s, 6H, $(CH_3)_2$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*). Elemental analysis calculated for $C_{38}H_{48}Zr_1Cl_2$: C, 68.44; H, 7.25. Found: C, 62.90; H, 6.97.

Preparation of 6.

6,6-(pentamethylene)fulvene (cyclohexylfulvene). (Synthesis modified from reference 25) 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 hours before 40 mL of acetic acid were added, followed by 300 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and rotavapped to give 158.8 grams of a yellow oil that was subjected to Kugelrohr distillation under high vacuum. The first 20 grams 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 grams (61.1%).

cyclohexylcyclopentadiene. 15.66 grams (107.1 mmol) of cyclohexylfulvene were dissolved in 50 mL of tetrahydrofuran and this solution was added over 12 minutes to a stirred slurry of $LiAlH_4$ (4.500 g, 118.6 mmol) in 100 mL tetrahydrofuran at 0°C. After 15 hours 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 H_2O and 50 mL diethyl ether were added; the organic layer was isolated, and the aqueous layer was extracted with additional diethyl ether (2 x 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 methanol, acetone (20.0 mL, 272 mmol) and pyrrolidine (1.0 mL, 12 mmol). After stirring for 21 hours, 5 mL of acetic acid were injected, followed by 150 mL H_2O and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and with 10% aqueous NaOH (3 x 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)($C_{29}H_{36}$)H_2. 11.0 mL of an n-butyllithium solution (17.6 mmol, 1.6 M in hexanes) were syringed into a solution of octamethyloctahydrodibenzofluorene (6.603 g, 17.08 mmol) in 60 mL tetrahydrofuran. After stirring for 50 minutes, 3-cyclohexyl-6,6-dimethylfulvene (3.216 g, 17.08 mmol) was injected via syringe into the red slurry. After stirring for 18 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 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 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 hours, 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)($C_{29}H_{36}$)$ZrCl_2$ (6). 2.518 grams of Me_2C(3-cyclohexyl-C_5H_3)($C_{29}H_{36}$)Li_2 (4.29 mmol) and 1.00 g $ZrCl_4$ (4.29 mmol) were combined in a swivel frit apparatus. 30 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 18 hours of stirring. 40 mL of methylene chloride were 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 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 grams (58.5%) of **6** as an orange powder was obtained following *in vacuo* drying. MS (LC-MS) m/z 734.8 (M^+). ^1H 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-CH_3), 1.63 (m, 8H, Oct-CH_2), 2.08, 2.09 (s, 6H, $(CH_3)_2$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*). Elemental analysis calculated for $C_{43}H_{56}Zr_1Cl_2$: C, 70.26; H, 7.68. Found: C, 67.53; H, 7.76.

Preparation of 7.

2-methylcyclohexylfulvene. Pyrrolidine (20.0 mL, 240 mmol) was syringed into a solution of 2-methylcyclohexanone (25.0 mL, 206 mmol) and cyclopentadiene (30.0 mL, 364 mmol) in 50 mL of methanol. The reaction was stirred for 47 hours before 25 mL of acetic acid were added, followed by 300 mL H_2O and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and rotavapped to give 34.24 grams (97.9%) of a yellow oil after *in vacuo* drying.

2-methylcyclohexylcyclopentadiene. 32.00 grams (199.7 mmol) of 2-methylcyclohexylfulvene were dissolved in 100 mL of tetrahydrofuran and this solution was added over 5 minutes to a stirred slurry of $LiAlH_4$ (10.00 g, 266 mmol) in 100 mL tetrahydrofuran at 0°C. After 19 hours of stirring at room temperature, the reaction was cooled to 0°C and quenched by dropwise addition of 100 mL of water. Then 100 mL concentrated aqueous HCl in 300 mL water were added; the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give 31.59 grams (97.5%) of product as a light yellow oil.

3-(2-methylcyclohexyl)-6,6-dimethylfulvene.

To 2-methylcyclohexylcyclopentadiene (15.00 g, 92.44 mmol) was added 100 mL ethanol, acetone (25.0 mL, 340 mmol) and sodium methoxide (7.00 g, 130 mmol). After stirring for 63 hours, 200 mL water were added, followed by 100 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped. 17.30 grams (92.5%) of the product were obtained as a yellow liquid following purification by passing the neat liquid through a short column of alumina.

$Me_2C(3\text{-}(2\text{-methylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)H_2$. 13.0 mL of an n-butyllithium solution (20.8 mmol, 1.6 M in hexanes) were syringed into a solution of fluorene (3.286 g, 19.77 mmol) in 60 mL tetrahydrofuran. After stirring for 135 minutes, 3-(2-methylcyclohexyl)-6,6-dimethylfulvene (4.00 g, 19.8 mmol) was injected via syringe. After stirring for 21 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped to give the product in quantitative yield (7.29 g) as a light yellow oil.

$Me_2C(3\text{-}(2\text{-methylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2\text{-methylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)H_2$ (7.29 g, 19.8 mmol) in 50 mL diethyl ether with 26.0 mL of n-butyllithium solution (41.6 mmol, 1.6 M in hexanes) at 0°C. After stirring for 17 hours, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were condensed in. 7.14 grams (95.0%) of the dilithio salt as an orange powder were isolated by filtration and *in vacuo* drying.

$Me_2C(3\text{-}(2\text{-methylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (7). 2.449 grams of $Me_2C(3\text{-}(2\text{-methylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (6.437 mmol) and 1.500 g $ZrCl_4$ (6.437 mmol) were combined in a swivel frit apparatus. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 16 hours of stirring. 20 mL of methylene chloride were condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted in a cellulose extraction thimble overnight with 150 mL diethyl ether. The volume of the filtrate was reduced to 30 mL and 0.823 grams (24.2%) of **7** as an orange powder were obtained following collection at 0°C and *in vacuo* drying. ^{1}H NMR shows all four possible diastereomers present in an approximate 1:1:1:1 ratio. MS (LC-MS) m/z 528.7 (M^+). ^{1}H NMR (C_6D_6): δ 0.59, 0.61, 0.61, 0.63 (s, 3H, cyclohexyl(CH_3)), 0.88 - 1.70 (m, 9H, cyclohexyl-*H*), 1.82, 1.82, 1.83, 1.83, 1.83, 1.85, 1.85, 1.87 (s, 6H, C(CH_3)$_2$), 2.89 (m, 1H, 1-*H*-cyclohexyl), 5.27, 5.32, 5.42, 5.44, 5.50, 5.53, 5.72, 5.90, 6.00, 6.08, 6.21, 6.24 (m, 3H, Cp-*H*), 6.93 - 7.36 (t, 4H, Flu-*H*), 7.41 - 7.87 (d, 4H, Flu-*H*). Elemental analysis calculated for $C_{28}H_{30}Zr_1Cl_2$: C, 63.61; H, 5.72. Found: C, 59.92; H, 5.42.

Preparation of 8.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)H_2$. 15.5 mL of an n-butyllithium solution (24.8 mmol, 1.6 M in hexanes) were syringed into a solution of fluorene (4.047 g, 24.35 mmol) in 60 mL tetrahydrofuran. After stirring for 45 minutes, 3-cyclohexyl-6,6-dimethylfulvene (4.58 g, 24.3 mmol) was injected via syringe. After stirring for 15 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)H_2$ (8.63 g, 24.3 mmol) in 50 mL 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 hours, the solvent was removed by vacuum transfer and 75 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield as a red-orange powder.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)ZrCl_2$ (8). 2.500 grams of $Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)Li_2$ (6.82 mmol) and 1.59 g $ZrCl_4$ (6.82 mmol) were combined in a swivel frit apparatus. 30 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 17 hours of stirring. 40 mL of methylene chloride were 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 were obtained for a total of 1.261 grams (35.9%) of **8** as an orange powder following collection at 0°C and *in vacuo* drying. MS (LC-MS) m/z 514.7 (M^+). ^1H NMR (C_6D_6): δ 0.87 - 1.26 (m, 10H, cyclohexyl-*H*), 1.81, 1.82 (s, 6 H, $C(CH_3)_2$), 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*). Elemental analysis calculated for $C_{27}H_{28}Zr_1Cl_2$: C, 63.01; H, 5.48. Found: C, 57.74; H, 5.53.

Preparation of 9.

4-*t*-butylcyclohexylfulvene. Pyrrolidine (1.0 mL, 12 mmol) was syringed into a solution of 4-*t*-butylcyclohexanone (9.30 g, 60.3 mmol) and cyclopentadiene (10.0 mL, 121 mmol) in 100 mL of methanol. The reaction was stirred for 68 hours before the yellow precipitate was collected by suction filtration. A second crop was obtained by condensing the filtrate to 50 mL. The total product massed 10.43 grams (85.5%) after *in vacuo* drying.

4-*t*-butylcyclohexylcyclopentadiene. 8.24 grams (40.7 mmol) of 4-*t*-butylcyclohexylfulvene were dissolved in 50 mL of tetrahydrofuran and this solution was added over 12 minutes to a stirred slurry of $LiAlH_4$ (2.20 g, 58.0 mmol) in 50 mL tetrahydrofuran at 0°C. After 16 hours of stirring at room temperature, the reaction was cooled to 0°C and quenched by dropwise addition of 60 mL of aqueous NH_4Cl. Then 300 mL of water were added; the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (4 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to give the product as a light yellow oil in quantitative yield (8.32 g).

3-(4-*t*-butylcyclohexyl)-6,6-dimethylfulvene.

To 4-*t*-butylcyclohexylcyclopentadiene (8.32 g, 40.7 mmol) was added 50 mL methanol, acetone (15.0 mL, 204 mmol) and pyrrolidine (5.0 mL, 60 mmol). After stirring for 72 hours, 5 mL of acetic acid were injected, followed by 300 mL H_2O and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (4 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and with 10% aqueous NaOH (3 x 30 mL), dried over $MgSO_4$, filtered and rotavapped. The product was obtained in quantitative yield (9.95 g) as a yellow liquid and further purified by passing the neat liquid through a short column of alumina.

$Me_2C(3\text{-}(4\text{-}t\text{-butylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)H_2$. 16.0 mL of an n-butyllithium solution (25.6 mmol, 1.6 M in hexanes) were syringed into a solution of fluorene (4.080 g, 24.55 mmol) in 60 mL tetrahydrofuran. After stirring for 60 minutes, 3-(4-*t*-butylcyclohexyl)-6,6-dimethylfulvene (6.00 g, 24.5 mmol) was injected via syringe. After stirring for 15 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped to give the product in quantitative yield (10.08 g) as a light yellow oil.

$Me_2C(3\text{-}(4\text{-}t\text{-butylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(4\text{-}t\text{-butylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)H_2$ (10.08 g, 24.5 mmol) in 50 mL diethyl ether with 32.0 mL of n-butyllithium solution (51.2 mmol, 1.6 M in hexanes) at 0°C. After stirring for 17 hours, the solvent was removed by vacuum transfer and 100 mL of petroleum ether were condensed in. 9.27 grams (89.4%) of the dilithio salt as a red-orange powder were isolated by filtration and *in vacuo* drying.

$Me_2C(3\text{-}(4\text{-}t\text{-butylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (9). 1.813 grams of $Me_2C(3\text{-}(4\text{-}t\text{-butylcyclohexyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (4.29 mmol) and 1.00 g $ZrCl_4$ (4.29 mmol) were combined in a swivel frit apparatus. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 21 hours of stirring. 50 mL of methylene chloride were condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted in a cellulose extraction thimble overnight with 150 mL diethyl ether. 0.507 grams (20.7%) of **9** as an orange powder were obtained following collection at 0°C and *in vacuo* drying. ^{1}H NMR shows two diastereomers present in a 73:27 ratio. MS (LC-MS) *m*/*z* 570.8 (M^+). Major diastereomer: ^{1}H NMR (C_6D_6): δ 0.73 (s, 9H, C(C*H*$_3$)$_3$) 0.76 - 1.85 (m, 9H, cyclohexyl-*H*), 1.83, 1.83 (s, 6 H, C(C*H*$_3$)$_2$), 2.50 (m, 1H, 1-*H*-cyclohexyl), 5.40, 5.43, 6.24 (m, 3H, Cp-*H*), 7.01, 7.04, 7.31, 7.35 (t, $^3J_{HH}$ = 6.6, 7.7, 7.7, 7.3 Hz, 4H, Flu-*H*), 7.44, 7.47, 7.84, 7.86 (d, $^3J_{HH}$ = 9.1, 8.8, 7.3, 7.3 Hz, 4H, Flu-*H*). Minor diastereomer: ^{1}H NMR (C_6D_6): δ ^{1}H NMR (C_6D_6): δ 0.77 (s, 9H, C(C*H*$_3$)$_3$) 0.76 - 1.85 (m, 9H, cyclohexyl-*H*), 1.81, 1.81 (s, 6 H, C(C*H*$_3$)$_2$), 2.50 (m, 1H, 1-*H*-cyclohexyl), 5.31, 5.43, 6.09 (m, 3H, Cp-*H*), 7.01, 7.04, 7.31, 7.35 (t, $^3J_{HH}$ = 6.6, 7.7, 7.7, 7.3 Hz, 4H, Flu-*H*), 7.44, 7.47, 7.84, 7.86 (d, $^3J_{HH}$ = 9.1, 8.8, 7.3, 7.3 Hz, 4H, Flu-*H*). Elemental analysis calculated for $C_{31}H_{36}Zr_1Cl_2$: C, 65.24; H, 6.36. Found: C, 55.68; H, 5.82.

Preparation of 10.

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

norbornylcyclopentadiene. A solution of norbornylfulvene (14.37 g, 90.8 mmol) dissolved in 100 mL tetrahydrofuran was cooled to 0°C before $LiAlH_4$ (5.00 g, 132 mmol) was added over 2 minutes. After stirring at room temperature for 17 hours, the reaction was cooled to 0°C and 100 mL water were added dropwise over 1 hour. Then, 200 mL water/50 mL concentrated aqueous HCl and 100 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the crude product as a light yellow oil in quantitative yield.

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

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

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

$Me_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (10). In the glove box, 2.44 grams of $Me_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)Li_2$ (6.44 mmol) were combined with $ZrCl_4$ (1.50 g, 6.44 mmol) in a 100 mL round bottom flask. This was equipped with a 180° needle valve and 40 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 24 hours of stirring, solvent was removed. Then 30 mL of dichloromethane were added and removed, followed by addition and removal of 30 mL diethyl ether. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of diethyl ether. The filtrate volume was reduced to 30 mL and the precipitated product was collected on a swivel frit and dried *in vacuo*: 1.26 grams of **5** (37.2%) in a 54:46 diastereomeric ratio. MS (LC-MS) *m/z* 526.6 (M^+). Major diastereomer (54%): ^{1}H NMR (C_6D_6): δ 1.01 - 1.35 (m, 8H, norbornyl-*H*), 1.89 - 2.07 (m, 2H, norbornyl-*H*), 1.82, 1.83 (s, 6 H, $C(CH_3)_2$), 3.20 (m, 1H, 2-*H*-norbornyl), 5.42, 5.45, 6.09 (t, $^3J_{HH}$ = 3.3, 3.3, 2.9 Hz, 3H, Cp-*H*), 7.00, 7.03, 7.35, 7.35 (t, $^3J_{HH}$ = 7.7, 7.7, 7.3, 7.3 Hz, 4H, Flu-*H*), 7.45, 7.47, 7.84, 7.86 (d, $^3J_{HH}$ = 8.1, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 23.52, 29.71, 34.05, 37.25, 40.13, 41.00, 43.61, (norbornyl-*C*), 28.58, 28.66 (CH_3), 40.51 (CH_3CCH_3), 65.70, 79.12, 114.31, 122.59, 122.88, 123.15, 140.29 (Cp- and Flu-CH_0), 102.73, 103.79, 116.17 (Cp-CH_1), 123.49, 123.58, 124.64, 124.74, 124.80, 124.84, 128.76, 128.84 (Flu-CH_1). Minor diastereomer (46%): ^{1}H NMR (C_6D_6): δ 1.01 - 1.35 (m, 8H, norbornyl-*H*), 1.89 - 2.07 (m, 2H, norbornyl-*H*), 1.79, 1.83 (s, 6 H, $C(CH_3)_2$), 3.13 (m, 1H, 2-*H*-norbornyl), 5.23, 5.54, 6.04 (t, $^3J_{HH}$ = 3.0, 2.9, 2.9 Hz, 3H, Cp-*H*), 6.98, 7.03, 7.30, 7.30 (t, $^3J_{HH}$ = 7.7, 7.7, 7.7, 7.7 Hz, 4H, Flu-*H*), 7.43, 7.45, 7.83, 7.84 (d, $^3J_{HH}$ = 8.4, 8.1, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 23.68, 29.80, 34.17, 36.97, 39.39, 41.53, 43.29, (norbornyl-*C*), 28.58, 28.58 (CH_3), 40.55 (CH_3CCH_3), 65.65, 79.02, 113.27, 122.55, 122.88, 123.40, 138.57 (Cp- and Flu-CH_0), 102.31, 103.69, 117.44 (Cp-CH_1), 123.37, 123.71, 124.64, 124.74, 124.80, 124.84, 128.84, 128.92 (Flu-*C*H_1). Elemental analysis calculated for $C_{28}H_{28}Zr_1Cl_2$: C, 63.86; H, 5.36. Found: C, 61.78, 61.58; H, 5.03, 5.23.

Preparation of 11.

6,6'-(tricyclo[3.3.1.1]decane)fulvene (adamantylfulvene). (Synthesis modified from reference 20) 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 hours before the yellow precipitate was collected by suction filtration, rinsed with a small volume of methanol and dried *in vacuo*. 25.71 grams (77.9%) of adamantylfulvene were 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). Elemental analysis calculated for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.20, 90.22; H, 8.39, 8.50.

2-adamantylcyclopentadiene. 6.00 grams (30.3 mmol) of adamantylfulvene were dissolved in 30 mL of tetrahydrofuran and this solution added over 30 minutes to at stirred slurry of $LiAlH_4$ (1.40 g, 0.0369 mol) at 0°C. After 5 hours 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 H_2O, 25 mL concentrated HCl, and 50 mL diethyl ether were added, the organic layer isolated, and the aqueous layer extracted with addition diethyl ether (3 x 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 methanol, 50 mL ethanol, 20 mL tetrahydrofuran, 36 mL acetone (0.49 mol) and 0.5 mL pyrrolidine (0.006 mol). After stirring for 48 hours, 5 mL of acetic acid were injected, followed by 200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 40 mL). The combined organic layers were extracted with H_2O (3 x 25 mL) and with 10% aqueous NaOH (3 x 25 mL), dried over $MgSO_4$, filtered and rotavapped. The obtained yellow solid was further purified by overnight Soxhlet extraction by 150 mL 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. Elemental analysis calculated for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 82.23, 82.23; H, 8.78, 8.82.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$. 10.5 mL of an n-butyllithium solution (1.6 M in hexanes, 0.0168 mol) was syringed into a solution of sublimed fluorene (2.77 g, 0.0166 mol) in 60 mL tetrahydrofuran. After stirring for 5 hours, a solution of 3-(2-adamantyl)-6,6-dimethylfulvene (4.00 g, 0.0166 mol) in 40 mL tetrahydrofuran was injected over 2 minutes. After stirring for 20 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer isolated, and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$ (6.77 g, 16.6 mmol) in 75 mL 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 hours, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield as an orange powder.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (11). 2.00 grams of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$ (0.00478 mol) and 1.114 g sublimed $ZrCl_4$ (0.00478 mol) were combined in a swivel frit apparatus. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 14 hours of stirring. 40 mL of methylene chloride were 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 grams (55.5%) of **2** as an orange powder following collection at 0°C and *in vacuo* drying. MS (LC-MS) *m/z* 566.5 (M^+). ^1H NMR (C_6D_6): δ 1.36 - 2.04 (m, 14H, adamantyl-*H*), 1.84, 1.86 (s, 6 H, $C(CH_3)_2$), 3.32 (s, 1H, 2-*H*-adamantyl), 5.44, 5.48, 6.18 (m, 3H, Cp-*H*), 6.95, 7.03, 7.29, 7.34 (t, $^3J_{HH}$ = 7.7, 7.7, 8.0, 8.0 Hz, 4H, Flu-*H*), 7.41, 7.49, 7.84, 7.84 (d, $^3J_{HH}$ = 8.8, 9.1, 7.7, 7.7 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.58, 28.65, (CH_3), 27.90, 27.93, 31.98, 32.41, 32.62, 32.66, 37.84, 38.50, 38.66 (adamantyl-*C*), 43.83 (2-*C*-adamantyl), 102.56, 103.02, 116.65 (Cp-CH_1), 123.41, 123.67, 124.61, 124.67, 124.76, 124.83, 128.81, 128.81 (benzo-CH_1), 139.93 (9-Flu-*C*), CH_0, not determined. Elemental analysis calculated for $C_{31}H_{32}ZrCl_2$: C, 65.70; H, 5.69. Found: C, 63.46, 61.93; H, 5.57, 5.42.

Preparation of 12.

3, 3, 5, 5-tetramethylcyclohexylfulvene. Hexane washed sodium spheres (2.40 g, 104 mmol) were slowly added to 100 mL absolute ethanol. The sodium had full reacted before cyclopentadiene (6.0 mL, 72.6 mmol) and 3, 3, 5, 5-tetramethylcyclohexanone (10.0 mL, 57.1 mmol) were added. After 30 hours, the reaction was poured into 200 mL water and 100 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL), dried over $MgSO_4$, filtered, and rotavapped to produce the product in quantitative yield as a yellow oil. MS (GC-MS) *m/z* 202.3 (M^+).

1-(cyclopentadienyl)-3, 3, 5, 5-tetramethylcyclohexane. A 500 mL flask was charged with $LiAlH_4$ (2.50 g, 65.9 mmol) and 200 mL tetrahydrofuran. An addition funnel containing 3, 3, 5, 5-tetramethylcyclohexylfulvene (11.89 g, 58.8 mmol) dissolved in 50 mL tetrahydrofuran was attached. The vessel was cooled to 0°C before dropwise addition over 25 minutes. After 17 hours of stirring at room temperature, the vessel was cooled to 0°C and 20 mL of water were added dropwise. Then, aqueous NH_4Cl (100 mL) and water (200 mL) were added before the organic layer was isolated. 15 mL of concentrated aqueous HCl were added to the aqueous layer and it was extracted with diethyl ether (3 x 50 mL).

The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide 11.87 grams of product (98.8%) as a light orange oil. MS (GC-MS) *m/z* 204.3 (M^+).

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

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

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

$Me_2C(3\text{-}(3, 3, 5, 5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (12). In the glove box, 1.81 grams of $Me_2C(3\text{-}(3, 3, 5, 5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)Li_2$ (4.29 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 15 hours of stirring, solvent was removed. 40 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal. Then, 30 mL of diethyl ether were condensed in and the slurry was warmed and stirred. The obtained orange solid was extracted several times on the frit with refluxing diethyl ether before the filtrate was condensed to 20 mL. The precipitate was collected on the frit and dried *in vacuo* to afford the product **12**: 0.16 grams (6.6%). Second and third crops were obtained: 0.13 g and 0.23 g (21.2% for all three crops). MS (LC-MS) *m / z* 570.6 (M^+). ^1H NMR (C_6D_6): δ 0.78, 0.81, 1.00, 1.01 (s, 12H, cyclohexyl(CH_3)), 0.88 - 1.12 (m, 6H, cyclohexyl-*H*), 1.83, 1.86 (s, 6 H, $C(CH_3)_2$), 3.03 (t, $^3J_{HH}$ = 12.4 Hz, 1H, 1-*H*-cyclohexyl), 5.41, 5.43, 6.13 (t, $^3J_{HH}$ = 4.0, 4.0, 4.0 Hz, 3H, Cp-*H*), 6.94, 7.03, 7.30, 7.34 (t, $^3J_{HH}$ = 8.0, 8.8, 8.1, 7.3 Hz, 4H, Flu-*H*), 7.49, 7.49, 7.81, 7.82 (d, $^3J_{HH}$ = 8.8, 8.8, 7.7, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 26.77, 27.23, 28.47, 28.52, 28.62, 28.67 (CH_3), 31.44 (1-cyclohexyl-*C*), 32.05, 39.71, 40.50, 43.45, 49.00, 52.01 (cyclohexyl and Me*C*Me CH_0 and CH_2), 102.69, 102.74, 115.19 (Cp-CH_1), 123.56, 123.58, 123.58, 124.62, 124.73, 124.73, 124.78, 124.80 (benzo-CH_1), 141.29 (9-Flu-*C*), CH_0, not determined. Elemental analysis calculated for $C_{31}H_{36}Zr_1Cl_2$: C, 65.24; H, 6.36. Found: C, 60.96, 61.75; H, 5.53, 5.60.

Preparation of 13.

6,6-diphenylfulvene. (Synthesis modified from reference 26) 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 ethanol. The solid was refluxed in 200 mL methanol for 1 hour. Upon cooling the solid was collected, rinsed with 75 mL methanol, and dried *in vacuo* for 48 hours to provide the product as an orange powder: 136.18 g (86.2%). MS (GC-MS) *m/z* 230.3 (M^+). Elemental analysis calculated 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 tetrahydrofuran. An addition funnel containing 6,6-diphenylfulvene (20.00 g, 86.84 mmol) dissolved in 100 mL tetrahydrofuran was attached. The vessel was cooled to 0°C before dropwise addition over 45 minutes. After 22 hours of stirring at room temperature, the vessel was cooled to 0°C and 60 mL of aqueous NH_4Cl solution were added dropwise. Then, 300 mL water and 20 mL of concentrate aqueous HCl were added before the organic layer was isolated. The aqueous layer was extracted with diethyl ether (3 x 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 methanol, acetone (20.0 mL, 272 mmol), and pyrrolidine (5.0 mL, 60 mmol). After stirring for 67 hours, the yellow precipitate was collected by suction filtration, was washed with 20 mL methanol, and was dried *in vacuo*: 8.24 grams (70.3%).

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{29}H_{36})H_2$. A 250 mL flask was charged with octamethyloctahydrodibenzofluorene (2.988 g, 7.729 mmol), evacuated, and backfilled with argon before 60 mL tetrahydrofuran and 5.2 mL n-butyllithium solution (8.3 mmol, 1.6 M in hexanes) were syringed in. The orange solution was stirred for 4 hours before a solution of 3-(diphenylmethyl)-6,6-dimethylfulvene (2.105 g, 7.728 mmol) in 25 mL tetrahydrofuran was syringed in. Following an additional 30 hours, the stirred reaction was quenched by slow addition of 60 mL aqueous NH_4Cl. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{29}H_{36})Li_2$. A round bottom flask containing 5.093 grams (7.728 mmol) of $Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{29}H_{36})H_2$ was attached to a swivel frit and evacuated before 50 mL of diethyl ether were condensed in. At 0°C, 10.4 mL of n-butyllithium solution (16.6 mmol, 1.6 M in hexanes) were syringed in over 2 minutes. After stirring for 26 hours at room temperature, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield (5.185 g) as an orange powder.

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (13). In the glove box, 2.879 grams of $Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{29}H_{36})Li_2$ (4.29 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 17 hours of stirring, solvent was removed. 20 mL of methylene chloride were 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 grams of **13** (22.6%). MS (LC-MS) m/z 818.8 (M^+). ^1H NMR (C_6D_6): δ 1.08, 1.20, 1.23, 1.29, 1.30, 1.30, 1.51, 1.58 (s, 24H, Oct-CH_3), 1.63 (m, 8H, Oct-CH_2), 1.90, 2.04 (s, 6H, $(CH_3)_2C$-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, $CHPh_2$), 6.91 - 7.15 (m, 10H, phenyl-*H*), 7.46, 6.65, 8.29, 8.31 (s, 4H, Oct-*H*). Elemental analysis calculated for $C_{50}H_{56}Zr_1Cl_2$: C, 73.32; H, 6.89. Found: C, 65.09; H, 6.86.

Preparation of 14.

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)H_2$. A 250 mL flask was charged with fluorene (3.661 g, 22.03 mmol), evacuated, and backfilled with argon before 50 mL tetrahydrofuran and 14.0 mL n-butyllithium solution (22.4 mmol, 1.6 M in hexanes) were syringed in. The orange solution was stirred for 1 hour before a solution of 3-(diphenylmethyl)-6,6-dimethylfulvene (6.00 g, 22.03 mmol) in 15 mL tetrahydrofuran was syringed in. Following an additional 16 hours, the stirred reaction was quenched by slow addition of 60 mL aqueous NH_4Cl. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)Li_2$. A round bottom flask containing 9.66 grams (22.0 mmol) of $Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)H_2$ was attached to a swivel frit and evacuated before 75 mL of diethyl ether were condensed in. At 0°C, 28.0 mL of n-butyllithium solution (44.8 mmol, 1.6 M in hexanes) were syringed in over 2 minutes. After stirring for 18 hours at room temperature, the red precipitate was collected and dried *in vacuo* to provide the product in quantitative yield (9.92 g).

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)ZrCl_2$ (14). In the glove box, 1.933 grams of $Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)Li_2$ (4.29 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 24 hours of stirring solvent was removed. 50 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal. The solid was extracted for 64 hours 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 grams of **14** (59.2%). MS (LC-MS) m/z 598.5 (M^+). ^1H 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*). Elemental analysis calculated for $C_{34}H_{28}Zr_1Cl_2$: C, 68.21; H, 4.71. Found: C, 52.61; H, 3.82.

Preparation of 15.

6,6'-(tricyclo[3.3.1.1]decane)fulvene (adamantylfulvene). 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 liter round bottom flask. After stirring for 77 hours, the yellow precipitate was collected by suction filtration and washed with 50 mL methanol. After *in vacuo* drying, 49.56 grams adamantylfulvene were obtained (83.4%). MS (GC-MS) *m* / *z* 198.3 (M^+). Elemental analysis calculated for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.20, 90.22; H, 8.39, 8.50.

3-(2-methyl-2-adamantyl)-6,6-dimethylfulvene. A 500 mL flask was charged with adamantylfulvene (18.00 g, 90.77 mmol), equipped with a 180° needle valve, and charged with 120 mL 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 minutes. Dimethoxyethane (10 mL) was syringed in and the reaction was stirred at room temperature for 8 days when 60 mL aqueous NH_4Cl solution were slowly added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried *in vacuo* to provide 19.46 grams of (2-methyl-2-adamantyl)cyclopentadiene as a light yellow oil (theoretical yield). To this was added 30 mL acetone (409 mmol), 100 mL methanol, and 10 mL pyrrolidene (120 mmol). After stirring for 96 hours, the yellow precipitate was collected by filtration, rinsed with 50 mL 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$_0$). Elemental analysis calculated for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.57; H, 10.04.

$Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. 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 aqueous NH_4Cl were slowly added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide $Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)H_2$ in theoretical yield (13.23 g). The flask was attached to a swivel frit and charged with 50 mL diethyl ether before n-butyllithium solution (42.0 mL, 67.2 mmol, 1.6 M in hexanes) was syringed in over 4 minutes at 0°C. After 23 hours, solvent is removed and 75 mL petroleum ether are added by vacuum transfer. The red solid is broken up, stirred, collected on the frit, and dried *in vacuo*: 15.85 grams (13.60 g theoretical yield).

$Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (15). A 100 mL flask was charged with $Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (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 hours, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL 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^+). ^1H NMR (C_6D_6): δ 1.32 - 2.62 (m, 14H, adamantyl-*H*), 1.73, 1.85, 1.89 (s, 9H, CH_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, (CH_3), 41.68 (2-*C*-adamantyl), 42.07 (2-CH_3-adamantyl), 102.54, 105.28, 120.28 (Cp-CH_1), 123.81, 124.17, 124.36, 124.46, 124.51, 125.25, 127.94, 129.10 (benzo-CH_1), 112.14, 120.68, 123.68, 125.72, 127.82, 129.55, 139.05, 145.94 (CH_0). Elemental analysis calculated for $C_{32}H_{34}Zr_1Cl_2$: C, 66.18; H, 5.90. Found: C, 57.60; H, 5.23.

Preparation of 16.

$Me_2C(3\text{-}(3, 3, 5, 5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)HfCl_2$ (16). In the glove box, 1.649 grams of $Me_2C(3\text{-}(3, 3, 5, 5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)Li_2$ (3.903 mmol) were combined with $HfCl_4$ (1.250 g, 3.903 mmol) in a 100 mL round bottom flask. This was attached to a 180° needle valve and 50 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 41 hours of stirring, solvent was removed. 20 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal. Then, 30 mL of diethyl ether were condensed in and the slurry was warmed and stirred. Solvent was removed and the obtained orange solid was extracted in a cellulose extraction thimble overnight with 150 mL diethyl ether. The volume of the filtrate was reduced to 30 mL and the yellow precipitate was collected on the frit and dried *in vacuo* to afford the product **16**: 0.305 grams (11.9%). MS (LC-MS) m/z 658.7 (M^+). ^1H NMR (C_6D_6): δ 0.77, 0.82, 1.00, 1.01 (s, 12H, cyclohexyl(CH_3)), 0.86 - 1.13 (m, 6H, cyclohexyl-*H*), 1.84, 1.87 (s, 6 H, $C(CH_3)_2$), 3.05 (t, $^3J_{HH}$ = 12.4 Hz, 1H, 1-*H*-cyclohexyl), 5.36, 5.38, 6.08 (t, $^3J_{HH}$ = 2.6, 3.3, 2.6 Hz, 3H, Cp-*H*), 6.93, 7.02, 7.28, 7.32 (t, $^3J_{HH}$ = 7.7, 7.3, 8.4, 8.4 Hz, 4H, Flu-*H*), 7.43, 7.55, 7.80, 7.82 (d, $^3J_{HH}$ = 8.8, 9.1, 4.0, 4.0 Hz, 4H, Flu-*H*). Elemental analysis calculated for $C_{31}H_{36}Hf_1Cl_2$: C, 56.58; H, 5.51. Found: C, 42.79; H, 4.48.

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 6110 drying system equipped with an OXYSORB™ column. Polymerizations were conducted in a 3 oz. Lab Crest glass reaction vessel and were stirred with a magnetic stir bar. Monomer was condensed into the vessel over several minutes at 0°C. The vessel was then equilibrated at either 0°C or at 20°C with an ice or water bath for 10 minutes. A given reaction commenced upon injection of a toluene solution of the metallocene into the vessel with a 2.5 mL Hamilton syringe rated to 200 psi. Temperature maintenance was monitored by an affixed pressure gauge. Polymerization reactions were vented and quenched with a small volume of methanol/concentrated HCl (12:1) and the polymers were separated from hydrolyzed aluminoxanes by precipitation from methanol, followed by filtration. Residual amounts of toluene and methanol were removed from the obtained polymers by *in vacuo* drying. See Table 7 for complete polymerization results.

The pentad distributions for those polymers prepared at 20°C (only those for T_p = 0°C are shown in the text) and for polymerization Entries 1 - 6 are as follows:

metallocene	**5**	**6**	**7**	**8**	**2**	**9**	**10**	**11**	**16**
mmmm	2.4	7.3	15.1	14.5	18.3	22.7	28.0	31.4	45.6
mmmr	3.5	7.5	10.3	11.0	11.6	12.7	13.3	14.7	15.3
rmmr	3.7	4.1	5.4	6.4	5.5	5.3	4.8	4.5	2.6
mmrr	9.5	14.9	20.0	22.7	22.5	22.6	21.7	23.1	14.5
mmrm + rrmr	4.1	7.2	3.5	1.9	1.9	1.3	2.2	0.9	4.7
mrmr	3.3	1.8	1.4	0.9	0.8	0.7	1.0	0.4	1.4
rrrr	55.8	36.5	25.0	21.5	21.3	16.3	12.3	8.2	5.7
rrrm	12.9	15.6	12.6	13.2	11.7	10.4	9.4	8.5	3.1
mrrm	4.8	5.0	6.7	7.9	6.5	8.1	7.3	8.4	6.9

metallocene	**12**	**13**	**14**	Ent 1	Ent 2	Ent 3	Ent 4	Ent 5	Ent 6
mmmm	47.9	76.4	81.2	26.4	26.0	27.2	28.4	34.2	40.1
mmmr	14.3	11.9	7.1	14.3	14.6	15.7	16.5	16.8	16.4
rmmr	2.8	0.0	0.0	6.5	5.9	4.5	3.7	2.9	3.0
mmrr	16.8	8.4	7.9	23.2	23.6	22.7	20.2	17.4	15.8
mmrm + rrmr	2.0	0.0	0.0	2.2	2.2	3.0	5.5	6.6	6.4
mrmr	1.2	0.0	0.0	0.6	0.6	0.6	1.2	2.7	2.1
rrrr	4.0	0.0	0.0	9.6	9.9	8.9	6.3	3.7	2.7
rrrm	4.1	0.0	0.0	9.0	9.1	8.2	7.7	5.8	4.8
mrrm	6.9	3.3	3.8	8.3	8.0	9.1	10.4	9.8	8.8

Table 7. Results of MAO-cocatalyzed polymerizations. [a]

Met. (mg)	T_p (°C)	Time (min.)	Yield (g)	Activity gP / (gmet·h)	T_m [b] (°C)	[m] (%)	M_w	M_w / M_n
4 (2.0)	0	10	1.16	3500	154	2.5	535,000	2.00
4 (2.0)	20	10	4.79	14000	153		310,000	2.03
5 (1.5)	0	15	0.37	980	130	14.6		
5 (1.5)	20	5	0.83	6600	117	18.1		
6 (2.0)	0	20	0.36	530	103	22.0		
6 (2.0)	20	20	5.55	8300	n.o.	30.9		
7 (1.0)	0	15	0.92	3700	n.o.	40.0		
7 (1.0)	20	10	3.90	23000	n.o.	43.2		
8 (1.0)	0	10	0.71	4300	n.o.	41.7		
8 (1.0)	20	10	4.01	24000	n.o.	44.6		
2 (1.0)	0	15	1.43	5700	n.o.	50.4	80,000	1.81
2 (1.0)	20	10	4.95	30000	n.o.	48.0		
9 (1.0)	0	30	0.98	2000	n.o.	54.7		
9 (1.0)	20	15	3.02	12000	n.o.	53.0		
10 (1.0)	0	15	1.31	5200	n.o.	57.6	105,000	1.93
10 (1.0)	20	10	3.74	22000	n.o.	58.4		
11 (0.5)	0	30	1.50	6000	n.o.	62.3	134,000	3.15
11 (0.5)	20	10	1.08	13000	n.o.	62.7	81,900	4.38
16 (5.0)	0	60	0.03	6	76	71.3		
16 (5.0)	20	60	0.65	130	74	73.9		
12 (2.0)	0	30	1.57	1600	98	75.3	77,400	2.01
12 (2.0)	20	15	3.54	7100	91	75.0		
13 (2.7)	0	20	0.05	60	125	89.2		
13 (2.7)	20	20	0.14	150	135	92.5		
14 (2.0)	0	20	0.32	480	137	94.7		
14 (2.0)	20	20	0.47	710	138	92.3		
15 (2.0)	0	10	1.38	4100	159	>98	160,000	1.91
15 (2.0)	20	10	2.13	6400	156	>98	124,000	1.90
Entry 1	0	30	0.13	510	n.o.	60.1		
Entry 2	20	10	0.25	2900	n.o.	59.8		
Entry 3	40	10	0.44	5300	n.o.	60.6		
Entry 4	60	10	0.18	2100	n.o.	62.1		
Entry 5	75	30	0.15	610	n.o.	67.3		
Entry 6	90	60	0.21	420	n.o.	71.6		

[a] 1000 equivalents MAO and 2.0 mL toluene, except polymerizations with **11** used 2000 equivalents MAO and 1.0 mL toluene; 30 mL propylene, except polymerizations with **15** used 55 mL propylene. Entries 1 - 6 employed 0.5 mg of metallocene **11**, 2000 equivalents MAO, 30.0 mL toluene and 3 mL propylene. [b] n.o. = not observed.

Representative Polymerization Procedures.

Polymerization with 12 at 0°C. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.203 g, 3.50 mmol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of **12** (0.002 g, 3.5×10^{-3} mmol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 30 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Polymerization with 12 at 20°C. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.203 g, 3.50 mmol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of **12** (0.002 g, 3.5×10^{-3} mmol) in toluene (2.0 mL) was injected and the reaction stirred in a 20°C water bath for 15 minutes. 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/minute) 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.[27] 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 seconds and a minimum of 1000 scans were used.

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13. The forbidden pentad intensity could also arise from site epimerization processes, which will be ignored for the present model.

14. Obviously, mr and rm triads occur in hemiisotactic polypropylene as in mmrrmmmmrr; mr an rm triads are considered stereodefective when they replace mm or rr triads otherwise present in a sequence, as in (mm)(rr)(mr)(mm)(rr).

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

16. See Appendix H for a detailed explanation of the equations shown in Figure 12.

17. A similar principal mode of stereoerror formation has been suggested for doubly bridged C_1-symmetric metallocene catalysts. Veghini, D.; Henling, L.; Burkhardt, T.; Bercaw, J. E. *J. Amer. Chem. Soc.* **1999** *121*, 564-573.

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Chapter 5

Isotactic-hemiisotactic Polypropylene Formation with C_1-symmetric, Bridged Metallocene Catalysts: A New Strategy for the Synthesis of Elastomeric Polypropylene

ABSTRACT: Isotactic-hemiisotactic polypropylene has a tacticity in which every other stereocenter is of the same configuration and the intervening stereocenters tend to align with their neighbors. Control of this alignment, as quantified by the parameter α, is achieved by proper R substituent selection in the catalyst system $R'_2C(3\text{-}R\text{-}C_5H_3)(C_{13}H_8)MCl_2$ / MAO. For R = 2-adamantyl, R' = Ph, and M = Zr or Hf, α is approximately 0.60 and the isotactic-hemiisotactic polypropylene obtained is elastomeric. Its properties are rationalized by the statistical existence of isotactic stereoblocks among an otherwise amorphous hemiisotactic medium. The isotactic block length distribution can be calculated: for a chain with M_n = 200,000 and α = 0.62, there are 15 isotactic blocks of 21 monomer units or longer, and the longest contains 27 units.

5.1 Introduction

The mechanical properties of a given polymer can generally be classified as rigid, flexible, or elastic. While metallocene catalysts are capable of producing polymers that fall into each of these classifications, the most intense efforts have been directed at surpassing existing systems in their aptitude for making rigid isotactic polypropylene and rigid or flexible polyethylene.[1] More recently, growing efforts to devise metallocene catalysts capable of producing elastomeric polymers have revealed several different viable strategies: ethylene/α-olefin copolymers[2]; high molecular weight atactic polypropylene[3]; binary isotactic/atactic compatibilized polypropylene[4]; isotactic-atactic polypropylene[5]; stereoblock isotactic-atactic polypropylene[6]; and isotactic polypropylene with controllable stereoerror sequences.[7] Although the structure/property relationship of each of these regimes is not fully understood, the elastomeric properties undoubtedly rely on the existence of physical crosslinks in the presence of an amorphous phase. In the case of high molecular weight materials, the crosslinks can be simple chain entanglements. In the other examples, segments from several different polymer chains participate in crystalline regions, which physically connect the chains and provide crosslinks in an otherwise amorphous phase.

One of the best understood systems is that initially developed by Coates and Waymouth.[6,8] Their unbridged metallocene (2-phenylindenyl)$_2$ZrCl$_2$, in the presence of methylaluminoxane (MAO), isomerizes between chiral and achiral coordination geometries during the formation of a given polypropylene chain. Since the chiral isomer is isospecific and the achiral isomer is aspecific, stereoblock isotactic-atactic polypropylene is obtained.

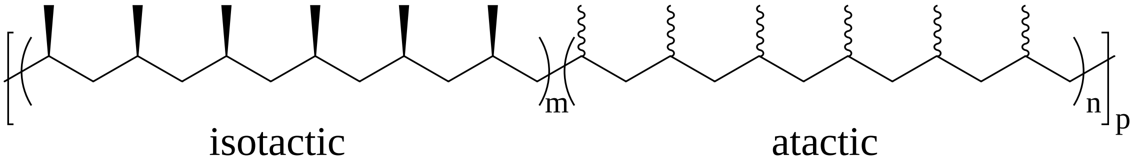


Figure 1. Stereoblock isotactic-atactic polypropylene.

Owing to the chelate effect, bridged metallocene catalysts tend to be more stable at elevated polymerization temperatures, and often behave more predictably when adsorbed on a support, a common industrial tactic. With this in mind, we sought to devise a bridged metallocene catalyst that provided isotactic polypropylene segments to participate in crystallites, but formed hemiisotactic polypropylene segments—instead of atactic—to constitute the amorphous phase. As the amorphous phase in an elastomer, hemiisotactic polypropylene might impart new and interesting properties in an elastomeric isotactic-hemiisotactic regime.

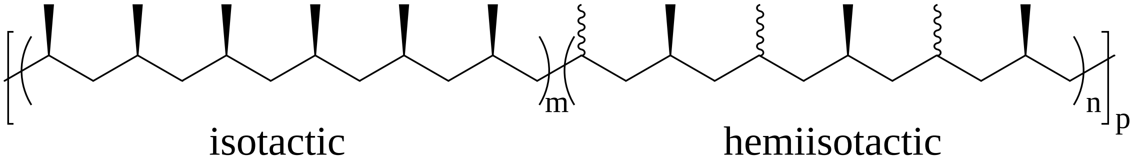


Figure 2. Stereoblock isotactic-hemiisotactic polypropylene.

5.2 Catalyst Design

Isotactic polypropylene is obtained when monomer insertions occur via the same enantioface (Figure 3, $\alpha = 1$). Hemiisotactic polypropylene is obtained when every other monomer inserts with the same enantioface and the intervening monomers insert aspecifically ($\alpha = 0.5$). Finally, syndiotactic polypropylene is obtained when every other monomer inserts with the same enantioface and the intervening monomers insert via the opposite enantioface ($\alpha = 0$). By modifying the hemiisospecific metallocene precatalyst $Me_2C(3\text{-methyl-}C_5H_3)(C_{13}H_8)ZrCl_2$ **1** developed by Ewen and Razavi,[9] it is possible to arrive at the desired isotactic-hemiisotactic microstructure. There are two very important catalyst design features.

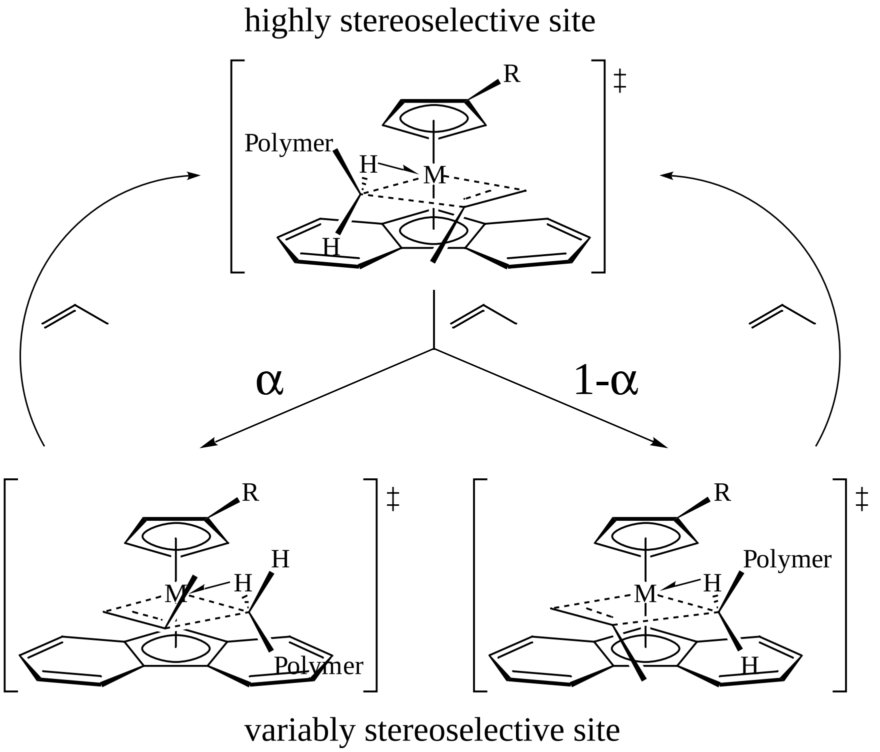
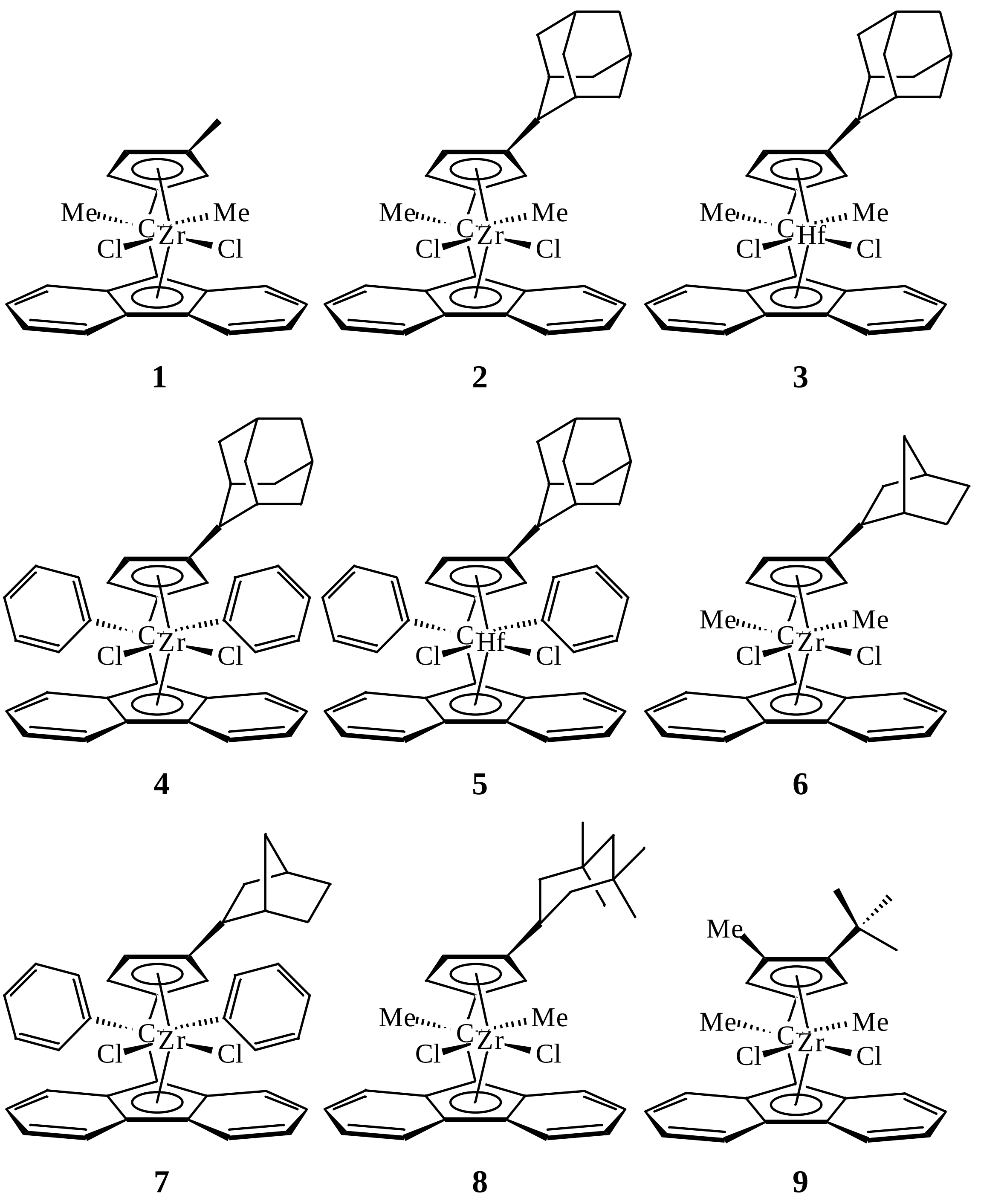


Figure 3. Proposed two-site mechanism for propylene polymerization at a C_1-symmetric metallocene having one highly stereoselective site and one variably stereoselective site.

