Chiral *Ansa* Metallocenes with Cp Ring-Fused to Thiophenes and Pyrroles: Syntheses, Crystal Structures, and Isotactic Polypropylene Catalysts

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Abstract: Syntheses, crystal structures, and polymerization data for new isospecific metallocenes (heterocenes) having cyclopentenyl ligands b-fused to substituted thiophenes (Tp) and pyrroles (Pyr) are reported. The C_2- and C_1-symmetric heterocenes are dimethylsilyl bridged, have methyl groups adjacent to the bridgehead carbon atoms, and have aryl substituents protruding in the front. *rac*-Me_2Si(2,5-Me_2-3-Ph-6-Cp[b]Tp)$_2ZrCl_2$/MAO (MAO = methyl alumoxanes) is the most active metallocene catalyst for polypropylene reported to date. *rac*-Me_2Si(2,5-Me_2-3-Ph-6-Cp[b]Tp)$_2ZrCl_2$ and *rac*-Me_2Si(2,5-Me_2-1-Ph-4-Cp[b]Pyr)$_2ZrCl_2$ have the same structure, and the former is 6 times more active, produces half the total enantiofacial errors, and is 3.5 times less regiospecific in propylene polymerizations at the same conditions. *rac*-Me_2Si(2-Me-4-Ph-1-Ind)$_2ZrCl_2$/MAO is 3.5 times lower in activity than *rac*-Me_2Si(2,5-Me_2-3-Ph-6-Cp[b]Tp)$_2ZrCl_2$ catalyst, and while the former is the more stereospecific and the less regiospecific, the sum of these two enantioface errors is the same for both species. Fine-tuning the heterocene sterics by changing selected hydrogen atoms on the ligands to methyl groups influenced their catalyst activities, stereospecificites, regiospecificites, and isotactic polypropylene (IPP) M_w. Thus, both substituting a hydrogen atom adjacent to the phenyl ring with a methyl group on an azapentalenyl ligand system and replacing one and then two hydrogens on the phenyl ring with methyls on thiopentalenyl ligands provided increased polymer T_m and M_w with increasing ligand bulk. Polymer molecular weights are sensitive to and inversely proportional to MAO concentration, and the catalyst activities increase when hydrogen is added for molecular weight control. The polymer T_m values with the thiopentalenyls as TIBAL/[Ph_3C][$B(C_6F_5)_4$] systems were higher than with MAO as catalyst activator. A racemic C_1, pseudo-*meso* complex with a hybrid dimethylsilyl-bridged 2-Me-4-Ph-1-Ind/2,5-Me_2-4-Ph-1-Cp[b]Pyr ligand produced the first sample of IPP with all the steric pentad intensities fitting the enantiomorphic site control model. Speculative mechanistic considerations are offered regarding electronic effects of the heteroatoms and steric effects of the ligand structures, the preferred phenyl torsion angles, and anion effects.

Introduction

The discovery that group 4 metallocenes catalyze stereospecific polymerization to isotactic polypropylene (IPP)[1,2] according to the enantiomorphic site-controlled model[3] resulted in a lot of research targeting better catalyst activities, improved stereo- and regioselectivities, and higher polypropylene molecular weights.[4] Structural modifications to a prototype *rac*-Me_2Si[indenyl]$_2ZrCl_2$ (**1**)[5] led to promising catalysts with higher efficiencies, higher molecular weight polymers, stereospecificities approaching those of commercial catalysts, and higher regiospecificities.[6,7] This quest for a "rational design" of catalysts has focused on the trends seen from comparison of polymerization results to catalyst structural parameters that affect the nonbonded energies in preinsertion and termination assemblies.[8]

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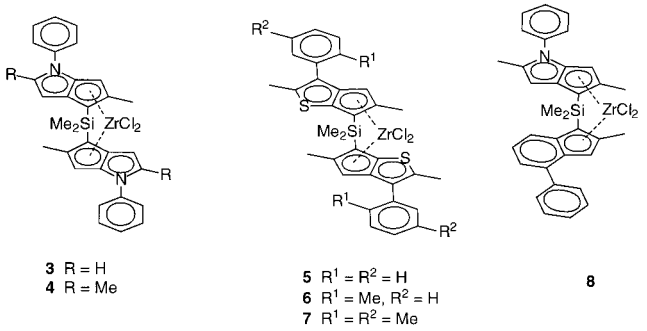
Chart 1



One of these indenyl-type catalysts, *rac*-Me_2Si(2-Me-4-Ph-1-indenyl)$_2ZrCl_2$ (**2**),[6] was adopted in this contribution as a benchmark for comparisons with similarly substituted cyclopenta[*b*]thiophenes and cyclopenta[*b*]pyrroles.

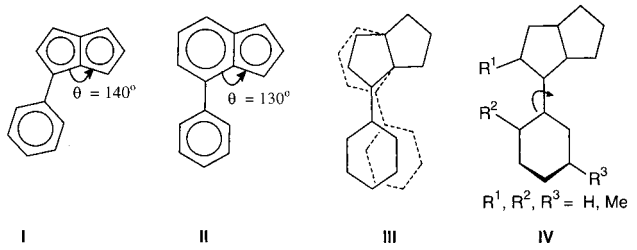
The first C_2-symmetric heterocene in this series (**4**, Chart 1) had an activity close to that of **2**, and C_s- and C_1-symmetric complexes having isopropylidene-bridged cyclopentadienyl and cyclopentyl[1,2-*b*:4,3-*b*′]dithiophene ligands had activities similar to those of fluorenyl analogues and obeyed the same symmetry rules for polypropylene tacticity versus catalyst symmetry.[9] Ligand effects have now been investigated in more detail, and the present paper reports our results on the preparation, characterization, and polymerization behavior of new heterocene complexes with ligands that are dimethylsilyl-bridged, have a methyl group adjacent to the bridgehead carbon atom, and have aryl substituents protruding out in the front of the catalysts by analogy with **2** (Chart 1).