The first is proper selection of the R substituent at the 3 position of the cyclopentadienyl ring. This allows one to control the specificity at the variably stereoselective site (Figure 3).[10] For R = methyl, the parameter α is 0.50 and the intervening stereocenters tend to be stereorandom with respect to their neighbors, yielding amorphous hemiisotactic polypropylene.[11] For R = 3,3,5,5-tetramethylcyclohexyl, α is 0.75 and the intervening stereocenters tend to be substantially aligned with their neighbors, resulting in a crystalline, rigid material (T_m = 98°C). However, if R = 2-adamantyl, α has an intermediate value near 0.60, the intervening stereocenters are moderately aligned with their neighbors, and polypropylene incorporating both amorphous and crystalline phases can be acquired.

The second important design feature is the metallocene bridge, as this impacts the molecular weight of the polymer.[12] The statistical likelihood of obtaining isotactic segments capable of participating in crystallites is proportional to the molecular weight, as is the statistical likelihood of obtaining hemiisotactic segments long enough to behave as amorphous connectors of these crystallites. For these reasons the elastomeric properties will be very sensitive to molecular weight.

Several catalyst systems have been prepared that meet the required design features and provide elastomeric polypropylene. Figure 4 describes several metallocene dichloride catalyst precursors investigated which, when combined with MAO, make isotactic-hemiisotactic polypropylene. Figure 5 illustrates the single crystal X-ray structure of metallocene precatalyst **4**.[13]



1 2 3

4 5 6

7 8 9

Figure 4. Metallocene dichloride precatalysts investigated for isotactic-hemiisotactic polypropylene formation.

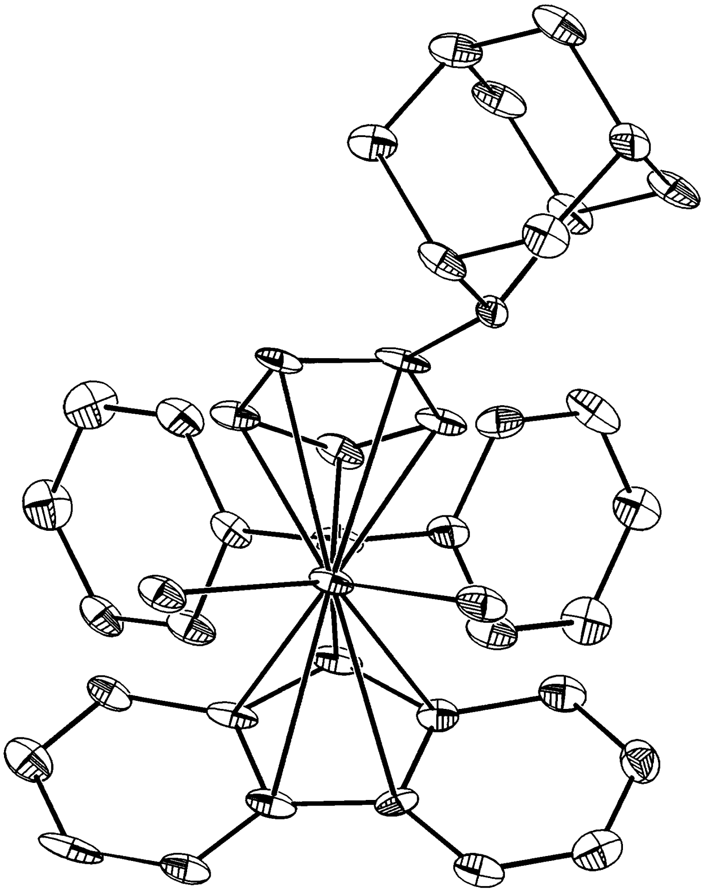


Figure 5. X-ray crystal structure of $Ph_2C(\eta^5\text{-}C_{13}H_8)(\eta^5\text{-}3\text{-}(2\text{-adamantyl})C_5H_3)ZrCl_2$ (**4**). Ellipsoids are shown with 50% probability. Hydrogen atoms are omitted.

5.3 Synthesis and Characterization of Elastomeric Isotactic-hemiisotactic Polypropylene

Table 1 tabulates the polymerization results and Table 2 provides data from the thermal and mechanical property testing. Figure 6 depicts the ^{13}C NMR spectrum of the methyl region for the polymer given by Entry 8 (from **4**/MAO, R = 2-adamantyl). Marked deviation from the ideal hemiisotactic pentad distribution[14] (18.75: 12.5: 6.25: 25: 0: 0: 18.75: 12.5: 6.25) is apparent; nonetheless, the mmrm, rrmr, and mrmr pentads are still virtually absent.

Table 1. Polymerization data with **1-9**/MAO in liquid propylene.

Entry	Metallocene (mg)	MAO (equiv.)	T_p (°C)	Toluene (mL)	C_3H_6 (mL)	Time (min.)	Yield (g)	Activity (gP/(gmet·h))	T_m [a] (°C)	m (%)	mmmm (%)	M_w	M_w/M_n
1	**1** (1.0)	1000	0	2.0	30	15	1.43	5710	n.o.	50.4	21.6	80,000	1.81
2	**1** (1.0)	1000	20	2.0	30	10	4.95	29700	n.o.	49.6	18.3		
3	**2** (0.5)	2000	0	1.0	30	30	1.50	6020	n.o.	62.3	28.4	134,000	3.15
4	**2** (0.5)	2000	20	1.0	30	10	1.08	12900	88	62.7	31.4	81,900	4.38
5	**2** (2.0)	1000	0	2.0	55	60	9.96	5000	n.o.	61.0	28.0		
6	**3** (5.0)	1000	0	2.0	30	60	0.15	30	n.o.	64.4	32.0		
7	**3** (5.0)	1000	20	2.0	30	60	2.34	470	n.o.	66.4	34.0		
8	**4** (15)	1000	0	2.0	350	90	23.22	1030	115	57.8	27.2	638,000	2.33
9	**4** (15)	1000	20	2.0	350	30	27.76	3700	125	55.7	25.3	435,000	2.14
10	**4** (2.0)	1000	0	2.0	180	180	11.27	1900	147	57.9	25.9	1,081,000	2.33
11	**4** (6.0)	1000	0	2.0	200	70	26.02	3700	146	58.7	26.6	1,006,000	2.42
12	**4** (2.0)	1000	0	2.0	200	360	13.85	1200	125	58.8	27.7	802,000	2.43
13	**5** (5.0)	1000	0	2.0	55	60	0.19	38	134	58.8	26.6		
14	**5** (5.0)	1000	20	2.0	55	60	1.92	384	n.o.	58.8	28.1		
15	**5** (15)	1000	20	2.0	55	60	8.03	540	135	57.6	24.0	806,000	1.93
16	**6** (1.0)	1000	0	2.0	30	15	1.31	5220	122	57.6	27.5	105,000	1.93
17	**6** (1.0)	1000	20	2.0	30	10	3.74	22500	n.o.	58.4	28.0		
18	**7** (2.0)	1000	0	2.0	55	60	8.38	4190	148	43.8	14.7	572,000	2.55
19	**7** (2.0)	1000	20	2.0	55	30	12.50	12500	147	50.6	18.5	390,000	2.32
20	**8** (2.0)	1000	0	2.0	30	30	1.57	1570	98	75.3	49.3	77,400	2.01
21	**8** (2.0)	1000	20	2.0	30	15	3.54	7070	91	75.0	47.9		
22	**9** (1.0)	1000	0	2.0	30	3	1.23	24600	n.o.	57.5	26.9	653,000	1.87
23	**9** (0.5)	1000	20	1.0	30	3	1.12	44700	n.o.	61.0	30.0	397,000	2.31
24	**9** (1.0)	1000	20	2.0	55	15	10.22	41000	149	63.0	31.8	535,000	2.21

[a] n.o. = melting temperature not observed.

Table 2. Thermal and mechanical properties of elastomeric polypropylenes.

Entry	5	8	9	10	11	12	15	18	19	24
Thermal Properties										
melt flow rate (g/600 s, 230°C)		0.1	0.41							
T_g (°C)		-3	-3							
T_m (°C)	n.o.	115	125	147	146	125	135	148	147	149
H_{m° (J/g)		9.3	6.8	5.4	4.5	0.5	0.7	6.6	6.5	2.2
T_c (°C)		66	62	88	86	78		87	82	79
H_{c° (J/g)		4.6	2.7	8.7	3.1	1.9		7.1	7.8	3.6
Mechanical Properties										
initial modulus (psi)	1007 ±44	679	712				509±23	483±23		1100±33
stress at 100% strain (psi)	226±2						222±24	155±1		260±4
stress at 200% strain (psi)	249±3						313±7	170±1		305±3
stress at 300% strain (psi)	180±2						415±9	174±1		366±3
stress at 400% strain (psi)	325±3						530±12	181±1		459±6
stress at 500% strain (psi)	379±2						660±14	191±1		586±9
stress at 1000% strain (psi)	895±10						N A	328±8		N A
stress at break (psi)	1233±27	1215	1230				1219±70	642±43		1763±299
strain at break (%)	1245±30	756	813				792±32	1447±45		910±75
% recovery, trial 1	11.3						0.70	3.70		3.60
% recovery, trial 2	7.60						2.10	5.70		3.40
% recovery, trial 3	9.10						1.8	5.00		4.9
% recovery, average [a]	9.33						1.53	4.80		3.97
tensile stress relaxation (%)[b]		27	28							
tensile hysteresis: [c]										
cumulative set (%) [d]		6.5	7.3							
retained force (%) [e]		51	49							
[m] (%)	61.0	57.8	55.7	57.9	58.7	58.8	57.6	43.8	50.6	63.0
M_n	43,000[f]	273,000	204,000	463,000	416,000	330,000	417,000	224,000	168,000	242,000

[a] Recovery from 200% strain (%) = (final length - initial length)/(initial length) where initial length = 0.5000 inch. [b] 50% elongation stress decay, 5 minutes. [c] 3 cycles, 100% elongation, 30 second hold at extension, 60 second hold at recovery. [d] 2 cycles. [e] 2nd cycle, (stress at 50% on recovery)/(stress at 100% on extension before hold). [f] Estimated based on Entry 3, performed with the same catalyst at the same temperature.

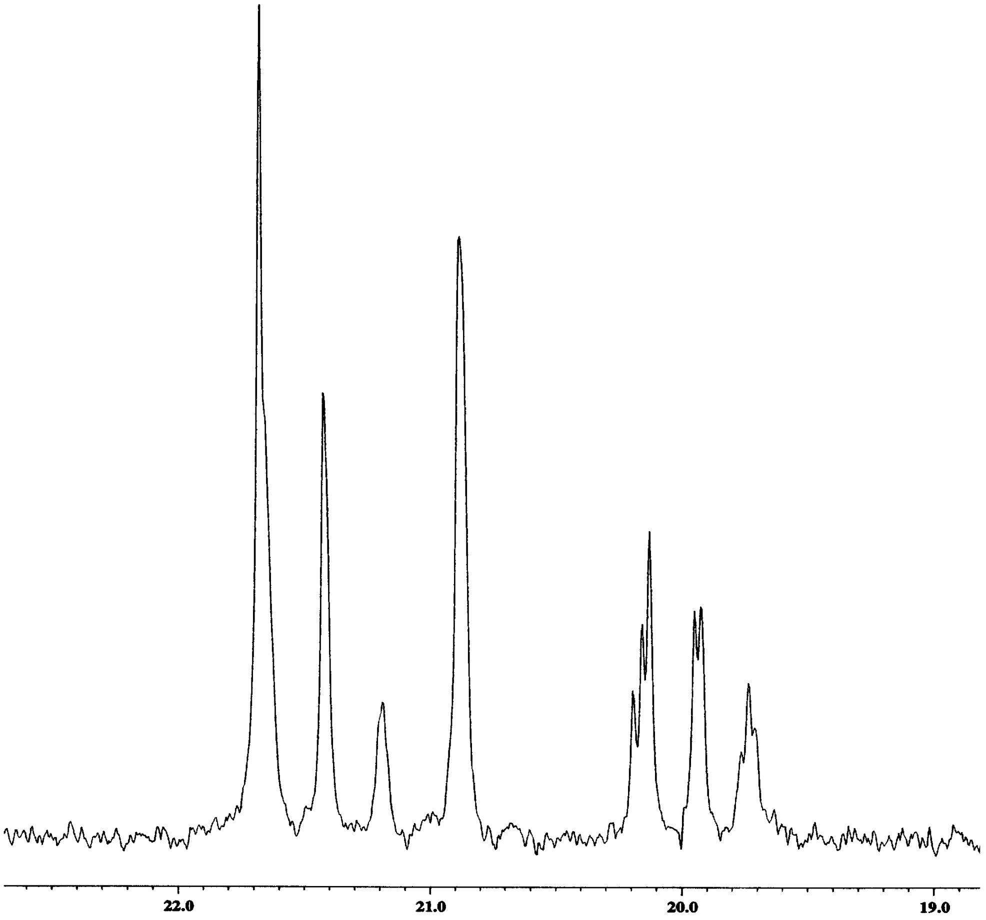


Figure 6. ^{13}C NMR of the methyl region for polypropylene prepared with **4**/MAO at 0°C (Entry 8). The pentad distribution was determined: 27.2% mmmm; 13.2% mmmr; 5.5% rmmr; 22.2% mmrr; 1.2% mmrm + rrmr; 0.6% mrmr; 12.5% rrrr; 9.1% rrrm; 8.5% mrrm.

The ideal α parameter is approximately 0.60 and a molecular weight in the vicinity of M_n = 200,000 is suitable. Those metallocenes with an isopropylidene bridge (R' = Me) generally produce polymer of too low molecular weight to realize good elasticity. However, the metallocenes bearing a diphenylmethylidene bridge (R' = Ph) provide polymer molecular weights great enough that isotactic segments competent for crystallite formation are present, as evidenced by detection of melting temperatures[15] and definitive elastomeric behavior.

5.4 Derivation of Isotactic Block Length Distribution for Isotactic-hemiisotactic Polypropylene

One can calculate the isotactic block length distribution for isotactic-hemiisotactic polypropylene. For a hemiisotactic regime, only sequential rr and mm triads are allowed. Therefore, only isotactic blocks containing an odd number of monomers will be allowed and an isotactic block will be defined by $(rr)(mm)^{(s)}(rr)$, where s is the number of repeating mm triads.[16] The probability of creating an isotactic block of length n will be given by $P_n = (1-\alpha)(\alpha)^{((n-1)/2)}(1-\alpha)$, and the number of blocks with length n in a given polymer chain is $N_n = P_n (P_d)$, where P_d is the degree of polymerization.[17]

For a polymer with $\alpha = 0.62$ and $M_n = 100{,}000$, this analysis predicts that the longest isotactic segment present ($N_n \geq 1$) will contain 25 monomer units and there will be a total of 7 blocks of 21 monomer units or longer. Doubling the molecular weight ($M_n = 200{,}000$) results in a polymer for which the longest isotactic segment is 27 monomer units long, but for which there are 15 blocks of 21 monomer units or longer.

For a polymer with $\alpha = 0.50$, the longest isotactic segments present will contain only 19 or 21 monomer units, for $M_n = 100{,}000$ or $M_n = 200{,}000$, respectively. Such a polymer does not contain isotactic blocks in great enough number or length to form the crystalline regions necessary for elastomeric polypropylene.

Finally, for a polymer with $\alpha = 0.75$, the longest isotactic segments present will contain 35 or 39 monomer units and there will be 33 or 67 blocks of length 21 or greater, for $M_n = 100{,}000$ or $M_n = 200{,}000$, respectively. Clearly these will be present at the expense of the requisite amorphous hemiisotactic segments and a rigid polymer will result.

5.5 Conclusions

It is evident that the parameter α largely dictates the length of the isotactic blocks, whereas the molecular weight correlates with the number of such blocks per polymer chain. The effects of altering these parameters and the mechanistic processes (including mistake processes) of forming elastomeric isotactic-hemiisotactic polypropylene are presently under further investigation.

5.6 Experimental Section

General Considerations. Unless otherwise noted, all reactions and procedures are carried out under an inert atmosphere of argon or nitrogen using standard glove box, Schlenk and high vacuum line techniques.[18] Solvents are dried according to standard procedures. The following reagents were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%); 2-adamantanone (99%); fluorene (98%); n-butyllithium (1.6 M in hexanes); zirconium tetrachloride (99.5%); norcamphor (98%); and 3, 3, 5, 5-tetramethylcyclohexanone (98%). Dicyclopentadiene and di(methylcyclopentadiene) were obtained from Aldrich and cracked following standard procedures prior to use. Hafnium tetrachloride (99%) was obtained from Cerac and used as received. **Instrumentation.** NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC-MS were acquired with a Hewlett Packard 5890 Series II Gas Chromatograph connected to a Hewlett Packard 5989A Mass Spectometer. The GC was equipped with a column of dimensions 7.1 m x 0.1μm having an HP-1 phase (Crosslinked Methyl Silicone Gum). LC-MS were acquired with a Hewlett Packard 1090 Series II Liquid Chromatograph with a toluene phase (solvent dried over sodium/benzophenone). The LC was connected to a Hewlett Packard 59980B Particle Beam Interface, and this was connected to a Hewlett Packard 5989A Mass Spectrometer.

Metallocene Syntheses.

Preparation of 1. The synthesis of **1** was performed as described in the literature.[19]

Preparation of 2.

6,6'-(tricyclo[3.3.1.1]decane)fulvene (adamantylfulvene). (Synthesis modified from reference 20) 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 hours before the yellow precipitate was collected by suction filtration, rinsed with a small volume of methanol and dried *in vacuo*. 25.71 grams (77.9%) of adamantylfulvene were isolated. MS (GC-MS) *m/z* 198.3 (M^+). ^1H 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-CH_1), 135.81, 167.38 (fulvene-CH_0). Elemental analysis calculated for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.20, 90.22; H, 8.39, 8.50.

2-adamantylcyclopentadiene. 6.00 grams (30.3 mmol) of adamantylfulvene were dissolved in 30 mL of tetrahydrofuran and this solution added over 30 minutes to a stirred slurry of $LiAlH_4$ (1.40 g, 0.0369 mol) at 0°C. After 5 hours 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 H_2O, 25 mL concentrated HCl, and 50 mL diethyl ether were added, the organic layer isolated, and the aqueous layer extracted with additional diethyl ether (3 x 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 methanol, 50 mL ethanol, 20 mL tetrahydrofuran, 36 mL acetone (0.49 mol) and 0.5 mL pyrrolidine (0.006 mol).

After stirring for 48 hours, 5 mL of acetic acid were injected, followed by 200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 40 mL). The combined organic layers were extracted with H_2O (3 x 25 mL) and with 10% aqueous NaOH (3 x 25 mL), dried over $MgSO_4$, filtered and rotavapped. The obtained yellow solid was further purified by overnight Soxhlet extraction by 150 mL 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. Elemental analysis calculated for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 82.23, 82.23; H, 8.78, 8.82.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$. 10.5 mL of an n-butyllithium solution (1.6 M in hexanes, 0.0168 mol) were syringed into a solution of fluorene (2.77 g, 0.0166 mol) in 60 mL tetrahydrofuran. After stirring for 5 hours, a solution of 3-(2-adamantyl)-6,6-dimethylfulvene (4.00 g, 0.0166 mol) in 40 mL tetrahydrofuran was injected over 2 minutes. After stirring for 20 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer isolated, and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$ (6.77 g, 16.6 mmol) in 75 mL 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 hours, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield as an orange powder.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (2). 2.00 grams of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$ (0.00478 mol) and 1.114 g $ZrCl_4$ (0.00478 mol) were combined in a swivel frit apparatus. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 14 hours of stirring. 40 mL of methylene chloride were 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 grams (55.5%) of **2** as an orange powder following collection at 0°C and *in vacuo* drying. MS (LC-MS) *m/z* 566.5 (M^+). ^1H NMR (C_6D_6): δ 1.36 - 2.04 (m, 14H, adamantyl-*H*), 1.84, 1.86 (s, 6 H, $C(CH_3)_2$), 3.32 (s, 1H, 2-*H*-adamantyl), 5.44, 5.48, 6.18 (m, 3H, Cp-*H*), 6.95, 7.03, 7.29, 7.34 (t, $^3J_{HH}$ = 7.7, 7.7, 8.0, 8.0 Hz, 4H, Flu-*H*), 7.41, 7.49, 7.84, 7.84 (d, $^3J_{HH}$ = 8.8, 9.1, 7.7, 7.7 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.58, 28.65 (C-$(CH_3)_2$), 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-CH_1), 123.41, 123.67, 124.61, 124.67, 124.76, 124.83, 128.81, 128.81 (Flu-CH_1), 139.93 (9-Flu-*C*),CH_0 not determined. Elemental analysis calculated 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.

Preparation of 3.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)HfCl_2$ (3). 2.00 grams of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$ (4.78 mmol) and 1.531 g $HfCl_4$ (4.78 mol) were combined in a 100 mL flask equipped with a 180° needle valve. 50 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 47 hours of stirring. 20 mL of methylene chloride were condensed in and removed in order to quench unreacted ligand. Then the yellow solid was extracted in cellulose extraction thimble with 150 mL of refluxing methylene chloride for 48 hours. Solvent was removed from the filtrate and 30 mL diethyl ether were condensed in. The yellow solid was collected on the frit and dried *in vacuo*: 1.771 g (56.7%). MS (LC-MS) *m/z* 654.7 (M^+). ^1H NMR (C_6D_6): δ 1.11 - 2.04 (m, 14H, adamantyl-*H*), 1.85, 1.88 (s, 6 H, $C(CH_3)_2$), 3.37 (s, 1H, 2-*H*-adamantyl), 5.40, 5.43, 6.12 (m, 3H, Cp-*H*), 6.94, 7.01, 7.27, 7.33 (t, $^3J_{HH}$ = 7.0, 7.7, 7.0, 7.3 Hz, 4H, Flu-*H*), 7.46, 7.55, 7.84, 7.84 (d, $^3J_{HH}$ = 8.8, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 28.82, 28.88 (C-$(CH_3)_2$), 27.90, 27.90, 32.08, 32.40, 32.65, 32.70, 37.86, 38.53, 38.68, 43.77 (adamantyl-*C*), 99.90, 100.22, 115.73 (Cp-*C*H_1), 123.16, 123.42, 124.27, 124.42, 124.54, 124.66, 128.61, 128.64 (Flu-*C*H_1), 138.42 (9-Flu-*C*),*C*H_0 not determined. Elemental analysis calculated for $C_{31}H_{32}Hf_1Cl_2$: C, 56.93; H, 4.93. Found: C, 54.80; H, 4.97.

Preparation of 4.

adamantylfulvene. (Synthesis modified from reference 20) 2-adamantanone (40.22 g, 267.7 mmol), methanol (200 mL), cyclopentadiene (51.0 mL, 618.9 mmol), and pyrrolidine (20.0 mL, 239.6 mmol) were added to a 1 liter round bottom flask. After stirring for 70 hours, the yellow precipitate was collected by suction filtration and washed with 50 mL methanol. After *in vacuo* drying, 45.59 grams adamantylfulvene were obtained (85.9%). MS (GC-MS) *m/z* 198.3 (M^+).

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

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

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

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (4). 2.834 grams of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$ (5.340 mmol) were combined with $LiCH_2$(trimethylsilane) (1.006 g, 10.68 mmol) in a 250 mL round bottom flask. 50 mL of tetrahydrofuran were condensed in and this was stirred at room temperature for 17 hours, when the solvent was removed. In the glove box, zirconium tetrachloride (1.245 g, 5.343 mmol) was added. 60 mL of petroleum ether were condensed in and the reaction stirred at room temperature for 52 hours. Solvent was removed and 20 mL of dichloromethane were condensed in, stirred, and removed. Then, 50 mL of diethyl ether were condensed in, stirred, and removed. The solid was extracted overnight in a cellulose extraction thimble with 150 mL methylene chloride. The obtained solution was filtered through a frit. Solvent was removed, 15 mL of diethyl ether were condensed in, and the orange solid was broken up, collected at 0°C, and dried *in vacuo* to give 0.778 grams of product **3** (21.1%). MS (LC-MS) *m*/*z* 690.9 (M^+). Elemental analysis calculated for $C_{41}H_{36}Zr_1Cl_2$: C, 71.28; H, 5.25. Found: C, 68.78; H, 5.21.

Alternate Preparation of 4.

adamantylfulvene. (Synthesis modified from reference 20) 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 liter round bottom flask. After stirring for 77 hours, the yellow precipitate was collected by suction filtration and washed with 50 mL methanol. After *in vacuo* drying, 49.56 grams adamantylfulvene were obtained (83.4%). MS (GC-MS) m/z 198.3 (M^+).

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

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

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

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

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (4). In the glove box, 4.657 grams of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$ (8.582 mmol) were combined with $ZrCl_4$ (2.000 g, 8.583 mmol) in a 100 mL round bottom flask. This was equipped with a 180° needle valve and 60 mL petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 46 hours of stirring, solvent was removed. The solid was extracted for two days in a cellulose extraction thimble with 150 mL methylene chloride. The obtained solution was filtered through a frit and condensed to 15 mL. After sitting for 1 hour, the formed precipitate was collected on the frit and dried *in* *vacuo*: 2.443 g of product **3** were obtained (41.2%). MS (LC-MS) *m* / *z* 690.7 (M^+). ^1H NMR (C_6D_6): δ 1.46 - 2.10 (m, 14H, adamantyl-*H*), 3.36 (s, 1H, 2-*H*-adamantyl), 5.73, 5.74 (s, 2H, Cp-*H*), 6.28 (t, $^3J_{HH}$ = 2.9 Hz, 1H, Cp-*H*), 6.93, 6.97, 7.02, 7.04, 7.12, 7.14 (t, $^3J_{HH}$ = 7.3, 7.3, 7.4, 7.4, 7.3, 6.6 Hz, 6H, phenyl-*H*), 7.59, 7.60, 7.82, 7.95 (d, $^3J_{HH}$ = 8.1, 8.1, 8.1, 8.4 Hz, 4H, phenyl-*H*), 6.49, 6.55, 7.90, 7.90 (d, $^3J_{HH}$ = 8.8, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*), 6.71, 6.77, 7.28, 7.33 (t, $^3J_{HH}$ = 7.0, 7.0, 7.4, 7.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 27.90, 28.03, 32.30, 32.48, 32.51, 32.72, 37.88, 38.48, 38.64 (adamantyl-*C*), 43.88 (2-*C*-adamantyl), 104.23, 104.57, 116.06 (Cp-CH_1), 121.30, 121.43, 122.98, 123.28 (Flu-CH_0), 123.82, 124.02, 124.53, 124.68, 124.14, 125.28, 126.65, 126.65, 127.20, 127.26, 128.06, 128.06, 129.04, 129.04, 129.13, 129.13, 129.26, 129.39 (phenyl- and Flu-CH_1), 139.39 (9-Flu-*C*), 145.01, 145.11 (ipso-*C*), other CH_0 not determined. Elemental analysis calculated for $C_{41}H_{36}Zr_1Cl_2$: C, 71.28; H, 5.25. Found: C, 63.48, 63.71; H, 4.46, 4.57.

Preparation of 5.

$Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)HfCl_2$ (5). In the glove box, 3.388 grams of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$ (6.244 mmol, prepared as given in the alternate preparation of **3**) were combined with $HfCl_4$ (2.000 g, 6.244 mmol) in a 100 mL round bottom flask. This was equipped with a 180° needle valve and 60 mL petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 30 hours of stirring, solvent was removed. The solid was extracted overnight in a cellulose extraction thimble with 150 mL methylene chloride. The obtained solution was filtered through a frit and condensed to 30 mL. After sitting for 1 hour, the formed precipitate was collected on the frit and dried *in vacuo*: 1.547 g of product **5** were obtained (31.8%). A second crop was obtained from toluene: 1.237 g (57.3% for both crops). MS (LC-MS) *m* / *z* 778.8 (M^+). ^1H NMR (C_6D_6): δ 1.45 - 2.09 (m, 14H, adamantyl-*H*), 3.41 (s, 1H, 2-*H*-adamantyl), 5.68, 5.69 (s, 2H, Cp-*H*), 6.21 (t, $^3J_{HH}$ = 3.0 Hz, 1H, Cp-*H*), 6.93, 6.98, 7.02, 7.04, 7.12, 7.14 (t, $^3J_{HH}$ = 7.3, 7.3, 7.7, 7.7, 8.0, 8.0 Hz, 6H, phenyl-*H*), 7.60, 7.60, 7.83, 7.96 (d, $^3J_{HH}$ = 7.4, 7.4, 8.1, 7.7 Hz, 4H, phenyl-*H*), 6.54, 6.60, 7.89, 7.89 (d, $^3J_{HH}$ = 8.8, 9.2, 8.4, 8.4 Hz, 4H, Flu-*H*), 6.71, 6.77, 7.26, 7.31 (t, $^3J_{HH}$ = 7.7, 7.7, 7.3, 7.0 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 27.91, 28.01, 32.42, 32.47, 32.59, 32.72, 37.93, 38.53, 38.67 (adamantyl-*C*), 43.83 (2-*C*-adamantyl), 101.61, 101.92, 115.20 (Cp-CH_1), 120.19, 120.27, 121.51, 121.87 (Flu-CH_0), 123.62, 123.83, 124.45, 124.57, 124.79, 124.92, 126.68, 126.68, 127.18, 127.24, 127.84, 127.85, 128.99, 128.99, 129.12, 129.12, 129.29, 129.41 (phenyl- and Flu-CH_1), 137.91 (9-Flu-*C*), 145.28, 145.38 (ipso-*C*), other CH_0 not determined. Elemental analysis calculated for $C_{41}H_{36}Hf_1Cl_2$: C, 63.29; H, 4.66. Found: C, 66.36, 66.16; H, 4.66, 4.69.

Preparation of 6.

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

norbornylcyclopentadiene. A solution of norbornylfulvene (14.37 g, 90.8 mmol) dissolved in 100 mL tetrahydrofuran was cooled to 0°C before $LiAlH_4$ (5.00 g, 132 mmol) was added over 2 minutes. After stirring at room temperature for 17 hours, the reaction was cooled to 0°C and 100 mL water were added dropwise over 1 hour. Then, 200 mL water/50 mL concentrated aqueous HCl and 100 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the crude product as a light yellow oil in quantitative yield.

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

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

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

$Me_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (6). In the glove box, 2.44 grams of $Me_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)Li_2$ (6.44 mmol) were combined with $ZrCl_4$ (1.50 g, 6.44 mmol) in a 100 mL round bottom flask. This was equipped with a 180° needle valve and 40 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 24 hours of stirring, solvent was removed. Then 30 mL of dichloromethane were added and removed, followed by addition and removal of 30 mL diethyl ether. The solid was extracted overnight in a cellulose extraction thimble with 150 mL of diethyl ether. The filtrate volume was reduced to 30 mL and the precipitated product was collected on a swivel frit and dried *in vacuo*: 1.26 grams of **5** (37.2%) in a 54:46 diastereomeric ratio. MS (LC-MS) m/z 526.6 (M^+). Major diastereomer (54%): ^1H NMR (C_6D_6): δ 1.01 - 1.35 (m, 8H, norbornyl-*H*), 1.89 - 2.07 (m, 2H, norbornyl-*H*), 1.82, 1.83 (s, 6 H, $C(CH_3)_2$), 3.20 (m, 1H, 2-*H*-norbornyl), 5.42, 5.45, 6.09 (t, $^3J_{HH}$ = 3.3, 3.3, 2.9 Hz, 3H, Cp-*H*), 7.00, 7.03, 7.35, 7.35 (t, $^3J_{HH}$ = 7.7, 7.7, 7.3, 7.3 Hz, 4H, Flu-*H*), 7.45, 7.47, 7.84, 7.86 (d, $^3J_{HH}$ = 8.1, 8.8, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 23.52, 29.71, 34.05, 37.25, 40.13, 41.00, 43.61, (norbornyl-*C*), 28.58, 28.66 (CH_3), 40.51 (CH_3CCH_3), 65.70, 79.12, 114.31, 122.59, 122.88, 123.15, 140.29 (Cp- and Flu-CH_0), 102.73, 103.79, 116.17 (Cp-CH_1), 123.49, 123.58, 124.64, 124.74, 124.80, 124.84, 128.76, 128.84 (Flu-CH_1). Minor diastereomer (46%): ^1H NMR (C_6D_6): δ 1.01 - 1.35 (m, 8H, norbornyl-*H*), 1.89 - 2.07 (m, 2H, norbornyl-*H*), 1.79, 1.83 (s, 6 H, $C(CH_3)_2$), 3.13 (m, 1H, 2-*H*-norbornyl), 5.23, 5.54, 6.04 (t, $^3J_{HH}$ = 3.0, 2.9, 2.9 Hz, 3H, Cp-*H*), 6.98, 7.03, 7.30, 7.30 (t, $^3J_{HH}$ = 7.7, 7.7, 7.7, 7.7 Hz, 4H, Flu-*H*), 7.43, 7.45, 7.83, 7.84 (d, $^3J_{HH}$ = 8.4, 8.1, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 23.68, 29.80, 34.17, 36.97, 39.39, 41.53, 43.29, (norbornyl-*C*), 28.58, 28.58 (CH_3), 40.55 (CH_3CCH_3), 65.65, 79.02, 113.27, 122.55, 122.88, 123.40, 138.57 (Cp- and Flu-CH_0), 102.31, 103.69, 117.44 (Cp-CH_1), 123.37, 123.71, 124.64, 124.74, 124.80, 124.84, 128.84, 128.92 (Flu-CH_1). Elemental analysis calculated for $C_{28}H_{28}Zr_1Cl_2$: C, 63.86; H, 5.36. Found: C, 61.78, 61.58; H, 5.03, 5.23.

Preparation of 7.

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

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

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

$Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (7). In the glove box, 3.24 grams of $Ph_2C(3\text{-}(2\text{-norbornyl})C_5H_3)(C_{13}H_8)Li_2$ (6.44 mmol) were combined with $ZrCl_4$ (1.50 g, 6.44 mmol) in a 100 mL round bottom flask. This was equipped with a 180° needle valve and 60 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 24 hours of stirring, solvent was removed. The solid was extracted overnight in a cellulose extraction thimble with 150 mL methylene chloride. The solvent was removed and the solid redissolved in 75 mL toluene and 25 mL methylene chloride. The obtained solution was filtered through a frit, all solvent was removed, and 40 mL toluene were condensed in. The orange solid was broken up, stirred, collected on the frit and dried *in vacuo* to afford the product **5** in a 64:36 diastereomeric ratio: 1.81 grams (43.2%). MS (LC-MS) *m/z* 650.5 (M^+). Major diastereomer (64%): ^1H NMR (C_6D_6): δ 0.99-1.40 (m, 8H, norbornyl-*H*), 1.83-2.09 (m, 2H, norbornyl-*H*), 3.09 (m, 1H, 2-*H*-norbornyl), 5.53, 5.71, 6.19 (t, $^3J_{HH}$ = 3.0, 2.9, 2.6 Hz, 3H, Cp-*H*), 6.91-7.13 (m, 6H, phenyl-*H*), 7.56, 7.56, 7.75, 7.75 (d, $^3J_{HH}$ = 8.1, 8.1, 7.7, 7.7 Hz, 4H, phenyl-*H*), 6.49, 6.53, 7.89, 7.89 (d, $^3J_{HH}$ = 8.8, 8.8, 8.1, 8.1 Hz, 4H, Flu-*H*), 6.78, 6.81, 7.31, 7.33 (t, $^3J_{HH}$ = 7.7, 7.7, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 23.91, 29.78, 34.42, 37.34, 40.19, 41.64, 43.41 (norbornyl-*C*), 58.33 (Ph*C*Ph), 78.20, 109.96, 121.26, 121.61, 123.10, 123.30, 138.11, 145.00, 145.00 (Cp-, phenyl-, and Flu-CH_0), 104.38, 105.22, 115.76 (Cp-CH_1), 123.97, 123.97, 124.61, 124.69, 125.30, 125.30, 126.68, 126.73, 127.26, 127.31, 128.03, 128.11, 128.23, 129.05, 129.08, 129.17, 129.29, 129.36 (phenyl- and Flu-CH_1). Minor diastereomer: ^1H NMR (C_6D_6): δ 0.99-1.40 (m, 8H, norbornyl-*H*), 1.83-2.09 (m, 2H, norbornyl-*H*), 3.19 (m, 1H, 2-*H*-norbornyl), 5.66, 5.80, 6.11 (t, $^3J_{HH}$ = 2.9, 2.9, 2.6 Hz, 3H, Cp-*H*), 6.91-7.13 (m, 6H, phenyl-*H*), 7.58, 7.60, 7.79, 7.79 (d, $^3J_{HH}$ = 8.1, 8.1, 8.0, 8.0 Hz, 4H, phenyl-*H*), 6.45, 6.58, 7.91, 7.91 (d, $^3J_{HH}$ = 8.8, 8.8, 8.1, 8.1 Hz, 4H, Flu-*H*), 6.76, 6.78, 7.29, 7.33 (t, $^3J_{HH}$ = 7.7, 7.7, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 23.88, 29.66, 34.14, 37.02, 39.45, 40.93, 44.04 (norbornyl-*C*), 58.33 (Ph*C*Ph), 78.43, 108.97, 121.37, 121.50, 123.00, 123.30, 139.95, 144.92, 145.20 (Cp-, phenyl-, and Flu-CH_0), 103.63, 105.16, 116.84 (Cp-CH_1), 123.67, 124.07, 124.61, 124.74, 125.13, 125.39, 126.57, 126.64, 127.26, 127.31, 128.09, 128.11, 128.18, 129.08, 129.17, 129.29, 129.36, 129.45 (phenyl- and Flu-CH_1). Elemental analysis calculated for $C_{38}H_{32}Zr_1Cl_2$: C, 70.13; H, 4.96. Found: C, 71.10, 70.50; H, 4.71, 4.64.

Preparation of 8.

3, 3, 5, 5-tetramethylcyclohexylfulvene. Hexane washed sodium spheres (2.40 g, 104 mmol) were slowly added to 100 mL absolute ethanol. The sodium had fully reacted before cyclopentadiene (6.0 mL, 72.6 mmol) and 3, 3, 5, 5-tetramethylcyclohexanone (10.0 mL, 57.1 mmol) were added. After 30 hours, the reaction was poured into 200 mL water and 100 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with water (3 x 50 mL), dried over $MgSO_4$, filtered, and rotavapped to produce the product in quantitative yield as a yellow oil. MS (GC-MS) m/z 202.3 (M^+). ^1H NMR ($CDCl_3$): δ 0.97 (s, 12H, CH_3), 1.04 (s, 2H, CH_2), 2.39 (s, 4H, CH_2), 6.52, 6.52 (m, 4H, fulvene-*H*).

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

3-(3, 3, 5, 5-tetramethylcyclohexyl)-6, 6-dimethylfulvene. A 500 mL flask was charged with 1-(cyclopentadienyl)-3, 3, 5, 5-tetramethylcyclohexane (11.87 g, 58.1 mmol), 100 mL methanol, acetone (30 mL, 430 mmol), and pyrrolidine (1.0 mL, 12 mmol). After stirring for 52 hours, 5 mL of acetic acid were added, along with 200 mL water and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL).

The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, rotavapped, dried *in vacuo*, and pushed through a short column of alumina to provide the product in quantitative yield as a yellow oil. MS (GC-MS) *m / z* 244.4 (M^+).

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

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

$Me_2C(3\text{-}(3, 3, 5, 5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (8). In the glove box, 1.81 grams of $Me_2C(3\text{-}(3, 3, 5, 5\text{-tetramethylcyclohexyl})C_5H_3)(C_{13}H_8)Li_2$ (4.29 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 15 hours of stirring, solvent was removed. 40 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal. Then, 30 mL of diethyl ether were condensed in and the slurry was warmed and stirred. The obtained orange solid was extracted several times on the frit with refluxing diethyl ether before the filtrate was condensed to 20 mL. The precipitate was collected on the frit and dried *in vacuo* to afford the product **7**: 0.16 grams (6.6%). Second and third crops were obtained: 0.13 g and 0.23 g (21.2% for all three crops). MS (LC-MS) *m / z* 570.6 (M^+). ^{1}H NMR (CD_2Cl_2): δ 0.83, 0.83, 0.90, 0.99 (s, 12H, cyclohexyl(C*H*$_3$)), 0.88 - 1.27 (m, 6H, cyclohexyl-*H*), 2.33, 2.35 (s, 6 H, C(C*H*$_3$)$_2$), 2.69 (t, $^3J_{HH}$ = 12.4 Hz, 1H, 1-*H*-cyclohexyl), 5.46, 5.69, 5.99 (t, $^3J_{HH}$ = 2.6, 3.3, 2.6 Hz, 3H, Cp-*H*), 7.24, 7.26, 7.51, 7.53 (t, $^3J_{HH}$ = 7.7, 7.7, 7.7, 7.5 Hz, 4H, Flu-*H*), 7.82, 7.86, 8.12, 8.12 (d, $^3J_{HH}$ = 8.8, 9.2, 8.4, 8.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 26.77, 27.23, 28.47, 28.52, 28.62, 28.67 (*C*H$_3$), 31.44 (1-cyclohexyl-*C*), 32.05, 39.71, 40.50, 43.45, 49.00, 52.01 (cyclohexyl and Me*C*Me *C*H$_0$ and *C*H$_2$), 102.69, 102.74, 115.19 (Cp-*C*H$_1$), 123.56, 123.58, 123.58, 124.62, 124.73, 124.73, 124.78, 124.80 (benzo-*C*H$_1$), 141.29 (9-Flu-*C*), *C*H$_0$, not determined. Elemental analysis calculated for $C_{31}H_{36}Zr_1Cl_2$: C, 65.24; H, 6.36. Found: C, 60.96, 61.75; H, 5.53, 5.60.

Preparation of 9.

3, 6, 6-trimethylfulvene. A 1 liter flask was charged with 400 mL 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 hours, 50 mL of acetic acid were added, followed by 1200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (5 x 100 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and rotavapped to give 158.8 grams of a red-orange oil that was subjected to Kugelrohr distillation under high vacuum. The first 15 grams 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 grams (94.0%).

$Me_2C(3\text{-methyl-}C_5H_3)(C_{13}H_8)H_2$. 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 and 240 mL of diethyl ether were added via syringe. 210.0 mL of n-butyllithium in hexanes (1.6 M, 336.0 mmol) were syringed in at room temperature over 20 minutes. After shaking and stirring the obtained yellow slurry for 1 hour, 3, 6, 6-trimethylfulvene (40.00g, 332.8 mmol) was syringed in over 25 minutes, providing a clear, red solution. After stirring for 17 hours, the vessel was cooled to 0°C and 60 mL aqueous NH_4Cl solution were added. The slurry was filtered and the aqueous layer removed. The obtained solid was extracted from a cellulose extraction thimble with 500 mL diethyl ether/hexanes for two 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 grams, respectively (43.4% for all three crops). MS (GC-MS) m/z 286.3 (M^+). Elemental analysis calculated 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. 11.86 grams of $Me_2C(3\text{-methyl-}C_5H_3)(C_{13}H_8)H_2$ (41.41 mmol) were combined with 200 mL acetone (2720 mmol) and 15.0 mL pyrrolidine (180 mmol). After stirring for 30 minutes, a homogeneous solution is obtained and stirring is ceased. The product slowly crystallized, and after 30 days the yellow crystals were collected by filtration. These were combined with 100 mL methanol, brought to a boil for 4 hours, and stirred overnight as the vessel cooled. Collection by suction filtration, rinsing with 25 mL methanol, and *in vacuo* drying afforded 8.15 grams of the desired product (60.3%). MS (GC-MS) m/z 326.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.02, 1.02 (s, 6H, $C(CH_3)_2$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 (CH_3), 39.38 (CH_0), 55.66 (9-Flu-CH_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). Elemental analysis calculated for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 90.83, 91.12; H, 7.33, 7.26.

Me_2C(3-*t*-butyl-4-methyl-C_5H_2)($C_{13}H_8$)H_2. A 250 mL round bottom flask was charged with 5.087 grams of 2, 6, 6-trimethyl-4-(C(methyl)$_2$(9-fluorenyl))-fulvene (15.58 mmol). This was evacuated before 100 mL diethyl ether were condensed in. 75.0 mL of methyllithium in diethyl ether (1.4 M, 105 mmol) were added by syringe, giving an orange homogeneous solution after 1 hour. 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 H_2O. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped to provide the product in quantitative yield (5.34 g) as a light yellow oil, which slowly began to crystallize.

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

Me_2C(3-*t*-butyl-4-methyl-C_5H_2)($C_{13}H_8$)$ZrCl_2$ (9). In the glove box, 2.28 grams of Me_2C(3-*t*-butyl-4-methyl-C_5H_2)($C_{13}H_8$)Li_2 (6.44 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly, and after 23 hours of stirring, solvent was removed. 30 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal; 30 mL of diethyl ether were 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 methylene chloride. The obtained solution was filtered through a frit, all solvent was removed, and 50 mL diethyl ether were condensed in. The pink solid was broken up, stirred, collected on the frit and dried *in vacuo* to afford the product **9**: 1.60 grams (49.5%). MS (LC-MS) m/z 502.3 (M^+). ^{1}H NMR (C_6D_6): δ 1.25 (s, 9H, $C(CH_3)_3$) 1.82, 1.85 (s, 6 H, $C(CH_3)_2$), 2.09 (s, 3H, Cp-CH_3), 5.20, 5.50 (d, $^3J_{HH}$ = 3.6, 3.6 Hz, 3H, Cp-H), 6.98, 6.98, 7.31, 7.31 (t, $^3J_{HH}$ = 7.0, 7.0, 7.3, 7.3 Hz, 4H, Flu-H), 7.41, 7.47, 7.82, 7.85 (d, $^3J_{HH}$ = 8.4, 8.4, 8.0, 8.4 Hz, 4H, Flu-H). ^{13}C NMR (CD_2Cl_2): δ 16.08, 28.24, 28.75 (CH_3), 29.17 ($C(CH_3)_3$), 33.52, 39.85 (CH_0), 78.40, 110.49, 121.76, 123.65, 123.79, 128.00, 140.84 (Cp and Flu CH_0), 102.93, 108.11 (Cp-CH_1), 123.42, 123.64, 124.45, 124.55, 124.68, 124.96, 128.33, 128.80 (Flu-CH_1). Elemental analysis calculated 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.

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 6110 drying system equipped with an OXYSORB™ column. Polymerizations were conducted in Lab Crest glass reaction vessels (12 oz. for propylene volumes greater than 60 mL, or 3 oz. for propylene volumes less than 60 mL) and 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°C or at 20°C with an ice or water bath for 10 minutes. A given reaction commenced upon injection of a toluene solution of the metallocene into the vessel with a 2.5 mL Hamilton syringe rated to 200 psi. Temperature maintenance was monitored by an affixed pressure gauge. Polymerization reactions were vented and quenched with a small volume of methanol/concentrated HCl (12:1) and the polymers were separated from hydrolyzed aluminoxanes by precipitation from methanol. Toluene and methanol were removed from the obtained polymers by *in vacuo* drying.

Representative Polymerization Procedures.

Entry # 100. In the glove box, a 12 oz. Lab Crest pressure reactor was charged with MAO (1.260 g, 21.7 mmol [Al]). Propylene (350 mL) was condensed in at 0°C over 2 hours. A solution of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ **4** (0.015 g, 0.022 mmol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 90 minutes. The reaction was vented and quenched with methanol/HCl. 23.22 grams of elastomeric polypropylene were obtained.

Entry # 222. In the glove box, a 3 oz. Lab Crest pressure reactor was charged with MAO (1.118 g, 19.3 mmol [Al]). Propylene (55 mL) was condensed in at 0°C over 20 minutes. The vessel was then equilibrated at 20°C for 10 minutes with a water bath. A solution of $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)HfCl_2$ **5** (0.015 g, 0.019 mmol) in toluene (2.0 mL) was injected and the reaction stirred in a 20°C water bath for 60 minutes. The reaction was vented and quenched with methanol/HCl. 8.03 grams of elastomeric polypropylene were obtained.

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

Mechanical properties were determined by BP-Amoco (Entries 100 and 101) and by Exxon (all remaining Entries). BP-Amoco used standard protocol and the test specimens were compression molded according to ASTM D1708.

For mechanical testing, the crosshead separation rate was 50.8 cm./min. Exxon used the following protocol:

Plaques suitable for physical property testing were compression molded on a Carver hydraulic press. 6.5g of polymer was molded between brass plates (0.05" thick) lined with Teflon coated aluminum foil. A 0.033" thick chase with a square opening 4" x 4" was used to control sample thickness. After one minute of preheat at 120, under minimal pressure, the hydraulic load was gradually increased to ~10,000 - 15,000 lbs. at which it was held for three minutes. Subsequently the sample and molding plates were cooled for three minutes under ~10,000 to 15,000 lbs. load between the water cooled platens of the press. Plaques were allowed to equilibrate at room temperature for a minimum of one week prior to physical property testing. Dogbones for tensile testing were cut from compression molded plaques using a mallet handle die. Specimen dimensions were those specified in ASTM D 1708. Tensile properties were measured on an Instron model 4502 equipped with a 22.48 lb. load cell and pneumatic jaws fitted with serrated grip faces. Five specimens of each sample were tested. Deformation was performed at a constant crosshead speed of 5.0 in./min. with a data sampling rate of 25 points/second. Jaw separation prior to testing was 0.876", from which strains were calculated assuming affine deformation. Initial modulus, stress and strain at yield (where evident), stress at 100%, 200%, 300%, 400%, 500% and 1,000% strain, and stress and strain at break were calculated. A minimum of five specimens from each plaque were tested, the results being reported as the average value. All stresses quoted are "engineering" values, *i.e.*, they are calculated based upon the original cross-sectional area of the specimen, taking no account of reduced cross-section as a function of increasing strain. Strain values in excess of 500% are questionable; most samples pulled out of the grips to some extent at higher strains. Thus, the strain calculated from crosshead separation is larger than the strain experienced in the gauge region of the sample. This phenomenon was particularly apparent in samples that exhibited high degrees of strain hardening. Elastic recovery experiments were performed on the Instron 4502 tensile tester using samples with the same specimen dimensions as those used in tensile experiments. Three specimens of each sample were tested. Prior to testing a pair of fiducial ink marks were placed on the gauge region of the sample 0.5" apart (with an Ultra Fine Point Sharpie marker pen). The sample was extended to a nominal 200% elongation (crosshead displacement 1.752") at a crosshead speed of 20 in./min. Once it reached this extension, the crosshead travel was automatically reversed and the crosshead returned to its original position at 20 in./min. The sample was immediately removed from the grips and the separation of the ink marks was measured with calipers. Recovery from the fiducial marks is calculated according to: Recovery from 200% strain (%) = 100 (E - 0.5)/(0.5), where E = Fiducial mark separation after 24 hours. Results: All samples drew affinely. No samples exhibited a yield peak. All samples strain whitened to some extent. This was particularly noticeable in the sample from Entry 15, in which the whitening was irreversible.

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.[21] 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 seconds and a minimum of 1000 scans were used. The complete pentad distributions for the polymers presented follow (The percentages may not sum exactly to 100.0 on account of rounding.):

Entry	1	2	3	4	5	6	7	8
mmmm	21.6	18.3	28.4	31.4	28.0	32.0	34.0	27.2
mmmr	10.9	11.6	15.5	14.7	14.3	15.3	15.3	13.2
rmmr	6.0	5.5	5.3	4.5	5.7	4.6	5.1	5.5
mmrr	21.8	22.5	24.7	23.1	24.6	23.5	21.5	22.2
mmrm + rrmr	1.3	1.9	0.8	0.9	1.1	1.2	1.4	1.2
mrmr	0.6	0.8	0.4	0.4	0.5	0.4	0.9	0.6
rrrr	23.1	21.3	7.9	8.2	8.1	7.5	6.6	12.5
rrrm	10.3	11.7	7.4	8.5	8.9	6.9	7.0	9.1
mrrm	4.4	6.5	9.5	8.4	9.0	8.7	8.0	8.5

Entry	9	10	11	12	13	14	15	16
mmmm	25.3	25.9	26.6	27.7	26.6	28.1	24.0	27.5
mmmr	13.2	13.6	13.9	13.4	13.2	13.5	14.9	12.9
rmmr	5.0	5.8	5.5	5.2	6.3	5.0	6.1	5.1
mmrr	21.5	23.4	23.5	22.6	23.1	22.3	24.0	21.3
mmrm + rrmr	2.3	1.2	1.3	1.4	1.3	1.6	1.0	2.0
mrmr	0.6	0.6	0.7	0.8	0.7	0.5	0.2	1.1
rrrr	11.6	12.2	11.4	12.3	12.7	11.1	11.8	13.6
rrrm	11.1	9.4	9.4	9.0	8.9	10.2	9.4	8.8
mrrm	9.3	7.8	7.8	7.5	7.2	7.7	8.5	7.8

Entry	17	18	19	20	21	22	23	24
mmmm	28.0	14.7	18.5	49.3	47.9	26.9	30.0	31.8
mmmr	13.3	9.8	13.4	13.2	14.3	13.4	15.1	15.3
rmmr	4.8	6.1	6.7	3.2	2.8	4.8	3.1	3.0
mmrr	21.7	22.7	21.6	15.5	16.8	20.4	19.2	19.3
mmrm + rrmr	2.2	2.9	1.6	2.6	2.0	4.2	5.2	5.4
mrmr	1.0	0.6	0.8	1.0	1.2	0.2	1.2	1.4
rrrr	12.3	21.1	20.4	3.5	4.0	11.7	8.9	8.0
rrrm	9.4	13.4	10.6	4.3	4.1	10.8	8.7	7.8
mrrm	7.3	8.6	6.5	7.3	6.9	7.6	8.6	8.1

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5.7 References and Notes

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10. For metallocene **9** it is presumed that the more stereoselective insertion occurs while the chain is in the proximity of the *t*-butyl

group, but is directed away from it, towards the benzo substituent. See Chapter 6 of this thesis.

11. The parameter α is equivalent to the m dyad percentage since the α insertion provides an (mm) triad and the (1-α) insertion provides an (rr) triad.

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13. X-ray analysis was performed on two crystals. For the structure shown (**4**), the asymmetric unit contains one metallocene and 1.5 molecules of benzene. The dihedral angle between the Cp plane and the plane that divides the adamantyl group into two equivalent hemispheres is 56.9°. The asymmetric unit of the second crystal contained two metallocenes and 4 molecules of benzene. The corresponding dihedral angles were found to be 73.0° and 112.3°. See Appendix E for X-ray crystallographic data obtained for both crystals.

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15. The DSC traces obtained—except those for Entries 141 and 142, which are typical for moderately isotactic specimens—generally show very faint (H_m < 1 J/g) and narrow (5 - 20°C) melting temperatures which vary by several degrees on the temperature axis, depending on the thermal history of the sample. Where these were widely erratic,

unusually broad, or absent, a designation of "not observed" is employed.

16. This model assumes that no site epimerization is operating and that the stereoselectivity of the more stereoselective site is perfect. While these assumptions are not strictly true, the presented analysis does not deviate greatly from the case where these mistakes do occur to a very minor degree, as seen with the catalysts presented (typically, [mmrm] + [rrmr] + [mrmr] = 1 - 3%, except for **9**: 4 - 6%). A treatment that does include such factors will be presented in a forthcoming manuscript.
17. The relationship between s and n is given by: $s = ((n-1)/2)$. For example, the sequence (rr)(mm)^9(rr) contains n = 19 monomers in its isotactic stereoblock. $P_d = M_n$ / (monomer molecular weight = 42). For a detailed derivation, see Appendix I.
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Chapter 6

The Mechanism of Isotactic Polypropylene Formation with C_1-symmetric Metallocene Catalysts

ABSTRACT: The previously proposed mechanism for isotactic polypropylene formation by the C_1-symmetric catalyst system $Me_2C(3\text{-}t\text{-butyl-}C_5H_3)(9\text{-}C_{13}H_8)ZrCl_2$ / MAO is one in which a site epimerization follows each monomer insertion. Evidence gathered here supports an alternating mechanism in which both sites of the metallocene wedge are utilized for monomer insertion—akin to that occurring for C_2-symmetric systems. The site epimerization mechanism can compete with the alternating mechanism at higher temperatures, as evidenced by an increase in isotacticity for dilute polymerizations conducted at increasing temperatures. Comparative polymerizations between $Me_2C(3\text{-R-}C_5H_3)(C_{13}H_8)ZrCl_2$ and $Me_2C(3\text{-R-}C_5H_3)(Oct)ZrCl_2$, where Oct = octamethyloctahydrodibenzofluorenyl, are most readily interpreted as the bulky Oct ligand influencing insertions on both sides of the metallocene wedge. For various R groups (methyl, cyclohexyl and diphenylmethyl), the Oct ligand increases the syndiotacticity of the obtained polymers, consistent with employment of the alternating mechanism. Additional evidence that both sites can be employed for insertion in the presence of a *t*-butyl group is found in the catalyst system $Me_2C(C_{13}H_8)(3\text{-}t\text{-butyl-4-methyl-}C_5H_2)ZrCl_2$ / MAO, from which essentially hemiisotactic polypropylene is obtained. For an Oct-containing catalyst system with R = 2-methyl-2-adamantyl, unprecedentedly high isotacticity (>99% [mmmm]) is observed for a fluorenyl-based metallocene catalyst. Melting temperatures for such isotactic polymers can be as high as 167°C and molecular weights (M_w) are as high as 370,000 (T_p = 0°C). This high stereoselectivity is consistent with operation of the site epimerization mechanism because these C_1-symmetric catalysts are known to have at least one site that is highly stereoselective (99%). Further modification to R = 2-phenyl-2-adamantyl provides a catalyst system with such large steric bulk, that it is essentially inactive towards propylene polymerization. At this extreme both the alternating and the site epimerization mechanisms are halted.

6.1 Introduction

Shortly following the report of Ewen et al.[1] demonstrating the MAO-cocatalyzed formation of syndiotactic polypropylene with fluorenyl-containing metallocenes of the type $Me_2C(C_{13}H_8)(C_5H_4)MCl_2$ (*e.g.*, M = Zr, **1**), several authors prepared cyclopentadienyl-substituted variants of the parent C_s-symmetric 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.

Principal authors 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** (Figure 1) produces syndiotactic polypropylene via a Cossee[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 Cossee type mechanism in which one site is enantiospecific and the other site is aspecific. In contrast, **3** produces isotactic polypropylene. The exact mechanism of isotactic polypropylene formation with this C_1-symmetric metallocene is currently under debate.

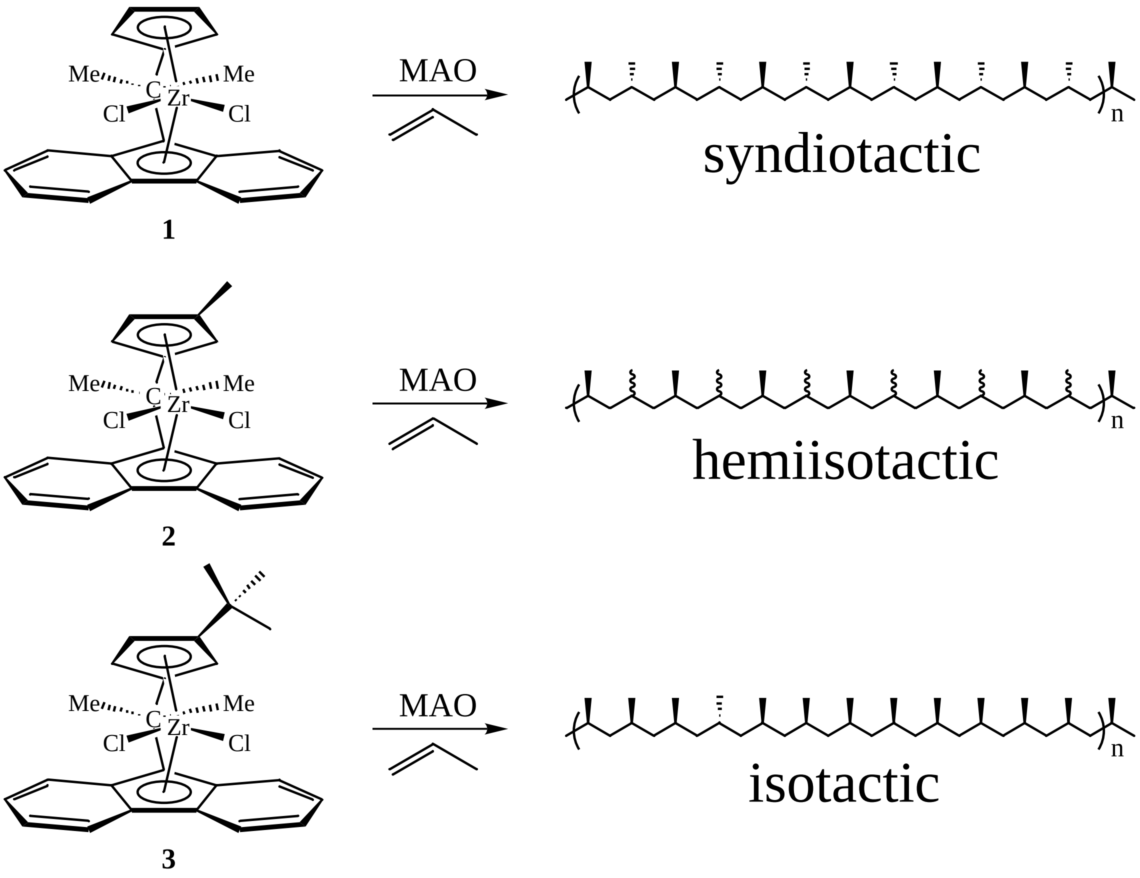


Figure 1. The nature of the cyclopentadienyl substituent greatly affects the tacticity of the resulting polypropylene.

6.2 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. These are the site epimerization mechanism (Figure 2) and the alternating mechanism (Figure 3).

The vast majority of published reports for isotactic polypropylene formation with metallocenes based on **3** invoke the site epimerization mechanism[8] to account for the observed isospecificity.[2c, 2d, 3c, 4a, 4b, 8, 9] As described in Figure 2, the growing polymer chain is directed away from the benzo substituent of the fluorenyl ligand in the transition state for monomer insertion. The methyl group of the incoming monomer is directed in a *trans* fashion away from the growing polymer chain. Following migratory insertion, the growing polymer chain moves away from the bulky *tert*-butyl substituent in a unimolecular site epimerization process that epimerizes the metal center. This regenerates the original coordination site for monomer insertion. Hence, only one site of the metallocene is employed for monomer insertion.

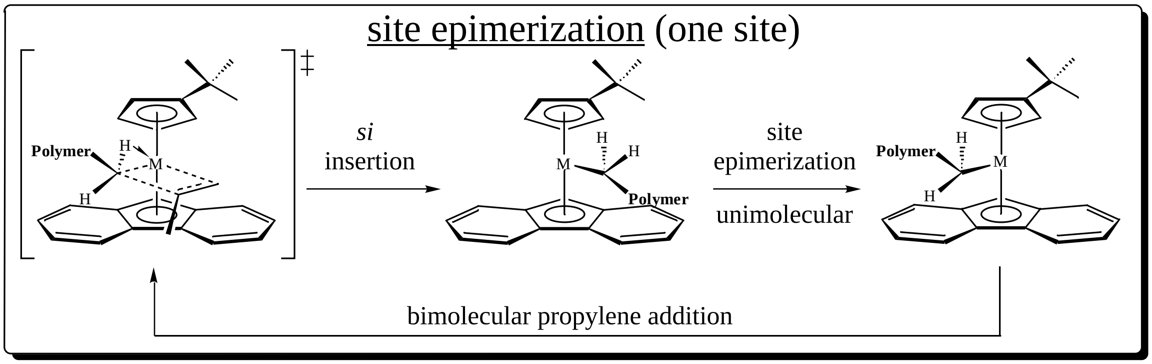


Figure 2. The site epimerization mechanism in which only one site of the metallocene is employed for monomer insertion.

As shown in Figure 3, a second limiting mechanism is possible. 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 and the benzo substituent. In order for the resulting polymer to be isotactic, the *tert*-butyl group must prevail and the growing polymer chain is 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.

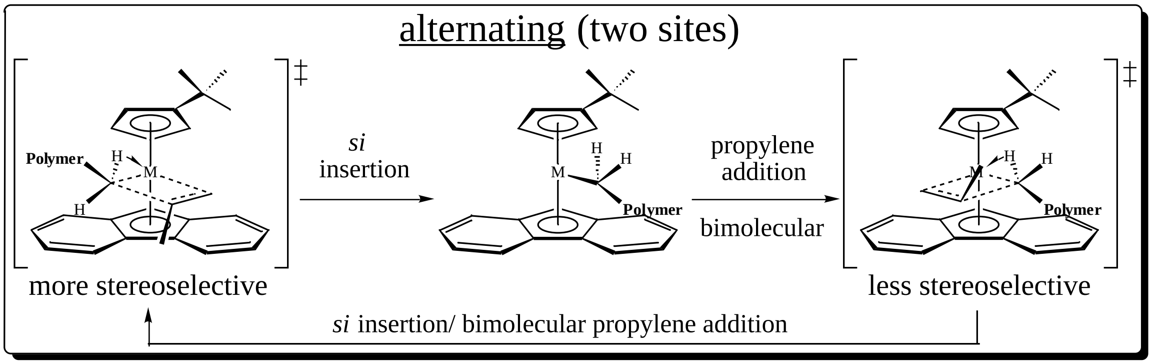


Figure 3. The alternating mechanism in which both sites of the metallocenes are employed for monomer insertion.

6.3 Differentiating Between the Site Epimerization and the Alternating Mechanisms

Despite the strong, sometimes dogmatic and emotional support for the site epimerization mechanism, there has been little convincing evidence presented in its defense. It is hoped that, through several carefully designed experiments, it will be possible to determine which of the two mechanisms, or combination thereof, most accurately describes the polymerization behavior of selected C_1-symmetric metallocene catalysts.

6.3.1 Expected Pentad Distributions

Polymer stereochemistry provides a permanent record of the stereochemical mechanism for monomer enchainment. Therefore, polymer tacticity can be compared to the polymer stereochemistry predicted by each of the possible mechanisms. Table 1 presents this 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[10] which is predicted by the site epimerization mechanism. The second is a triad model for which $P_{mr} = 0$. This model is generally applicable to catalysts with two sites and employs one independent parameter. One site is assumed to be perfectly stereoselective and the other has a stereoselectivity equal to P_{mm}. The third is a triad model for which $P > 0$. This model also applies to catalysts with two sites, but employs two independent parameters. The stereoselectivity of one site is given by (1-P_{rr}) and the stereoselectivity of the other site is given by (1-P_{mr}). Both triad models assume that no site epimerization is occurring.[11]

The RMS errors[12] provided by these fits are too similar to draw definitive conclusions. The enantiomorphic site control model predicts that **3**/MAO is employing one site with a stereoselectivity of 95.2%. The triad model (P > 0) predicts that **3**/MAO employs two sites, one with a stereoselectivity of 99.2% and the other with a stereoselectivity of 91.8%. Related polymers subjected to these models have also provided inconclusive results.

Table 1. Statistical analysis of a polymer made with **3**/MAO.

Pentad (%)	observed[a]	enantiomorphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	78.02	78.01	78.20	77.86
mmmr	9.37	7.95	7.72	8.17
rmmr	0.52	0.21	0.40	0.37
mmrr	7.06	7.95	8.53	7.49
mrmm + rmrr + mrmr	0.91	1.28	0.00	1.58
rrrr	0.28	0.21	0.48	0.37
rrrm	0.68	0.43	0.80	0.75
mrrm	3.16	3.97	3.86	3.41
m	91.90	90.78	90.59	90.94
r	8.10	9.22	9.41	9.06
Parameters		$\alpha = 0.952$	$P_{mm} = 0.906$ $P_{rr} = 0.094$	$P_{mm} = 0.901$ $P_{rr} = 0.082$ $P_{mr} = 0.008$ $P_{rm} = 0.008$
RMS error		0.687	0.886	0.523

[a] See Reference 4a.

6.3.2 Effect of Polymerization Temperature and Monomer Concentration on Isotacticity

For the site epimerization mechanism (Figure 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 alternating mechanism will be sensitive to changes in polymerization temperature and monomer concentration, as shown in Figure 4. As the polymerization temperature increases or the monomer concentration decreases, the depicted 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, one would anticipate an increase in polymerization temperature or a decrease in monomer concentration to effect a polymer of increased isotacticity.

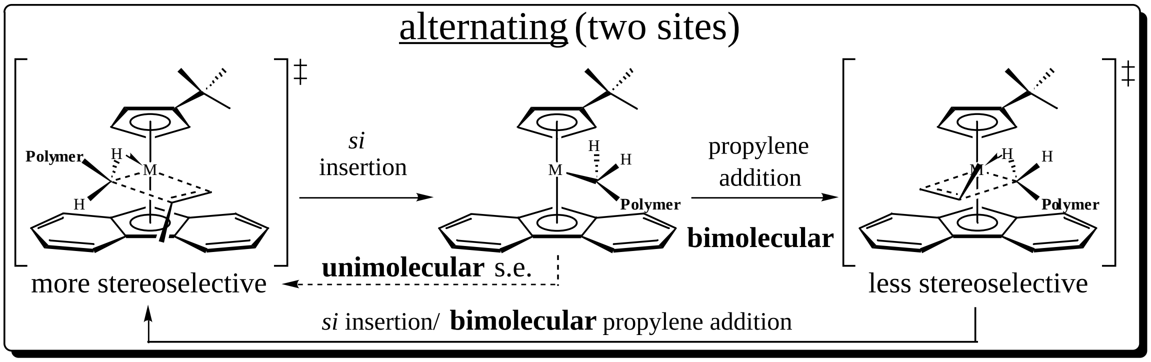
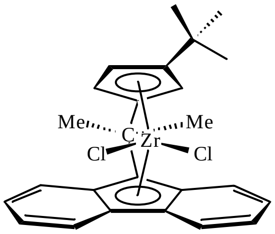
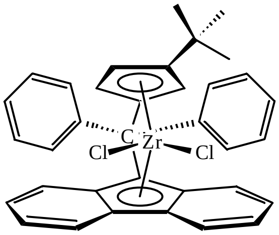


Figure 4. A unimolecular site epimerization will compete with bimolecular propagation at increased polymerization temperatures or decreased monomer concentration.

The literature reports propylene polymerizations with **3**/MAO conducted in liquid monomer at varying polymerization temperatures.[4] This results in a shallow dependence of isotacticity on polymerization temperature, as shown in Table 2. However, for a similar series of experiments conducted in dilute monomer (10% by volume in toluene), isotacticity is found to increase 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 Δmmmm values of 4.7%, 10.8%, and 11.9% for polymerization temperatures of 20°C, 40°C, and 60°C, respectively. Metallocene polymerization system **4**/MAO reveals similar trends, albeit with diminished magnitude (Table 2).

These results demonstrate that isotacticity can increase with increasing polymerization temperature and decreasing monomer concentration. The two-site alternating mechanism is likely dominant, but can yield to the site epimerization mechanism under certain conditions. These results are consistent with a recent report that **3**/MAO provides polymers of increasing isotacticity as the monomer concentration is progressively decreased.[13]

Table 2. 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**		
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			**10% monomer in toluene**		
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 Reference 4b.

6.3.3 Steric Perturbation of the Fluorenyl Ligand

In addition to performing polymerizations under various reaction conditions, an alternative probative approach is steric modification of the parent metallocene. To this end we have incorporated the 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo [b, h] fluorenyl[14] (Oct) ligand into various C_1-symmetric metallocenes.

A substitution of the fluorenyl (Flu) ligand for the Oct ligand is expected to result in increased stereoselectivity at the more stereoselective site (Figure 5) since the Oct ligand is expected to be a better polymer chain directing substituent than the Flu ligand during the propagative transition state. However, a substitution of the Flu ligand for the Oct ligand is expected to result in decreased stereoselectivity at the less stereoselective site (Figure 5) since the Oct ligand is expected to compete more favorably with the opposing R substituent for directing the polymer chain during the propagative transition state.

Therefore, if one observes increased isotacticity upon substitution of Flu for 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 for Oct, the alternating mechanism is likely operative since it employs both the more stereoselective site and the less stereoselective site.

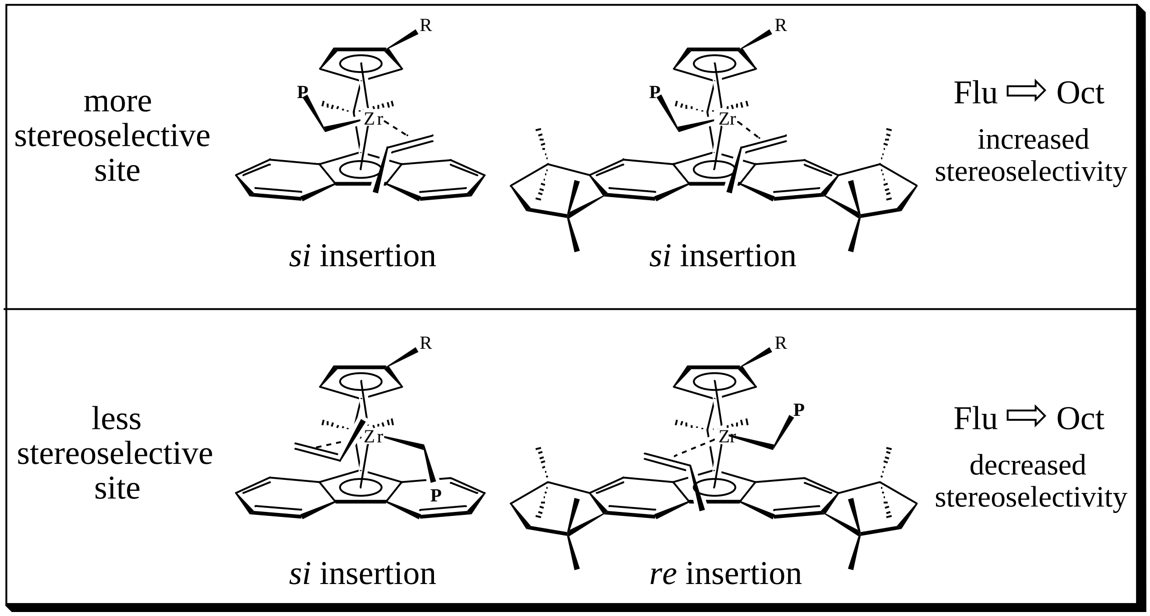
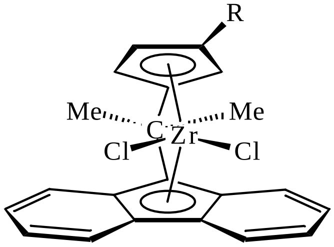
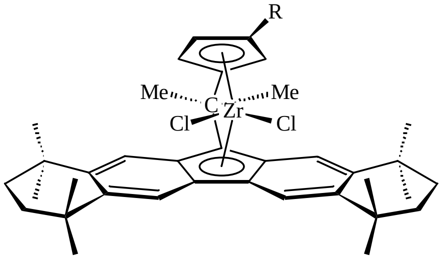
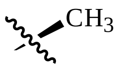
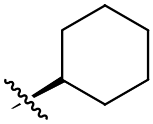
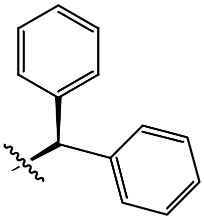


Figure 5. Steric perturbation of the fluorenyl ligand will alter the stereoselectivity of the two sites differently.

Fluorenyl-containing metallocenes **5**, **6**, and **7** were prepared as were Oct-containing metallocenes **8**, **9**, and **10** (Table 3). For R = methyl, cyclohexyl and diphenylmethyl, the isotacticity decreases substantially upon substitution of the Flu ligand for the Oct ligand. This is especially noteworthy for R = diphenylmethyl; the isospecificity of **7** is greater than that of **3**, whereas the isospecificity of **10** is less than that of **3**. These results implicate operation of the alternating mechanism for which the Oct ligand can perturb the stereochemistry of insertion at *both* sites of the metallocene.

Table 3. Comparative polymerizations between fluorenyl-containing and Oct-containing metallocenes for various R substituents.

						
R	T_p (°C)	T_m (°C)	mmmm (%)	T_p (°C)	T_m (°C)	mmmm (%)
	**5**			**8**		
	0	none	21.6	0	129.8	2.4
	20	none	18.3	20	116.8	2.4
	**6**			**9**		
	0	none	13.2	0	103.0	5.1
	20	none	14.5	20	none	7.3
	**7**			**10**		
	0	136.6	86.1	0	124.7	74.4
	20	137.8	81.2	20	135.4	76.4

6.3.4 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**, the incorporation of a methyl substituent on the cyclopentadienyl ligand opposed to it was accomplished in the synthesis of **11** (Figure 6). Because the condensation of Me$_2$C(C$_{13}$H$_9$)(3-

methyl-C_5H_4) with acetone occurs selectively at the four position of the cyclopentadienyl moiety—away from the tertiary alkyl substituent—$Me_2C(C_{13}H_8)$(3-*t*-butyl-4-methyl-C_5H_2)$ZrCl_2$ (**11**) was obtained as a single (racemic) stereoisomer. This was confirmed by determination of the crystal structure by X-ray diffraction, as shown in Figure 7.[15]

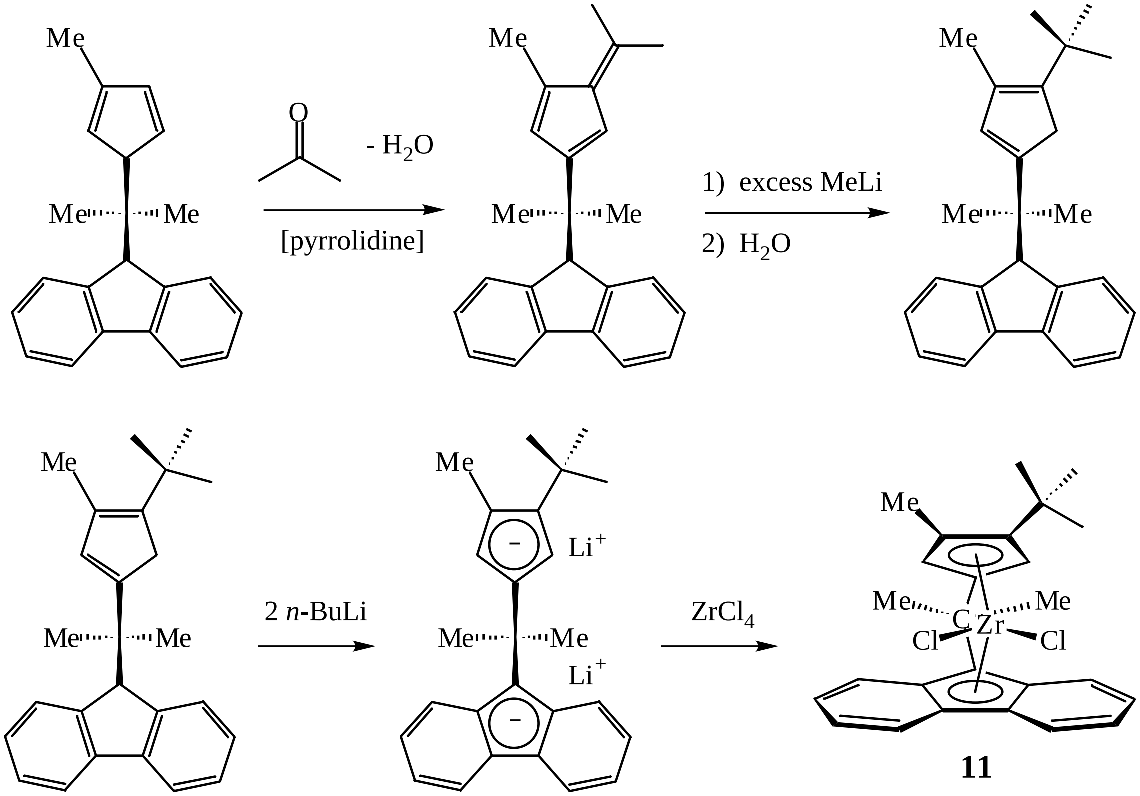


Figure 6. Synthetic route for the stereoselective synthesis of *rac*-$Me_2C(C_{13}H_8)$(3-*t*-butyl-4-methyl-C_5H_2)$ZrCl_2$ (**11**).

Table 4 tabulates the pentad distributions measured for polypropylenes obtained with **11**/MAO under a variety of polymerization conditions. The pentad distributions are largely independent of changes in polymerization temperature and monomer concentration, with the polymerization performed at 80°C in 10% monomer being the most affected by reaction conditions. As a representative example, the ^{13}C NMR of the methyl region for the polymer obtained in liquid monomer at 20°C is displayed in Figure 8.

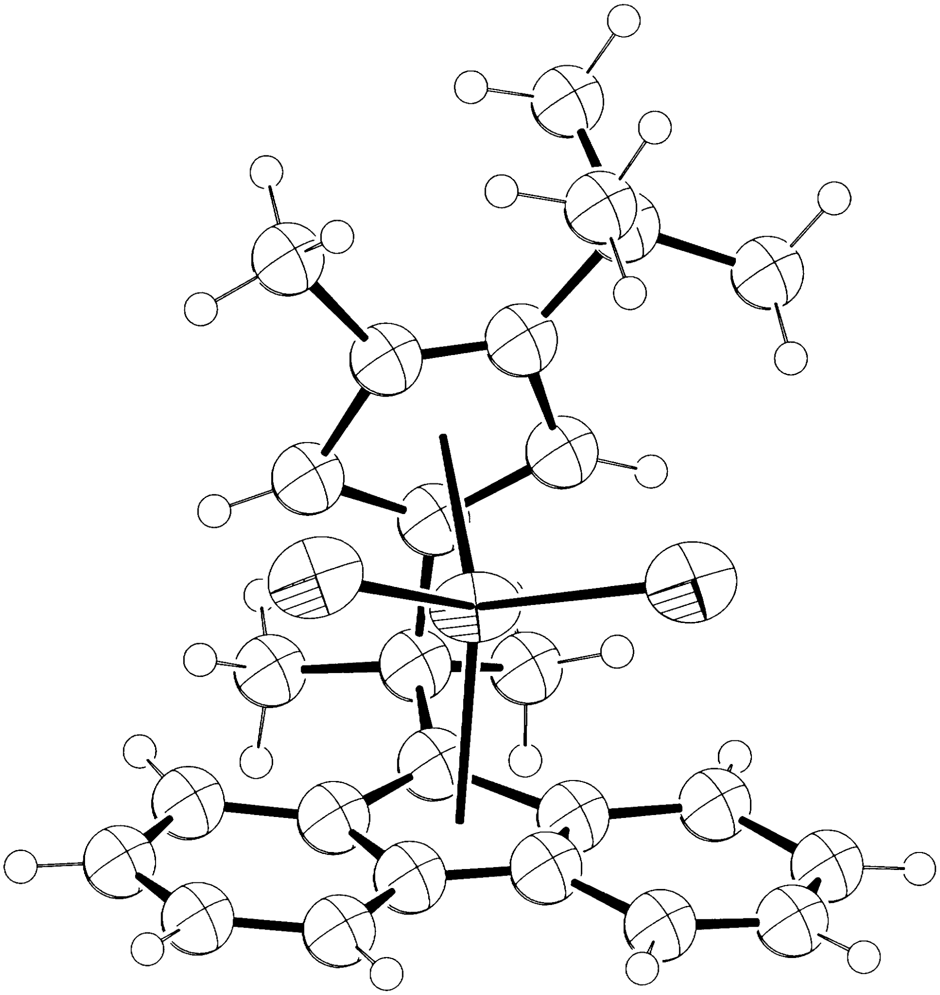


Figure 7. X-ray crystal structure of $Me_2C(C_{13}H_8)(3\text{-}t\text{-butyl-4-methyl-}C_5H_2)ZrCl_2$ (**11**). Thermal ellipsoids are shown with 50% probability.

Table 4. Pentad distributions obtained for polymers from **11**/MAO.

	liquid C_3H_6		10% C_3H_6 in toluene				
T_p (°C)	0	20	0	20	40	60	80
Pentad (%)							
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
mrmm + rmrr	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

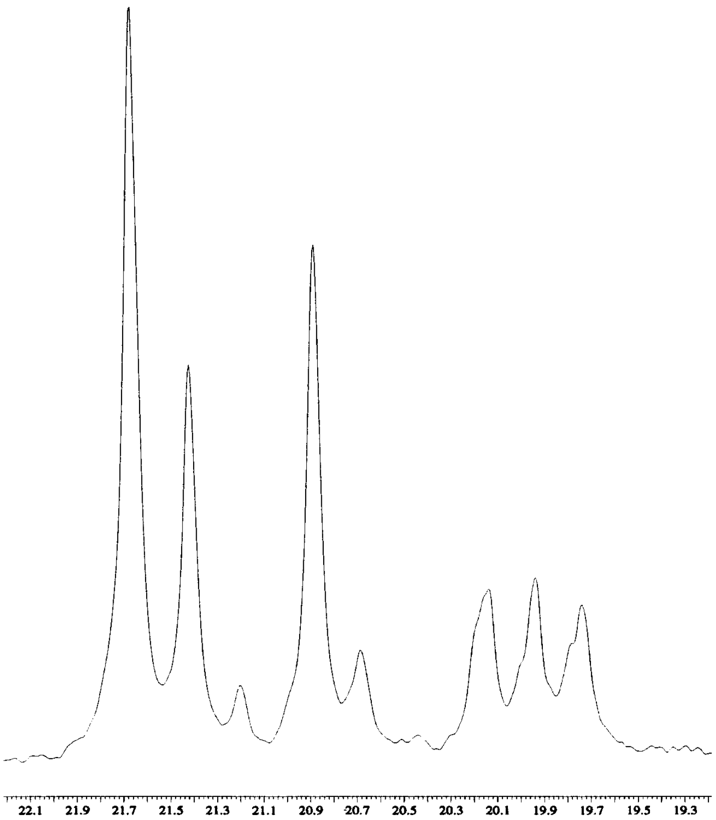


Figure 8. ^{13}C NMR of the methyl region for the polypropylene obtained with **11**/MAO in liquid monomer at 20°C.

The observed pentad distributions were subjected to a variety of statistical models. Table 5 shows this analysis for the polymer made with **11**/MAO at 20°C in liquid monomer.[17] 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 relative intensities of only four out of the ten pentads (#1, mmmm; #2, mmrr; #3, mmmr; and #9, rmmr). The triad models are each two site models. The triad model with $P_{mr} = 0$ has only one independent parameter, but correctly predicts the relative intensities of all seven allowed pentads. Not surprisingly, the triad model with $P_{mr} > 0$ having two independent parameters provides the best fit of all.

Table 5. Statistical analysis of a polymer made with **11**/MAO at 20°C in liquid monomer.

Pentad (%)	observed	chain end control	enantiomorphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	30.0	29.1	30.1	31.6	29.8
mmmr	15.1	21.0	16.7	14.6	16.0
rmmr	3.1	3.8	2.8	4.4	4.1
mmrr	19.2	7.6	16.7	23.5	20.6
mrmm + rmrr	5.2	23.8	11.3	0.0	5.2
mrmr	1.2	7.6	5.7	0.0	1.0
rrrr	8.9	0.5	2.8	9.8	7.7
rrrm	8.7	2.8	5.7	8.8	8.9
mrrm	8.6	3.8	8.3	7.3	6.7
m	61.0	73.4	66.4	62.3	63.3
r	39.0	26.6	33.6	37.7	36.7
Parameters		$\sigma = 0.734$	$\alpha = 0.786$	$P_{mm} = 0.624$ $P_{rr} = 0.376$	$P_{mm} = 0.598$ $P_{rr} = 0.331$ $P_{mr} = 0.035$ $P_{rm} = 0.035$
RMS error		8.73	3.53	2.44	0.99

The statistical calculations are most consistent with the operation of a two site, alternating mechanism for **11**/MAO since the single site models cannot adequately describe the resultant polymers, which are essentially hemiisotactic with a slight bias toward isotactic. The parameters derived from the triad model with $P_{mr} > 0$ are related to the stereoselectivities of the two sites, and predict the mechanism shown in Figure 9. At the more stereoselective site, the growing polymer chain is preferentially directed away from the *tert*-butyl group and the enantiofacial selectivity is 96.5% (= $1 - P_{mr}$). At the less stereoselective site, benzo and methyl are comparable in their abilities to direct the growing polymer chain. However, benzo is slightly more directing and the enantiofacial selectivity is 66.9% (= $1 - P_{rr}$). Contrary to steric arguments[4a, 2c] that claim monomer insertion cannot occur while the growing polymer chain is proximal to the *tert*-butyl group in **3**/MAO, the catalyst system **11**/MAO readily inserts monomer at both sites of the metallocene despite the presence of a bulky *tert*-butyl group.

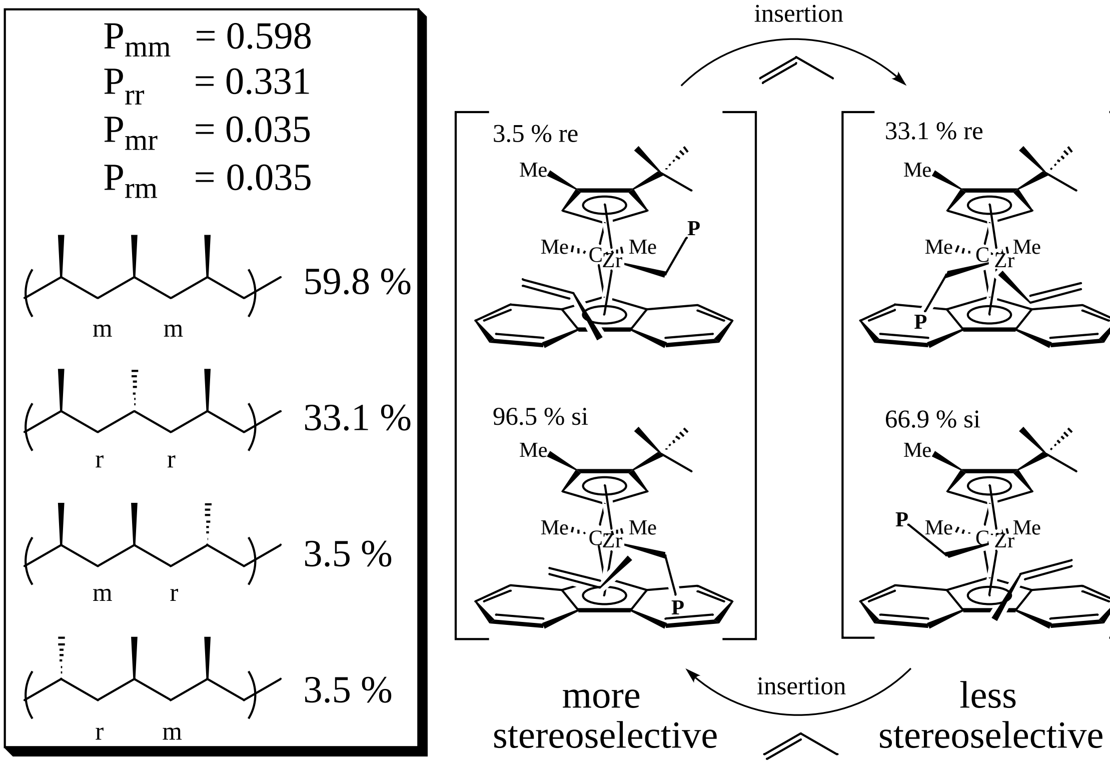
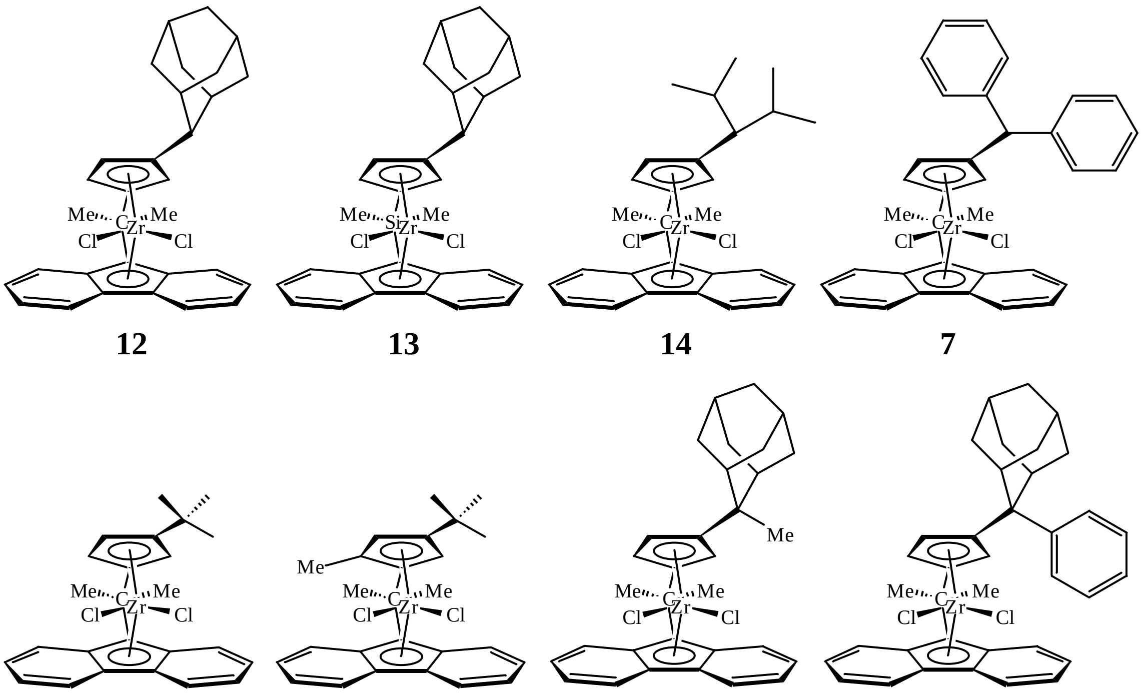


Figure 9. Predicted mechanism for polypropylene formation with **11**/MAO at 20°C in liquid monomer.

If indeed the alternating mechanism is operating for **3**/MAO, the statistical models suggest that one site is operating with 99.2% stereoselectivity and the other site is operating with 91.8% stereoselectivity (Table 1). This latter stereoselectivity should correspond to that of the more stereoselective site of **11**/MAO (96.5%) insofar as its methyl group has no effect on the stereochemistry of insertion. Similarly, the stereoselectivity of the less stereoselective site of **11**/MAO (66.9%) should correspond to the that of the less stereoselective site of the known hemiisotactic catalyst system $Me_2C(C_{13}H_8)$(3-methyl-C_5H_3)$ZrCl_2$/MAO[2a, 4b] (approximately 50%) insofar as its *tert*-butyl group has no effect on the stereoselectivity. These apparent stereoselectivity discrepancies represent small energy differences ($\Delta\Delta G^{\ddagger}$), and their magnitudes are proportional to the perturbation ($\Delta\alpha$ = +5% for the addition of methyl to **3** and $\Delta\alpha$ = +17% for addition of *tert*-butyl to $Me_2C(C_{13}H_8)$(3-methyl-C_5H_3)$ZrCl_2$).

6.3.5 Steric Perturbation of the 3-Cyclopentadienyl Substituent

Since **3**/MAO likely employs the alternating mechanism, steric perturbation of the 3-cyclopentadienyl substituent should have an effect on polymer stereochemistry much greater than previously thought. For this reason, the metallocenes shown in Figure 10 were prepared. Each was subjected to MAO-cocatalyzed propylene polymerizations at 0°C and 20°C, as reported in Table 6.



12 **13** **14** **7**

3 **15** **16** **17**

Figure 10. Metallocenes **3**, **7**, and **12-17** having various 3-cyclopentadienyl substituents.

Metallocene **12** incorporates a 2-adamantyl alkyl substituent in the 3 position of the cyclopentadienyl ring. **12**/MAO employs the alternating mechanism[18] and affords essentially hemiisotactic polypropylene with mmmm = 28.4%. While 2-adamantyl is large, it is not a tertiary alkyl substituent and is far inferior to *tert*-butyl in its ability to direct the growing polymer chain during the transition state for monomer insertion. Metallocene **13** is identical to **12** except that it bears a dimethylsilylene bridge. Such silicon-containing metallocenes often site epimerize more readily compared to their carbon analogs.[2d, 3d, 19] This is true of **13**/MAO as mmmm doubles to 60.2%. The site epimerization process allows this metallocene to employ the more stereoselective site to a greater degree.[20]

Metallocenes **14** and **7** produce polypropylene with isotacticities as high or higher than that produced by the parent metallocene **3**, despite the fact that they contain secondary alkyl substituents on the cyclopentadienyl ring. Therefore, it is not necessary to have a tertiary alkyl substituent to obtain isotactic polypropylene. Furthermore, 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.

Metallocene **15**, which is the 2-methyl analog of **3**, produces a polymer of considerably higher isotacticity, as measured by an increase in melting temperature of 18°C. The origin of this result is not fully understood but may be related to increases in isospecificities and molecular weights effected by α-methyl substitution.[3c, 21]

The second largest cyclopentadienyl substituent employed, 2-methyl-2-adamantyl,[22] is incorporated into metallocene **16**. This metallocene is capable of producing highly isotactic polypropylene (mmmm > 98%) with a melting temperature of 159°C. The high isospecificity 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 have turned on the site epimerization mechanism and metallocene **16** employs only one highly stereoselective site for monomer insertion. In either case, it is very difficult to rationalize the comparatively poor isospecificity of **3**/MAO (mmmm = 79.5%) if one claims that it employs the site epimerization mechanism.

Table 6. MAO-cocatalyzed polymerization results with **3**, **7**, **12**, **13**, **14**, **15**, **16**, **17**, and **18**.

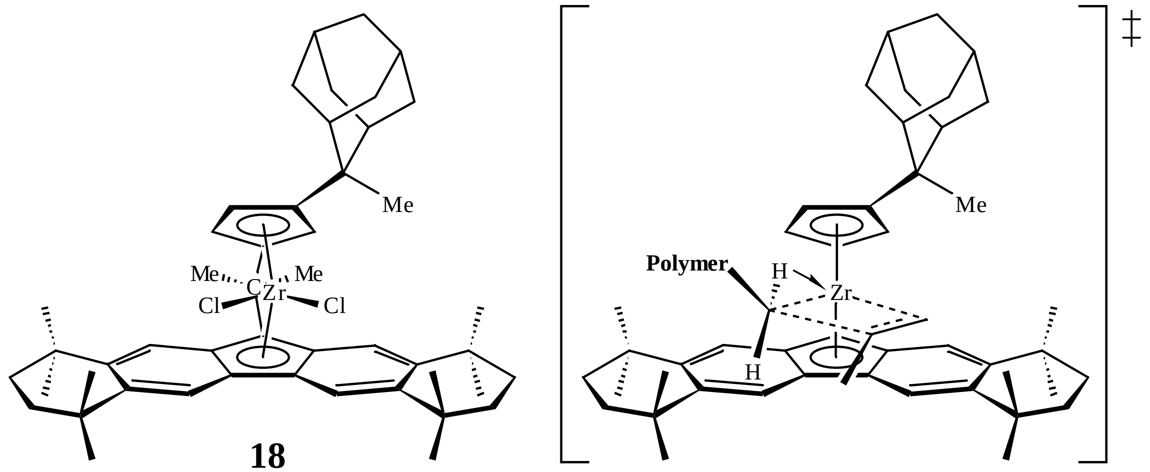
Entry	Metallocene (mg)	MAO (equiv.)	T_p (°C)	Toluene (mL)	C_3H_6 (mL)	Time (min.)	Yield (g)	Activity (gP/(gmet·h))	T_m [a] (°C)	m^4 (%)	M_w	M_w/M_n
1	**12** (0.5)	2000	0	1.0	30	30	1.50	6000	n.o.	28.4	134,000	3.15
2	**12** (0.5)	2000	20	1.0	30	10	1.08	13000	n.o.	31.4	81,900	4.38
3	**13** (1.0)	1000	0	2.0	30	15	0.18	730	109	60.2	360,000	1.75
4	**13** (1.0)	1000	20	2.0	30	15	1.62	6500	110	57.5	322,000	1.70
5	**14** (2.0)	1000	0	2.0	30	5	0.16	970	129	78.6	76,700	1.81
6	**14** (2.0)	1000	20	2.0	30	30	0.36	360	131	80.0	80,900	2.63
7	**7** (2.0)	1000	0	2.0	30	20	0.32	480	137	86.1		
8	**7** (2.0)	1000	20	2.0	30	20	0.47	710	138	81.2		
9	**3** (2.0)	1000	0	2.0	30	20	0.93	1400	126	79.5		
10	**3** (2.0)	1000	20	2.0	30	3	1.01	10000	125	81.5		
11	**15** (1.0)	1000	0	1.0	30	15	0.28	1100	144			
12	**15** (1.0)	1000	20	1.0	30	3	0.66	13000	139			
13	**16** (1.0)	1000	0	2.0	30	10	0.41	158	158	>98	171,00	1.93
14	**16** (1.0)	1000	20	2.0	30	10	0.83	5000	154	>98	113,000	1.93
15	**16** (2.0)	1000	0	2.0	55	60	3.88	1900	160	>98	157,000	2.48
16	**16** (2.0)	1000	20	2.0	55	10	2.13	6400	156		124,000	1.90
17	**16** (2.0)	1000	0	2.0	55	10	1.38	4100	159		160,000	1.91
18	**16** (2.0)	1000	0	30.0	3	180	0.87	140	158		102,000	1.82
19	**16** (2.0)	1000	20	30.0	3	90	0.50	170	148		54,400	2.08
20	**17** (3.0)	1000	0	2.0	30	120	0.03	4	n.o.			
21	**17** (3.0)	1000	20	2.0	30	120	0.02	3	n.o.			
22	**18** (2.0)	1000	0	2.0	30	20	0.29	440	167	>99	370,000	1.39
23	**18** (2.0)	1000	20	2.0	30	20	0.70	1100	163	>99	425,000	1.77

[a] n.o. = melting temperature not observed.

The largest cyclopentadienyl substituent employed, 2-phenyl-2-adamantyl, is incorporated into metallocene **17**. **17**/MAO is essentially inactive for propylene polymerization.[23] The cyclopentadienyl substituent is so large that both the alternating and site epimerization mechanisms have effectively halted.

6.4 Formation of Highly Isotactic Polypropylene with C_1-symmetric Metallocene Catalysts

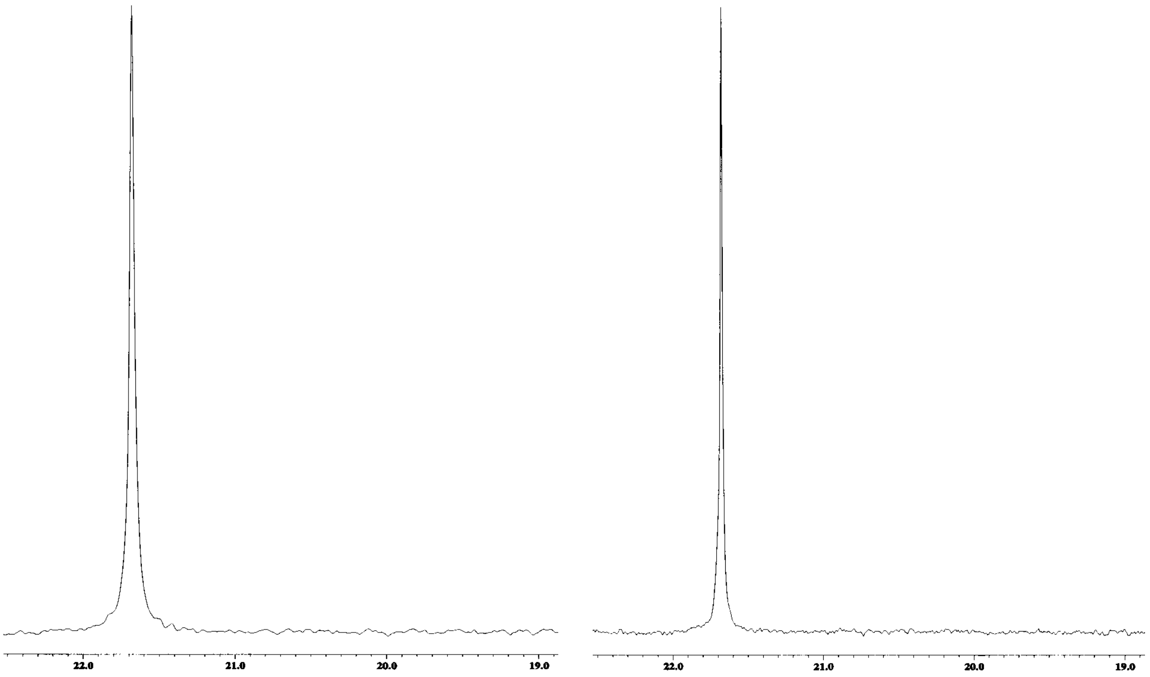
We sought to apply everything we learned about isotactic polypropylene formation to the design of a single, C_1-symmetric metallocene capable of producing highly isotactic polypropylene. Metallocene **18** (Figure 11) is the result of this endeavor and its structure arises from the identification of three important factors. First, the cyclopentadienyl substituent should be larger than *tert*-butyl, but not so large that it retards polymerization altogether. Therefore, the 2-methyl-2-adamantyl substituent has been incorporated into **18**. Second, factors that encourage site epimerization generally lead to polymers of higher isotacticity since the more stereoselective site is used preferentially. This can be accomplished, in principle, by altering polymerization conditions[24] or by the inclusion of a dimethylsilylene bridge. For **18**, 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 stereospecificity 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 **18** leads to greater isospecificity at the more stereoselective site.



18

Figure 11. Highly isospecific polymerization catalyst **18**/MAO likely employs a single propagative transition state.

The propylene polymerization results with **18**/MAO are given in Entries 22 and 23 of Table 5. Highly isotactic polypropylene is obtained, as stereoerrors are virtually absent by ^{13}C NMR analysis (mmmm > 99%, Figure 12). The polymers have high melting temperatures (167.0°C and 162.7°C) and large enthalpies of melt (92.0 J/g and 87.5 J/g, respectively). The high isospecificity of **18**/MAO suggests that it employs a single propagative transition state for monomer insertion, as depicted in Figure 11.



Entry 22

Entry 23

Figure 12. ^{13}C NMR of the methyl region for isotactic polypropylenes obtained with **18**/MAO.

6.5 Conclusions

The mechanism of isotactic polypropylene formation with $Me_2C(C_{13}H_8)$(3-*t*-butyl-C_5H_3)$ZrCl_2$/MAO (**3**/MAO) has been the topic of much recent debate. Despite the paucity of experimental evidence to support it, the majority of authors have invoked a site epimerization mechanism to explain the high isotacticities observed. The tacticity of this material is sufficiently isotactic that stereochemical analyses cannot conclusively discriminate 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 differentiate between 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 metallocenes/MAO. An increase in isotacticity is observed for polymerization conditions that favor unimolecular site epimerization over bimolecular propagation. Incorporation of the bulky Oct ligand effects an increase in syndiotacticity—a change consistent with an increase in stereoselectivity at one site and a decrease in stereoselectivity at a second site. The model system $Me_2C(C_{13}H_8)(3\text{-}t\text{-butyl-4-methyl-}C_5H_2)ZrCl_2$/MAO (**11**/MAO) produces essentially hemiisotactic PP, 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.

Three key elements contributed to the design of a highly isospecific metallocene catalyst system, $Me_2C(Oct)(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)ZrCl_2$/ MAO (**18**/MAO): incorporation of a cyclopentadienyl substituent larger than *tert*-butyl; considerable steric bulk on one side of the metallocene to encourage site epimerizations; and exploitation of the enhanced ability of the Oct ligand to direct the growing polymer chain during the transition state for monomer insertion. This catalyst system is capable of producing highly isotactic polypropylene (mmmm > 99%, T_m = 167°C) and demonstrates how the correct understanding of mechanism can lead to the rational design of improved catalysts.

6.6 Experimental Section

General Considerations. Unless otherwise noted, all reactions and procedures are carried out under an inert atmosphere of argon or nitrogen using standard glove box, Schlenk and high vacuum line techniques.[25] Solvents are dried according to standard procedures. The following were purchased from Aldrich and used as received: redistilled pyrrolidine (99.5+%); fluorene (98%); 2-adamantanone (99%); n-butyllithium (1.6 M in hexanes); methyllithium lithium bromide (1.5 M in diethyl ether); phenyllithium (1.8 M in cyclohexane/diethyl ether); zirconium tetrachloride (99.5%); aluminum chloride (99.99%); 2,5-dimethyl-2,5-hexanediol (99%); benzophenone (99%); nitromethane (96%); and 2,4-dimethyl-3-pentanone. Dicyclopentadiene and di(methylcyclopentadiene) were obtained from Aldrich and cracked following standard procedures prior to use. **Instrumentation.** NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC-MS were acquired with a Hewlett Packard 5890 Series II Gas Chromatograph connected to a Hewlett Packard 5989A Mass Spectometer. The GC was equipped with a column of dimensions 7.1 m x 0.1 μm having an HP-1 phase (Crosslinked Methyl Silicone Gum). LC-MS were acquired with a Hewlett Packard 1090 Series II Liquid Chromatograph with a toluene phase (solvent dried over sodium/benzophenone). The LC was connected to a Hewlett Packard 59980B Particle Beam Interface, and this was connected to a Hewlett Packard 5989A Mass Spectrometer.

Metallocene Syntheses.

Preparation of 3. Metallocene **3** was synthesized as described in the literature.[4a] MS (LC-MS) *m/z* 488.6 (M^+). Elemental analysis calculated for $C_{25}H_{26}Zr_1Cl_2$: C, 61.46; H, 5.36. Found: C, 43.94; H, 4.31.

Preparation of 4.

fluorenyllithium·diethyl ether. A 500 mL flask was charged with fluorene (47.00 grams, 282.8 mmol) and attached to a swivel frit before 200 mL diethyl ether were condensed in. n-butyllithium solution (180.0 mL, 288 mmol, 1.6 M in hexanes) was syringed in over 20 minutes at room temperature. After stirring for 18 hours, the yellow precipitate was collected and dried in vacuo: 50.64 g (72.7% based on the mono diethyl ether adduct).

3-*t*-butyl-6,6-diphenylfulvene. A argon-filled 1 L Schlenk flask was charged with 6,6-dimethylfulvene (40.15 g, 378.2 mmol) and 180 mL diethyl ether. At 0°C, methyllithium·lithium bromide solution (420 mL, 630 mmol, 1.5 M in diethyl ether) was syringed in over 25 minutes. The reaction was stirred for 7 days before it was cooled to 0°C and 60 mL aqueous NH_4Cl solution were slowly added, followed by 120 mL water. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped to provide 38.41 grams of *tert*-butylcyclopentadiene (83.1%). 15.00 grams of this material were combined with 100 mL ethanol and 22.37 grams 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 water and 200 mL diethyl ether were added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 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 grams were removed and the next fraction was collected as product at 60°C: 9.22 grams of red viscous oil (26.2%).

$Ph_2C(3\text{-}t\text{-butyl-}C_5H_3)(C_{13}H_8)H_2$. A 250 mL flask was charged with waxy 3-*tert*-butyl-6,6-diphenylfulvene (9.22 grams, 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 were slowly added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 x 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 grams (45.2%). MS (GC-MS) m/z 452.5 (M^+). Elemental analysis calculated for $C_{35}H_{32}$: C, 92.87; H, 7.13. Found: C, 91.37; H, 6.56.

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

$Ph_2C(3\text{-}t\text{-butyl-}C_5H_3)(C_{13}H_8)ZrCl_2$ (4). A 100 mL flask was charged with $Ph_2C(3\text{-}tert\text{-butyl-}C_5H_3)(C_{13}H_8)Li_2$ (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 hours, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL 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, $C(CH_3)_3$), 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, 4H, Flu-H), 6.96, 6.99, 7.85, 7.85 (t, $^3J_{HH}$ = 7.0, 7.7, 7.3, 7.3, 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 ($C(CH_3)_3$), 33.20 ($C(CH_3)_3$), 101.33, 105.86, 115.11 (Cp-CH_1), 121.05, 121.51, 123.27, 124.00 (fluorenyl-CH_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-CH_1 and Cp-CH_1), 145.03, 145.11 (ipso-C), 146.18 (9-fluorenyl-C), other CH_0, not determined. Elemental analysis calculated for $C_{35}H_{30}Zr_1Cl_2$: C, 68.61; H, 4.93. Found: C, 64.90; H, 4.56.

Preparation of 5. Metallocene **5** was synthesized as described in the literature.[4c]

Preparation of 6.

6,6-(pentamethylene)fulvene (cyclohexylfulvene). (Synthesis modified from reference 26) 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 hours before 40 mL of acetic acid were added, followed by 300 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and rotavapped to give 158.8 grams of a yellow oil that was subjected to Kugelrohr distillation under high vacuum. The first 20 grams 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 grams (61.1%).

cyclohexylcyclopentadiene. 15.66 grams (107.1 mmol) of cyclohexylfulvene were dissolved in 50 mL of tetrahydrofuran and this solution was added over 12 minutes to a stirred slurry of $LiAlH_4$ (4.500 g, 118.6 mmol) in 100 mL tetrahydrofuran at 0°C. After 15 hours 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 H_2O and 50 mL diethyl ether were added; the organic layer was isolated, and the aqueous layer was extracted with additional diethyl ether (2 x 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 methanol, acetone (20.0 mL, 272 mmol) and pyrrolidine (1.0 mL, 12 mmol). After stirring for 21 hours, 5 mL of acetic acid were injected, followed by 150 mL H_2O and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and with 10% aqueous NaOH (3 x 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.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)H_2$. 15.5 mL of an n-butyllithium solution (24.8 mmol, 1.6 M in hexanes) were syringed into a solution of fluorene (4.047 g, 24.35 mmol) in 60 mL tetrahydrofuran. After stirring for 45 minutes, 3-cyclohexyl-6,6-dimethylfulvene (4.58 g, 24.3 mmol) was injected via syringe. After stirring for 15 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)H_2$ (8.63 g, 24.3 mmol) in 50 mL 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 hours, the solvent was removed by vacuum transfer and 75 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield as a red-orange powder.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)ZrCl_2$ (6). 2.500 grams of $Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{13}H_8)Li_2$ (6.82 mmol) and 1.59 g $ZrCl_4$ (6.82 mmol) were combined in a swivel frit apparatus. 30 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 17 hours of stirring. 40 mL of methylene chloride were 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 were obtained for a total of 1.261 grams (35.9%) of **6** as an orange powder following collection at 0°C and *in vacuo* drying. MS (LC-MS) m/z 514.7 (M^+). ^1H NMR (C_6D_6): δ 0.87 - 1.26 (m, 10H, cyclohexyl-*H*), 1.81, 1.82 (s, 6 H, $C(CH_3)_2$), 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*). Elemental analysis calculated for $C_{27}H_{28}Zr_1Cl_2$: C, 63.01; H, 5.48. Found: C, 57.74; H, 5.53.

Preparation of 7.

6,6-diphenylfulvene. (Synthesis modified from reference 27) 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 ethanol. The solid was refluxed in 200 mL methanol for 1 hour. Upon cooling the solid was collected, rinsed with 75 mL methanol, and dried *in vacuo* for 48 hours to provide the product as an orange powder: 136.18 g (86.2%). MS (GC-MS) m/z 230.3 (M^+).

Elemental analysis calculated 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 tetrahydrofuran. An addition funnel containing 6,6-diphenylfulvene (20.00 g, 86.84 mmol) dissolved in 100 mL tetrahydrofuran was attached. The vessel was cooled to 0°C before dropwise addition over 45 minutes. After 22 hours of stirring at room temperature, the vessel was cooled to 0°C and 60 mL of aqueous NH_4Cl solution were added dropwise. Then, 300 mL water and 20 mL of concentrate aqueous HCl were added before the organic layer was isolated. The aqueous layer was extracted with diethyl ether (3 x 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 methanol, acetone (20.0 mL, 272 mmol), and pyrrolidine (5.0 mL, 60 mmol). After stirring for 67 hours, the yellow precipitate was collected by suction filtration, was washed with 20 mL methanol, and was dried *in vacuo*: 8.24 grams (70.3%).

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)H_2$. A 250 mL flask was charged with fluorene (3.661 g, 22.03 mmol), evacuated, and backfilled with argon before 50 mL tetrahydrofuran and 14.0 mL n-butyllithium solution (22.4 mmol, 1.6 M in hexanes) were syringed in. The orange solution was stirred for 1 hour before a solution of 3-(diphenylmethyl)-6,6-dimethylfulvene (6.00 g, 22.03 mmol) in 15 mL tetrahydrofuran was syringed in. Following an additional 16 hours, the stirred reaction was quenched by slow addition of 60 mL aqueous NH_4Cl. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)Li_2$. A round bottom flask containing 9.66 grams (22.0 mmol) of $Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)H_2$ was attached to a swivel frit and evacuated before 75 mL of diethyl ether were condensed in. At 0°C, 28.0 mL of n-butyllithium solution (44.8 mmol, 1.6 M in hexanes) were syringed in over 2 minutes. After stirring for 18 hours at room temperature, the red precipitate was collected and dried *in vacuo* to provide the product in quantitative yield (9.92 g).

$Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)ZrCl_2$ (7). In the glove box, 1.933 grams of $Me_2C(3\text{-(diphenylmethyl)-}C_5H_3)(C_{13}H_8)Li_2$ (4.29 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly and after 24 hours of stirring, solvent was removed. 50 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal. The solid was extracted for 64 hours 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 grams of **7** (59.2%). MS (LC-MS) m/z 598.5 (M^+). ^1H 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, $CHPh_2$), 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*). Elemental analysis calculated for $C_{34}H_{28}Zr_1Cl_2$: C, 68.21; H, 4.71. Found: C, 52.61; H, 3.82.

Preparation of 8.

2,5-dichloro-2,5-dimethylhexane. A 2 liter argon purged vessel was charged with 2,5-dimethyl-2,5-hexanediol (200.00 g, 1.368 mol) and concentrated aqueous hydrochloric acid (1.00 L, 12.2 mol HCl) was poured in. The white slurry was shaken and stirred for 17 hours. The white solid was collected by suction filtration and rinsed with 500 mL water. The solid was dissolved in 1.00 L 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 minutes) 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 (CH$_3$), 41.21 (CH$_2$), 70.13 (CH$_0$). Elemental analysis calculated 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 liter 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 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 nitromethane. The solution was added over 10 minutes and the purple reaction was stirred for 20 hours before it was slowly poured into 700 mL of ice water. The precipitate was collected by filtration and refluxed in 500 mL ethanol for 2 hours. Upon cooling, the solid was collected by filtration and this was refluxed in 300 mL hexanes for 2 hours. After cooling, the solid was collected by filtration and dried *in vacuo*, giving the product as a white powder: 62.53 grams (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 (CH$_3$), 34.68, 34.71 (CH$_0$), 35.50, 35.55 (CH$_2$), 36.47 (CH$_2$), 117.48, 123.31(CH$_1$), 139.20, 140.80, 143.50, 143.66 (CH$_0$). Elemental analysis calculated 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 liter flask was charged with 400 mL 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 hours, 50 mL of acetic acid were added, followed by 1200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (5 x 100 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and 10% aqueous NaOH (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and rotavapped to give 158.8 grams of a red-orange oil that was subjected to Kugelrohr distillation under high vacuum. The first 15 grams 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 grams (94.0%).

$Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})H_2$. 13.5 mL of an n-butyllithium solution (21.6 mmol, 1.6 M in hexanes) were syringed into a solution of octamethyloctahydrodibenzofluorene (8.00 g, 20.7 mmol) in 90 mL tetrahydrofuran. After stirring for 90 minutes, 3,6,6-trimethylfulvene (2.487 g, 20.7 mmol) was injected via syringe into the red solution. After stirring for 22 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})H_2$ (10.49 g, 20.7 mmol) in 75 mL 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 hours, the precipitate was isolated by filtration and *in vacuo* drying to provide the dianion as a yellow powder: 8.707 g (81.1%).

$Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (8). 3.34 grams of $Me_2C(3\text{-methyl-}C_5H_3)(C_{29}H_{36})Li_2$ (6.44 mmol) and 1.50 g $ZrCl_4$ (6.44 mmol) were combined in a swivel frit apparatus. 50 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 18 hours of stirring. 20 mL of methylene chloride were 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 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 grams (24.5%) of **8** as an orange-pink powder was obtained following *in vacuo* drying. MS (LC-MS) m/z 666.6 (M^+). ^1H NMR (C_6D_6): δ 1.20, 1.31, 1.31, 1.31, 1.31, 1.32, 1.50, 1.53 (s, 24H, Oct-CH_3), 1.65 (m, 8H, Oct-CH_2), 1.93 (s, 3H, Cp-CH_3), 2.03, 2.06 (s, 6H, $(CH_3)_2$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*). Elemental analysis calculated for $C_{38}H_{48}Zr_1Cl_2$: C, 68.44; H, 7.25. Found: C, 62.90; H, 6.97.

Preparation of 9.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{29}H_{36})H_2$. 11.0 mL of an n-butyllithium solution (17.6 mmol, 1.6 M in hexanes) were syringed into a solution of octamethyloctahydrodibenzofluorene (6.603 g, 17.08 mmol) in 60 mL tetrahydrofuran. After stirring for 50 minutes, 3-cyclohexyl-6,6-dimethylfulvene (3.216 g, 17.08 mmol) was injected via syringe into the red slurry. After stirring for 18 hours, 60 mL of a saturated NH_4Cl solution were added, the organic layer was isolated, and the aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{29}H_{36})Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{29}H_{36})H_2$ (9.82 g, 17.1 mmol) in 75 mL 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 hours, the precipitate was isolated by filtration and *in vacuo* drying to provide the dianion as an orange powder: 6.446 g (64.3%).

$Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (9). 2.518 grams of $Me_2C(3\text{-cyclohexyl-}C_5H_3)(C_{29}H_{36})Li_2$ (4.29 mmol) and 1.00 g $ZrCl_4$ (4.29 mmol) were combined in a swivel frit apparatus. 30 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 18 hours of stirring. 40 mL of methylene chloride were 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 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 grams (58.5%) of **9** as an orange powder was obtained following *in vacuo* drying. MS (LC-MS) m/z 734.8 (M^+). ^1H 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-CH_3), 1.63 (m, 8H, Oct-CH_2), 2.08, 2.09 (s, 6H, $(CH_3)_2$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*). Elemental analysis calculated for $C_{43}H_{56}Zr_1Cl_2$: C, 70.26; H, 7.68. Found: C, 67.53; H, 7.76.

Preparation of 10.

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 tetrahydrofuran and 5.2 mL n-butyllithium solution (8.3 mmol, 1.6 M in hexanes) were syringed in. The orange solution was stirred for 4 hours before a solution of 3-(diphenylmethyl)-6,6-dimethylfulvene (2.105 g, 7.728 mmol) in 25 mL tetrahydrofuran was syringed in. Following an additional 30 hours, the stirred reaction was quenched by slow addition of 60 mL aqueous NH_4Cl. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 x 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 grams (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 were condensed in. At 0°C, 10.4 mL of n-butyllithium solution (16.6 mmol, 1.6 M in hexanes) were syringed in over 2 minutes. After stirring for 26 hours at room temperature, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were 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)($C_{29}H_{36}$)$ZrCl_2$ (10). In the glove box, 2.879 grams of Me_2C(3-(diphenylmethyl)-C_5H_3)($C_{29}H_{36}$)Li_2 (4.29 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly and after 17 hours of stirring, solvent was removed. 20 mL of methylene chloride were 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 grams of **10** (22.6%). MS (LC-MS) *m/z* 818.8 (M^+). ^1H NMR (C_6D_6): δ 1.08, 1.20, 1.23, 1.29, 1.30, 1.30, 1.51, 1.58 (s, 24H, Oct-CH_3), 1.63 (m, 8H, Oct-CH_2), 1.90, 2.04 (s, 6H, $(CH_3)_2$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, $CHPh_2$), 6.91 - 7.15 (m, 10H, phenyl-*H*), 7.46, 6.65, 8.29, 8.31 (s, 4H, Oct-*H*). Elemental analysis calculated for $C_{50}H_{56}Zr_1Cl_2$: C, 73.32; H, 6.89. Found: C, 65.09; H, 6.86.

Preparation of 11.

$Me_2C(3\text{-methyl-}C_5H_3)(C_{13}H_8)H_2$. 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 and 240 mL of diethyl ether were added via syringe. 210.0 mL of n-butyllithium in hexanes (1.6 M, 336.0 mmol) were syringed in at room temperature over 20 minutes. After shaking and stirring the obtained yellow slurry for 1 hour, 3, 6, 6-trimethylfulvene (40.00g, 332.8 mmol) was syringed in over 25 minutes, providing a clear, red solution. After stirring for 17 hours, the vessel was cooled to 0°C and 60 mL aqueous NH_4Cl solution were added. The slurry was filtered and the aqueous layer removed. The obtained solid was extracted from a cellulose extraction thimble with 500 mL diethyl ether/hexanes for two 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 grams, respectively (43.4% for all three crops). MS (GC-MS) *m/z* 286.3 (M^+). Elemental analysis calculated 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. 11.86 grams of $Me_2C(3\text{-methyl-}C_5H_3)(C_{13}H_8)H_2$ (41.41 mmol) were combined with 200 mL acetone (2720 mmol) and 15.0 mL pyrrolidine (180 mmol). After stirring for 30 minutes, a homogeneous solution is obtained and stirring is ceased. The product slowly crystallized and after 30 days, the yellow crystals were collected by filtration.

These were combined with 100 mL methanol, brought to a boil for 4 hours, and stirred overnight as the vessel cooled. Collection by suction filtration, rinsing with 25 mL methanol, and *in vacuo* drying afforded 8.15 grams of the desired product (60.3%). MS (GC-MS) m/z 326.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.02, 1.02 (s, 6H, $C(CH_3)_2$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 (CH_3), 39.38 (CH_0), 55.66 (9-Flu-CH_1), 114.78, 130.54 (fulvene-CH_1), 119.30, 119.30, 126.07, 126.07, 126.52, 126.52, 126.92, 126.93 (Flu-CH_1), 132.75, 133.98, 140.86, 151.75 (fulvene-CH_0), 142.04, 142.04, 145.54, 145.54 (Flu-CH_0). Elemental analysis calculated for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 90.83, 91.12; H, 7.33, 7.26.

$Me_2C(3\text{-}t\text{-butyl-4-methyl-}C_5H_2)(C_{13}H_8)H_2$. A 250 mL round bottom flask was charged with 5.087 grams of 2, 6, 6-trimethyl-4-(C(methyl)$_2$(9-fluorenyl))-fulvene (15.58 mmol). This was evacuated before 100 mL diethyl ether were condensed in. 75.0 mL of methyllithium in diethyl ether (1.4 M, 105 mmol) were added by syringe, giving an orange homogeneous solution after 1 hour. 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 H_2O. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and rotavapped to provide the product in quantitative yield (5.34 g) as a light yellow oil, which slowly began to crystallize.

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

Me_2C(3-*t*-butyl-4-methyl-C_5H_2)($C_{13}H_8$)$ZrCl_2$ (11). In the glove box, 2.28 grams of Me_2C(3-*t*-butyl-4-methyl-C_5H_2)($C_{13}H_8$)Li_2 (6.44 mmol) were 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 petroleum ether were condensed in by vacuum transfer at -78°C. The vessel was allowed to warm slowly and after 23 hours of stirring, solvent was removed. 30 mL of methylene chloride were condensed in; the solution was warmed and stirred before solvent removal; 30 mL of diethyl ether were 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 methylene chloride. The obtained solution was filtered through a frit, all solvent was removed, and 50 mL diethyl ether were condensed in. The pink solid was broken up, stirred, collected on the frit and dried *in vacuo* to afford the product **11**: 1.60 grams (49.5%). MS (LC-MS) m/z 502.3 (M^+). ^1H NMR (CD_2Cl_2): δ 1.16 (s, 9H, C(CH_3)$_3$), 2.07 (s, 3H, Cp-CH_3), 2.30, 2.32 (s, 6 H, C(CH_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 (CH_3), 29.17 (C(CH_3)$_3$), 33.52, 39.85 (CH_0), 78.40, 110.49, 121.76, 123.65, 123.79, 128.00, 140.84 (Cp and Flu CH_0), 102.93, 108.11 (Cp-CH_1), 123.42, 123.64, 124.45, 124.55, 124.68, 124.96, 128.33, 128.80 (Flu-CH_1). Elemental analysis calculated 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.

Preparation of 12.

adamantylfulvene. (Synthesis modified from reference 22) 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 hours before the yellow precipitate was collected by suction filtration, rinsed with a small volume of methanol and dried *in vacuo*. 25.71 grams (77.9%) of adamantylfulvene were isolated. MS (GC-MS) m/z 198.3 (M^+). ^1H 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-CH_1), 135.81, 167.38 (fulvene-CH_0). Elemental analysis calculated for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.20, 90.22; H, 8.39, 8.50.

2-adamantylcyclopentadiene. 6.00 grams (30.3 mmol) of adamantylfulvene were dissolved in 30 mL of tetrahydrofuran and this solution added over 30 minutes to at stirred slurry of $LiAlH_4$ (1.40 g, 0.0369 mol) at 0°C. After 5 hours 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 H_2O, 25 mL concentrated HCl, and 50 mL diethyl ether were added, the organic layer isolated, and the aqueous layer extracted with addition diethyl ether (3 x 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 methanol, 50 mL ethanol, 20 mL tetrahydrofuran, 36 mL acetone (0.49 mol) and 0.5 mL pyrrolidine (0.006 mol). After stirring for 48 hours, 5 mL of acetic acid were injected, followed by 200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 40 mL). The combined organic layers were extracted with H_2O (3 x 25 mL) and with 10% aqueous NaOH (3 x 25 mL), dried over $MgSO_4$, filtered and rotavapped. The obtained yellow solid was further purified by overnight Soxhlet extraction with 150 mL 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. Elemental analysis calculated for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 82.23, 82.23; H, 8.78, 8.82.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)H_2$. 10.5 mL 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 tetrahydrofuran. After stirring for 5 hours, a solution of 3-(2-adamantyl)-6,6-dimethylfulvene (4.00 g, 0.0166 mol) in 40 mL tetrahydrofuran was injected over 2 minutes. After stirring for 20 hours, 60 mL of a saturated

NH_4Cl solution were added, the organic layer isolated, and the aqueous layer extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_4)(C_{13}H_8)H_2$ (6.77 g, 16.6 mmol) in 75 mL 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 hours, the solvent was removed by vacuum transfer and 50 mL of petroleum ether were condensed in. The dilithio salt was isolated by filtration and *in vacuo* drying in quantitative yield as an orange powder.

$Me_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$ (12). 2.00 grams of $Me_2C(3\text{-}(2\text{-adamantyl})C_5H_4)(C_{13}H_8)Li_2$ (0.00478 mol) and 1.114 g $ZrCl_4$ (0.00478 mol) were combined in a swivel frit apparatus. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 14 hours of stirring. 40 mL of methylene chloride were 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 grams (55.5%) of **12** as an orange powder following collection at 0°C and *in vacuo* drying. MS (LC-MS) m/z 566.5 (M^+). ^1H NMR (C_6D_6): δ 1.84, 1.86 (s, 6H, CH_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 ($C\text{-}(CH_3)_2$), 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-CH_1), 123.41, 123.67, 124.61, 124.67, 124.76, 124.83, 128.81, 128.81 (Flu-CH_1), 139.93 (9-Flu-*C*),CH_0 not determined. Elemental analysis calculated for $C_{31}H_{32}ZrCl_2$: C, 65.70; H, 5.69. Found: C, 63.46, 61.93; H, 5.57, 5.42.

Preparation of 13.

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

9-($ClMe_2Si$)-fluorene. A swivel frit was charged with fluorenyllithium (7.00 g, 40.66 mmol) and 80 mL 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 hours, 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-fluorenyl)$_2$ (MS (GC-MS) m/z 388.4 (M^+)), as reported by reference 28, occurs to about 10% (GC), but apparently does not affect the synthesis of **13**.

2-adamantylcyclopentadienyllithium. Adamantylcyclopentadiene (10.78 g, 53.81 mmol) was added to a swivel frit and 75 mL diethyl ether were 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 minutes. After stirring for 15 hours 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).

$Me_2Si(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. A swivel frit was charged with 9-($ClMe_2Si$)-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 hours. Solvent was removed and 50 mL diethyl ether were 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 minutes at room temperature. Solvent was removed after stirring for 20 hours. 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).

$Me_2Si(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (13). 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) were 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 hours. The solid was placed in a cellulose extraction thimble and was extracted overnight with 150 mL 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 (**4**) was collected on the frit and dried in vacuo: 0.707 g (14.1%). MS (LC-MS) m/z 582.7 (M^+). ^1H 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. Elemental analysis calculated for $C_{30}H_{32}Si_1Zr_1Cl_2$: C, 61.83; H, 5.53. Found: C, 58.63; H, 4.94.

Preparation of 14.

6,6-diisopropylfulvene. A 500 mL round bottom flask was charged with 150 mL 2,4-dimethyl-3-pentanone (1060 mmol), 60.0 mL cyclopentadiene (728 mmol), and 44.00 g sodium methoxide (815 mmol). The deep red slurry was placed on a mechanical shaker for 12 days. 300 mL aqueous NH_4Cl and 200 mL diethyl ether were added and the organic layer isolated. The aqueous layer was extracted with diethyl ether (5 x 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 grams (17.7%). ^1H NMR ($CDCl_3$): δ 1.28 (d, $^3J_{HH}$ = 7.0, 12H, C*H*$_3$), 3.11, (heptet, $^3J_{HH}$ = 7.0, 2H, *i*-Pr-*H*), 6.46, 6.64 (m, 4H, fulvene-*H*).

2,4-dimethyl-3-pentyl-cyclopentadiene. A 500 mL Schlenk flask was charged with 4.00 g $LiAlH_4$ (105 mmol) and 150 mL diethyl ether. An attached addition funnel was charged with 9.38 g 6,6-diisopropylfulvene (57.8 mmol) and 50 mL diethyl ether. The fulvene solution was added at 0°C over 15 minutes and rinsed down with an additional 50 mL of diethyl ether. The cold bath was removed and the reaction was stirred for 48 hours before it was cooled to 0°C and 50 mL 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 x 50 mL). The combined organic layers were filtered and rotavapped to yield 8.13 grams of product (85.6%) as a light yellow oil.

3-(2,4-dimethyl-3-pentyl)-6,6-dimethylfulvene. To 2,4-dimethyl-3-pentyl-cyclopentadiene (8.13 g, 49.5 mmol) was added 50 mL methanol, 30 mL acetone (409 mmol) and 10.0 mL pyrrolidine (120 mmol). After stirring for 10 days, 15 mL of acetic acid were injected, followed by 300 mL H_2O and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and with 10% aqueous NaOH (3 x 30 mL), dried over $MgSO_4$, filtered and rotavapped. This material was subjected to Kugelrohr distillation under high vacuum. 3 mL were 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.

$Me_2C(3\text{-}(2,4\text{-dimethyl-3-pentyl})\text{-}C_5H_3)(C_{13}H_8)H_2$. A 250 mL flask was charged 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 grams, 24.5 mmol) was injected. After 6 days, 60 mL of aqueous NH_4Cl solution were slowly added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-}(2,4\text{-dimethyl-3-pentyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. 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 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 hours, the solvent was removed by vacuum transfer and 75 mL of petroleum ether were condensed in. A red-orange powder was isolated in quantitative yield (9.36 g) by filtration and *in vacuo* drying.

$Me_2C(3\text{-}(2,4\text{-dimethyl-3-pentyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (14). 4.103 grams of $Me_2C(3\text{-}(2,4\text{-dimethyl-3-pentyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (10.73 mmol) and 2.500 g $ZrCl_4$ (10.73 mmol) were combined in a 100 mL round bottom flask, equipped with a 180° needle valve. 40 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 26 hours of stirring. 30 mL of methylene chloride were condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted in a cellulose extraction thimble for 48 hours with 150 mL diethyl ether. The filtrate volume was reduced to 75 mL and 0.491 grams (8.6%) of **14** as an orange powder were obtained following collection at 0°C and *in vacuo* drying. MS (LC-MS) m/z 530.7 (M^+). ^1H NMR (C_6D_6): δ 0.58, 0.90, 0.93, 1.01 (d, $^3J_{HH}$ = 7.0, 7.0, 7.0, 7.0, 12H, CH_3), 1.84, 1.86 (s, 6H, $C(CH_3)_2$), 2.25, 2.25 (m, 2H, $CH(CH_3)_2$), 2.57 (t, $^3J_{HH}$ = 2.4, 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*). Elemental analysis calculated for $C_{28}H_{32}Zr_1Cl_2$: C, 63.37; H, 6.08. Found: C, 56.61; H, 5.56.

Preparation of 15.

1,6,6-trimethyl-3-*t*-butyl-fulvene. To 3-*t*-butyl-methylcyclopentadiene (12.00 g, 88.08 mmol) was added 50 mL methanol, 25 mL acetone (340 mmol) and 20.0 mL pyrrolidine (240 mmol). After stirring for 5 days, 25 mL of acetic acid were injected, followed by 300 mL H_2O and 100 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (5 x 50 mL). The combined organic layers were extracted with H_2O (3 x 30 mL) and with 10% aqueous NaOH (3 x 30 mL), dried over $MgSO_4$, filtered and rotavapped. This material was subjected to Kugelrohr distillation under high vacuum. 4.9 g were distilled at 40°C and discarded. Product was obtained from the next fraction, obtained at 60°C: 11.75 g (75.7%) of an orange oil.

Me_2C(2-methyl-4-*t*-butyl-C_5H_2)($C_{13}H_8$)H_2. A 250 mL flask was charged fluorenyllithium diethyl ether adduct (9.513 g, 38.63 mmol). Diethyl ether (60 mL) was syringed in and a solution of 1,6,6-trimethyl-3-*t*-butyl-fulvene (6.810 grams, 38.63 mmol) in 40 mL diethyl ether was injected. After 15 hours, 60 mL of aqueous NH_4Cl solution were slowly added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 x 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide the product in quantitative yield (13.23 g) as a light yellow oil.

Me_2C(2-methyl-4-*t*-butyl-C_5H_2)($C_{13}H_8$)Li_2. The dianion was prepared by treating a solution of Me_2C(2-methyl-4-*t*-butyl-C_5H_2)($C_{13}H_8$)H_2 (13.23 g, 38.63 mmol) in 50 mL diethyl ether with 50.0 mL of n-butyllithium solution (80.0 mmol, 1.6 M in hexanes) at 0°C. After stirring for 43 hours, the pink precipitate was collected by filtration and dried in vacuo to provide 10.20 grams (74.5%) of product.

Me_2C(2-methyl-4-*t*-butyl-C_5H_2)($C_{13}H_8$)$ZrCl_2$ (15). 3.042 grams of Me_2C(2-methyl-4-*t*-butyl-C_5H_2)($C_{13}H_8$)Li_2 (8.584 mmol) and 2.000 g $ZrCl_4$ (8.583 mmol) were combined in a swivel frit. 50 mL of petroleum ether were condensed in at -78°C. This was allowed to warm slowly to room temperature before solvent removal after 16 hours of stirring. 40 mL of methylene chloride were condensed in and removed in order to quench unreacted ligand. Then the orange solid was extracted in a cellulose extraction thimble overnight with 150 mL methylene chloride. The filtrate was filtered on a swivel frit and the volume was reduced to 20 mL and 1.178 grams (27.3%) of **15** as an orange powder were obtained following collection at 0°C and *in vacuo* drying. MS (LC-MS) *m/z* 502.6 (M^+). ^1H NMR (C_6D_6): δ 1.16 (s, 9H, $C(CH_3)_3$), 1.89, 2.06, 2.10 (s, 9H, CH_3), 5.60, 6.02 (d, $^3J_{HH}$

= 2.9, 2.9 Hz, 2H, Cp-*H*), 6.91, 6.97, 7.24, 7.31 (t, $^3J_{HH}$ = 6.6, 6.6, 8.1, 7.7 Hz, 4H, Flu-*H*), 7.45, 7.69, 7.74, 7.84 (d, $^3J_{HH}$ = 9.2, 9.1, 8.4, 8.4 Hz, 4H, Flu-*H*). Elemental analysis calculated for $C_{26}H_{28}Zr_1Cl_2$: C, 62.13; H, 5.61. Found: C, 61.34; H, 5.27.

Preparation of 16.

adamantylfulvene. (Synthesis modified from reference 22) 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 liter round bottom flask. After stirring for 77 hours, the yellow precipitate was collected by suction filtration and washed with 50 mL methanol. After *in vacuo* drying, 49.56 grams adamantylfulvene were 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 adamantylfulvene (18.00 g, 90.77 mmol), equipped with a 180° needle valve, and charged with 120 mL 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 minutes. Dimethoxyethane (10 mL) was syringed in and the reaction was stirred at room temperature for 8 days when 60 mL aqueous NH_4Cl solution were slowly added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to provide 19.46 grams of (2-methyl-2-adamantyl)cyclopentadiene as a light yellow oil (theoretical yield). To this was added 30 mL acetone (409 mmol), 100 mL methanol, and 10 mL pyrrolidene (120 mmol). After stirring for 96 hours, the yellow precipitate was collected by filtration, rinsed with 50 mL 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$_0$). Elemental analysis calculated for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.57; H, 10.04.

$Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. 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 aqueous NH_4Cl were slowly added at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and rotavapped to provide $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)H_2$ in theoretical yield (13.23 g). The flask was attached to a swivel frit and charged with 50 mL diethyl ether before n-butyllithium solution (42.0 mL, 67.2 mmol, 1.6 M in hexanes) was syringed in over 4 minutes at 0°C. After 23 hours, solvent is removed and 75 mL petroleum ether are added by vacuum transfer. The red solid is broken up, stirred, collected on the frit, and dried in vacuo: 15.85 grams (13.60 g theoretical yield).

$Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (16). A 100 mL flask was charged with $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (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 hours, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL 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^+). ^1H NMR (C_6D_6): δ 1.32 - 2.62 (m, 14H, adamantyl-*H*), 1.73, 1.85, 1.89 (s, 9H, CH_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 (CH_0). Elemental analysis calculated for $C_{32}H_{34}Zr_1Cl_2$: C, 66.18; H, 5.90. Found: C, 57.60; H, 5.23.

Preparation of 17.

(2-phenyl-2-adamantyl)cyclopentadiene. A 300 mL flask was charged with adamantylfulvene (10.00 g, 50.43 mmol) and 75 mL diethyl ether were 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 hours, the vessel was cooled to 0°C and 60 mL of aqueous NH_4Cl solution were slowly added. The ether layer was isolated and the aqueous layer was extracted with diethyl ether (3 x 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) was added 100 mL methanol, 50 mL acetone (680 mmol) and 10.0 mL pyrrolidine (120 mmol). After stirring for 4 days, 100 mL methanol were added and the yellow precipitate was collected by suction filtration. The product was washed with 100 mL methanol and dried in vacuo: 14.76 grams (92.5%). MS (GC-MS) m/z 316.5 (M^+). ^1H NMR ($CDCl_3$): δ 1.63 - 2.22, 2.94 (m, 14H, adamantyl-*H*), 2.06, 2.10, (s, 6H, CH_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). Elemental analysis calculated for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 90.66; H, 8.56.

$Me_2C(3\text{-}(2\text{-phenyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)H_2$. A 300 mL flask was charged 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 hours before 60 mL of aqueous NH_4Cl solution were slowly added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 x 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.

$Me_2C(3\text{-}(2\text{-phenyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$. The dianion was prepared by treating a solution of $Me_2C(3\text{-}(2\text{-phenyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)H_2$ (6.10 g, 12.6 mmol) in 50 mL 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 hours, the solvent was removed and 50 mL of petroleum ether were condensed in. The product was isolated in quantitative yield (6.25 g) after filtration and in vacuo drying.

$Me_2C(3\text{-}(2\text{-phenyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (17). A 100 mL flask was charged with $Me_2C(3\text{-}(2\text{-phenyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)Li_2$ (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 hours, solvent was removed from the pink slurry. The solid was extracted in a cellulose extraction thimble with 150 mL methylene chloride overnight. The filtrate was attached to a swivel frit and filtered. The solvent was removed and 30 mL diethyl ether were 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, $C(CH_3)_2$), 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, 2 H, 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 ($C\text{-}(CH_3)_2$), 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-CH_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 -CH_1), 143.61, 144.27 (ipso-*C* and 9-Flu-*C*),CH_0 not determined. Elemental analysis calculated for $C_{37}H_{36}Zr_1Cl_2$: C, 69.13; H, 5.64. Found: C, 67.61; H, 5.39.

Preparation of 18.

$Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})Li_2$. 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 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 minutes. After 20 hours, 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 water were slowly syringed in at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, rotavapped, and dried in vacuo to provide $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})H_2$ 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 minutes. After 15 hours, solvent was removed and 50 mL petroleum ether were condensed in. The product slowly precipitated over 2 hours and was collect and dried in vacuo: 3.525 g (34.3%).

$Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (18). A swivel frit apparatus was charged with $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})Li_2$. (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 hours, 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 hours before the product was collected by filtration and dried in vacuo: 0.614 g (14.2%). MS (LC-MS) m/z 800.9 (M^+). ^1H 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, 27.55, 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). Elemental analysis calculated for $C_{48}H_{62}Zr_1Cl_2$: C, 71.96; H, 7.80. Found: C, 71.62; H, 7.37.

Preparation of 19.

(2-($CH_2Si(CH_3)_3$)-2-adamantyl)cyclopentadiene. A 250 mL flask was charged with adamantylfulvene (8.000 g, 40.34 mmol) and $LiCH_2Si(CH_3)_3$ (8.000 g, 84.96 mmol). 100 mL diethyl ether were condensed in and the reaction was stirred at room temperature for 16 hours when the vessel was cooled to 0°C and 60 mL aqueous NH_4Cl solution were slowly added. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (2 x 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-($CH_2Si(CH_3)_3$)-2-adamantyl)-6,6-dimethylfulvene. To (2-($CH_2Si(CH_3)_3$)-2-adamantyl)cyclopentadiene (11.56 g, 40.3 mmol) were added 100 mL acetone (1360 mmol) and 10.0 mL pyrrolidine (120 mmol). After stirring for 4 days, 10 mL of acetic acid were injected, followed by 200 mL H_2O and 200 mL diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (2 x 50 mL). The combined organic layers were extracted with H_2O (4 x 25 mL), dried over $MgSO_4$, filtered and rotavapped. This material was subjected to Kugelrohr distillation under high vacuum. 10.8 g were distilled at 60°C and discarded. Product was obtained from the next fraction, obtained at 120°C - 140°C: 10.54 g (80.0%) of a yellow oil.

Me$_2$C(C$_{13}$H$_8$)(3-(2-(CH$_2$Si(CH$_3$)$_3$)-2-adamantyl)-C$_5$H$_3$)H$_2$. A 250 mL flask was charged fluorenyllithium diethyl ether adduct (5.482 g, 22.26 mmol) and 3-(2-(CH$_2$Si(CH$_3$)$_3$)-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 hours before 60 mL of aqueous NH$_4$Cl solution were slowly added and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (3 x 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$_2$C(C$_{13}$H$_8$)(3-(2-(CH$_2$Si(CH$_3$)$_3$)-2-adamantyl)-C$_5$H$_3$)Li$_2$. The dianion was prepared by treating a solution of Me$_2$C(C$_{13}$H$_8$)(3-(2-(CH$_2$Si(CH$_3$)$_3$)-2-adamantyl)-C$_5$H$_3$)H$_2$ (10.97 g, 22.26 mmol) in 50 mL 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 hours, the solvent was removed and 75 mL of petroleum ether were condensed in. The product was isolated by decanting the solvent and drying the residue in vacuo: 8.013 g (71.3%).

Me$_2$C(C$_{13}$H$_8$)(3-(2-(CH$_2$Si(CH$_3$)$_3$)-2-adamantyl)-C$_5$H$_3$)ZrCl$_2$ (19). A 100 mL flask was charged with Me$_2$C(C$_{13}$H$_8$)(3-(2-(CH$_2$Si(CH$_3$)$_3$)-2-adamantyl)-C$_5$H$_3$)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 hours, solvent was removed. This was attached to a swivel frit, 70 mL toluene were 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$_6$D$_6$): δ -0.03 (s, 9H, Si(C*H*$_3$)$_3$), 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, C*H*$_3$), 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$_2$Cl$_2$): 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. Elemental analysis calculated 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 6110 drying system equipped with an OXYSORB^{TM} column. Polymerizations were conducted in a 3 oz. Lab Crest glass reaction vessel and were stirred with a magnetic stir bar. Monomer was condensed into the vessel over several minutes at 0°C. The vessel was then equilibrated at either 0°C or at 20°C with an ice or water bath for 10 minutes. A given reaction commenced upon injection of a toluene solution of the metallocene into the vessel with a 2.5 mL Hamilton syringe rated to 200 psi. Temperature maintenance was monitored by an affixed pressure gauge. Polymerization reactions were vented and quenched with a small volume of methanol/concentrated HCl (12:1) and the polymers were separated from hydrolyzed aluminoxanes by precipitation from methanol, followed by filtration. Residual amounts of toluene and methanol were removed from the obtained polymers by in vacuo drying. Polymerization reactions not fully described in the text are provided in Table 7.

Table 7. MAO-cocatalyzed polymerization results with **3**, **4**, **5**, **6**, **8**, **9**, **10**, and **11**.

Entry	Metallocene (mg)	MAO (equiv.)	T_p (°C)	Toluene (mL)	C_3H_6 (mL)	Time (min.)	Yield (g)	Activity (gP / (gmet·h))	T_m [a] (°C)	m^4 (%)	M_w	M_w / M_n
24	**3** (2.0)	1000	0	30.0	3	60	0.84	420	129	82.2		
25	**3** (2.0)	1000	20	30.0	3	10	0.56	1700	134	83.9		
26	**3** (2.0)	1000	40	30.0	3	5	0.50	3000	135	88.8		
27	**3** (2.0)	1000	60	30.0	3	5	0.38	2300	128	89.4		
28	**4** (2.0)	1000	0	2.0	30	15	0.45	900	120	74.1	431,000	1.74
29	**4** (2.0)	1000	20	2.0	30	5	1.77	11000	118	77.0	252,000	1.88
30	**4** (1.0)	1000	0	30	3	30	0.30	610	121	78.1		
31	**4** (1.0)	1000	20	30	3	15	1.71	6800	131	77.6		
32	**5** (1.0)	1000	0	2.0	30	15	1.43	5700	n.o.	21.6	80,000	1.81
33	**5** (1.0)	1000	20	2.0	30	10	4.95	30000	n.o.	18.3		
34	**6** (1.0)	1000	0	2.0	30	10	0.71	4300	n.o.	13.2		
35	**6** (1.0)	1000	20	2.0	30	10	4.01	24000	n.o.	14.5		
36	**8** (1.5)	1000	0	2.0	30	15	0.37	980	130	2.4		
37	**8** (1.5)	1000	20	2.0	30	5	0.86	6600	117	2.4		
38	**9** (2.0)	1000	0	2.0	30	20	0.36	530	103	5.1		
39	**9** (2.0)	1000	20	2.0	30	20	5.53	8300	n.o.	7.3		
40	**10** (2.7)	1000	0	2.0	30	20	0.05	60	125	74.4		
41	**10** (2.7)	1000	20	2.0	30	20	0.14	150	135	76.4		
42	**11** (1.0)	1000	0	2.0	30	3	1.23	25000	n.o.	26.9	653,000	1.87
43	**11** (0.5)	1000	20	1.0	30	3	1.12	45000	n.o.	30.0	397,000	2.31
44	**11** (1.0)	1000	0	30.0	3	10	1.90	11000	n.o.	28.5		
45	**11** (1.0)	1000	20	30.0	3	10	1.82	11000	n.o.	31.3		
46	**11** (1.0)	1000	40	30.0	3	10	1.16	7000	n.o.	32.4		
47	**11** (1.0)	1000	60	30.0	3	10	0.47	2800	n.o.	27.1		
48	**11** (1.0)	1000	80	30.0	3	10	0.10	600	n.o.	18.0		

[a] n.o. = melting temperature not observed.

Representative Polymerization Procedures.

Entry 13. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.100 g, 1.72 x 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**) (0.001 g, 1.7 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 10 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 14. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.100 g, 1.72 x 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**) (0.001 g, 1.7 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 20°C water bath for 10 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 15. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44 x 10^{-3} mol [Al]). Propylene (60 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**) (0.002 g, 3.4 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 60 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 16. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44 x 10^{-3} mol [Al]). Propylene (55 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**) (0.002 g, 3.4 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 20°C water bath for 10 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 17. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44 x 10^{-3} mol [Al]). Propylene (55 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-2-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**) (0.002 g, 3.4 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 10 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 18. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44 x 10^{-3} mol [Al]) and 28.0 mL toluene. Propylene (3 mL) was condensed in. A solution of $Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**), (0.002 g, 3.4 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 180 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 19. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.200 g, 3.44 x 10^{-3} mol [Al]) and 28.0 mL toluene. Propylene (3 mL) was condensed in. A solution of $Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{13}H_8)ZrCl_2$ (**16**) (0.002 g, 3.4 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 20°C water bath for 90 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 22. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.145 g, 2.50 x 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (**18**) (0.002 g, 2.5 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 0°C ice/water bath for 20 minutes. The reaction was vented and quenched with dilute HCl/methanol.

Entry 23. A 100 mL Lab Crest glass pressure reactor was charged with MAO (0.145 g, 2.50 x 10^{-3} mol [Al]). Propylene (30 mL) was condensed in at 0°C. A solution of $Me_2C(3\text{-}(2\text{-methyl-}2\text{-adamantyl})\text{-}C_5H_3)(C_{29}H_{36})ZrCl_2$ (**18**) (0.002 g, 2.5 x 10^{-6} mol) in toluene (2.0 mL) was injected and the reaction stirred in a 20°C water bath for 20 minutes. 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/minute) 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.[29] 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 seconds and a minimum of 1000 scans were used.

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6.7 References and Notes

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b) Janiak, C. in *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A.; Halterman, R. L., eds.; Wiley-VCH: Weinheim, 1998, pp. 547-623.

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

8. 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," Reference 2a.

c) "skipped-out insertions" and "chain migratory catalyst isomerization," Reference 2c.

c) "back-skip mechanism," Reference 2d.

d) "retention mechanism," Di Silvestro, G.; Sozzani, P.; Terragni, A. *Macromol. Chem. Phys.* **1996** *197*, 3209-3228.

e) "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.

f) "site-to-site chain migration," Reference 3c.

g) "side-to-side swing" and "back swing," Reference 4a.

h) "chain stationary insertion mechanism," Reference 4b.

9. Hefert, N.; Fink, G. *Makromol. Chem. Macromol. Symp.* **1993** *66*, 157.

10. a) Farina, M. *Top. Stereochem.* **1987** *17*, 1-111.

    b) Ewen, J. A. *J. Am. Chem. Soc.* **1984** *106* , 6355-6364

11. See Chapter 3 of this thesis for details regarding the triad models.

12. The least squares minimization was performed for the eight measured intensities (mmrm, rrmr, and mrmr were combined) according to RMS error = $(((\Sigma(I_{obs} - I_{calc})^2) / 8)^{0.5})$.

13. a) Ewen, J. A. 218th Amer. Chem. Soc. Nat. Meet., New Orleans 1999, INOR 261. b) This effect has also been identified in heterogeneous propylene polymerizations systems: Busico, V.; Cipullo, R.; Talarico, G.; Segre, A. L.; Chadwick, J. C. *Macromolecules* **1997** *30*, 4786-4790.

14. For the first reported synthesis of octamethyloctahydrodibenzofluorene, see: a) Gverdtsiteli, D. D.; Revazishvili, N. S.; Tsitsishvili, V. G.;

Kikoladze, V. S. *Soobshch. Akad. Nauk. Gruz. SSR* **1989** *133(1)*, 77-80; *Chem. Abstr.* **1989** *111*, 214206.

For the first reports of Oct employed as a transition metal ligand, see: b) Miller, S. A.; Bercaw, J. E. 217th Amer. Chem. Soc. Nat. Meet., Anaheim 1999, INOR 19.

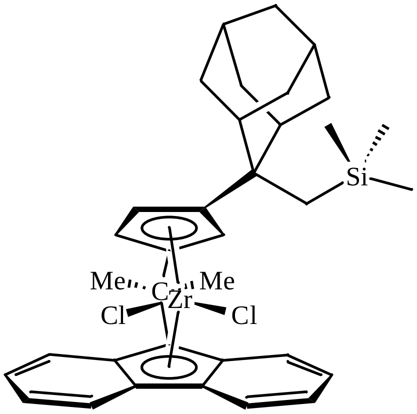
c) Miller, S. A.; Bercaw, J. E. 217th Amer. Chem. Soc. Nat. Meet., Anaheim 1999, INOR 151.

15. See Appendix F for X-ray crystallographic data of **11**.
16. The least squares minimization was performed for the nine measured intensities according to RMS error = $(((\Sigma(I_{obs} - I_{calc})^2) / 9)^{0.5})$.
17. The statistical analyses for the remaining polymers are found in Appendix K. The hemiisotactic triad model (P_{mr} = 0) excels the enantiomorphic site control model in liquid propylene. Above 60°C in dilute monomer, the enantiomorphic site control model provides better fits than either of the hemiisotactic triad models. The statistical results are consistent with increased employment of the site epimerization mechanism by **11** / MAO as the monomer concentration is decreased and the polymerization temperature is increased.
18. See Chapter 5 of this thesis.
19. Patsidis, K.; Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1996** *509*, 63-71.
20. See Chapter 2 of this thesis.
21. a) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989** *10*, 1853-1856.

    b) Spaleck, W.; Antberg, A.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem. Int. Ed. Eng.* **1992** *31*, 1347.
22. For previous examples of metallocenes bearing this substituent, see: Abrams, M. B.; Yoder, J. C.; Loeber, C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999** *18*, 1389-1401.

23. **18**/MAO is essentially inactive for ethylene polymerization as well (activity = 12 gP/(gmet·h) at 20°C). To test the suggestion that this metallocene simply deactivates by aryl C-H activation, $Me_2C(C_{13}H_8)(3\text{-}(2\text{-}(CH_2Si(CH_3)_3)\text{-}2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$ (**19**) was prepared and tested for its MAO-cocatalyzed polymerization behavior.

19



The obtained amorphous polypropylene (activity = 460 gP/(gmet·h) at 20°C) is attributed to impurities present in the metallocene (likely $Me_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$ based on the synthetic procedure) and the lack of any isotactic polypropylene suggests that the aliphatic substituent 2-$(CH_2Si(CH_3)_3)$-2-adamantyl effectively inhibits polymerization as well.

24. 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.

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

26. Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984** *49*, 1849-1853.

27. Thiele, J. *Chem. Ber.* **1900** *33*, 666.

28. Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995** *14,* 789-795.

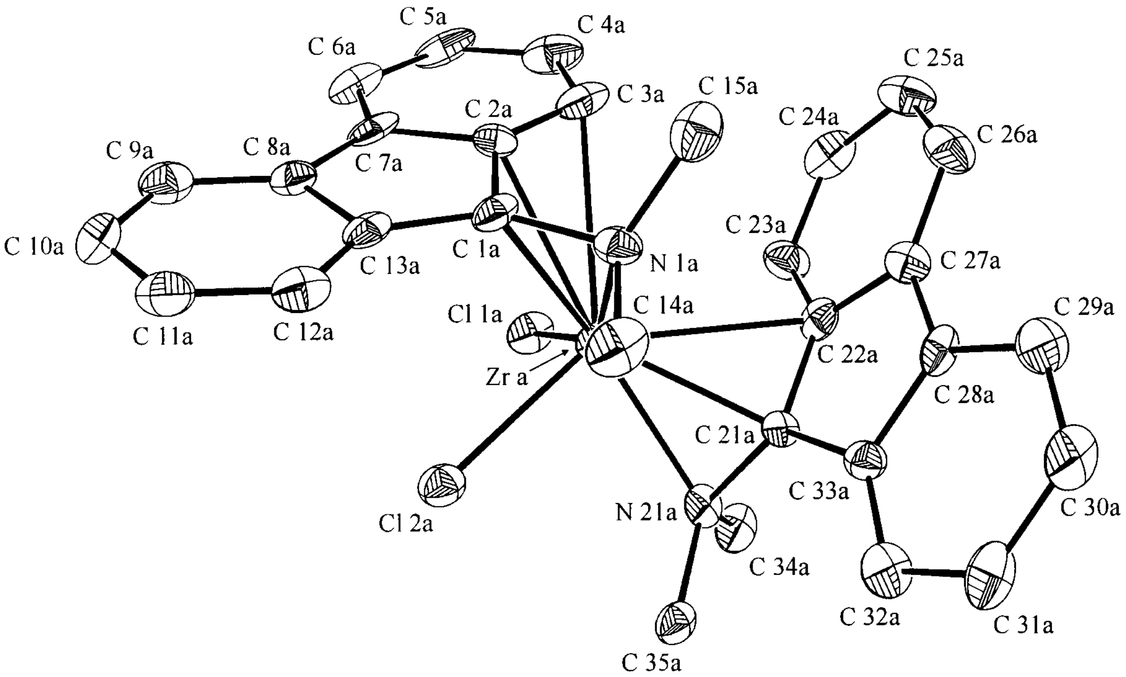
29. a) Busico, B.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. *Macromolecules* **1995** *28*, 1887-1892.

    b) Busico, B.; Cipullo, R.; Monaco, G.; Vacatello, M. *Macromolecules* **1997** *30*, 6251.

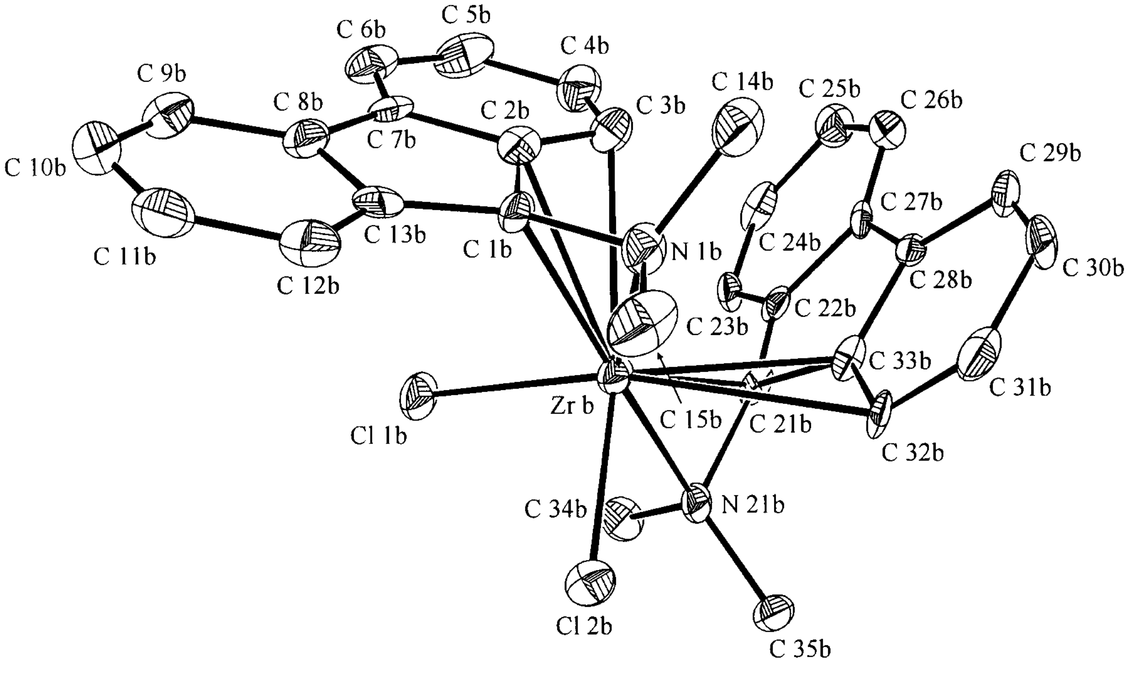
Appendix A

X-ray Crystal Structure Data for $(9\text{-}(Me_2N)\text{-}C_{13}H_8)_2ZrCl_2$

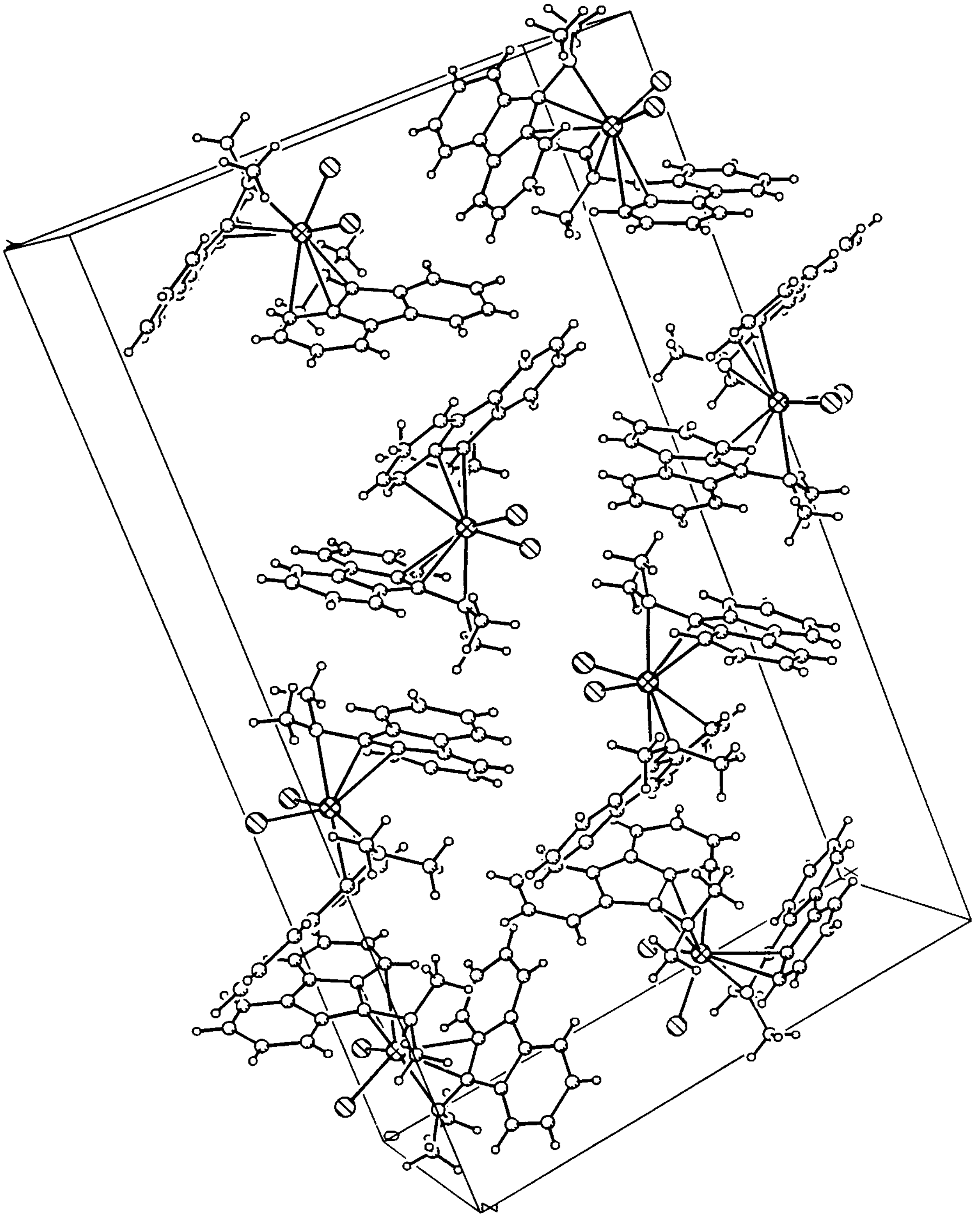
Cambridge Database (CCDC) 100582



Labeled view of molecule A with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $(9\text{-}(Me_2N)\text{-}C_{13}H_8)_2ZrCl_2$.

Empirical formula	$C_{30}H_{28}Cl_2N_2Zr$	
Formula weight	578.69	
Crystallization solvent	dichloromethane	
Crystal shape	irregular fragment	
Crystal size	0.37 x 0.29 x 0.08 mm	
Crystal color	almandine	
Data Collection		
Type of diffractometer	CAD-4	
Wavelength	0.71073Å MoK alpha	
Data collection temperature	160 K	
Lattice determination from	25 reflections	
Theta range for reflections used in lattice determination	11.4 to 13.1°	
Unit cell dimensions	a = 18.781(3)Å	alpha = 90°
	b = 30.088(9)Å	beta = 99.17(3)°
	c = 8.994(8)Å	gamma = 90°
Volume	5017(3)Å^3	
Z	8	
Crystal system and space group	Monoclinic P2(1)/n	
Density (calculated)	1.532 g/cm^3	
Absorption coefficient	0.674 mm^{-1}	
F(000)	2368	
Theta range for data collection	1.75 to 25.0°	
Index ranges	-22<=h<=22, -35<=k<=35, 0<=l<=10	
Data collection scan type	Omega-scans	
Reflections collected	19792	
Independent reflections	8829 [R(merge) = 0.08 GOF(merge) = 1.26]	
Absorption correction	None	
Number of standards	3 reflections measured every 60 min.	
Variation of standards	0.9%	
Structure Solution and Refinement		
Structure solution program	SHELXS-86 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Calculated geometric sites	
Structure refinement program	SHELXL-93 (Sheldrick, 1993)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	Restrained to calculated geometric sites	
Goodness-of-fit on F^2	1.132	
Final R indices [I>2sigma(I)]	R1 = 0.0747, wR2 = 0.0942	
R indices (all data)	R1 = 0.1487, wR2 = 0.1120	
Max shift/error	-0.001	
Average shift/error	0.000	
Largest diff. peak and hole	0.611 and -0.606 e.Å^{-3}	

Special Notes
These crystals were extremely fragile and were falling apart as they were being removed from the Paratone. Therefore, the data were weak and the refinement statistics were adversely affected.

Refinement on F^2 for ALL reflections except for 3 with very negative F^2 or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating _R_factor_obs, etc., and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $(9\text{-}(Me_2N)\text{-}C_{13}H_8)_2ZrCl_2$. U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
ZrA	620(1)	1008(1)	2018(1)	20(1)
Cl(1A)	362(1)	939(1)	-716(2)	28(1)
Cl(2A)	-599(1)	787(1)	2318(2)	27(1)
N(1A)	817(3)	1454(2)	4230(7)	23(2)
N(21A)	882(3)	249(2)	2181(6)	20(2)
C(1A)	265(4)	1675(2)	3155(8)	23(2)
C(2A)	480(4)	1839(2)	1797(8)	20(2)
C(3A)	1114(5)	1815(2)	1236(9)	30(2)
C(4A)	1140(5)	1956(2)	-267(10)	38(2)
C(5A)	520(5)	2120(2)	-1102(9)	34(2)
C(6A)	-126(5)	2150(2)	-566(8)	29(2)
C(7A)	-165(4)	2022(2)	891(9)	26(2)
C(8A)	-733(4)	2013(2)	1779(8)	22(2)
C(9A)	-1432(4)	2169(2)	1486(9)	29(2)
C(10A)	-1876(5)	2131(2)	2556(10)	32(2)
C(11A)	-1617(5)	1932(2)	3939(9)	31(2)
C(12A)	-932(4)	1776(2)	4259(9)	27(2)
C(13A)	-464(4)	1809(2)	3206(8)	22(2)
C(14A)	534(4)	1229(2)	5468(8)	33(2)
C(15A)	1421(4)	1740(2)	4894(9)	33(2)
C(21A)	1446(4)	486(2)	3166(8)	17(2)
C(22A)	1976(4)	749(2)	2548(8)	22(2)
C(23A)	2044(4)	897(2)	1111(8)	29(2)
C(24A)	2581(4)	1194(2)	933(9)	32(2)
C(25A)	3056(4)	1363(2)	2147(10)	33(2)
C(26A)	3009(4)	1207(2)	3573(10)	32(2)
C(27A)	2494(4)	907(2)	3802(8)	22(2)
C(28A)	2339(4)	684(2)	5129(8)	22(2)

C(29A)	2736(4)	685(2)	6598(9)	32(2)
C(30A)	2535(5)	411(2)	7680(9)	34(2)
C(31A)	1926(4)	132(3)	7329(9)	32(2)
C(32A)	1521(4)	138(2)	5903(8)	28(2)
C(33A)	1730(4)	403(2)	4776(8)	22(2)
C(34A)	1115(4)	-24(2)	982(8)	30(2)
C(35A)	417(4)	-27(2)	2982(8)	24(2)
ZrB	-4496(1)	905(1)	-2308(1)	19(1)
Cl(1B)	-4939(1)	954(1)	-4990(2)	28(1)
Cl(2B)	-5465(1)	416(1)	-1845(2)	29(1)
N(1B)	-4819(3)	1430(2)	-588(7)	25(2)
N(21B)	-3896(3)	237(2)	-2770(6)	20(2)
C(1B)	-4991(4)	1627(2)	-2072(8)	21(2)
C(2B)	-4419(4)	1754(2)	-2834(8)	18(2)
C(3B)	-3687(4)	1645(2)	-2622(9)	23(2)
C(4B)	-3279(4)	1751(2)	-3712(9)	30(2)
C(5B)	-3582(5)	1982(2)	-5004(10)	36(2)
C(6B)	-4300(4)	2100(2)	-5228(9)	29(2)
C(7B)	-4736(4)	1991(2)	-4181(8)	20(2)
C(8B)	-5485(4)	2044(2)	-4120(8)	25(2)
C(9B)	-6025(4)	2267(2)	-5101(9)	30(2)
C(10B)	-6702(5)	2294(2)	-4744(10)	38(2)
C(11B)	-6872(5)	2091(2)	-3487(10)	35(2)
C(12B)	-6362(4)	1852(2)	-2529(10)	31(2)
C(13B)	-5662(4)	1833(2)	-2833(9)	20(2)
C(14B)	-4327(4)	1712(2)	489(8)	33(2)
C(15B)	-5424(5)	1315(2)	175(9)	38(2)
C(21B)	-3374(4)	562(2)	-2074(7)	18(2)
C(22B)	-2699(4)	722(2)	-2469(8)	18(2)
C(23B)	-2384(4)	709(2)	-3764(8)	22(2)
C(24B)	-1751(4)	929(2)	-3830(8)	30(2)
C(25B)	-1392(4)	1172(2)	-2607(9)	29(2)
C(26B)	-1683(4)	1181(2)	-1304(9)	27(2)
C(27B)	-2318(4)	959(2)	-1210(7)	15(2)
C(28B)	-2722(4)	913(2)	36(7)	18(2)
C(29B)	-2589(4)	1069(2)	1497(8)	24(2)
C(30B)	-3073(4)	986(2)	2440(8)	33(2)
C(31B)	-3683(4)	742(2)	1974(8)	28(2)
C(32B)	-3830(4)	568(2)	516(8)	25(2)
C(33B)	-3347(4)	654(2)	-467(8)	17(2)
C(34B)	-3817(4)	136(2)	-4368(8)	28(2)
C(35B)	-3913(4)	-194(2)	-1988(8)	24(2)

Table 3. Selected bond lengths [Å] for (9-(Me_2N)-$C_{13}H_8$)$_2$ZrCl_2.

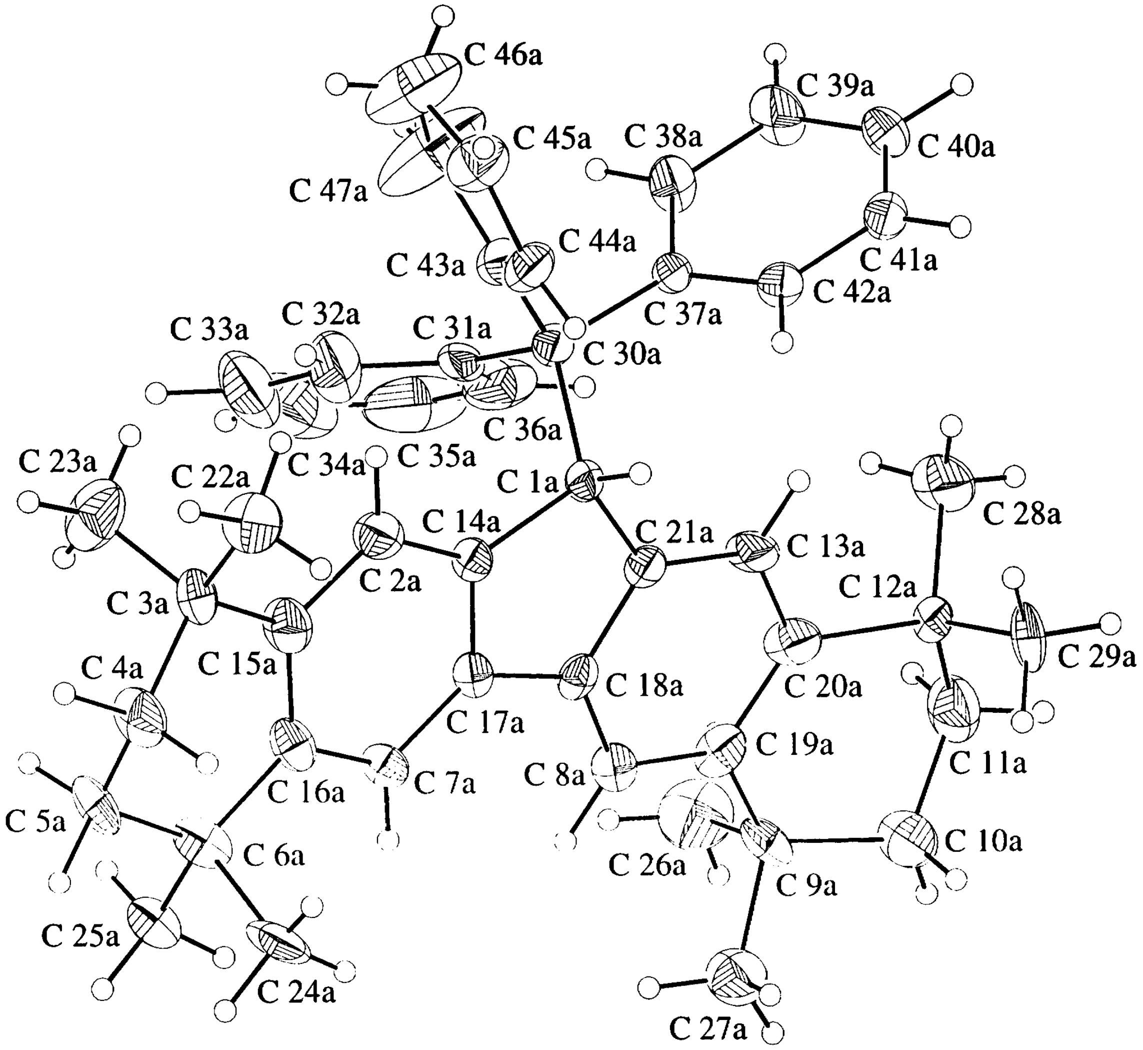
ZrA-C(21A)	2.330(7)
ZrA-N(21A)	2.337(5)
ZrA-N(1A)	2.379(6)
ZrA-C(1A)	2.394(7)
ZrA-Cl(1A)	2.438(2)
ZrA-Cl(2A)	2.439(2)

ZrA-C(2A)	2.516(7)
ZrA-C(22A)	2.633(7)
ZrA-C(3A)	2.731(7)
ZrA-C(23A)	2.939(8)
ZrB-C(21B)	2.326(7)
ZrB-N(1B)	2.357(6)
ZrB-N(21B)	2.373(5)
ZrB-C(1B)	2.384(7)
ZrB-Cl(2B)	2.427(2)
ZrB-Cl(1B)	2.428(2)
ZrB-C(2B)	2.605(6)
ZrB-C(33B)	2.614(7)
ZrB-C(3B)	2.736(7)
ZrB-C(32B)	2.834(7)

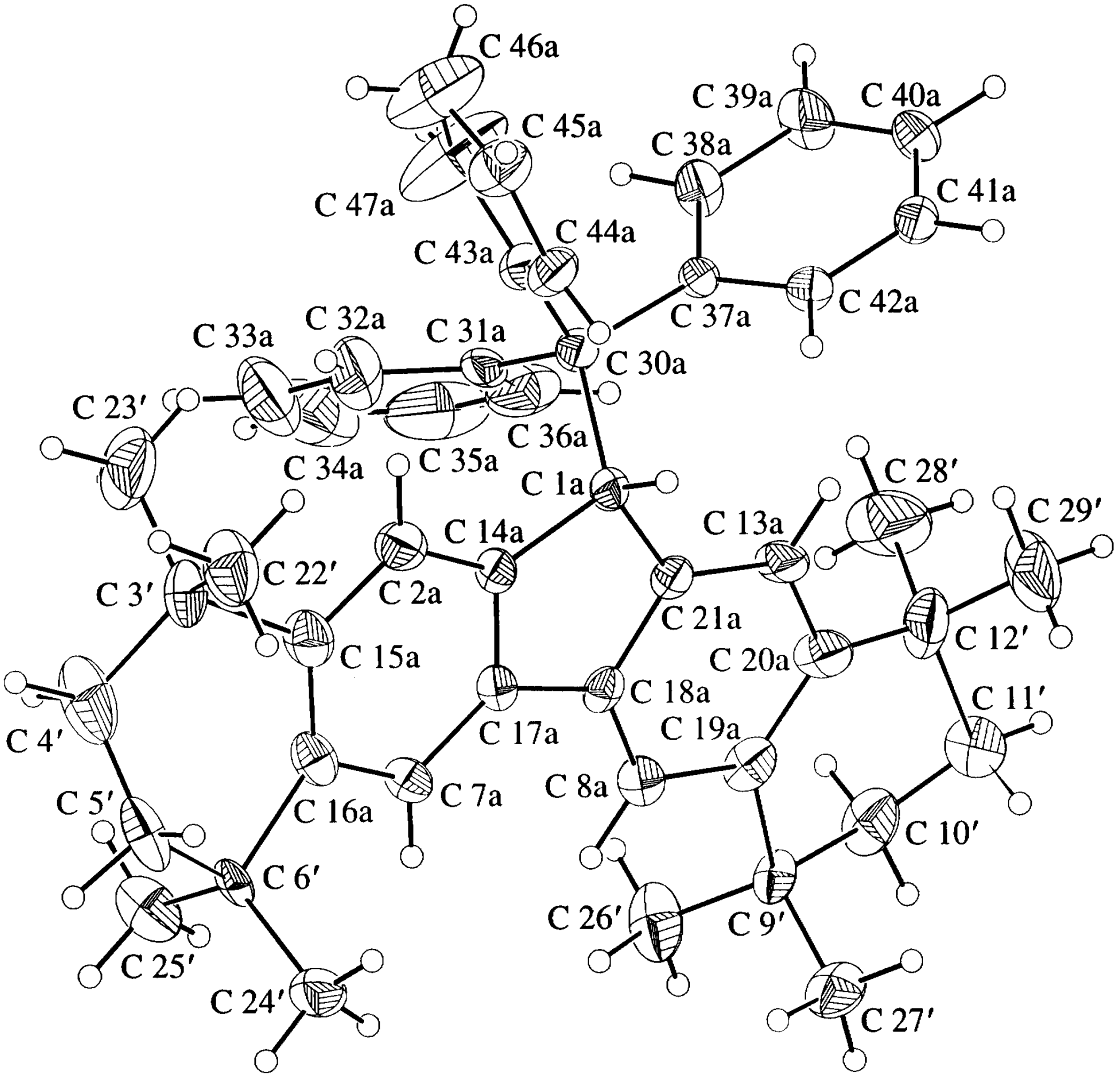
Appendix B

X-ray Crystal Structure Data for $Ph_2C(OctH)(C_5H_5)$

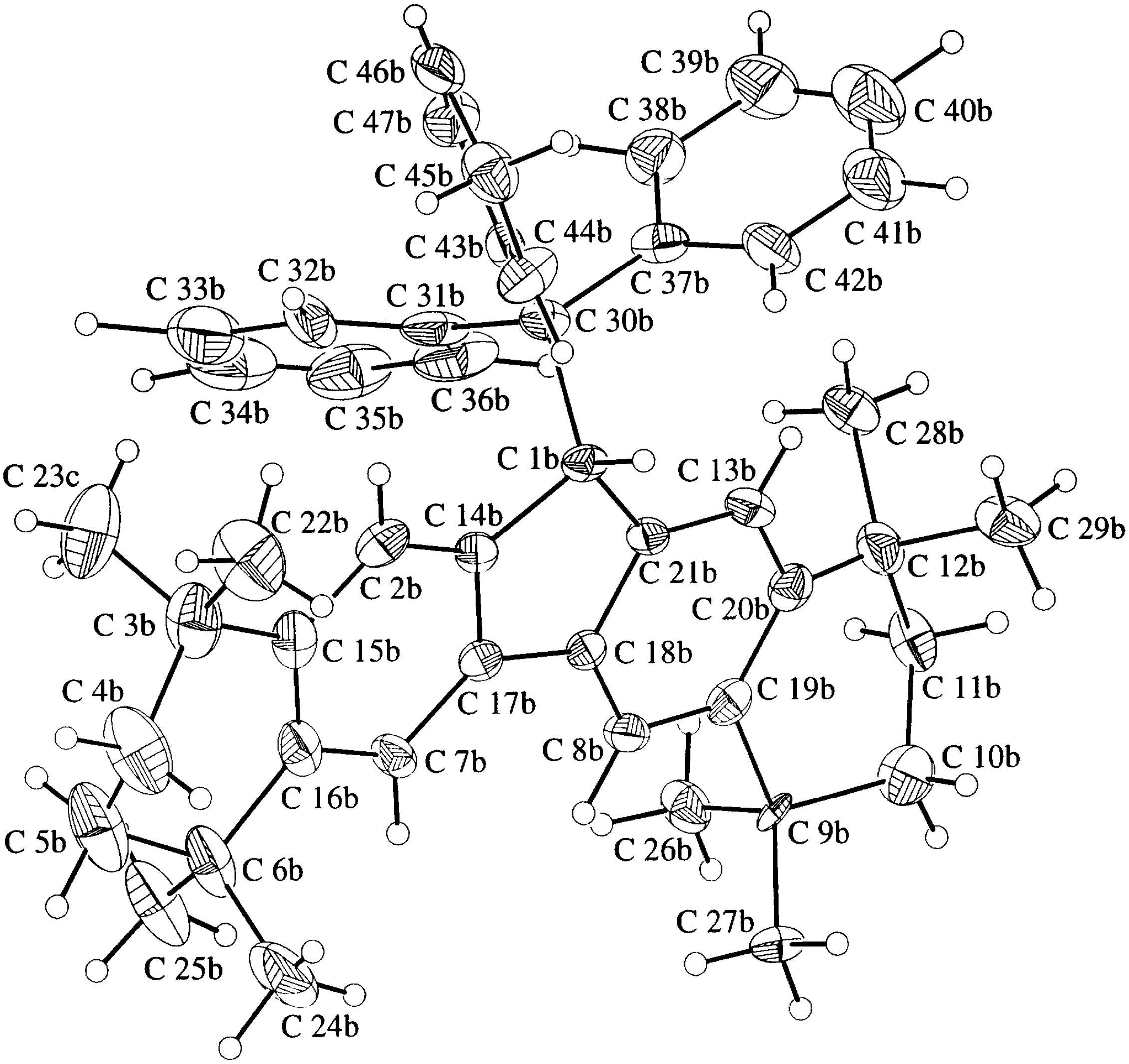
Cambridge Database (CCDC) 105607



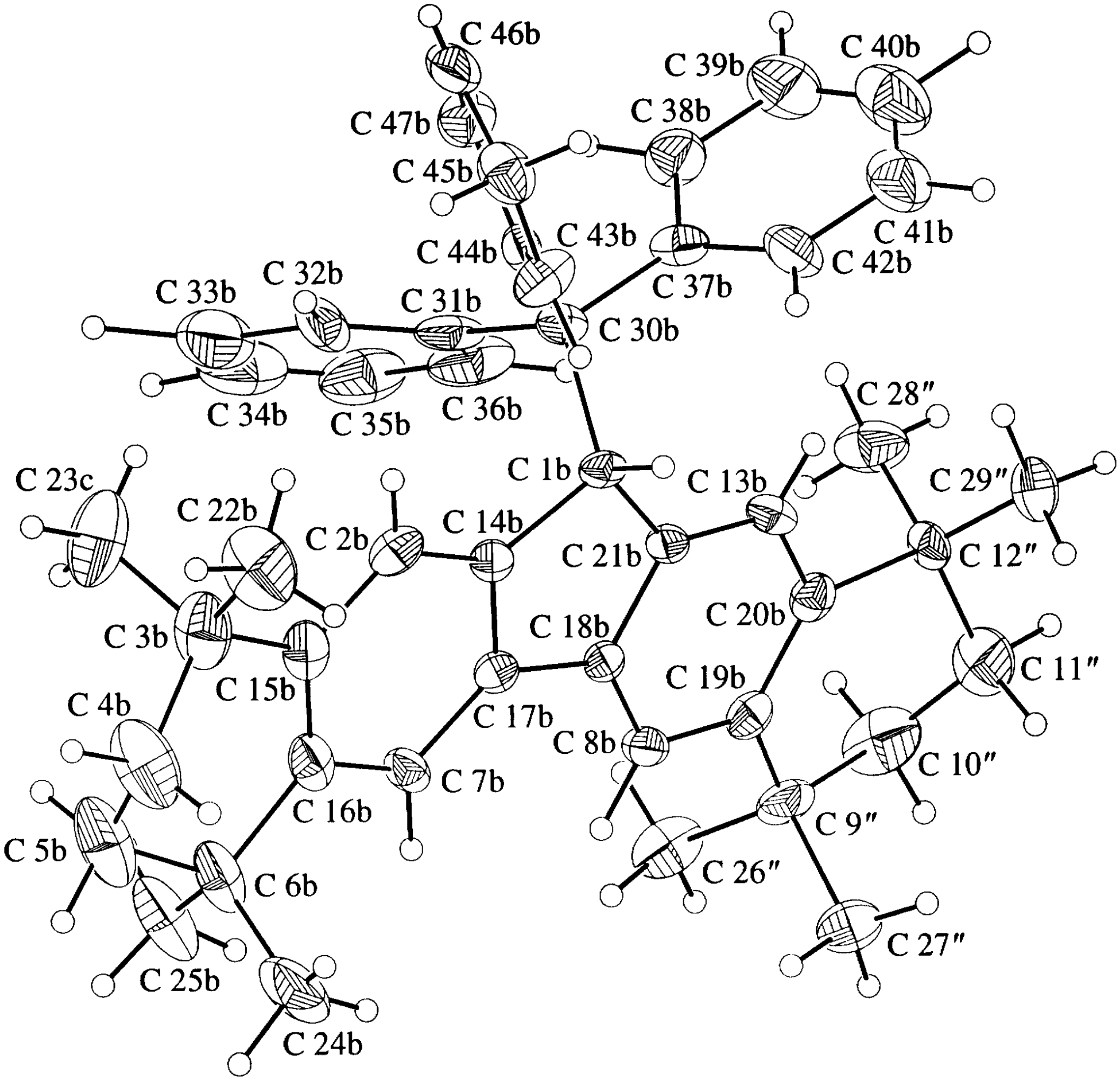
Labeled view of molecule A with 50% probability ellipsoids



Labeled view of molecule A (with alternate conformation) with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Labeled view of molecule B (with alternate conformation) with 50% probability ellipsoids

Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(OctH)(C_5H_5)$.

Empirical formula	C_{47} H_{52}	
Formula weight	616.93	
Crystallization solvent	ethanol	
Crystal habit	prismatic	
Crystal size	0.45 x 0.25 x 0.23 mm^3	
Crystal color	very slightly yellow	
Data Collection		
Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKa	
Data collection temperature	85 K	
Theta range for reflections used in lattice determination	10.7 to 12.9°	
Unit cell dimensions	a = 39.813(15) Å	alpha = 90°
	b = 12.631(6) Å	beta = 98.34(4)°
	c = 29.671(15) Å	gamma = 90°
Volume	14763(12) $Å^3$	
Z	16	
Crystal system	Monoclinic	
Space group	C2/c	
Density (calculated)	1.110 Mg/m^3	
F(000)	5344	
Theta range for data collection	1.6 to 23.0°	
Completeness to theta = 23.01°	99.8%	
Index ranges	-43<=h<=0, -13<=k<=13, -32<=l<=32	
Data collection scan type	Omega scans	
Reflections collected	22592	
Independent reflections	10265 [R_{int}= 0.057; GOF_{merge}= 1.02]	
Absorption coefficient	0.062 mm^{-1}	
Absorption correction	None	
Number of standards	3 reflections measured every 75 min.	
Variation of standards	-0.66%.	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometrically calculated positions	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	10265 / 795 / 1146	
Treatment of hydrogen atoms	Restrained angles, free distances	
Goodness-of-fit on F^2	1.696	
Final R indices [I>2s(I)]	R1 = 0.0739, wR2 = 0.1104	
R indices (all data)	R1 = 0.1286, wR2 = 0.1219	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	
Max shift/error	0.000	
Average shift/error	0.000	
Largest diff. peak and hole	0.751 and -0.454 e.$Å^{-3}$	

Special Refinement Details

This crystal diffracts weakly, therefore data was collected to a maximum 2θ value of only 23°. To further complicate matters the crystal is disordered and there are two molecules in the asymmetric unit. Some of the atoms in the disordered sites are very close to their equivalent atoms resulting in a tendency for the anisotropic displacement parameters (ADP) of these atom to become non-positive definite. Therefore, all of the atoms had a restraint placed on their ADP to approximate isotropic behavior. The treatment of the disordered sites is discussed below.

The disorder occurs in two places; the tetramethylcylcohexal groups on the ends of the flourinyl moiety, where in three of the four cases the pucker of the ring adopts both possible conformations and in the cylopentene rings. The first disorder was modeled and each disordered site was restrained to the geometry of the site where no disorder is observed. The second disorder was not modeled.

The hydrogen atoms of the Cp-ring in the B-molecule were located in the difference Fourier map and there is reasonable certainty where the CH_2 group is located within this Cp-ring. The hydrogen atoms of the Cp-ring in the A-molecule were not as apparent in the difference Fourier map and the position of the CH_2 group was inferred from the map and from the position in the other molecule. The bond distances within either Cp-ring offer no supporting evidence for the position of the CH_2 group. As noted in Table 1., the angular geometry of all hydrogens were restrained during the refinement.

The variances $[\sigma^2(Fo^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$, and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014<I>)^2$.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ph_2C(OctH)(C_5H_5)$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1A)	3955(1)	1315(3)	-1134(1)	23(1)
C(2A)	4272(1)	3024(3)	-1366(1)	33(1)
C(3A)	4540(4)	4774(10)	-1528(4)	28(3)
C(4A)	4427(2)	5828(6)	-1748(3)	38(3)
C(5A)	4278(4)	5721(14)	-2242(5)	34(4)
C(6A)	3973(5)	4999(19)	-2297(8)	33(6)
C(7A)	3742(1)	3253(3)	-2071(1)	24(1)
C(8A)	3233(1)	1210(3)	-2084(1)	25(1)
C(9A)	2732(5)	-1(15)	-2296(7)	33(5)
C(10A)	2472(2)	-653(8)	-2069(3)	45(3)
C(11A)	2641(5)	-1520(14)	-1774(6)	46(6)
C(12A)	2909(3)	-1141(9)	-1391(4)	21(3)
C(13A)	3433(1)	21(3)	-1311(1)	34(1)
C(14A)	4015(1)	2279(3)	-1422(1)	21(1)

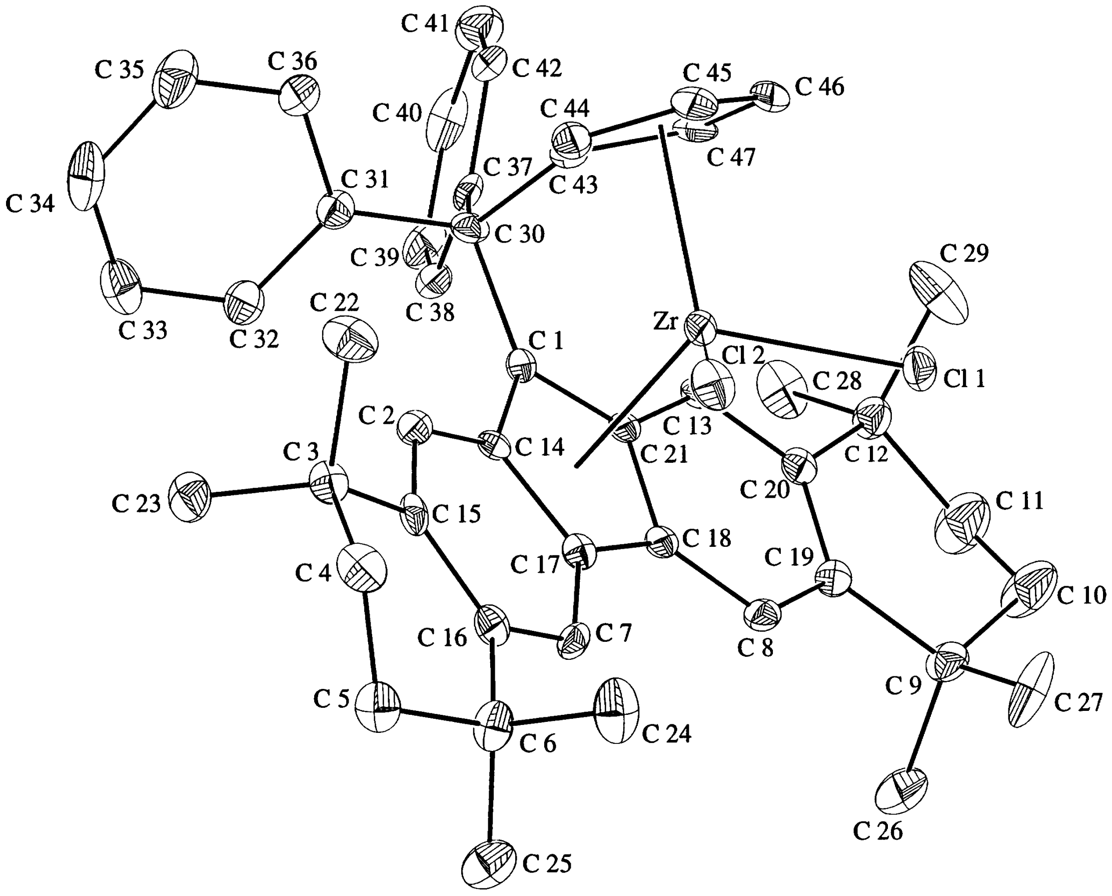
C(15A)	4267(1)	3895(3)	-1661(1)	34(1)
C(16A)	3992(1)	4031(3)	-2011(1)	28(1)
C(17A)	3753(1)	2377(3)	-1789(1)	21(1)
C(18A)	3521(1)	1486(3)	-1783(1)	22(1)
C(19A)	3041(1)	326(3)	-2004(1)	29(1)
C(20A)	3139(1)	-267(3)	-1604(1)	35(1)
C(21A)	3628(1)	876(3)	-1400(1)	22(1)
C(22A)	4644(4)	4969(11)	-1017(4)	40(3)
C(23A)	4852(3)	4346(9)	-1727(5)	52(3)
C(24A)	3674(4)	5656(18)	-2167(7)	46(5)
C(25A)	3841(4)	4786(18)	-2820(6)	34(4)
C(26A)	2850(2)	-673(9)	-2681(3)	61(3)
C(27A)	2531(3)	935(9)	-2534(4)	45(3)
C(28A)	3137(2)	-2106(7)	-1230(4)	50(3)
C(29A)	2754(2)	-715(7)	-984(3)	39(3)
C(30A)	4259(1)	504(3)	-1053(1)	25(1)
C(31A)	4333(1)	185(3)	-1530(1)	36(1)
C(32A)	4558(1)	771(4)	-1741(2)	74(2)
C(33A)	4617(2)	527(6)	-2188(3)	111(3)
C(34A)	4451(2)	-287(7)	-2407(2)	116(3)
C(35A)	4223(2)	-873(5)	-2218(2)	87(2)
C(36A)	4160(1)	-617(4)	-1779(1)	54(1)
C(37A)	4170(1)	-450(3)	-764(1)	20(1)
C(38A)	4298(1)	-1452(3)	-822(1)	31(1)
C(39A)	4233(1)	-2284(3)	-546(1)	40(1)
C(40A)	4040(1)	-2144(3)	-202(1)	31(1)
C(41A)	3924(1)	-1150(3)	-127(1)	27(1)
C(42A)	3989(1)	-316(3)	-403(1)	25(1)
C(43A)	4567(1)	969(3)	-759(1)	33(1)
C(44A)	4569(1)	1710(3)	-414(1)	34(1)
C(45A)	4900(1)	1855(3)	-165(1)	41(1)
C(46A)	5115(1)	1150(4)	-373(2)	83(2)
C(47A)	4898(1)	609(4)	-734(2)	89(2)
C(1B)	3944(1)	2004(3)	539(1)	21(1)
C(2B)	3878(1)	226(3)	998(1)	29(1)
C(3B)	3816(1)	-1466(3)	1423(2)	47(1)
C(4B)	3631(1)	-2521(3)	1320(2)	68(2)
C(5B)	3251(1)	-2408(4)	1230(2)	65(2)
C(6B)	3137(1)	-1754(3)	803(2)	43(1)
C(7B)	3258(1)	-5(3)	454(1)	25(1)
C(8B)	3123(1)	1980(3)	-245(1)	25(1)
C(9B)	2811(7)	2975(16)	-902(8)	13(5)
C(10B)	2913(3)	3819(10)	-1224(4)	40(5)
C(11B)	3032(4)	4823(12)	-974(6)	30(5)
C(12B)	3353(7)	4610(30)	-643(11)	34(9)
C(13B)	3671(1)	3330(3)	-104(1)	26(1)
C(14B)	3772(1)	989(3)	674(1)	22(1)
C(15B)	3677(1)	-664(3)	1053(1)	31(1)
C(16B)	3363(1)	-784(3)	777(1)	31(1)
C(17B)	3456(1)	864(3)	400(1)	22(1)
C(18B)	3396(1)	1757(3)	84(1)	19(1)
C(19B)	3114(1)	2901(3)	-504(1)	25(1)
C(20B)	3390(1)	3589(3)	-429(1)	25(1)
C(21B)	3677(1)	2434(3)	159(1)	20(1)

C(22B)	4199(1)	-1642(3)	1440(2)	61(1)
C(23C)	3757(1)	-1030(4)	1891(1)	73(2)
C(24B)	3147(1)	-2430(3)	377(2)	66(2)
C(25B)	2768(1)	-1412(3)	818(2)	63(2)
C(26B)	2512(7)	3358(17)	-679(9)	32(5)
C(27B)	2738(4)	1939(11)	-1162(6)	24(4)
C(28B)	3433(6)	5540(30)	-284(9)	31(6)
C(29B)	3654(5)	4770(30)	-927(9)	39(6)
C(30B)	4062(1)	2798(3)	943(1)	24(1)
C(31B)	3757(1)	2936(3)	1203(1)	36(1)
C(32B)	3739(1)	2334(4)	1596(2)	50(1)
C(33B)	3467(1)	2352(4)	1838(2)	65(2)
C(34B)	3206(1)	2991(4)	1659(2)	66(2)
C(35B)	3199(1)	3617(4)	1279(2)	56(2)
C(36B)	3485(1)	3575(4)	1037(2)	54(1)
C(37B)	4199(1)	3824(3)	756(1)	28(1)
C(38B)	4130(1)	4812(3)	912(1)	41(1)
C(39B)	4278(1)	5691(4)	741(2)	56(1)
C(40B)	4491(1)	5594(4)	432(2)	62(2)
C(41B)	4569(1)	4641(4)	284(2)	52(1)
C(42B)	4431(1)	3766(3)	449(1)	39(1)
C(43B)	4372(1)	2390(3)	1258(1)	27(1)
C(44B)	4589(1)	1617(3)	1179(1)	38(1)
C(45B)	4882(1)	1546(3)	1537(1)	38(1)
C(46B)	4832(1)	2372(4)	1875(1)	71(2)
C(47B)	4505(1)	2905(3)	1681(1)	49(1)
C(3')	4602(4)	4535(10)	-1659(4)	32(4)
C(4')	4564(3)	5305(8)	-2057(3)	59(4)
C(5')	4210(4)	5807(16)	-2157(7)	46(6)
C(6')	3909(5)	5067(18)	-2315(8)	21(5)
C(22')	4640(5)	5137(13)	-1207(4)	51(4)
C(23')	4920(4)	3847(11)	-1662(6)	63(4)
C(24')	3575(4)	5574(19)	-2239(7)	38(4)
C(25')	3952(4)	4740(20)	-2797(7)	44(5)
C(9')	2727(4)	82(13)	-2405(6)	24(4)
C(10')	2620(2)	-1069(6)	-2333(3)	42(3)
C(11')	2612(4)	-1353(15)	-1842(5)	45(5)
C(12')	2973(3)	-1323(11)	-1558(4)	46(4)
C(26')	2814(2)	236(7)	-2883(2)	46(3)
C(27')	2439(2)	843(9)	-2319(3)	38(3)
C(28')	3183(2)	-2266(7)	-1677(4)	72(4)
C(29')	2925(3)	-1383(10)	-1059(4)	67(4)
C(9")	2795(4)	3207(10)	-829(5)	34(4)
C(10")	2796(2)	4333(6)	-1009(3)	52(3)
C(11")	3141(2)	4685(8)	-1109(3)	45(3)
C(12")	3416(3)	4678(13)	-682(5)	24(4)
C(26")	2466(3)	3029(10)	-619(5)	42(3)
C(27")	2777(2)	2447(7)	-1247(3)	37(2)
C(28")	3329(3)	5532(14)	-348(5)	45(4)
C(29")	3758(3)	4848(12)	-835(4)	41(3)

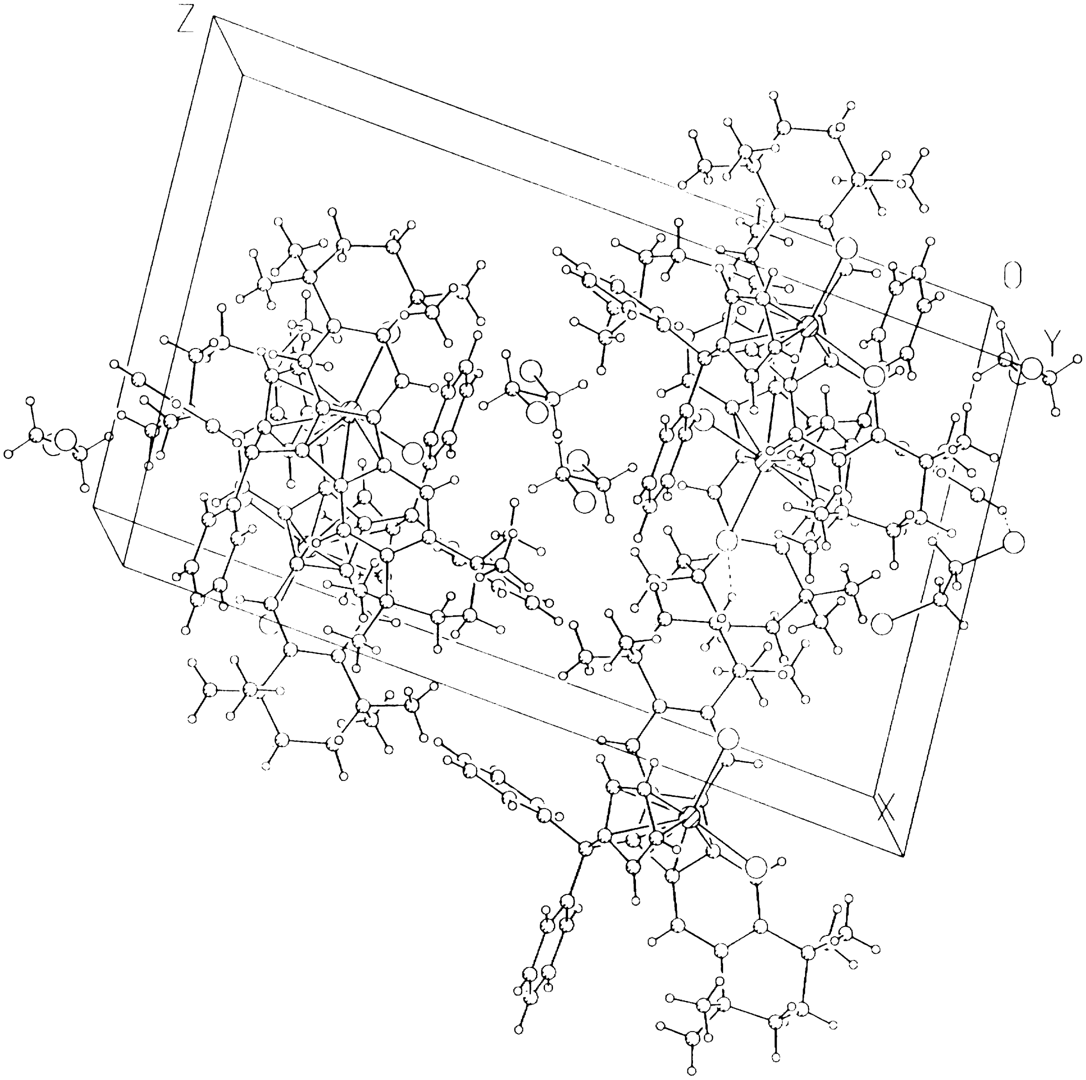
Appendix C

X-ray Crystal Structure Data for $Ph_2C(Oct)(C_5H_4)ZrCl_2$

Cambridge Database (CCDC) 112475



Labeled view with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(Oct)(C_5H_4)ZrCl_2$.

Empirical formula	$C_{47} H_{50} Cl_2 Zr (C_2 H_4 Cl_2)_{1.5}$	
Formula weight	925.48	
Crystallization solvent	1,2-dichloroethane	
Crystal habit	block	
Crystal size	0.44 x 0.33 x 0.32 mm^3	
Crystal color	ruby red	
Data Collection		
Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKa	
Data collection temperature	85 K	
Theta range for reflections used in lattice determination	15.4 to 16.2°	
Unit cell dimensions	a = 13.898(8) Å	alpha = 90°
	b = 13.698(10) Å	beta = 96.91(6)°
	c = 23.275(16) Å	gamma = 90°
Volume	4399(5) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Density (calculated)	1.397 Mg/m^3	
F(000)	1924	
Theta range for data collection	1.63 to 25.05°	
Completeness to theta = 25.05°	99.6%	
Index ranges	-16<=h<=16, -16<=k<=16, 0<=l<=27	
Data collection scan type	Omega scans	
Reflections collected	19403	
Independent reflections	7766 [R_{int}= 0.0242; GOF_{merge}= 1.21]	
Absorption coefficient	0.588 mm^{-1}	
Number of standards	3 reflections measured every 75 min.	
Variation of standards	-0.67%.	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Calculated sites	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	7766 / 7 / 527	
Treatment of hydrogen atoms	Geometrically restrained	
Goodness-of-fit on F^2	4.122	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0652, wR2 = 0.1422	
R indices (all data)	R1 = 0.0743, wR2 = 0.1433	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	
Max shift/error	0.004	
Average shift/error	0.000	
Extinction coefficient	0.0011(2)	
Largest diff. peak and hole	1.221 and -1.282 $e.Å^{-3}$	

Special Refinement Details

The unit cell contains 1,2-dichloroethane as a solvent of crystallization. One molecule sits on a center of inversion and therefore one half the molecule is in the list of atomic coordinates. Another molecule sits in a general position.

The variances [$\sigma^2(Fo^2)$] were derived from counting statistics plus an additional term, $(0.014I)^2$, and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014<I>)^2$.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $Ph_2C(Oct)(C_5H_4)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr	4117(1)	3727(1)	2430(1)	14(1)
Cl(1)	5858(1)	3773(1)	2662(1)	20(1)
Cl(2)	3726(1)	4493(1)	3318(1)	23(1)
C(1)	3183(3)	2464(3)	1900(2)	12(1)
C(2)	1958(3)	2889(3)	2638(2)	15(1)
C(3)	880(3)	3391(4)	3373(2)	18(1)
C(4)	932(4)	3516(4)	4027(2)	25(1)
C(5)	1267(4)	2596(4)	4351(2)	23(1)
C(6)	2323(4)	2355(4)	4278(2)	21(1)
C(7)	3315(3)	2038(3)	3469(2)	15(1)
C(8)	5253(3)	1435(3)	2828(2)	16(1)
C(9)	6970(4)	932(4)	2749(2)	21(1)
C(10)	7727(4)	1075(5)	2326(2)	38(2)
C(11)	7421(4)	819(5)	1725(2)	40(2)
C(12)	6547(3)	1438(4)	1450(2)	19(1)
C(13)	4895(3)	1914(3)	1657(2)	13(1)
C(14)	2800(3)	2482(3)	2456(2)	13(1)
C(15)	1796(3)	2875(3)	3217(2)	16(1)
C(16)	2474(3)	2410(3)	3639(2)	17(1)
C(17)	3510(3)	2084(3)	2888(2)	13(1)
C(18)	4352(3)	1817(3)	2616(2)	13(1)
C(19)	5979(3)	1314(3)	2472(2)	15(1)
C(20)	5787(3)	1553(3)	1876(2)	15(1)
C(21)	4145(3)	2048(3)	2002(2)	13(1)
C(22)	808(4)	4414(4)	3085(2)	28(1)
C(23)	-22(3)	2813(4)	3134(2)	25(1)
C(24)	3004(4)	3094(4)	4626(2)	31(1)
C(25)	2547(4)	1339(4)	4522(2)	28(1)
C(26)	6888(4)	-143(4)	2906(3)	42(2)

C(27)	7330(4)	1511(5)	3293(2)	39(2)
C(28)	6139(4)	863(4)	904(2)	28(1)
C(29)	6836(4)	2446(4)	1257(3)	37(2)
C(30)	2744(3)	3000(3)	1342(2)	15(1)
C(31)	1641(3)	3014(4)	1275(2)	17(1)
C(32)	1126(4)	2166(4)	1372(2)	21(1)
C(33)	130(4)	2156(4)	1298(2)	28(1)
C(34)	-380(4)	2990(5)	1116(2)	34(2)
C(35)	119(4)	3833(4)	999(2)	31(1)
C(36)	1126(4)	3836(4)	1069(2)	22(1)
C(37)	3031(3)	2539(4)	791(2)	16(1)
C(38)	3089(3)	1524(3)	731(2)	18(1)
C(39)	3293(4)	1100(4)	212(2)	23(1)
C(40)	3422(4)	1676(4)	-261(2)	29(1)
C(41)	3353(4)	2682(4)	-216(2)	27(1)
C(42)	3155(3)	3111(4)	304(2)	20(1)
C(43)	3203(3)	4000(3)	1471(2)	16(1)
C(44)	2889(4)	4708(3)	1858(2)	20(1)
C(45)	3649(4)	5379(4)	2015(2)	23(1)
C(46)	4441(4)	5088(3)	1749(2)	21(1)
C(47)	4188(3)	4230(3)	1423(2)	17(1)
Cl(10)	3763(1)	5127(1)	-651(1)	18(1)
C(110)	4612(5)	5383(6)	-23(3)	21(2)
Cl(11)	3961(1)	5151(1)	5505(1)	39(1)
Cl(12)	4410(1)	8254(1)	5472(1)	34(1)
C(111)	4219(7)	6351(2)	5235(3)	12(3)
C(112)	4250(8)	7034(2)	5767(3)	13(3)
C(114)	4190(9)	7023(3)	5230(4)	17(4)
C(113)	4200(10)	6398(3)	5786(4)	21(4)

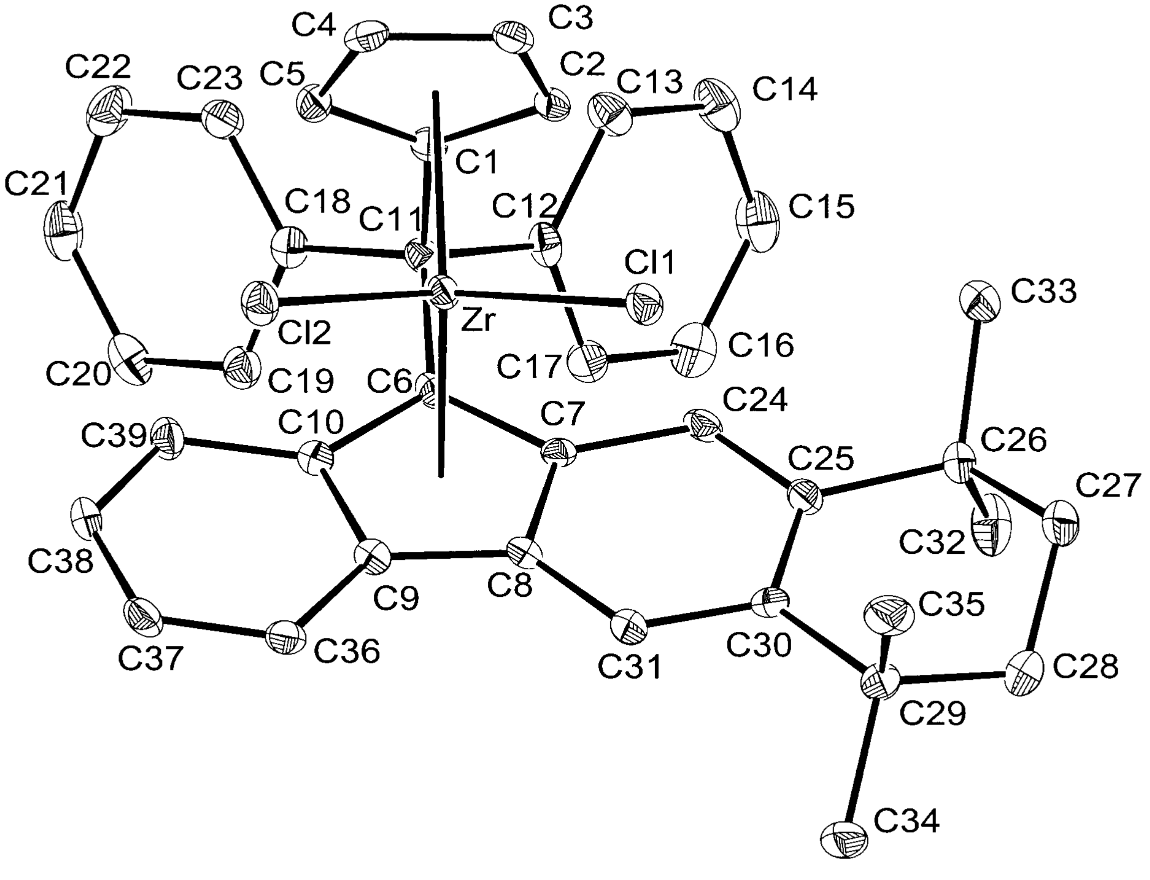
Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(Oct)(C_5H_4)ZrCl_2$.

Zr-Cent(1)	2.165(1)	C(43)-C(30)-C(1)	98.4(4)
Zr-Cent(2)	2.238(2)	Cent(1)-Zr-Cent(2)	117.76(4)
Zr-Pln(1)	2.163(3)	Pln(1)-Zr-Pln(2)	107.73(17)
Zr-Pln(2)	2.218(3)	Cl(1)-Zr-Cl(2)	96.79(7)
Zr-Cl(1)	2.4158(19)		
Zr-Cl(2)	2.4371(19)		
Zr-C(1)	2.411(5)		
Zr-C(44)	2.437(5)		
Zr-C(43)	2.458(5)		
Zr-C(47)	2.456(5)		
Zr-C(21)	2.509(5)		
Zr-C(14)	2.508(5)		
Zr-C(45)	2.514(5)		
Zr-C(46)	2.522(5)		
Zr-C(18)	2.666(5)		
Zr-C(17)	2.671(5)		

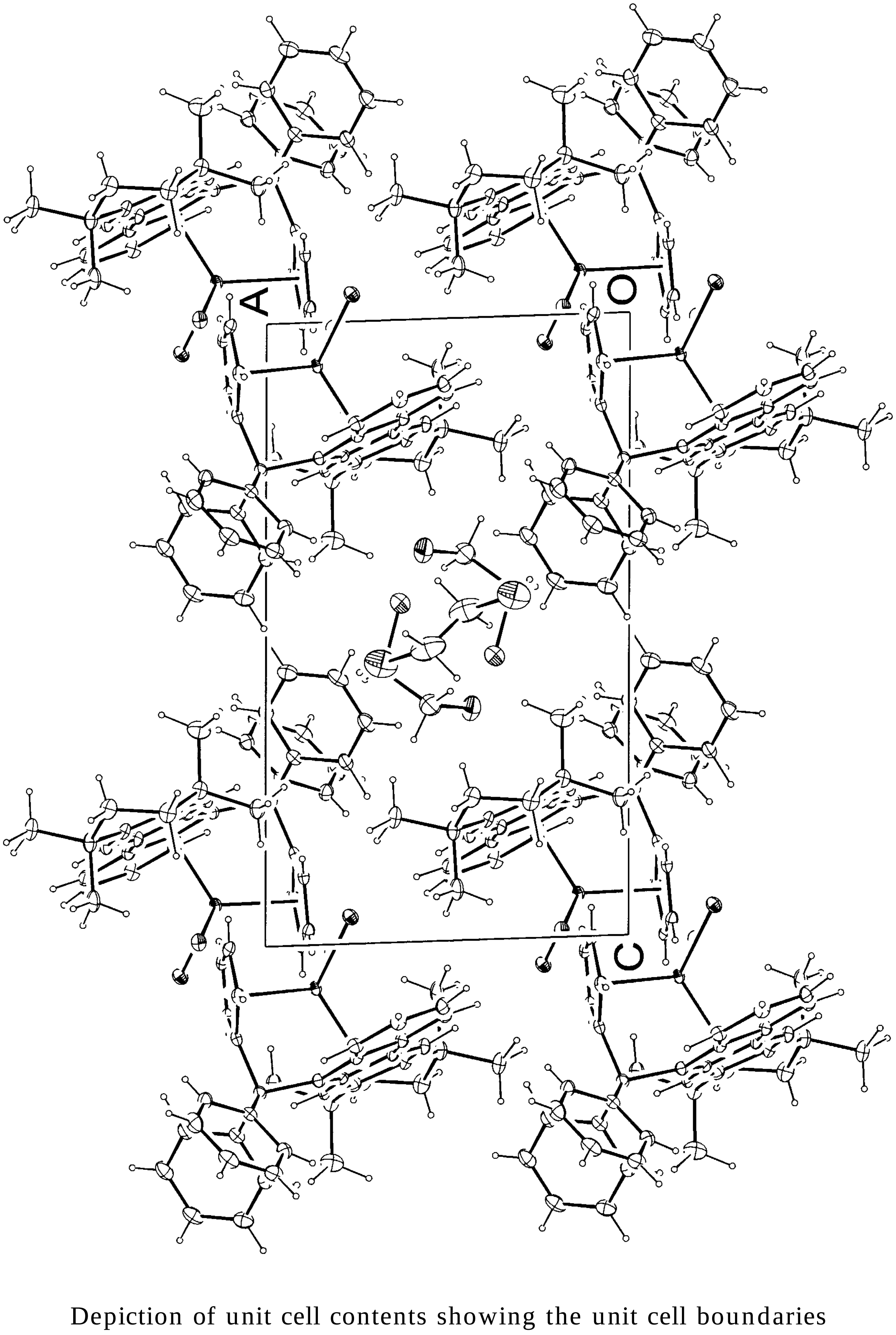
Appendix D

X-ray Crystal Structure Data for $Ph_2C(Tet)(C_5H_4)ZrCl_2$

Cambridge Database (CCDC) 137697



Labeled view with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(Tet)(C_5H_4)ZrCl_2$.

Empirical formula	$C_{42}H_{42}Cl_5Zr$ $[C_{39}H_{36}ClZr \cdot 3/2(C_2H_4Cl_2)]$	
Formula weight	815.28 [666.84 · 3/2(98.959)]	
Crystallization solvent	$ClCH_2CH_2Cl$	
Crystal habit	tabular	
Crystal size	0.40 x 0.36 x 0.18 mm^3	
Crystal color	tangerine	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker SMART 1000 ccd	
Wavelength	0.71073 Å MoKα	
Data collection temperature	98 K	
Theta range for 5986 reflections used in lattice determination	2.5 to 28.4°	
Unit cell dimensions	a = 9.1631(10) Å	α= 70.655(2)°
	b = 12.4550(13) Å	β= 87.699(2)°
	c = 16.7351(18) Å	γ = 87.820(2)°
Volume	1800.0(3) $Å^3$	
Z	2	
Crystal system	triclinic	
Space group	P $\bar{1}$ (#2)	
Density (calculated)	1.504 g/cm^3	
F(000)	838	
Theta range for data collection	1.79 to 28.45°	
Completeness to theta = 28.45°	89.6 %	
Index ranges	-11<=h<=11, -16<=k<=16, -21<=l<=21	
Data collection scan type	ω-scans at 3 fixed ϕ values	
Reflections collected	17128	
Independent reflections	8132 [R_{int}= 0.0406]	
Absorption coefficient	0.708 mm^{-1}	
Absorption correction	none	
Number of standards	initial 75 frames recollected at end	
Variation of standards	within counting statistics	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	direct methods	
Secondary solution method	difference map	
Hydrogen placement	geometric	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	8132 / 0 / 559	
Treatment of hydrogen atoms	refine xyz, U_{iso}'s fixed at 120% that of attached atom	
Goodness-of-fit on F^2	2.757	
Final R indices [I>2s(I)]	R1 = 0.0467, wR2 = 0.0847	
R indices (all data)	R1 = 0.0538, wR2 = 0.0855	
Type of weighting scheme used	calculated	
Weighting scheme used	$w=1/\sigma^2(F_o^2)$	
Max shift/error	0.030	
Average shift/error	0.001	
Largest diff. peak and hole	2.114 and -1.154 $e.Å^{-3}$	

Special Details

Several crystals were examined and appeared split, streaky and/or twinned. The crystal used had slightly split peaks. Paratone-N oil was used to mount the crystals on a glass fiber. Three runs of data were collected with 30 second long, –0.3° wide ω-scans at three values of φ (0, 120 and 240°) with the detector 5 cm (nominal) distant at a θ of -28°. The initial cell for data reduction was based on reflections found in the data frames. [The crystal to detector distance was held constant (the value based on other samples) since it decreased with further refinement.] The cell thus obtained was used for another cycle of unrestrained data integration with SAINT v6.02. [For data processing, all SAINT defaults were used, except: box size optimization was enabled, periodic orientation matrix updating was disabled, no Laue class integration restraints were used, the model profiles from all nine areas were blended, and for the post-integration global least squares refinement, no constraints were applied.] The final box sizes were somewhat larger than typical. Absorption correction with SADABS did not improve the data and was not used.

There is one molecule of phenyl$_2$C(Tet)(Cp)ZrCl$_2$ in the asymmetric unit as well as one and one half (the latter on a center of inversion) molecules of ClCH$_2$CH$_2$Cl. As seen in the view along the *b*-axis, the solvent molecules lie in a channel parallel to the axis. These solvent molecules are slightly disordered; four of the five peaks over |1| e.Å^{-3} in the final difference map are near the chlorine atoms in the solvent molecules. [The peaks are: 2.11 e.Å^{-3} at 0.86 Å from Cl3, -1.15 e.Å^{-3} at 0.48 Å from Cl5,-1.13 e.Å^{-3} at 0.66 Å from Cl3, -1.06 e.Å^{-3} at 0.55 Å from Cl5, with 1.26 e.Å^{-3} at 0.80 Å from Zr.]

Two outlier reflections (0 1 0 and 2 3 8) were omitted from the final dataset. Refinement of F^2 is against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. The $\sigma^2(F_o^2)$ include the default instrument error constant of 0.005I. SAINT uses model profiles to improve the determination of weak reflections; however, it does not calculate the σ's for these weak reflections properly.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for Ph$_2$C(Tet)(C$_5$H$_4$)ZrCl$_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U$_{eq}$
Zr	8626(1)	7234(1)	693(1)	11(1)
Cl1	8170(1)	9255(1)	108(1)	16(1)
Cl2	7661(1)	6672(1)	-432(1)	16(1)
C1	10797(3)	6364(2)	1464(2)	12(1)
C2	11047(3)	7543(2)	1104(2)	13(1)
C3	11183(3)	7823(2)	216(2)	15(1)
C4	11004(3)	6839(2)	14(2)	15(1)
C5	10744(3)	5937(2)	777(2)	14(1)
C6	8535(3)	6145(2)	2181(2)	12(1)
C7	7877(3)	7222(2)	2164(2)	11(1)
C8	6482(3)	7360(2)	1789(2)	13(1)
C9	6235(3)	6345(2)	1579(2)	13(1)
C10	7488(3)	5595(2)	1826(2)	13(1)
C11	10151(3)	5786(2)	2349(2)	12(1)
C12	10783(3)	6218(2)	3021(2)	14(1)
C13	12203(3)	6634(2)	2925(2)	18(1)

C14	12775(3)	6982(3)	3547(2)	22(1)
C15	11989(3)	6886(3)	4284(2)	23(1)
C16	10599(3)	6463(3)	4389(2)	22(1)
C17	10004(3)	6127(2)	3765(2)	16(1)
C18	10423(3)	4489(2)	2682(2)	13(1)
C19	9476(3)	3803(2)	3295(2)	16(1)
C20	9767(3)	2652(2)	3650(2)	20(1)
C21	11009(3)	2164(3)	3399(2)	22(1)
C22	11954(3)	2831(3)	2793(2)	23(1)
C23	11664(3)	3986(2)	2445(2)	17(1)
C24	8385(3)	8147(2)	2376(2)	13(1)
C25	7552(3)	9115(2)	2265(2)	14(1)
C26	8188(3)	10060(2)	2544(2)	16(1)
C27	7314(3)	11178(2)	2203(2)	20(1)
C28	5686(3)	11012(3)	2287(2)	21(1)
C29	5173(3)	10306(2)	1761(2)	18(1)
C30	6121(3)	9229(2)	1923(2)	14(1)
C31	5628(3)	8339(2)	1689(2)	14(1)
C32	8164(4)	9652(3)	3514(2)	25(1)
C33	9771(3)	10274(3)	2211(2)	19(1)
C34	3552(3)	10037(3)	2004(2)	22(1)
C35	5269(3)	11002(3)	820(2)	22(1)
C36	5036(3)	6053(2)	1197(2)	15(1)
C37	5104(3)	5030(2)	1048(2)	17(1)
C38	6336(3)	4298(2)	1270(2)	16(1)
C39	7525(3)	4551(2)	1642(2)	15(1)
Cl3	5662(1)	3177(1)	3723(1)	40(1)
Cl4	3698(1)	3272(1)	5447(1)	33(1)
C40	4537(4)	4329(3)	3798(2)	35(1)
C41	3228(4)	3929(3)	4373(2)	28(1)
Cl5	3170(1)	9461(1)	4485(1)	54(1)
C42	4474(6)	10370(4)	4703(3)	56(1)

Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(Tet)(C_5H_4)ZrCl_2$.

Zr-Cp1	2.158
Zr-Cp2	2.242
Zr-Pln1	2.1551(12)
Zr-Pln2	2.2226(12)
Zr-Cl1	2.4063(7)
Zr-Cl2	2.4229(7)
Zr-C1	2.431(3)
Zr-C2	2.430(2)
Zr-C3	2.502(3)
Zr-C4	2.524(3)
Zr-C5	2.455(3)
Zr-C6	2.408(3)
Zr-C7	2.524(3)
Zr-C8	2.669(3)
Zr-C9	2.657(3)
Zr-C10	2.507(3)

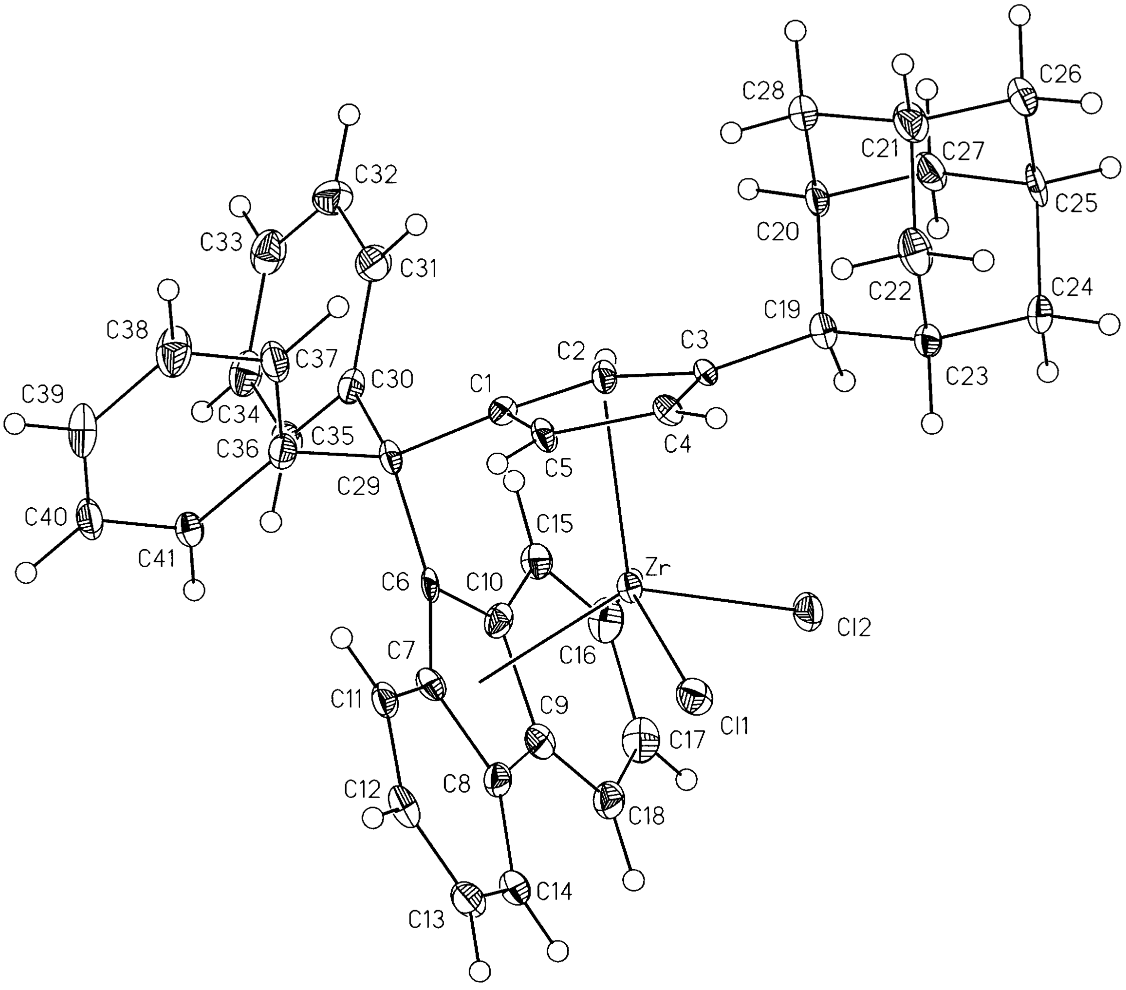
Cp1-Zr-Cp2	118.1
Cp1-Zr-Cl1	108.9
Cp1-Zr-Cl2	109.1
Cp2-Zr-Cl1	109.5
Cp2-Zr-Cl2	111.7
Cl1-Zr-Cl2	98.84(2)
Pln1-Pln2	72.2(1)
C1-C11-C6	99.1(2)

Symmetry transformations used to generate equivalent atoms:
(i) -x+1,-y+2,-z+1
Cp1 is the centroid formed by C1, C2, C3, C4, C5
Cp2 is the centroid formed by C6, C7, C8, C9, C10
Pln1 is the plane formed by C1, C2, C3, C4, C5
Pln2 is the plane formed by C6, C7, C8, C9, C10

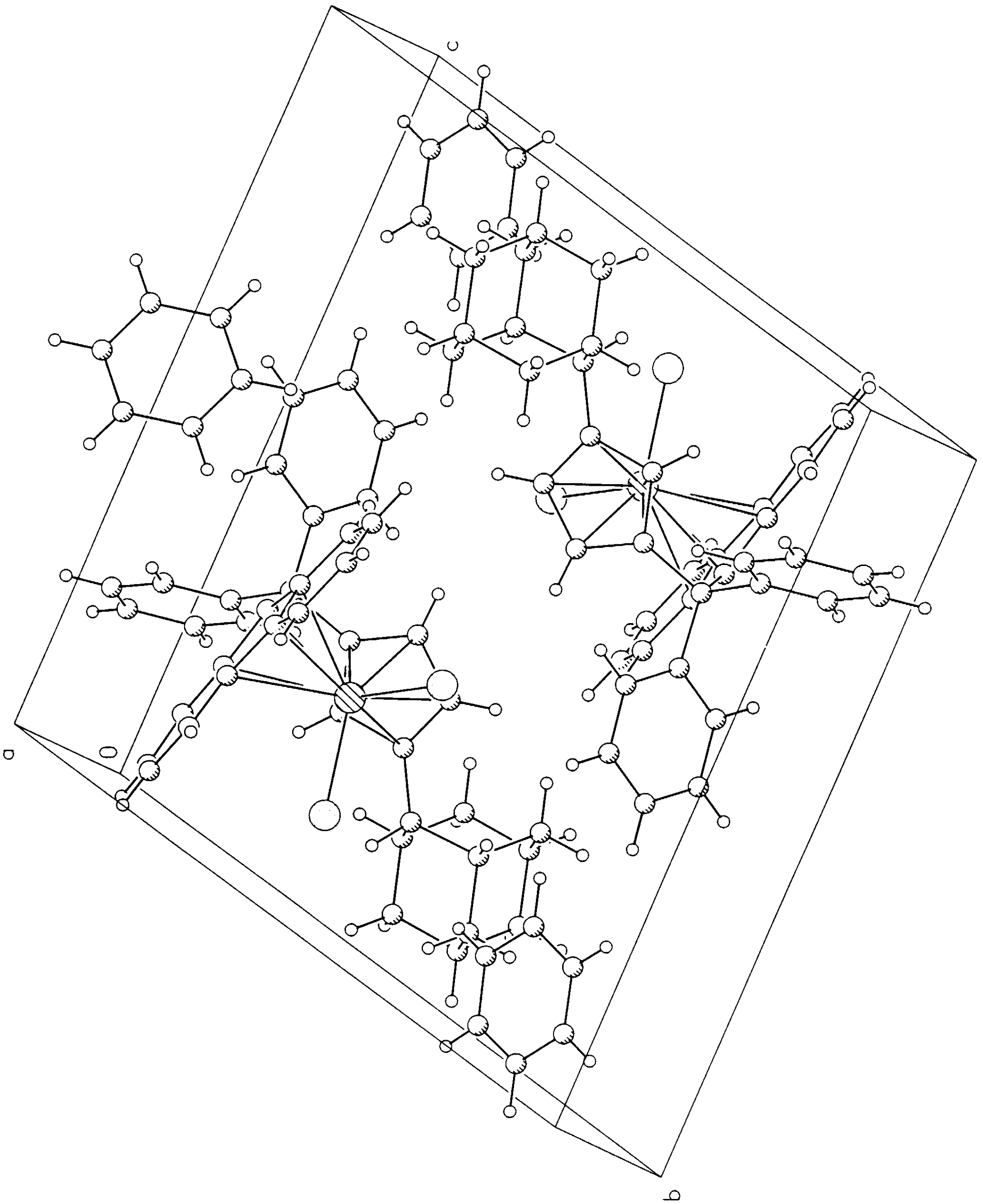
Appendix E

X-ray Crystal Structure Data for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_{1.5}$

Cambridge Database (CCDC) 137247



Labeled view with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-}adamantyl)\text{-}C_5H_3)ZrCl_2$.

Empirical formula	$C_{50}H_{45}Cl_2Zr(C_6H_6)_{1.5}$	
Formula weight	808.03	
Crystallization solvent	benzene	
Crystal habit	thick blade	
Crystal size	0.42 x 0.41 x 0.08 mm^3	
Crystal color	red	
Data Collection		
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å MoKα	
Data collection temperature	98(2) K	
Theta range for 5068 reflections used in lattice determination	2.57 to 28.16°	
Unit cell dimensions	a = 9.4262(18) Å	α= 103.984(3)°
	b = 13.514(3) Å	β= 90.944(3)°
	c = 15.357(3) Å	γ = 90.162(3)°
Volume	1898.0(6) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.414 Mg/m^3	
F(000)	838	
Theta range for data collection	2.16 to 28.36°	
Completeness to theta = 28.36°	89.1%	
Index ranges	-12<=h<=12, -17<=k<=16, -20<=l<=20	
Data collection scan type	phi and omega scans	
Reflections collected	18178	
Independent reflections	8454 [R_{int}= 0.0815]	
Absorption coefficient	0.467 mm^{-1}	
Absorption correction	None	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Difference Fourier map	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	8454 / 0 / 520	
Treatment of hydrogen atoms	Restrained	
Goodness-of-fit on F^2	1.776	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0525, wR2 = 0.0956	
R indices (all data)	R1 = 0.0663, wR2 = 0.0976	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	
Max shift/error	0.000	
Average shift/error	0.000	
Largest diff. peak and hole	1.462 and -0.927 e.$Å^{-3}$	

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr	6553(1)	3885(1)	2787(1)	11(1)
Cl(1)	7850(1)	5325(1)	3681(1)	18(1)
Cl(2)	6836(1)	4307(1)	1364(1)	18(1)
C(1)	4449(3)	3150(2)	3311(2)	12(1)
C(2)	4040(3)	3386(2)	2489(2)	12(1)
C(3)	3983(3)	4469(2)	2600(2)	12(1)
C(4)	4436(3)	4911(3)	3479(2)	15(1)
C(5)	4738(3)	4111(2)	3916(2)	13(1)
C(6)	6529(3)	2201(2)	3069(2)	11(1)
C(7)	7713(3)	2703(2)	3617(2)	14(1)
C(8)	8845(3)	2813(2)	3038(2)	15(1)
C(9)	8391(3)	2389(2)	2125(2)	14(1)
C(10)	6951(3)	2024(2)	2154(2)	14(1)
C(11)	7900(3)	3121(2)	4559(2)	14(1)
C(12)	9168(3)	3584(3)	4870(2)	18(1)
C(13)	10272(3)	3670(3)	4293(2)	19(1)
C(14)	10131(3)	3288(3)	3384(2)	17(1)
C(15)	6242(3)	1627(3)	1315(2)	16(1)
C(16)	6941(4)	1574(3)	531(2)	20(1)
C(17)	8369(3)	1890(3)	522(2)	21(1)
C(18)	9080(3)	2303(3)	1312(2)	18(1)
C(19)	3487(3)	4940(2)	1860(2)	14(1)
C(20)	1925(3)	4636(3)	1580(2)	16(1)
C(21)	1020(3)	6326(3)	2424(2)	21(1)
C(22)	2552(3)	6651(3)	2739(2)	21(1)
C(23)	3601(3)	6119(3)	2039(2)	16(1)
C(24)	3288(3)	6392(3)	1146(2)	18(1)
C(25)	1761(3)	6071(3)	825(2)	18(1)
C(26)	718(3)	6594(3)	1531(2)	21(1)
C(27)	1606(3)	4914(3)	693(2)	18(1)
C(28)	913(3)	5170(3)	2300(2)	19(1)
C(29)	5005(3)	2131(2)	3398(2)	12(1)
C(30)	4160(3)	1214(2)	2811(2)	15(1)
C(31)	2701(3)	1310(3)	2669(2)	18(1)
C(32)	1930(3)	480(3)	2192(2)	23(1)
C(33)	2573(4)	-449(3)	1867(2)	21(1)
C(34)	4010(4)	-545(3)	2013(2)	19(1)

C(35)	4791(3)	289(2)	2488(2)	16(1)
C(36)	4938(3)	1969(2)	4358(2)	14(1)
C(37)	3867(3)	2422(3)	4923(2)	19(1)
C(38)	3751(4)	2218(3)	5767(2)	25(1)
C(39)	4692(4)	1572(3)	6043(2)	25(1)
C(40)	5749(4)	1110(3)	5478(2)	19(1)
C(41)	5870(3)	1307(2)	4634(2)	15(1)
C(42)	6897(4)	7423(4)	1155(3)	40(1)
C(43)	7633(4)	8044(5)	1862(3)	55(2)
C(44)	8235(5)	8948(4)	1765(4)	48(1)
C(45)	8127(5)	9208(4)	989(4)	54(1)
C(46)	7385(5)	8592(4)	277(4)	50(1)
C(47)	6773(5)	7715(4)	364(3)	42(1)
C(48)	-278(5)	9278(4)	5476(3)	47(1)
C(49)	217(5)	8980(4)	4616(3)	48(1)
C(50)	503(5)	9700(4)	4142(3)	43(1)

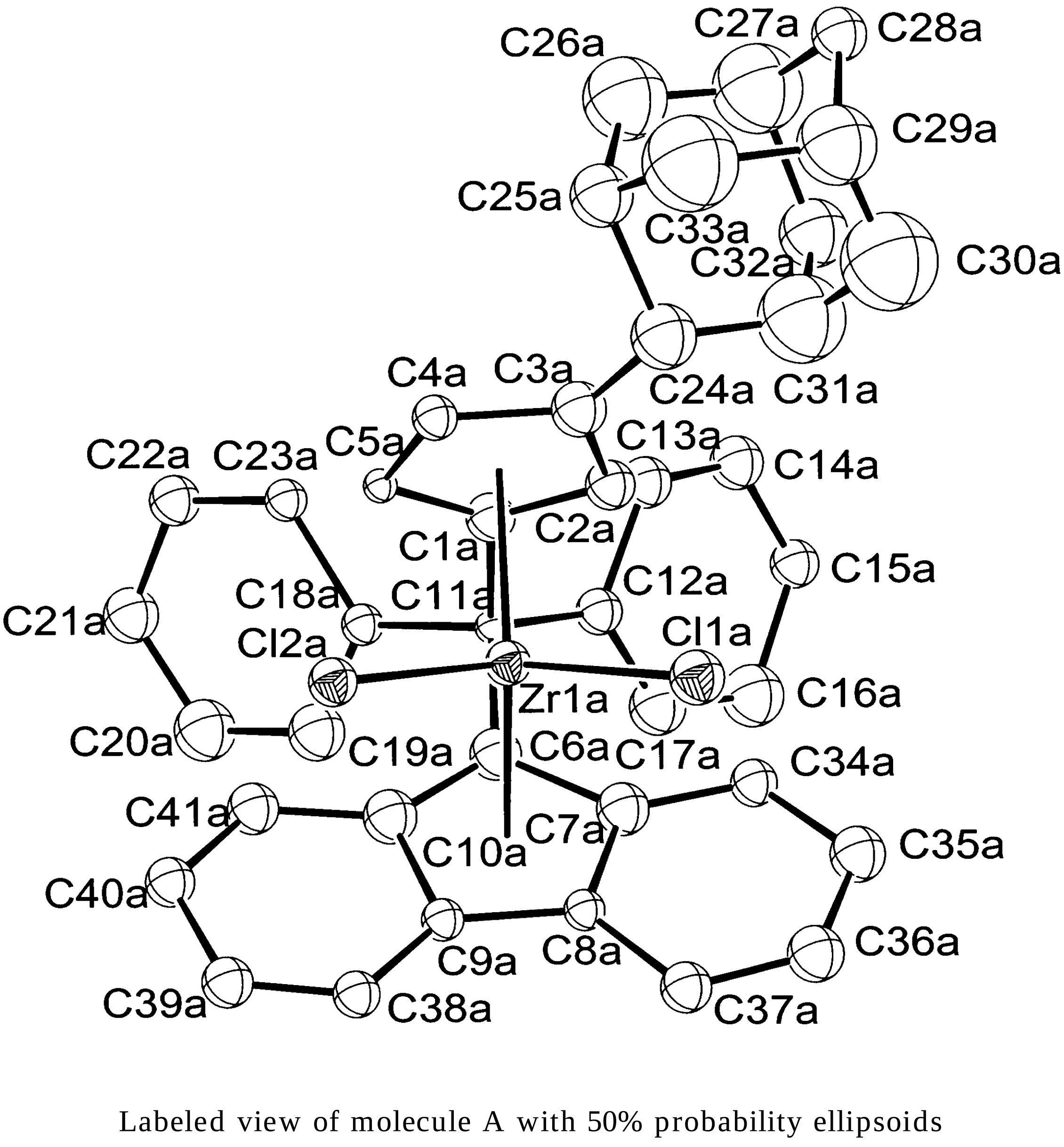
Table 3. Selected bond lengths [Å] and angles ¶] for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$.

Zr-Pln(1)	2.1732(26)
Zr-Pln(2)	2.2362(30)
Zr-Cent(1)	2.1776(7)
Zr-Cent(2)	2.2486(7)
Zr-Cl(1)	2.4098(8)
Zr-Cl(2)	2.4062(9)
Zr-C(6)	2.416(3)
Zr-C(5)	2.424(3)
Zr-C(1)	2.448(3)
Zr-C(2)	2.466(3)
Zr-C(10)	2.499(3)
Zr-C(7)	2.514(3)
Zr-C(4)	2.532(3)
Zr-C(3)	2.583(3)
Zr-C(8)	2.678(3)
Zr-C(9)	2.684(3)
Pln(1)-Zr-Pln(2)	108.18(25)
Cent(1)-Zr-Cent(2)	118.02(3)
Cl(2)-Zr-Cl(1)	96.83(3)
C(1)-C(29)-C(6)	99.6(2)

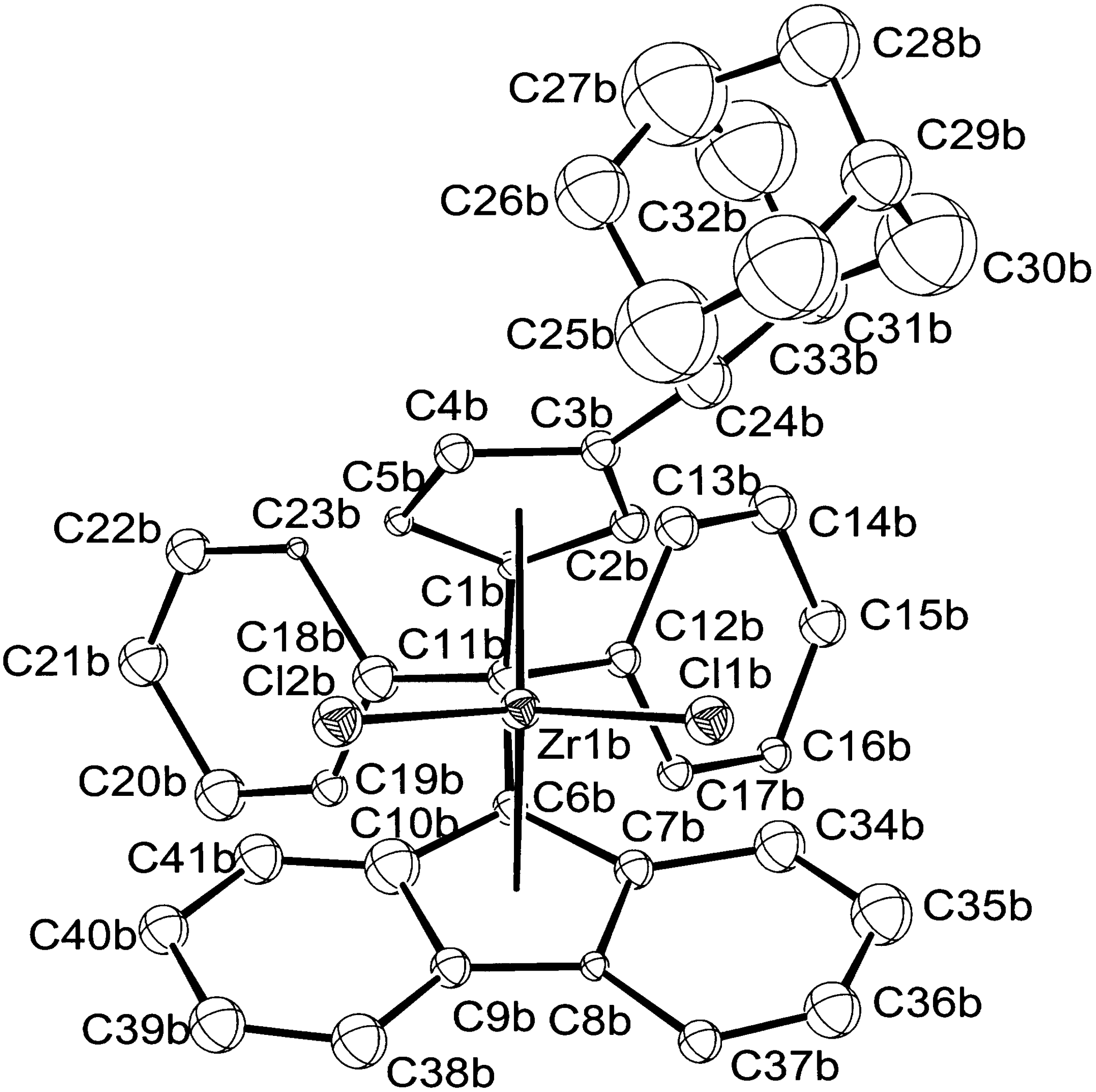
Pln(1) is the plane defined by C1, C2, C3, C4 and C5.
Pln(2) is the plane defined by C6, C7, C8, C9 and C10.
Cent(1) is the centroid of C1, C2, C3, C4 and C5.
Cent(2) is the centroid of C6, C7, C8, C9 and C10.

X-ray Crystal Structure Data for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_2$

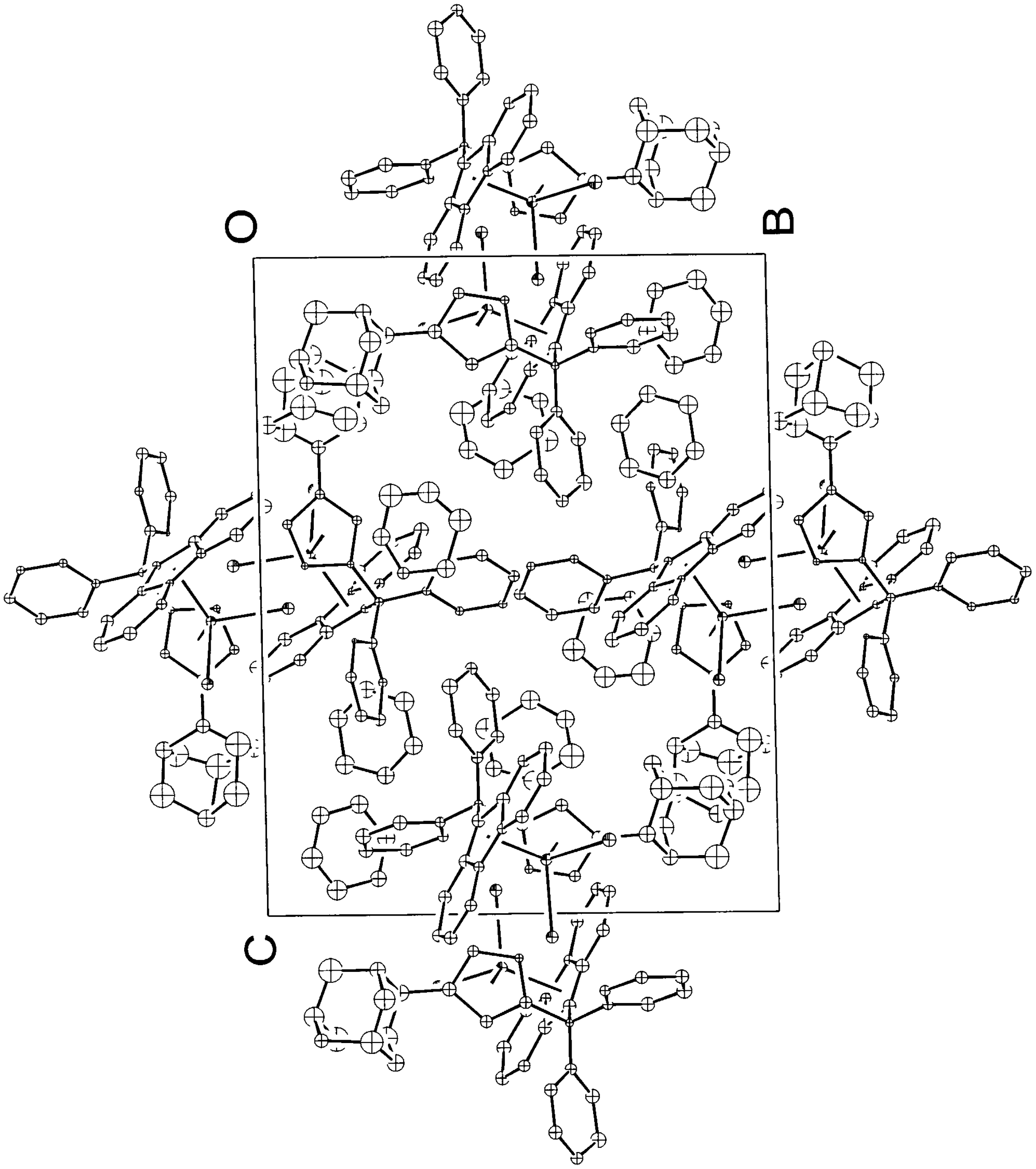
Cambridge Database (CCDC) 137247



Labeled view of molecule A with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal Data and Structure Refinement for $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$.

Empirical formula	$C_{53}H_{48}Cl_2Zr$ [$C_{41}H_{36}Cl_2Zr \cdot 2(C_6H_6)$]	
Formula weight	847.09 [690.87 · 2(78.11)]	
Crystallization solvent	benzene	
Crystal habit	blade	
Crystal size	0.48 x 0.09 x 0.04 mm^3	
Crystal color	bright red	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	CAD4	
Wavelength	0.71073 Å MoKα	
Data collection temperature	84 K	
Theta range for 25 reflections used in lattice determination	11 to 14°	
Unit cell dimensions	a = 13.242(6) Å	α= 82.67(3)°
	b = 17.098(10) Å	β= 73.29(3)°
	c = 21.311(5) Å	γ = 67.26(5)°
Volume	4261(3) $Å^3$	
Z	4	
Crystal system	Triclinic	
Space group	P $\bar{1}$ (#2)	
Density (calculated)	1.320 g/cm^3	
F(000)	1760	
Theta range for data collection	1.5 to 20°	
Completeness to theta = 20.00°	100.0 %	
Index ranges	-12<=h<=12, -16<=k<=16, -20<=l<=20	
Data collection scan type	ω–scan	
Reflections collected	17254	
Independent reflections	7934 [R_{int}= 0.0897; GOF_{merge}= 1.01]	
Absorption coefficient	0.419 mm^{-1}	
Absorption correction	ψ–scan (North, Phillips & Matthews, 1968)	
Max. and min. transmission	1.29 and 0.60	
Number of standards	3 reflections measured every 75 min	
Variation of standards	0.41%	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	direct methods	
Secondary solution method	difference map	
Hydrogen placement	geometric	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	7934 / 0 / 449	
Treatment of hydrogen atoms	no refinement	
Goodness-of-fit on F^2	2.909	
Final R indices [$I>2\sigma(I)$]	R1 = 0.1567, wR2 = 0.2781	
R indices (all data)	R1 = 0.2372, wR2 = 0.2922	
Type of weighting scheme used	calculated	
Weighting scheme used	$w=1/\sigma^2(F_o^2)$	
Max shift/error	0.005	
Average shift/error	0.000	

Largest diff. peak and hole 3.985 and -3.956 e.Å^{-3}

Special Details

A tiny bright red blade was mounted on a glass fiber with Paratone-N oil. Data were collected with 1.4° ω-scans. The individual backgrounds were replaced by a background function of 2θ derived from those reflections with $I < 3\sigma(I)$; a number of high backgrounds were removed from this calculation. The GOF_merge was 1.01 (7932 multiples) in point group $\bar{1}$; R_merge was 0.069 for 5527 duplicates with $F_o > 0$. Ψ–scan data were used for the absorption correction. One outlier reflection (0 1 1) was omitted from the refinement.

Weights w are calculated as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. The refinement of F^2 is as always against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

The asymmetric unit consists of two molecules, with different orientations of the adamantyl group, and four molecules of benzene. Overlaps of the two molecules with each other and with the structure obtained from a different solvate are provided. Since the crystal was small and the unit cell large, a 2θ limit of 40° was used in collecting data. The background is anisotropic and, as a result, reflections with small values of h were apparently truncated. Coupled with the lack of high angle data, this systematic error caused most atoms to go non-positive definite during refinement. Consequently all heavy atoms were refined isotropically; no hydrogen atom parameters were refined. Not surprisingly, the largest excursions in the final difference map are big (~4 e.Å^{-3}) and near the two Zr atoms. Nonetheless, this structure adequately shows the conformations of the two molecules.

This crystal was obtained from the same vial and had the same habit as $Ph_2C(C_{13}H_8)$(3-(2-adamantyl)-$C_5H_3)ZrCl_2 \cdot (C_6H_6)_{1.5}$, which was examined months later. It is interesting to speculate that the structure of $Ph_2C(C_{13}H_8)$(3-(2-adamantyl)-$C_5H_3)ZrCl_2 \cdot (C_6H_6)_{1.5}$ may have resulted from the slow loss of benzene from $Ph_2C(C_{13}H_8)$(3-(2-adamantyl)-$C_5H_3)ZrCl_2 \cdot (C_6H_6)_2$ accompanied by rearrangement of the molecules.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Ph_2C(3-(2-adamantyl)$C_5H_3)(C_{13}H_8)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr1A	2375(2)	4540(2)	816(1)	21(1)
Cl1A	3856(6)	3298(4)	1108(3)	31(2)
Cl2A	3143(6)	4458(4)	-359(3)	25(2)
C1A	330(20)	4997(16)	1352(11)	25(7)
C2A	860(20)	4216(16)	1637(11)	26(7)
C3A	1260(20)	3503(17)	1140(11)	32(7)
C4A	1010(20)	3986(15)	562(10)	21(7)
C5A	480(19)	4884(14)	672(9)	12(6)
C6A	1340(20)	5854(16)	1413(11)	28(7)
C7A	2270(20)	5358(17)	1734(11)	29(7)
C8A	3290(20)	5390(15)	1289(10)	18(6)

C9A	3060(20)	5865(15)	713(10)	19(6)
C10A	1830(20)	6121(17)	799(11)	30(7)
C11A	130(20)	5846(14)	1669(10)	10(6)
C12A	-310(20)	5851(16)	2374(11)	22(7)
C13A	-1090(20)	5450(16)	2688(11)	27(7)
C14A	-1630(20)	5521(16)	3339(11)	30(7)
C15A	-1410(20)	5930(15)	3736(11)	24(7)
C16A	-650(20)	6356(17)	3462(12)	40(8)
C17A	-160(20)	6265(16)	2791(11)	33(7)
C18A	-680(20)	6605(15)	1396(10)	18(6)
C19A	-680(20)	7390(17)	1394(11)	33(7)
C20A	-1470(20)	8108(18)	1196(11)	39(8)
C21A	-2320(20)	8065(17)	979(11)	32(7)
C22A	-2390(20)	7281(15)	986(10)	26(7)
C23A	-1610(20)	6556(16)	1182(9)	18(6)
C24A	1750(30)	2551(18)	1188(12)	44(8)
C25A	1200(20)	2112(18)	836(13)	41(8)
C26A	20(30)	2230(20)	1285(14)	75(11)
C27A	-30(40)	1960(20)	1937(17)	86(12)
C28A	680(20)	984(16)	1906(11)	31(7)
C29A	1970(30)	850(20)	1546(14)	68(11)
C30A	2320(40)	1280(30)	1888(18)	100(14)
C31A	1650(30)	2260(20)	1877(16)	82(12)
C32A	550(30)	2420(19)	2255(13)	49(9)
C33A	2020(30)	1200(20)	838(16)	97(14)
C34A	2290(20)	4939(15)	2317(10)	23(7)
C35A	3340(20)	4507(17)	2500(12)	32(7)
C36A	4350(20)	4548(17)	2040(11)	34(7)
C37A	4350(20)	4999(15)	1471(11)	27(7)
C38A	3750(20)	6041(15)	130(10)	23(7)
C39A	3370(20)	6451(16)	-359(11)	27(7)
C40A	2200(20)	6685(16)	-322(11)	25(7)
C41A	1480(20)	6543(15)	261(10)	27(7)
Zr1B	2710(2)	9015(2)	5509(1)	16(1)
Cl1B	1250(6)	8919(4)	6468(3)	23(2)
Cl2B	1810(6)	10527(4)	5325(3)	24(2)
C1B	4771(19)	8241(14)	5337(9)	8(6)
C2B	4257(19)	8099(15)	5998(9)	14(6)
C3B	3810(20)	8809(15)	6395(10)	15(6)
C4B	4000(20)	9456(15)	5945(9)	15(6)
C5B	4566(18)	9134(13)	5316(9)	8(6)
C6B	3840(20)	7975(14)	4661(9)	12(6)
C7B	2940(20)	7681(14)	5043(10)	15(6)
C8B	1878(19)	8230(14)	4928(9)	8(6)
C9B	2090(20)	8853(15)	4479(10)	16(6)
C10B	3310(20)	8739(17)	4312(11)	29(7)
C11B	5030(20)	7702(15)	4762(10)	13(6)
C12B	5600(20)	6770(14)	4924(9)	12(6)
C13B	6290(20)	6508(15)	5358(10)	18(6)
C14B	6900(20)	5672(15)	5454(10)	22(7)
C15B	6800(20)	5054(16)	5138(10)	21(6)
C16B	6117(19)	5284(14)	4715(9)	12(6)
C17B	5517(19)	6134(14)	4612(9)	12(6)

C18B	5830(20)	7864(15)	4138(10)	21(7)
C19B	5910(20)	7663(14)	3535(9)	13(6)
C20B	6640(20)	7745(16)	2967(11)	25(7)
C21B	7470(20)	8099(15)	3028(11)	23(7)
C22B	7430(20)	8281(15)	3619(10)	20(6)
C23B	6693(18)	8196(13)	4173(9)	5(5)
C24B	3360(20)	8815(17)	7111(11)	32(7)
C25B	2900(40)	9490(30)	7390(18)	103(15)
C26B	3800(30)	9800(20)	7454(14)	54(9)
C27B	4750(40)	9100(30)	7728(18)	107(15)
C28B	4130(30)	8920(20)	8521(14)	66(10)
C29B	3050(30)	8836(19)	8513(14)	49(9)
C30B	3560(40)	7990(20)	8161(17)	101(14)
C31B	4170(30)	8037(19)	7471(12)	47(9)
C32B	5100(40)	8280(30)	7541(18)	99(14)
C33B	2360(40)	9430(30)	8148(17)	105(15)
C34B	2950(20)	6983(16)	5501(10)	25(7)
C35B	1940(20)	6851(17)	5842(12)	36(8)
C36B	930(20)	7423(16)	5685(11)	31(7)
C37B	860(20)	8058(15)	5245(9)	18(6)
C38B	1360(20)	9550(16)	4205(10)	30(7)
C39B	1750(20)	10113(17)	3777(11)	31(7)
C40B	2940(20)	9970(16)	3609(10)	23(7)
C41B	3630(20)	9268(15)	3888(10)	23(7)
C1	860(30)	8430(20)	2283(14)	60(10)
C2	1800(30)	7650(19)	2112(13)	48(9)
C3	2240(30)	7090(20)	2564(13)	53(9)
C4	1790(30)	7260(20)	3240(14)	63(10)
C5	860(30)	7989(19)	3427(14)	48(9)
C6	430(30)	8550(20)	2987(13)	53(9)
C7	4540(30)	7660(20)	1163(13)	50(9)
C8	4400(30)	8180(20)	1678(14)	53(9)
C9	4500(30)	8940(20)	1514(13)	49(9)
C10	4770(30)	9120(20)	874(15)	74(11)
C11	4940(30)	8640(20)	383(15)	66(10)
C12	4830(20)	7834(19)	549(13)	42(8)
C13	6240(20)	5533(19)	2207(13)	44(8)
C14	7020(30)	4760(20)	2014(15)	64(10)
C15	7100(40)	4000(30)	2388(18)	101(14)
C16	6500(30)	4110(20)	2945(14)	55(9)
C17	5610(30)	4790(20)	3245(14)	60(10)
C18	5510(30)	5660(20)	2812(15)	76(11)
C19	1280(20)	2783(15)	4803(11)	23(7)
C20	620(30)	3620(20)	4741(13)	55(9)
C21	800(30)	3910(30)	4011(16)	84(12)
C22	1510(30)	3310(20)	3589(17)	76(11)
C23	2040(30)	2570(30)	3631(18)	89(13)
C24	1930(30)	2370(20)	4255(13)	49(9)

Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$.

Zr1A-Cp1A	2.183
Zr1A-Cp2A	2.248
Zr1A-Pl1A	2.177(13)
Zr1A-Pl2A	2.226(12)
Zr1A-Cl2A	2.416(6)
Zr1A-Cl1A	2.428(7)
Zr1A-C6A	2.43(2)
Zr1A-C5A	2.45(2)
Zr1A-C2A	2.45(3)
Zr1A-C1A	2.46(3)
Zr1A-C7A	2.49(2)
Zr1A-C10A	2.51(3)
Zr1A-C4A	2.55(3)
Zr1A-C3A	2.63(3)
Zr1A-C8A	2.66(3)
Zr1A-C9A	2.71(3)
Zr1B-Cp1B	2.202
Zr1B-Cp2B	2.248
Zr1B-Pl1B	2.196(11)
Zr1B-Pl2B	2.200(19)
Zr1B-Cl1B	2.414(7)
Zr1B-Cl2B	2.427(7)
Zr1B-C6B	2.42(2)
Zr1B-C5B	2.46(2)
Zr1B-C2B	2.46(2)
Zr1B-C1B	2.47(2)
Zr1B-C7B	2.48(2)
Zr1B-C10B	2.49(2)
Zr1B-C4B	2.54(2)
Zr1B-C3B	2.61(2)
Zr1B-C8B	2.63(2)
Zr1B-C9B	2.63(2)
Cp1A-Zr1A-Cp2A	117.9
Cp1A-Zr1A-Cl1A	109.7
Cp1A-Zr1A-Cl2A	108.9
Cp2A-Zr1A-Cl1A	110.2
Cp2A-Zr1A-Cl2A	110.7
Cl2A-Zr1A-Cl1A	97.5(2)
Pl1A-Pl2A	74(1)
C6A-C11A-C1A	99.1(18
Cp1B-Zr1B-Cp2B	117.8
Cp1B-Zr1B-Cl1B	109.0
Cp1B-Zr1B-Cl2B	110.0
Cp2B-Zr1B-Cl1B	111.6
Cp2B-Zr1B-Cl2B	110.5
Cl1B-Zr1B-Cl2B	95.6(2)

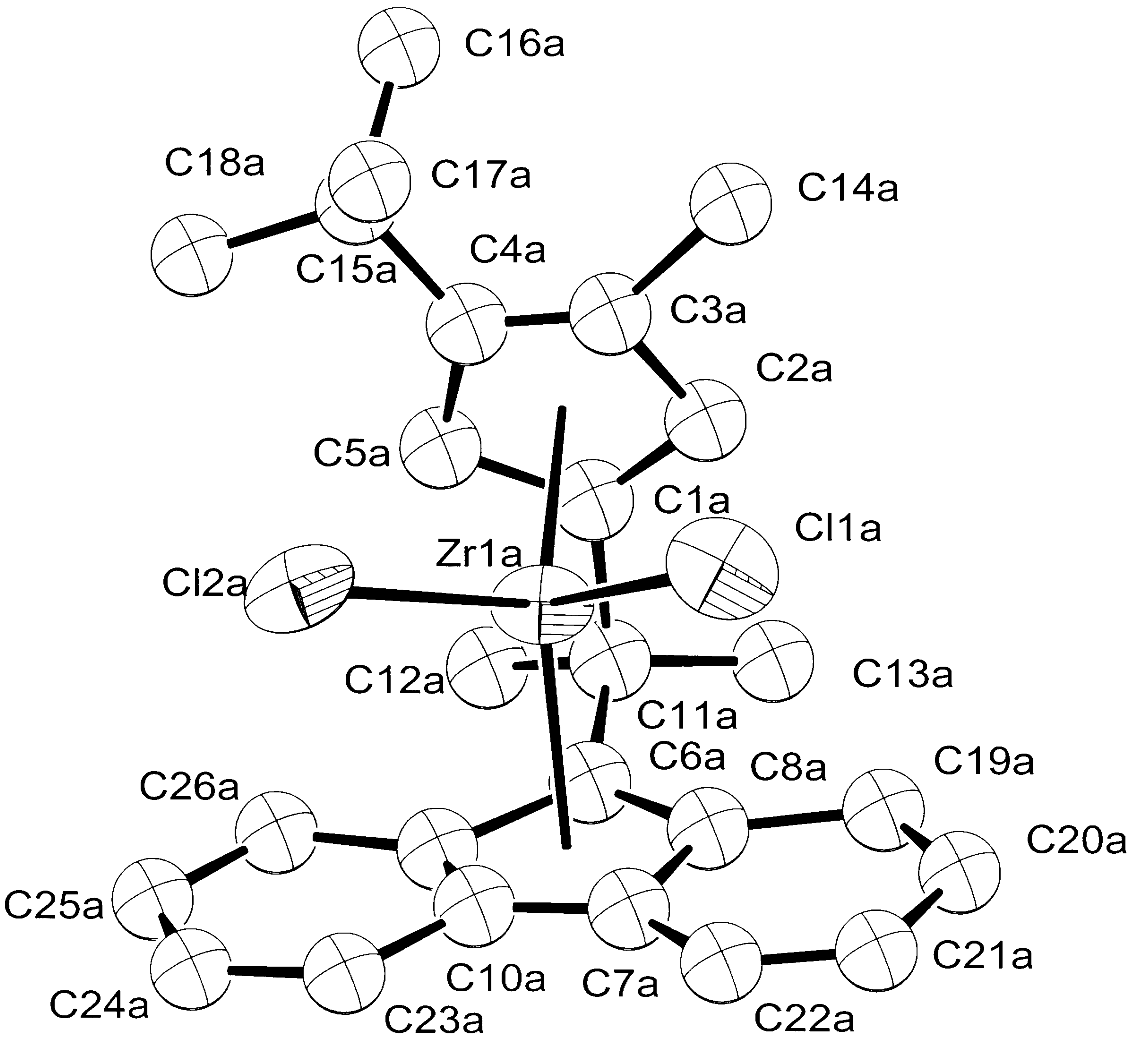
Pl1B-Pl2B	73(1)
C1B-C11B-C6B	100.3(17)

Cp1A is the centroid formed by C1A, C2A, C3A, C4A, C5A
Cp2A is the centroid formed by C6A, C7A, C8A, C9A, C10A
Pl1A is the plane formed by C1A, C2A, C3A, C4A, C5A
Pl2A is the plane formed by C6A, C7A, C8A, C9A, C10A
Cp1B is the centroid formed by C1B, C2B, C3B, C4B, C5B
Cp2B is the centroid formed by C6B, C7B, C8B, C9B, C10B
Pl1B is the plane formed by C1B, C2B, C3B, C4B, C5B
Pl2B is the plane formed by C6B, C7B, C8B, C9B, C10B

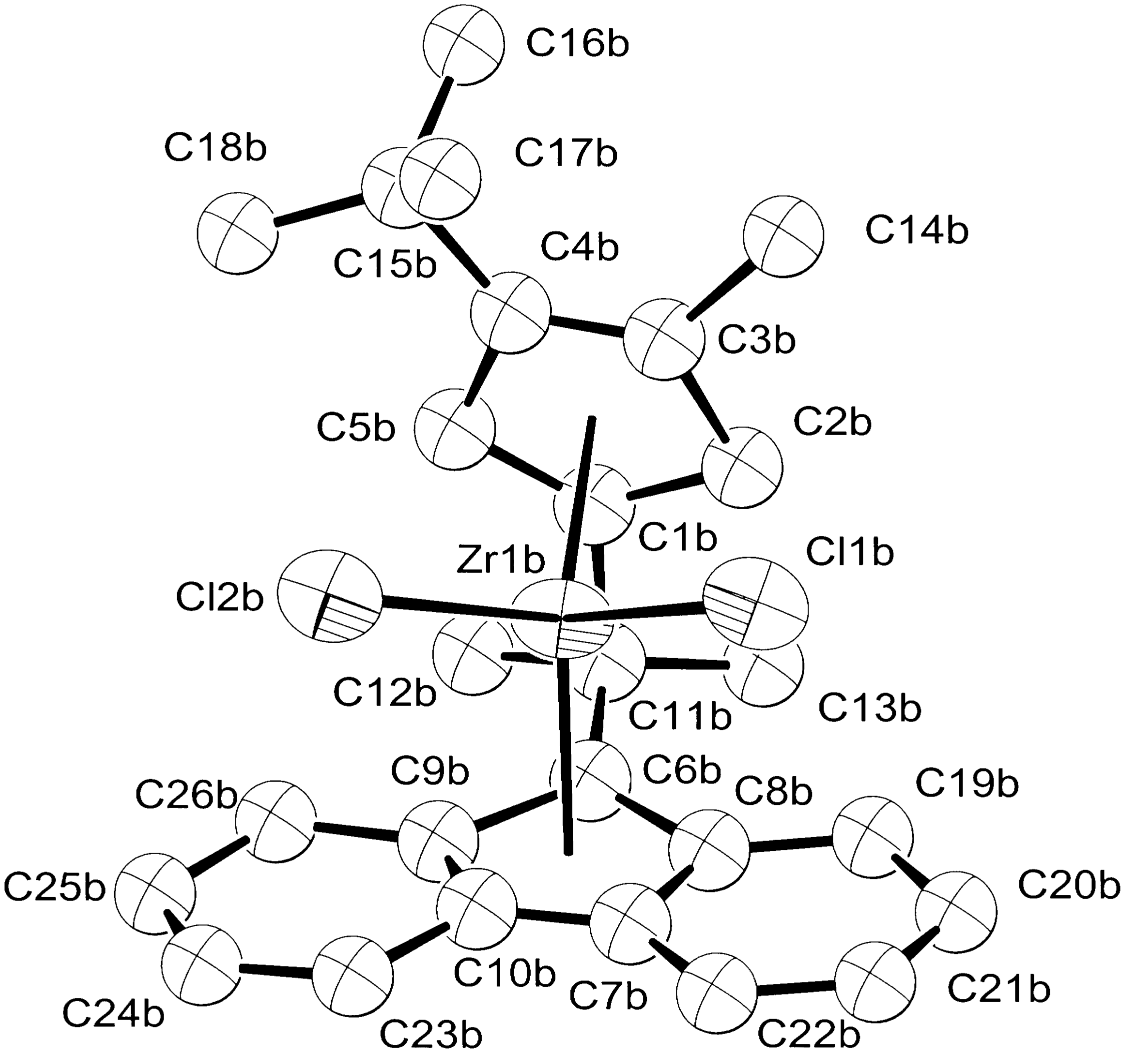
Appendix F

X-ray Crystal Structure Data for $Me_2C(C_{13}H_8)(3\text{-}t\text{-butyl-4-methyl-}C_5H_2)ZrCl_2$

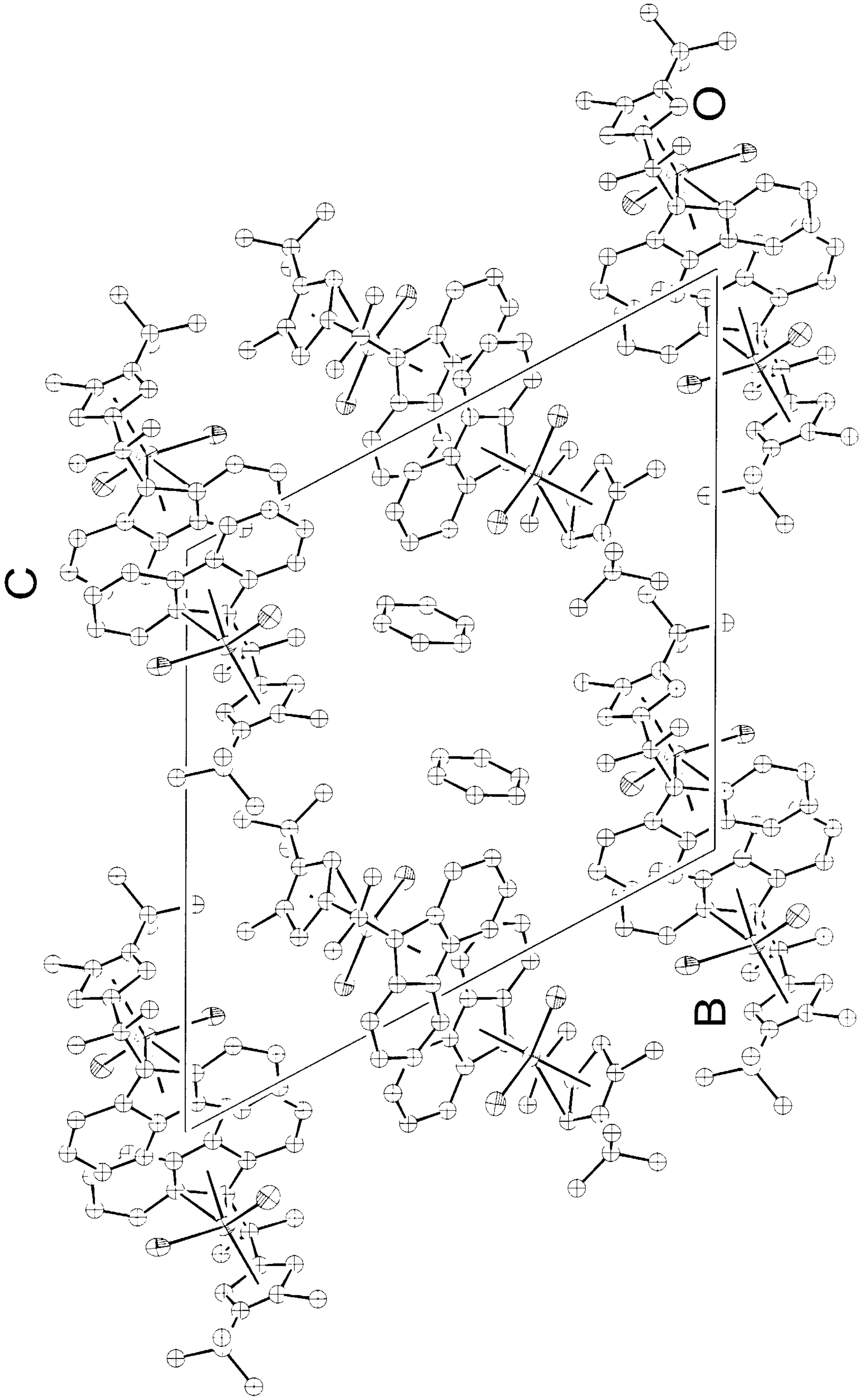
Cambridge Database (CCDC) 137698



Labeled view of molecule A with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Depiction of unit cell with idealized benzene present (40% of the time)

Table 1. Crystal data and structure refinement for $Me_2C(C_{13}H_8)$(3-*t*-butyl-4-methyl-C_5H_2)$ZrCl_2$.

Empirical formula	$C_{27.22}H_{29.22}Cl_2Zr$ ($C_{26}H_{28}Cl_2Zr \cdot 0.204\ C_6H_6$)	
Formula weight	518.57 (502.63 · 15.94)	
Crystallization solvent	benzene / n-heptane	
Crystal habit	plate	
Crystal size	0.11 x 0.04 x 0.01 mm^3	
Crystal color	dichroic red - pale red	
Data Collection		
Preliminary photos	Rotation	
Type of diffractometer	Bruker SMART 1000 ccd	
Data collection program	SMART v5.054	
Wavelength	0.71073 Å MoKα	
Data collection temperature	98 K	
Theta range for 272 reflections used in lattice determination	2.3 to 14.3°	
Unit cell dimensions	a = 9.286(3) Å	α= 61.037(14)°
	b = 17.711(6) Å	β= 81.471(14)°
	c = 17.903(6) Å	γ = 78.713(15)°
Volume	2521.2(13) $Å^3$	
Z	4	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Density (calculated)	1.366 Mg/m^3	
F(000)	1066	
Theta range for data collection	2.24 to 28.74°	
Completeness to theta = 28.74°	88.9 %	
Index ranges	-12<=h<=12, -23<=k<=23, -24<=l<=24	
Data collection scan type	Ω–scans at 6 fixed ϕ–values	
Reflections collected	37091	
Data reduction program	Saint v6.02	
Independent reflections	11631 [R_{int}= 0.8639; GOF_{merge}= 0.744]	
Absorption coefficient	0.660 mm^{-1}	
Absorption correction	None	
Number of standards	initial 75 frames recollected at end	
Variation of standards	within counting statistics	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference map	
Hydrogen placement	Geometric	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	11631 / 0 / 284	
Treatment of hydrogen atoms	no refinement, U_{iso}'s fixed at 120% that of attached atom	
Goodness-of-fit on F^2	0.744	
Final R indices [$I>2\sigma(I)$]	R1 = 0.1142, wR2 = 0.1959	
R indices (all data)	R1 = 0.6696, wR2 = 0.3262	
Type of weighting scheme used	Calculated	
Weighting scheme used	$w=1/\sigma^2(F_o^2)$	
Max shift/error	0.021	

Average shift/error	0.000
Largest diff. peak and hole	0.829 and -0.644 e·Å^{-3}

Special Details

The crystal used was very small and did not diffract well, especially at high θ values. The first three runs of data were collected with 60 second long, –0.3° wide ω–scans at three values of φ (0, 120 and 240°) with the detector 5 cm (nominal) distant at a θ of -28°. A second set of three runs were collected with the detector at 0° θ and φ values of 60, 180 and 300°; other parameters were not changed. The initial cell for data reduction was based on 171 reflections found in the data frames. The paucity of high angle data made it difficult to refine some of the machine parameters. [Cell volumes obtained from preliminary refinements varied by more than 10%.] Therefore values for the X-center, Y-center and distance correction (based on values from cell refinements on more suitable crystals) were held fixed; likewise, the pitch, roll and yaw were not refined.

The cell thus obtained was used for data integration with SAINT v6.02. [For data processing, all SAINT defaults were used, except: box size optimization was enabled, periodic orientation matrix updating was disabled, no Laue class integration restraints were used, the model profiles from all nine areas were blended, and for the post-integration global least squares refinement, no constraints were applied.] The globally-determined cell seemed to be fairly stable with no constraints. However, this cell was used as the initial, fixed cell for another round of data integration. Several more cycles were performed. The final cell appeared converged and produced reasonable correction factors, compared to other samples.

The final dataset is extremely weak, with a mean I/σ of 0.75. SAINT uses profiles based on stronger reflections to model weak reflections and thus improve the accuracy of the intensities for these reflections. However, even this latest version of SAINT does not calculate the σ's for these weak reflections properly. The systematic error in weighting leads to ridiculous GOF's (theoretical minimum value of 1) for both data merging (0.744) and subsequent refinement (0.744).

Nonetheless, the structure does seem satisfactory. There are two molecules in the asymmetric unit. The Zr and Cl atoms were refined anisotropically (although some ellipsoids are quite flattened) and all carbon atoms in the molecules were refined isotropically. No restraints or constraints were used for these two molecules. The variation in isotropic displacement parameters is consistent with the structure of the molecules. The t-butyl group on molecule A shows evidence of some rotational disorder. All the displacement parameters are a little larger than is typical for low-temperature structures. This could be due to processing of the weak data and/or crystal problems caused by solvent disorder.

There is a cavity in the center of the cell which appears to be a repository for disordered solvent. Nothing was obvious in difference maps. A benzene molecule was fitted to 6 of the 9 largest difference peaks in this area. Two of the other three peaks were near the center of symmetry. During the early stages of refinement, this solvent was constrained to be a rigid group. At the end, the coordinates of the six carbon atoms were refined independently but all carbon atoms were shared one isotropic displacement parameter and one population parameter, which refined to 0.408(15). The final geometry of the benzene is poor. There is room for more solvent in this region as well. There is another program which tries to compensate for such regions of disordered solvent, but given the quality of the data it seemed best not to do anything which might appear to make the results look better than they are. The ORTEPIII view of the unit cell contents along the *a*-axis clearly shows the solvent channel.

Four reflections were omitted from the final dataset; the beamstop apparently interfered with three low angle reflections (011, 010 and 001) and the fourth (012) was an outlier. Omitting data past a θ cutoff did not improve the refinement. Refinement of F^2 is against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

The table of calculated and observed structure factors was produced with a program which lists values for negative F's instead of 0's; this program calculates slightly different values for $\sigma(F_o)$, which doesn't matter since refinement of course uses F_o^2 and $\sigma(F_o^2)$.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Me_2C(C_{13}H_8)$(3-*t*-butyl-4-methyl-C_5H_2)$ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr1A	3315(2)	8006(2)	751(2)	48(1)
Cl1A	5052(6)	8106(4)	1568(4)	64(2)
Cl2A	4900(6)	8261(4)	-520(4)	60(2)
C1A	1530(30)	7004(17)	1399(18)	73(9)
C2A	2520(30)	6708(16)	2075(17)	79(9)
C3A	3860(30)	6344(17)	1764(19)	74(10)
C4A	3760(20)	6401(13)	1053(15)	28(7)
C5A	2270(30)	6860(16)	715(17)	73(9)
C6A	700(20)	8569(15)	758(15)	47(8)
C7A	1350(20)	8949(14)	1165(15)	32(7)
C8A	2160(20)	9607(13)	513(14)	19(6)
C9A	2150(20)	9606(13)	-240(15)	23(6)
C10A	1230(20)	9058(13)	-169(14)	29(7)
C11A	90(20)	7695(15)	1209(14)	41(7)
C12A	-880(20)	7578(14)	675(14)	60(8)
C13A	-740(20)	7513(14)	2063(13)	56(8)
C14A	4950(30)	5880(18)	2507(18)	121(12)
C15A	4870(30)	5930(15)	693(15)	46(8)
C16A	4830(30)	4982(19)	1264(18)	128(13)
C17A	6500(40)	6100(20)	700(20)	199(18)
C18A	4470(40)	6140(20)	-167(19)	151(14)
C19A	1330(20)	8809(15)	2044(16)	50(8)
C20A	1970(20)	9288(15)	2214(15)	48(8)
C21A	2810(20)	9939(15)	1559(15)	49(8)
C22A	2890(20)	10061(13)	773(14)	27(6)
C23A	2740(20)	10136(14)	-1060(14)	38(7)
C24A	2480(20)	10090(13)	-1761(13)	29(7)
C25A	1570(20)	9485(14)	-1687(15)	51(8)
C26A	1020(20)	8956(14)	-885(14)	38(7)
Zr1B	8090(2)	8131(2)	6542(2)	46(1)
Cl1B	9305(6)	8917(4)	7004(4)	54(2)
Cl2B	10224(6)	7634(4)	5869(4)	58(2)
C1B	6140(30)	7310(16)	7343(14)	47(8)
C2B	6520(30)	7680(16)	7860(15)	68(9)
C3B	8070(30)	7060(20)	8180(19)	95(11)

C4B	8350(20)	6525(15)	7836(14)	36(7)
C5B	7180(30)	6669(16)	7231(15)	67(9)
C6B	5620(20)	8582(13)	6061(13)	25(6)
C7B	5970(20)	9376(14)	6010(14)	30(7)
C8B	7110(20)	9713(13)	5358(13)	18(6)
C9B	7510(20)	9185(13)	4984(13)	18(6)
C10B	6590(20)	8552(14)	5300(13)	31(7)
C11B	4800(20)	7886(14)	6745(14)	36(7)
C12B	4220(20)	7313(13)	6488(13)	38(7)
C13B	3590(20)	8217(15)	7224(14)	72(9)
C14B	8870(30)	7090(16)	8893(15)	87(10)
C15B	9590(30)	5743(16)	8054(15)	53(8)
C16B	9190(30)	5141(15)	8944(14)	73(9)
C17B	11030(20)	6059(15)	8074(14)	69(9)
C18B	9720(20)	5431(14)	7407(13)	52(8)
C19B	5460(20)	9797(14)	6530(14)	45(7)
C20B	5990(20)	10516(14)	6335(14)	45(8)
C21B	7120(20)	10824(15)	5683(14)	47(8)
C22B	7700(20)	10450(14)	5186(14)	36(7)
C23B	8490(20)	9304(14)	4252(14)	36(7)
C24B	8630(20)	8755(14)	3916(14)	43(7)
C25B	7760(30)	8081(16)	4226(15)	69(9)
C26B	6800(20)	7974(14)	4949(13)	32(7)
C1	5450(70)	5900(40)	5210(40)	63(12)
C2	3910(70)	7300(40)	3810(40)	63(12)
C3	2930(70)	6850(40)	4500(40)	63(12)
C4	6330(70)	6120(40)	4550(40)	63(12)
C5	5310(60)	6890(40)	3870(40)	63(12)
C6	3800(70)	6370(40)	5020(40)	63(12)

Table 3. Selected bond lengths [Å] and angles [°] for $Me_2C(C_{13}H_8)$(3-*t*-butyl-4-methyl-C_5H_2)$ZrCl_2$.

Zr1A-Cp1A	2.203
Zr1A-Cp2A	2.254
Zr1A···Pln1A	2.190
Zr1A···Pln2A	2.237
Zr1A-Cl2A	2.413(7)
Zr1A-C1A	2.41(3)
Zr1A-Cl1A	2.416(7)
Zr1A-C6A	2.44(2)
Zr1A-C5A	2.45(3)
Zr1A-C7A	2.51(2)
Zr1A-C2A	2.51(2)
Zr1A-C10A	2.55(2)
Zr1A-C4A	2.58(2)
Zr1A-C3A	2.59(3)
Zr1A-C9A	2.62(2)
Zr1A-C8A	2.67(2)

Zr1B-Cp1B	2.191
Zr1B-Cp2B	2.226
Zr1B···Pln1B	2.170
Zr1B···Pln2B	2.213
Zr1B-C1B	2.39(2)
Zr1B-Cl2B	2.407(6)
Zr1B-C6B	2.42(2)
Zr1B-Cl1B	2.428(7)
Zr1B-C2B	2.44(2)
Zr1B-C10B	2.52(2)
Zr1B-C5B	2.53(2)
Zr1B-C7B	2.55(2)
Zr1B-C9B	2.562(19)
Zr1B-C3B	2.61(3)
Zr1B-C8B	2.64(2)
Zr1B-C4B	2.65(2)

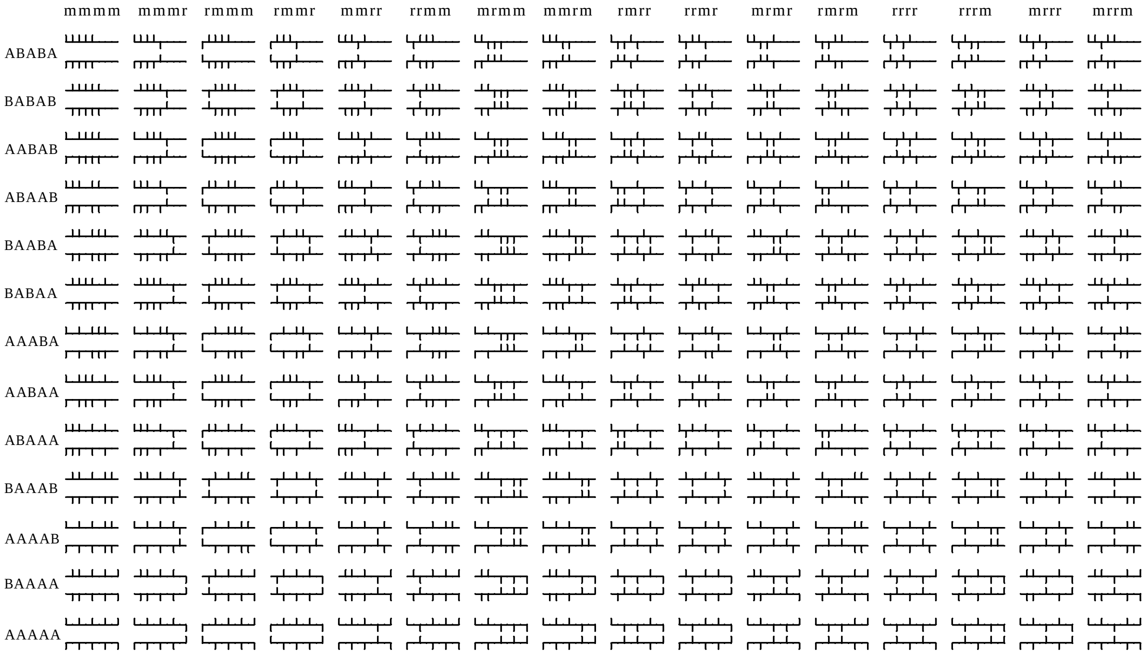
Cp1A-Zr1A-Cp2A	121.0
Cp1A-Zr1A-Cl1A	108.5
Cp1A-Zr1A-Cl2A	110.7
Cp2A-Zr1A-Cl1A	109.9
Cp2A-Zr1A-Cl2A	107.6
Pln1A-Pln2A	107.9
Cl2A-Zr1A-C1A	127.1(7)
Cl2A-Zr1A-Cl1A	97.7(2)
C1A-Zr1A-Cl1A	122.7(7)
C6A-C11A-C1A	103.0(19)

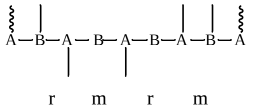
Cp1B-Zr1B-Cp2B	119.6
Cp1B-Zr1B-Cl1B	107.8
Cp1B-Zr1B-Cl2B	111.7
Cp2B-Zr1B-Cl1B	109.0
Cp2B-Zr1B-Cl2B	108.9
Pln1B-Pln2B	106.2
C1B-Zr1B-Cl2B	125.1(6)
C1B-Zr1B-Cl1B	124.7(6)
Cl2B-Zr1B-Cl1B	97.5(2)
C6B-C11B-C1B	98.1(17)

Appendix G

Representation of 416 Possible Pentads in the Unidirectional Site Epimerization Model

A pentad created by the unidirectional site epimerization model will employ one of 13 possible site sequences. It will result in one of the 16 possible pentads and can begin with the first insertion occurring in one of 2 orientations. The total of 416 (= 13 x 16 x 2) pentads are depicted schematically below.





rmrm made via BAAAB

Appendix H

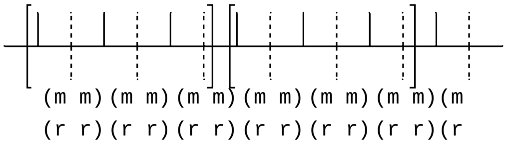
Predicted Effects of Stereoerrors on Dyad and Pentad Quotients for Hemiisotactic Polypropylene

Stereoerrors in the formation of hemiisotactic polypropylene can arise via three possible scenarios. The first is an enantiofacial misinsertion at the more stereoselective site. The second is a site epimerization process (site epimerization mistake I) in which the growing polymer chain migrates away from the cyclopentadienyl R substituent in a unimolecular process prior to bimolecular monomer insertion. This event will skip the insertion at the variably stereoselective site. The third is a site epimerization process (site epimerization mistake II) in which the growing polymer chain migrates toward the cyclopentadienyl R substituent prior to monomer insertion. This event will skip the insertion at the highly stereoselective site.

$\alpha = 0.612$

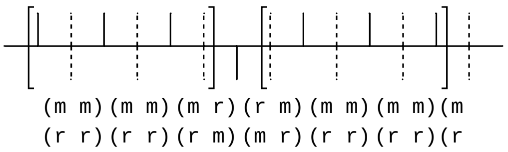
$\beta = 0.388$

$$\frac{[m]}{[r]} \qquad \frac{[mmmm]}{[rrrr]}$$



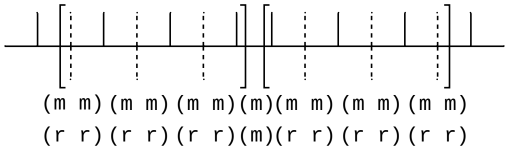
$$\frac{10\alpha + \alpha}{10\beta + \beta} = 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 2\alpha^2 + 2\alpha^3}{2\beta^2 + 2\beta^3 + 2\beta^2 + 2\beta^3} = 2.89$$

perfect hemiisotactic PP



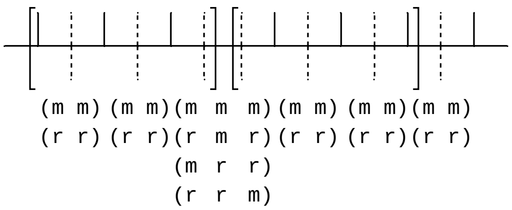
$$\frac{10\alpha + 2\beta}{10\beta + 2\alpha} < 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 0}{2\beta^2 + 2\beta^3 + 0} = 2.89$$

misinsertion mistake



$$\frac{10\alpha + 1}{10\beta + 0} > 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 4\alpha^2}{2\beta^2 + 2\beta^3 + 0} > 2.89$$

site epimerization mistake I



$$\frac{10\alpha + \alpha^2 + \beta^2}{10\beta + 2\alpha\beta} < 1.58 \qquad \frac{2\alpha^2 + 2\alpha^3 + 4\alpha^3}{2\beta^2 + 2\beta^3 + 2\alpha\beta^2} > 2.89$$

site epimerization mistake II

These three scenarios will lead to the stereoerrors, [m]/[r] dyad quotients, and [mmmm]/[rrrr] pentad quotients shown.

For perfect hemiisotactic polypropylene the bulk polymer contribution to stereochemistry is represented by the twelve stereocenters held in two sets of brackets. For each set of brackets, [m] is given by 5α and [r] is given by 5β. [mmmm] is given by the sum of α^2—the case where a pentad spans two (mm) triads—and α^3, the case where a pentad spans three (mm) triads. Similarly, [rrrr] is given by the sum of β^2 and β^3. The boundary between the brackets affects one dyad and four pentads. For the boundary region, [m] is given by α and [r] is given by β; and, [mmmm] is given by $2\alpha^2 + 2\alpha^3$, and [rrrr] is given by $2\beta^2 + 2\beta^3$. For the two bracketed regions and the boundary region, the values for the dyads and pentads will give the quotients shown.

In the event of isolated stereoerrors, the bracketed regions will contribute identically ([m] = 10α; [r] = 10β; [mmmm] = $2\alpha^2 + 2\alpha^3$; and [rrrr] = $2\beta^2 + 2\beta^3$); but, the contribution to stereochemistry made by the boundary region will vary depending on the identity of the stereoerror.

For the enantiofacial misinsertion mistake, the boundary between the brackets affects two dyads and five pentads. [m] is given by 2β and [r] is given by 2α. [mmmm] and [rrrr] are each zero, since none of the five boundary pentads can be either mmmm or rrrr.

For site epimerization mistake I, the boundary between the brackets affects one dyad and four pentads. [m] is given by $\alpha + \beta = 1$ and [r] is zero. [mmmm] is given by $4\alpha^2$ since each pentad spans two (mm) triads and the isolated (m) dyad. [rrrr] is zero since each possible pentad contains the isolated (m) dyad.

For site epimerization mistake II, the boundary between the brackets affects one dyad and four pentads. [m] is given by $\alpha^2 + \beta^2$ since an m dyad will result for either α^2 or β^2. [r] is given by $2\alpha\beta$ since an r dyad will result for either $\alpha\beta$ or $\beta\alpha$. [mmmm] is given by $4\alpha^3$ since each pentad spans three stereocenters of variable stereochemistry. [rrrr] is given by $2\alpha\beta^2$ since only two of the possible pentads can give rise to rrrr, each with a probability of $\alpha\beta\beta$.

For values of $\alpha = 0.612$ and $\beta = 0.388$, the following numerical values are obtained:

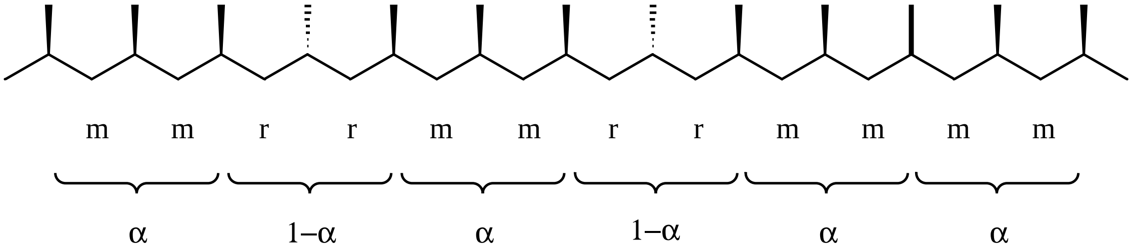
$\frac{[m]}{[r]}$	$\alpha = 0.612$ $\beta = 0.388$	$\frac{[mmmm]}{[rrrr]}$
$\frac{10\alpha + \alpha}{10\beta + \beta} = 1.577$	perfect hemiisotactic PP	$\frac{2\alpha^2 + 2\alpha^3 + 2\alpha^2 + 2\alpha^3}{2\beta^2 + 2\beta^3 + 2\beta^2 + 2\beta^3} = 2.889$
$\frac{10\alpha + 2\beta}{10\beta + 2\alpha} = 1.351$	misinsertion mistake	$\frac{2\alpha^2 + 2\alpha^3 + 0}{2\beta^2 + 2\beta^3 + 0} = 2.889$
$\frac{10\alpha + 1}{10\beta + 0} = 1.835$	site epimerization mistake I	$\frac{2\alpha^2 + 2\alpha^3 + 4\alpha^2}{2\beta^2 + 2\beta^3 + 0} = 6.474$
$\frac{10\alpha + \alpha^2 + \beta^2}{10\beta + 2\alpha\beta} = 1.526$	site epimerization mistake II	$\frac{2\alpha^2 + 2\alpha^3 + 4\alpha^3}{2\beta^2 + 2\beta^3 + 2\alpha\beta^2} = 3.528$

Appendix I

Derivation of the Isotactic Block Length Distribution for Isotactic-hemiisotactic Polypropylene

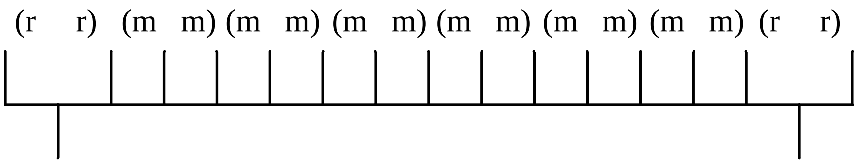
Derivation for $\gamma = 0$

For a hemiisotactic regime, every other stereocenter is of the same stereochemistry and the intervening stereocenters are of variable stereochemistry. Therefore, as in the hemiisotactic polymer shown below, a given polymer can be represented by a string of mm and rr triads. This disallows the pentads containing isolated m and r dyads: mmrm, rrmr and mrmr. For a given triad, if the probability of obtaining an mm triad is defined as α, then the probability of obtaining an rr triad is $1-\alpha$.



An isotactic block is defined as a collection of m dyads terminated on either end by an r dyad. Since only (mm) and (rr) triads are allowed for hemiisotactic polypropylene, an isotactic block must be a collection of (mm) triads terminated on either end by (rr) triads: $(rr)(mm)^{(s)}(rr)$, where s is the number of repeating (mm) triads. The probability of such a sequence will be the product of the individual probabilities.

For example, the isotactic block drawn below containing 13 monomer units is described by $(rr)(mm)^{(6)}(rr)$ and the probability of forming it will be $P_{13} = (1-\alpha)(\alpha)^{(s)}(1-\alpha)$, where s = 6. Since the variables s and n are related as $s = ((n-1)/2)$, we can generalize for the probability of obtaining an isotactic block containing n repeating monomer units: $P_n = (1-\alpha)(\alpha)^{((n-1)/2)}(1-\alpha)$, for n = odd.



For a given polymer chain, the number of blocks of length n present will be given by $N_n = P_n (P_d)$, where P_d is the degree of polymerization—the number of monomers in that chain given by the number average molecular weight/monomer molecular weight = $M_n/42$ for polypropylene.[1] In the table below, the calculated values for N_n is given as a function of M_n and α. For example, a polymer chain of M_n = 100,000 and α = 0.50 is expected to have 4.65 isotactic blocks containing 15 monomer units. This is a statistical average and the actual number of isotactic blocks containing 15 monomer units will be an integral value near 4.65.

Similarly, this polymer chain is expected to have 0.0045 isotactic blocks containing 35 monomer units. While most chains will not contain an isotactic block of this length, statistically, one out of every 222 (= 1/0.0045) chains will.

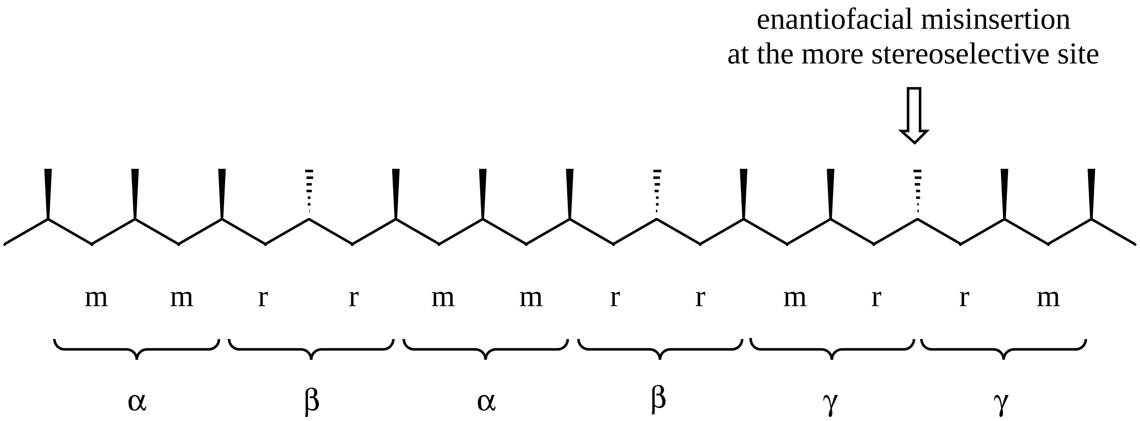
Although the probability of finding an isotactic block of exactly 21 monomer units in a given chain is less than unity, the probability of finding one greater than or equal to 21 monomer units is 1.16, the sum of the N_n values for n = 21 through n = 99. (An exhaustive calculation would compute up to n = P_d.) This suggests that there will be, statistically, at least one isotactic block having 21 or more monomer units in a chain for which M_n = 100,000 and α = 0.50.

M_n =	100,000	200,000	100,000	200,000	100,000	200,000
α =	0.50	0.50	0.62	0.62	0.75	0.75
n	N_n	N_n	N_n	N_n	N_n	N_n
1	595.2381	1190.4762	343.8095	687.6190	148.8095	297.6190
3	297.6190	595.2381	213.1619	426.3238	111.6071	223.2143
5	148.8095	297.6190	132.1604	264.3208	83.7054	167.4107
7	74.4048	148.8095	81.9394	163.8789	62.7790	125.5580
9	37.2024	74.4048	50.8025	101.6049	47.0843	94.1685
11	18.6012	37.2024	31.4975	62.9950	35.3132	70.6264
13	9.3006	18.6012	19.5285	39.0569	26.4849	52.9698
15	4.6503	9.3006	12.1076	24.2153	19.8637	39.7273
17	2.3251	4.6503	7.5067	15.0135	14.8978	29.7955
19	1.1626	2.3251	4.6542	9.3084	11.1733	22.3466
21	0.5813	1.1626	2.8856	5.7712	8.3800	16.7600
23	0.2906	0.5813	1.7891	3.5781	6.2850	12.5700
25	0.1453	0.2906	1.1092	2.2184	4.7137	9.4275
27	0.0727	0.1453	0.6877	1.3754	3.5353	7.0706
29	0.0363	0.0727	0.4264	0.8528	2.6515	5.3030
31	0.0182	0.0363	0.2644	0.5287	1.9886	3.9772
33	0.0091	0.0182	0.1639	0.3278	1.4915	2.9829
35	0.0045	0.0091	0.1016	0.2032	1.1186	2.2372
37	0.0023	0.0045	0.0630	0.1260	0.8389	1.6779
39	0.0011	0.0023	0.0391	0.0781	0.6292	1.2584
41	0.0006	0.0011	0.0242	0.0484	0.4719	0.9438
43	0.0003	0.0006	0.0150	0.0300	0.3539	0.7079
45	0.0001	0.0003	0.0093	0.0186	0.2654	0.5309
47	0.0001	0.0001	0.0058	0.0115	0.1991	0.3982
49	0.0000	0.0001	0.0036	0.0072	0.1493	0.2986
51	0.0000	0.0000	0.0022	0.0044	0.1120	0.2240
53	0.0000	0.0000	0.0014	0.0028	0.0840	0.1680
55	0.0000	0.0000	0.0009	0.0017	0.0630	0.1260
57	0.0000	0.0000	0.0005	0.0011	0.0472	0.0945
59	0.0000	0.0000	0.0003	0.0007	0.0354	0.0709
61	0.0000	0.0000	0.0002	0.0004	0.0266	0.0531
63	0.0000	0.0000	0.0001	0.0003	0.0199	0.0399
65	0.0000	0.0000	0.0001	0.0002	0.0149	0.0299
67	0.0000	0.0000	0.0000	0.0001	0.0112	0.0224
69	0.0000	0.0000	0.0000	0.0001	0.0084	0.0168
71	0.0000	0.0000	0.0000	0.0000	0.0063	0.0126
73	0.0000	0.0000	0.0000	0.0000	0.0047	0.0095
75	0.0000	0.0000	0.0000	0.0000	0.0035	0.0071
77	0.0000	0.0000	0.0000	0.0000	0.0027	0.0053
79	0.0000	0.0000	0.0000	0.0000	0.0020	0.0040
81	0.0000	0.0000	0.0000	0.0000	0.0015	0.0030
83	0.0000	0.0000	0.0000	0.0000	0.0011	0.0022
85	0.0000	0.0000	0.0000	0.0000	0.0008	0.0017
87	0.0000	0.0000	0.0000	0.0000	0.0006	0.0013
89	0.0000	0.0000	0.0000	0.0000	0.0005	0.0009
91	0.0000	0.0000	0.0000	0.0000	0.0004	0.0007
93	0.0000	0.0000	0.0000	0.0000	0.0003	0.0005
95	0.0000	0.0000	0.0000	0.0000	0.0002	0.0004
97	0.0000	0.0000	0.0000	0.0000	0.0001	0.0003
99	0.0000	0.0000	0.0000	0.0000	0.0001	0.0002
Sum N_n for $n \geq 21$	1.16	2.33	7.59	15.19	33.52	67.04

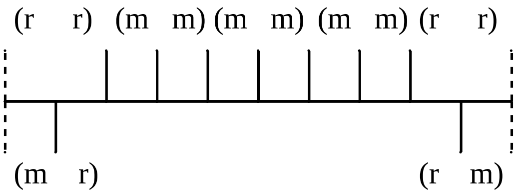
$$N_n = [(1-\alpha)(\alpha)^{((n-1)/2)}(1-\alpha)] \cdot [M_n / 42]$$

Derivation for $\gamma > 0$

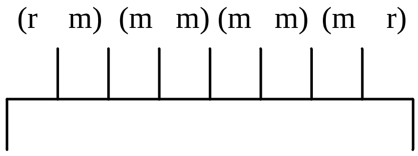
The above derivation was performed for the triad model with $\gamma = 0$. However, to the extent that the enantioselectivity at the more stereoselective site is not perfect, γ will be greater than zero. As shown below, such an enantiofacial misinsertion will give rise to two γ triads, each of which is (mr) or (rm). For a given triad, the probability of obtaining an (mm) triad is defined as α, the probability of obtaining an (rr) triad is β, the probability of obtaining an (mr) triad is γ, and the probability of obtaining an (rm) triad is also γ (hence, $\alpha + \beta + \gamma + \gamma = 1$).



An isotactic block is defined as a collection of m dyads terminated on either end by r dyads. For the scenario with $\gamma > 0$, all four triads will be possible: (mm), (rr), (mr), and (rm). An isotactic block of odd length can be formed in one of two ways—(mr or rr)$(mm)^{(s)}$(rr or rm) *or* (rm)$(mm)^{(s-1)}$(mr)—as depicted by the examples below:



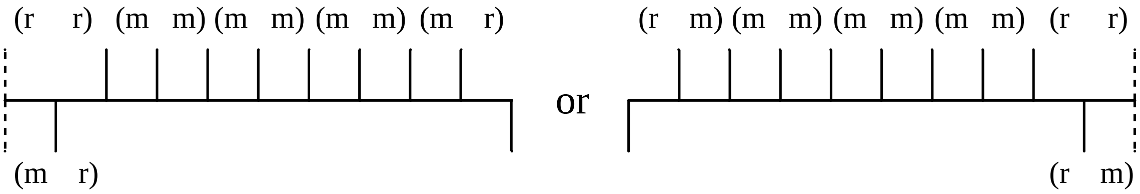
or



$P_{n(odd)}$ will then equal the sum of the probabilities $P(mr\ or\ rr)(mm)^{(s)}(rr\ or\ rm) + P(rm)(mm)^{(s-1)}(mr)$. Since $s = (n-1)/2$, the expression for $P_{n(odd)}$ is:

$$P_{n(odd)} = (\gamma + \beta)(\alpha)^{((n-1)/2)}(\beta + \gamma) + (\gamma)(\alpha)^{((n-3)/2)}(\gamma)$$

An isotactic block of even length can be formed in two ways—$(mr\ or\ rr)(mm)^{(s)}(mr)$ or $(rm)(mm)^{(s)}(rr\ or\ rm)$—as depicted by the examples below:



$P_{n(even)}$ will then equal twice the probability $P(mr\ or\ rr)(mm)^{(s)}(mr)$. Since $s = (n-2)/2$, the expression for $P_{n(even)}$ is:

$$P_{n(even)} = 2(\gamma + \beta)(\alpha)^{((n-2)/2)}(\gamma)$$

For a given polypropylene chain with number average molecular weight M_n, the number of isotactic blocks of length n is given by N_n as follows:

$$N_{n(odd)} = [(\gamma + \beta)(\alpha)^{((n-1)/2)}(\beta + \gamma) + (\gamma)(\alpha)^{((n-3)/2)}(\gamma)] \cdot [M_n / 42]$$

and

$$N_{n(even)} = [2(\gamma + \beta)(\alpha)^{((n-2)/2)}(\gamma)] \cdot [M_n / 42]$$

In the table below, the calculated values for N_n are given as a function of M_n and α; γ has arbitrarily been set to 0.01, which corresponds to an enantioselectivity of 0.99 at the more stereoselective site. Note that $\alpha + \gamma + \gamma = 0.50, 0.62$, and 0.75 so that a direct comparison can be made with the table

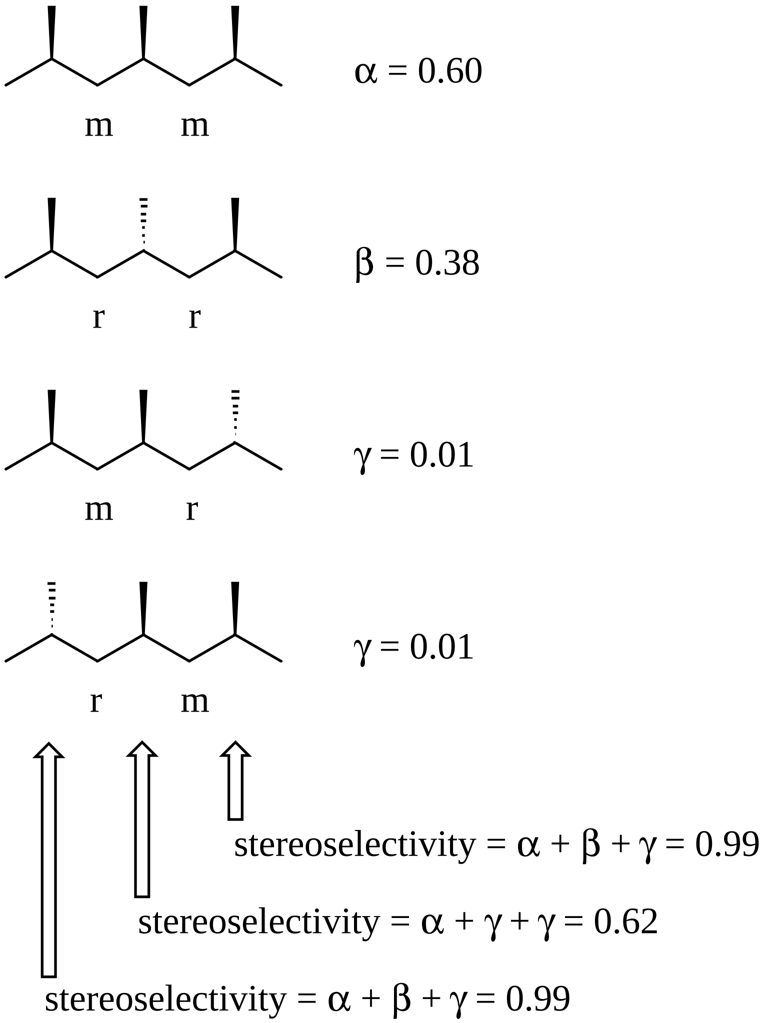
M_n =	100,000	200,000	100,000	200,000	100,000	200,000
α =	0.48	0.48	0.60	0.60	0.73	0.73
β =	0.50	0.50	0.38	0.38	0.25	0.25
$\alpha+\gamma+\gamma$ =	0.50	0.50	0.62	0.62	0.75	0.75
γ =	0.01	0.01	0.01	0.01	0.01	0.01
n	N_n	N_n	N_n	N_n	N_n	N_n
1	619.7817	1239.5635	362.5397	725.0794	161.2785	322.5571
2	24.2857	48.5714	18.5714	37.1429	12.3810	24.7619
3	297.4952	594.9905	217.5238	435.0476	117.7333	235.4667
4	11.6571	23.3143	11.1429	22.2857	9.0381	18.0762
5	142.7977	285.5954	130.5143	261.0286	85.9453	171.8907
6	5.5954	11.1909	6.6857	13.3714	6.5978	13.1956
7	68.5429	137.0858	78.3086	156.6171	62.7401	125.4802
8	2.6858	5.3716	4.0114	8.0229	4.8164	9.6328
9	32.9006	65.8012	46.9851	93.9703	45.8003	91.6005
10	1.2892	2.5784	2.4069	4.8137	3.5160	7.0319
11	15.7923	31.5846	28.1911	56.3822	33.4342	66.8684
12	0.6188	1.2376	1.4441	2.8882	2.5667	5.1333
13	7.5803	15.1606	16.9147	33.8293	24.4070	48.8139
14	0.2970	0.5941	0.8665	1.7329	1.8737	3.7473
15	3.6385	7.2771	10.1488	20.2976	17.8171	35.6342
16	0.1426	0.2851	0.5199	1.0398	1.3678	2.7355
17	1.7465	3.4930	6.0893	12.1785	13.0065	26.0129
18	0.0684	0.1369	0.3119	0.6239	0.9985	1.9969
19	0.8383	1.6766	3.6536	7.3071	9.4947	18.9894
20	0.0328	0.0657	0.1872	0.3743	0.7289	1.4578
21	0.4024	0.8048	2.1921	4.3843	6.9311	13.8623
22	0.0158	0.0315	0.1123	0.2246	0.5321	1.0642
23	0.1931	0.3863	1.3153	2.6306	5.0597	10.1195
24	0.0076	0.0151	0.0674	0.1348	0.3884	0.7768
25	0.0927	0.1854	0.7892	1.5783	3.6936	7.3872
26	0.0036	0.0073	0.0404	0.0809	0.2835	0.5671
27	0.0445	0.0890	0.4735	0.9470	2.6963	5.3927
28	0.0017	0.0035	0.0243	0.0485	0.2070	0.4140
29	0.0214	0.0427	0.2841	0.5682	1.9683	3.9366
30	0.0008	0.0017	0.0146	0.0291	0.1511	0.3022
31	0.0103	0.0205	0.1705	0.3409	1.4369	2.8738
32	0.0004	0.0008	0.0087	0.0175	0.1103	0.2206
33	0.0049	0.0098	0.1023	0.2046	1.0489	2.0978
34	0.0002	0.0004	0.0052	0.0105	0.0805	0.1610
35	0.0024	0.0047	0.0614	0.1227	0.7657	1.5314
36	0.0001	0.0002	0.0031	0.0063	0.0588	0.1176
37	0.0011	0.0023	0.0368	0.0736	0.5590	1.1179
38	0.0000	0.0001	0.0019	0.0038	0.0429	0.0858
39	0.0005	0.0011	0.0221	0.0442	0.4080	0.8161
40	0.0000	0.0000	0.0011	0.0023	0.0313	0.0626
41	0.0003	0.0005	0.0133	0.0265	0.2979	0.5957
42	0.0000	0.0000	0.0007	0.0014	0.0229	0.0457
43	0.0001	0.0003	0.0080	0.0159	0.2174	0.4349
44	0.0000	0.0000	0.0004	0.0008	0.0167	0.0334
45	0.0001	0.0001	0.0048	0.0095	0.1587	0.3175
46	0.0000	0.0000	0.0002	0.0005	0.0122	0.0244
47	0.0000	0.0001	0.0029	0.0057	0.1159	0.2318
48	0.0000	0.0000	0.0001	0.0003	0.0089	0.0178
49	0.0000	0.0000	0.0017	0.0034	0.0846	0.1692
50	0.0000	0.0000	0.0001	0.0002	0.0065	0.0130
Sum N_n for $n \geq 21$	0.80	1.61	5.76	11.52	27.40	54.79

$N_{n(odd)} = [(\gamma + \beta)(\alpha)^{((n-1)/2)}(\beta + \gamma) + (\gamma)(\alpha)^{((n-3)/2)}(\gamma)] \cdot [M_n / 42]$

and $N_{n(even)} = [2(\gamma + \beta)(\alpha)^{((n-2)/2)}(\gamma)] \cdot [M_n / 42]$

above for which $\gamma = 0$. In other words, the stereoselectivity at the variably stereoselective site is the same for both this and the preceding analysis. However, this analysis includes a highly stereoselective site that is not 100% enantioselective (as above, for $\gamma = 0$), but only 99% enantioselective.

The relationship between the enantioselectivity of the more stereoselective site and parameters α, β, and γ is: enantioselectivity $= \alpha + \beta + \gamma$. The relationship between the enantioselectivity of the variably stereoselective site and the parameters α, β, and γ is: enantioselectivity $= \alpha + \gamma + \gamma$. These relationships are illustrated by the following example:

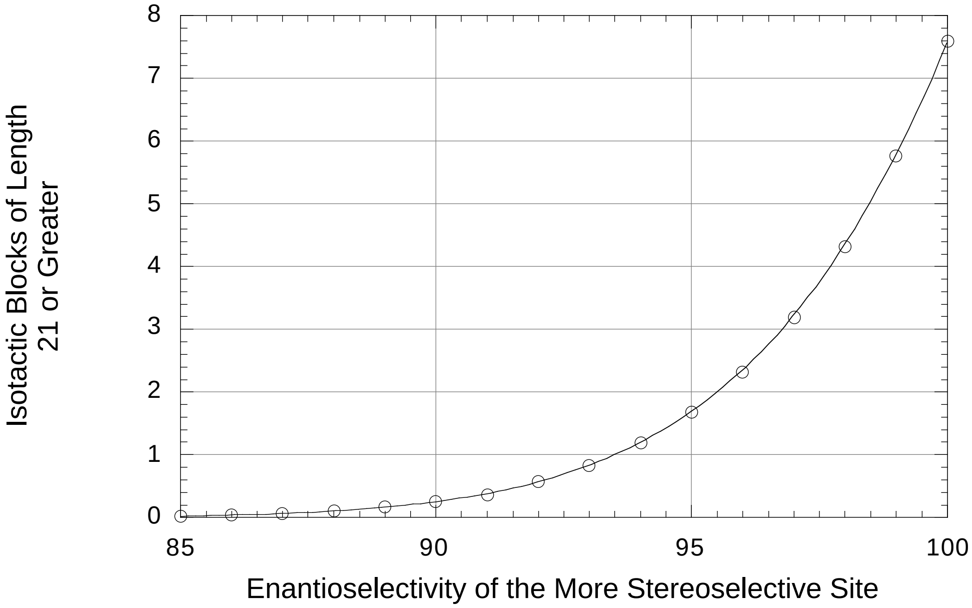


For the analysis with $\gamma = 0.1$, a polymer chain of $M_n = 100{,}000$ and $\alpha = 0.50$ is expected to have 3.64 isotactic blocks containing 15 monomer units. This is a statistical average and the actual number of isotactic blocks containing 15 monomer units will be an integral value near 3.64.

Similarly, this polymer chain is expected to have 0.0024 isotactic blocks containing 35 monomer units. While most chains will not contain an isotactic block of this length, statistically, one out of every 417 (= 1/0.0024) chains will.

Although the probability of finding an isotactic block of exactly 21 monomer units in a given chain is less than unity, the probability of finding one greater than or equal to 21 monomer units is 0.80, the sum of the N_n values for n = 21 through n = 50. (An exhaustive calculation would compute up to $n = P_d$.) This suggests that there will be, statistically, almost one isotactic block having 21 or more monomer units in a chain for which $M_n = 100{,}000$ and $\alpha = 0.50$.

The isotactic block length distribution is quite sensitive to the stereoselectivity of the more stereoselective site. Compare the polymers for which $M_n = 100{,}000$ and $\alpha + \gamma + \gamma = 0.62$. For the catalyst with $\gamma = 0$ (perfectly enantioselective at the more stereoselective site), the number of isotactic blocks of length 21 or greater is, statistically, 7.59 per chain. However, for the catalyst with $\gamma = 0.01$ (99% enantioselective at the more stereoselective site), the number of isotactic blocks of length 21 or greater drops to 5.76. This is a loss of almost 2 blocks per chain for a slight decrease of enantioselectivity from 100% to 99%. The following graph illustrates the precipitous drop of this parameter as the enantioselectivity decreases. By the time the enantioselectivity drops to 90%, only one in 4.0 (= 1/0.25) chains contain an isotactic block of length 21 or greater.



References and Notes

1. For a related treatment calculating the isotactic block length distribution in samples of stereoblock isotactic-atactic polypropylene, see Coates, G. W., Ph.D. Dissertation, Stanford University (1994).

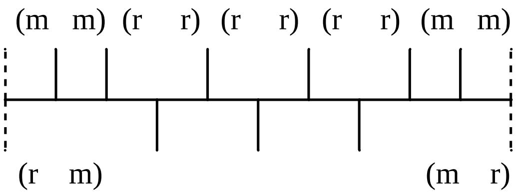
Appendix J

Derivation of the Syndiotactic Block Length Distribution for Syndiotactic-hemiisotactic Polypropylene

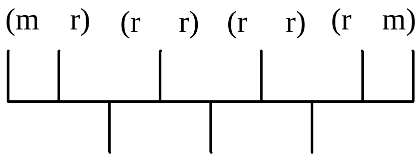
Derivation for $\gamma > 0$

For a given triad, the probability of obtaining an (mm) triad is defined as α, the probability of obtaining an (rr) triad is β, the probability of obtaining an (mr) triad is γ, and the probability of obtaining an (rm) triad is also γ (hence, $\alpha + \beta + \gamma + \gamma = 1$).

A syndiotactic block is defined as a collection of r dyads terminated on either end by m dyads. For the scenario with $\gamma > 0$, all four triads will be possible: (mm), (rr), (mr), and (rm). An syndiotactic block of odd length can be formed in one of two ways—(rm or mm)$(rr)^{(s)}$(mm or rm) *or* (mr)$(rr)^{(s-1)}$(rm)—as depicted by the examples below:



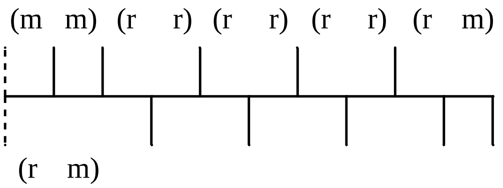
or



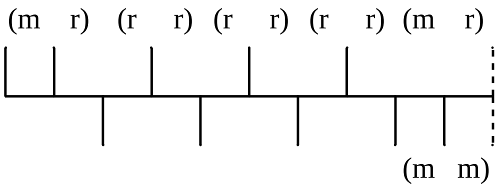
$P_{n(odd)}$ will then equal the sum of the probabilities P(rm or mm)$(rr)^{(s)}$(mm or rm) + P(mr)$(rr)^{(s-1)}$(rm). Since $s = (n-1)/2$, the expression for $P_{n(odd)}$ is:

$$P_{n(odd)} = (\gamma + \alpha)(\beta)^{((n-1)/2)}(\alpha + \gamma) + (\gamma)(\beta)^{((n-3)/2)}(\gamma)$$

A syndiotactic block of even length can be formed in two ways—(rm or mm)$(rr)^{(s)}$(rm) *or* (mr)$(rr)^{(s)}$(mm or mr)—as depicted by the examples below:



or



$P_{n(even)}$ will then equal the twice the probability P(rm or mm)(rr)$^{(s)}$(rm). Since s = (n-2)/2, the expression for $P_{n(even)}$ is:

$$P_{n(even)} = 2(\gamma + \alpha)(\beta)^{((n-2)/2)}(\gamma)$$

For a given polypropylene chain with number average molecular weight M_n, the number of isotactic blocks of length n is given by N_n as follows:

$$N_{n(odd)} = [(\gamma + \alpha)(\beta)^{((n-1)/2)}(\alpha + \gamma) + (\gamma)(\beta)^{((n-3)/2)}(\gamma)] \cdot [M_n / 42]$$

and

$$N_{n(even)} = [2(\gamma + \alpha)(\beta)^{((n-2)/2)}(\gamma)] \cdot [M_n / 42]$$

Note that the results are identical to those obtained for the isotactic block length distribution with the exchange of the parameters α and β.

Appendix K

Complete Statistical Analysis for Polypropylenes from $Me_2C(C_{13}H_8)$(3-*t*-butyl-4-methyl-$C_5H_2)ZrCl_2$/MAO

Table 1. Statistical analysis of a polymer made with **11**/MAO at 0°C in liquid monomer (Entry 42).

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	26.9	24.1	29.1	27.4	26.3
mmmr	13.4	20.6	16.7	14.2	15.2
rmmr	4.8	4.4	2.9	5.0	4.7
mmrr	20.4	8.8	16.7	24.2	22.2
mrmm + rmrr	4.2	24.3	11.7	0.0	3.8
mrmr	0.2	8.8	5.9	0.0	0.7
rrrr	11.7	0.8	2.9	12.0	10.2
rrrm	10.8	3.8	5.9	10.0	10.1
mrrm	7.6	4.4	8.3	7.1	6.7
m	57.5	70.0	65.8	58.8	59.6
r	42.5	30.0	34.2	41.2	40.4
Parameters		$\sigma = 0.701$	$\alpha = 0.781$	$P_{mm} = 0.588$ $P_{rr} = 0.412$	$P_{mm} = 0.570$ $P_{rr} = 0.378$ $P_{mr} = 0.026$ $P_{rm} = 0.026$
RMS error		9.72	4.97	1.97	1.09

Table 2. Statistical analysis of a polymer made with **11**/MAO at 20°C in liquid monomer (Entry 43).

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	30.0	29.1	30.1	31.6	29.8
mmmr	15.1	21.0	16.7	14.6	16.0
rmmr	3.1	3.8	2.8	4.4	4.1
mmrr	19.2	7.6	16.7	23.5	20.6
mrmm + rmrr	5.2	23.8	11.3	0.0	5.2
mrmr	1.2	7.6	5.7	0.0	1.0
rrrr	8.9	0.5	2.8	9.8	7.7
rrrm	8.7	2.8	5.7	8.8	8.9
mrrm	8.6	3.8	8.3	7.3	6.7
m	61.0	73.4	66.4	62.3	63.3
r	39.0	26.6	33.6	37.7	36.7
Parameters		$\sigma = 0.734$	$\alpha = 0.786$	$P_{mm} = 0.624$ $P_{rr} = 0.376$	$P_{mm} = 0.598$ $P_{rr} = 0.331$ $P_{mr} = 0.035$ $P_{rm} = 0.035$
RMS error		8.73	3.53	2.44	0.99

Table 3. Statistical analysis of a polymer made with **11**/MAO at 0°C in 10% monomer in toluene (Entry 44).

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	28.5	27.1	30.0	31.3	27.2
mmmr	16.1	20.9	16.7	14.6	16.0
rmmr	2.9	4.0	2.8	4.5	4.3
mmrr	18.3	8.1	16.7	23.5	20.6
mrmm + rmrr	6.5	24.0	11.4	0.0	6.1
mrmr	2.3	8.1	5.7	0.0	1.2
rrrr	6.9	0.6	2.8	9.9	8.4
rrrm	9.2	3.1	5.7	8.9	9.6
mrrm	9.3	4.0	8.3	7.3	6.6
m	61.1	72.2	66.3	62.1	61.5
r	38.9	27.8	33.7	37.9	38.5
Parameters		$\sigma = 0.722$	$\alpha = 0.786$	$P_{mm} = 0.621$ $P_{rr} = 0.379$	$P_{mm} = 0.573$ $P_{rr} = 0.343$ $P_{mr} = 0.042$ $P_{rm} = 0.042$
RMS error		8.01	2.80	3.33	1.63

Table 4. Statistical analysis of a polymer made with **11**/MAO at 20°C in 10% monomer in toluene (Entry 45).

Pentad (%)	observed	chain end control	enantiomorphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	31.3	30.8	31.9	34.9	31.8
mmmr	17.6	21.1	16.7	14.8	17.5
rmmr	2.2	3.6	2.6	4.0	3.5
mmrr	18.1	7.2	16.7	22.7	17.1
mrmm + rmrr	10.0	23.6	10.6	0.0	9.8
mrmr	2.3	7.2	5.3	0.0	2.0
rrrr	4.4	0.4	2.6	8.2	4.7
rrrm	5.8	2.5	5.3	7.9	7.5
mrrm	8.3	3.6	8.3	7.4	6.1
m	66.4	74.5	67.5	65.1	67.2
r	33.6	25.5	32.5	34.9	32.8
Parameters		$\sigma = 0.745$	$\alpha = 0.796$	$P_{mm} = 0.651$ $P_{rr} = 0.349$	$P_{mm} = 0.603$ $P_{rr} = 0.259$ $P_{mr} = 0.069$ $P_{rm} = 0.069$
RMS error		6.56	1.33	4.37	1.09

Table 5. Statistical analysis of a polymer made with **11**/MAO at 40°C in 10% monomer in toluene (Entry 46).

Pentad (%)	observed	chain end control	enantiomorphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	32.4	32.2	33.1	35.3	32.8
mmmr	16.4	21.1	16.6	14.8	17.0
rmmr	3.2	3.5	2.5	3.9	3.5
mmrr	17.4	6.9	16.6	22.6	17.9
mrmm + rmrr	7.9	23.4	10.1	0.0	8.2
mrmr	2.8	6.9	5.1	0.0	1.6
rrrr	5.6	0.4	2.5	8.1	5.1
rrrm	5.6	2.3	5.1	7.8	7.5
mrrm	8.6	3.5	8.3	7.4	6.3
m	66.1	75.3	68.2	65.4	67.2
r	33.9	24.7	31.8	34.6	32.8
Parameters		$\sigma = 0.753$	$\alpha = 0.802$	$P_{mm} = 0.654$ $P_{rr} = 0.346$	$P_{mm} = 0.615$ $P_{rr} = 0.271$ $P_{mr} = 0.057$ $P_{rm} = 0.057$
RMS error		7.10	1.55	3.68	1.14

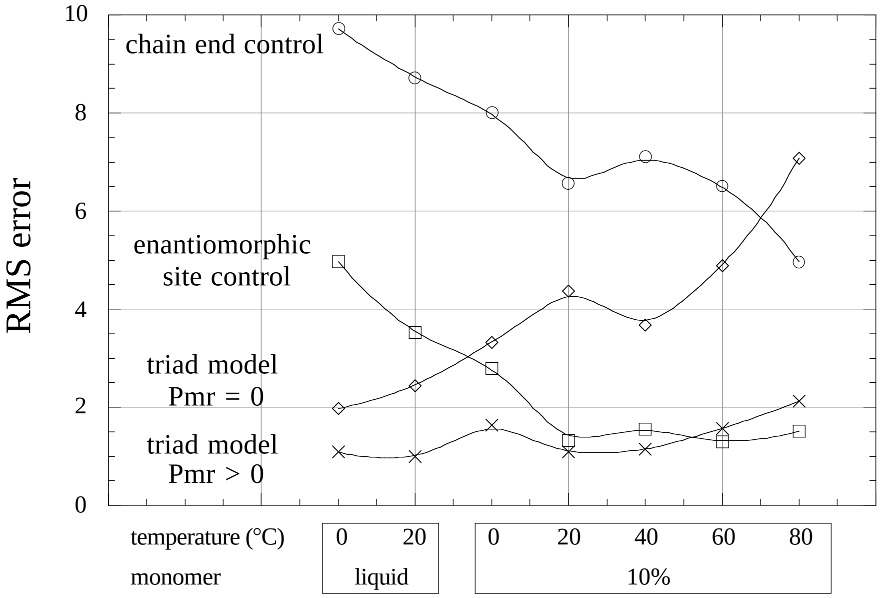
Table 6. Statistical analysis of a polymer made with **11**/MAO at 60°C in 10% monomer in toluene (Entry 47).

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	27.1	25.0	27.8	31.4	27.5
mmmr	15.6	20.7	16.6	14.6	17.4
rmmr	3.3	4.3	3.1	4.4	3.9
mmrr	17.5	8.6	16.6	23.5	17.6
mrmm + rmrr	10.3	24.3	12.3	0.0	10.8
mrmr	4.5	8.6	6.1	0.0	2.4
rrrr	4.9	0.7	3.1	9.8	5.7
rrrm	7.4	3.5	6.1	8.9	8.6
mrrm	9.5	4.3	8.3	7.3	6.1
m	62.1	70.7	65.0	62.2	64.2
r	37.9	29.3	35.0	37.8	35.8
Parameters		$\sigma = 0.707$	$\alpha = 0.774$	$P_{mm} = 0.622$ $P_{rr} = 0.378$	$P_{mm} = 0.564$ $P_{rr} = 0.280$ $P_{mr} = 0.078$ $P_{rm} = 0.078$
RMS error		6.51	1.30	4.89	1.57

Table 7. Statistical analysis of a polymer made with **11**/MAO at 80°C in 10% monomer in toluene (Entry 48).

Pentad (%)	observed	chain end control	enantio-morphic site control	triad model $P_{mr} = 0$	triad model $P_{mr} > 0$
mmmm	18.0	13.7	18.9	25.0	18.1
mmmr	14.1	17.7	15.8	13.9	16.8
rmmr	3.6	5.7	4.1	5.3	4.8
mmrr	16.3	11.3	15.8	24.6	16.4
mrmm + rmrr	14.6	24.9	16.6	0.0	15.9
mrmr	7.5	11.3	8.3	0.0	4.6
rrrr	6.6	2.3	4.1	13.6	6.9
rrrm	9.1	7.3	8.3	10.7	10.8
mrrm	10.1	5.7	7.9	6.9	5.7
m	54.9	60.9	59.3	56.5	58.1
r	45.1	39.1	40.7	43.5	41.9
Parameters		$\sigma = 0.609$	$\alpha = 0.715$	$P_{mm} = 0.565$ $P_{rr} = 0.435$	$P_{mm} = 0.456$ $P_{rr} = 0.293$ $P_{mr} = 0.126$ $P_{rm} = 0.126$
RMS error		4.97	1.51	7.08	2.12

The following graph plots the RMS error as a function of polymerization condition. In liquid propylene, the hemiisotactic triad models provide the best fits. In dilute monomer, the triad model that employs two independent parameters excels the enantiomorphic site control model up to approximately 60°C. At this point, the single parameter enantiomorphic site control model provides the best fits. The statistical results are consistent with increased employment of the site epimerization mechanism by **11**/MAO as the monomer concentration is decreased and the polymerization temperature is increased.



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