The chosen mode of ring fusion has one heterocycle double bond aligned with the methylcyclopentenes of these cyclopentadienoid-like systems since b-fusion results in preferential metalation with *n*-BuLi at the desired active methylene group and also improves anionic delocalization relative to c-fused heterocyclic nuclei.[10] Electronic and steric ligand effects were investigated for sulfur and nitrogen heteroatoms and with the interchanging of hydrogen atoms and methyl groups adjacent to (**3**, **4**) and on the pendant phenyl rings (**5**−**7**), respectively (Chart 1). **8** is C_1 symmetrical and has the dimethylsilyl-bridged azapentalenyl and indenyl ligands in a pseudo-*meso* arrangement.

The importance of metallocene symmetries, bridges, and ligand substituents for producing polypropylenes with microtacticity control is well known.[4,11] New catalyst structural variants introduced in this study are illustrated in Chart 2.

There is 10° difference in the ligand mouth angles subtended between the 5/5 and 5/6 rings in the front of the complexes (Chart 2, **I**, **II**). Structures having differing mouth angles superimposed on each other are depicted as **III**, where the relative dispositions of the pendant phenyl rings are shown. **IV** indicates the positions at which H atoms and methyl groups

Chart 2



were interchanged to determine influences of the positions and sizes of substituents on the heterocycles and which can also influence the preferred torsion angles between the phenyl group and the Cp plane.

A rare opportunity that is offered by studying heterocenes is the possibility of better separating ligand steric and electronic effects since catalysts with ligands that are structurally equivalent around the non-Cp coordination sites but which are, at the same time, electronically dissimilar from each other because of the heteroatoms can be compared.[12] There are no measurements of electron-donating abilities of the ligands but, by definition, S is a soft, polarizable atom and nitrogen is hard.[13] The Pauling electronegativities for C (2.55), S (2.58), and N (3.04)[14] reflect the relative inductive electron-withdrawing power of these atoms.[12] Carbon and sulfur have the same electronegativity, while nitrogen is one of the most electronegative elements; only oxygen and fluorine exceed it in this respect. The azapentalenyl ligands for **4** are therefore structurally equivalent around the non-Cp coordination sites and are relatively poor electron donors compared with the isostructural thiopentalenyl ligands for **5**.

Modification of the sterics with heterocenes was done with selected hydrogen atoms on the parent ligands being changed to methyl groups and determining the influences of ligand bulk on catalyst activities, stereospecificities, regiospecificities, and on the IPP molecular weights. This approach was based on the findings that bulkier 4-indenyl ring-fused aromatics improve catalyst performance while aryl substituents in the 5-indenyl position do not.[6,7] The methyl substitutions were selected as a matter of expediency and because methyl and aromatic CH substituents typically have equivalent effects on stereoregulation.[5,11] The steric effect of methyl substitution adjacent to the phenyl ring on a heterocene was also investigated, not withstanding the aforementioned unimportance of the 5-indenyl position.

A goal with metallocenes and polypropylene is the creation of a stable of catalysts that can be used to tailor polypropylene microstructures ranging from amorphous or low-melting elastomeric materials to hard, perfectly isotactic polypropylene. A wide variety of C_1- and C_2-symmetric heterocenes and indenyl-type and fluorenyl-type metallocenes produce high-molecular-weight IPP with a wide range of melting points.[4e,15] The extreme high and low ends of stereoregulation have not been reported before. In an effort to attain a very low end of stereoregulation, we investigated **8**, which produced the first sample of isotactic

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Table 1. Crystallographic Data for **3**, **5**, **6**, and **8**

	compound			
	3	**5**	**6**·CH_2Cl_2	**8**·0.5CH_2Cl_2
formula	$C_{30}H_{28}Cl_2N_2SiZr$	$C_{32}H_{30}Cl_2S_2SiZr$	$C_{35}H_{36}Cl_4S_2SiZr$	$C_{33.5}H_{32}Cl_3NSiZr$
formula weight	606.75	668.89	781.87	674.26
space group	$P4_12_12$	$P2_1/c$	$P\bar{1}$	$I2/a$
a, Å	12.7198(2)	9.5183(2)	11.7096(2)	13.7403(2)
b, Å	12.7198(2)	35.7383(3)	12.6751(2)	17.3226(2)
c, Å	34.1068(2)	8.8314(2)	12.7721(2)	26.3308(3)
A, deg	−	−	96.9974(7)	−
β, deg	−	91.6932(11)	106.8513(5)	91.6470(2)
γ, deg	−	−	100.2661(3)	−
V, Å^3	5518.25(6)	3002.85(7)	1754.65(3)	6264.61(8)
Z, Z′	8	4	2	8
cryst color, habit	orange block	yellow plate	yellow block	yellow blade
D(calc), g cm^{-3}	1.461	1.480	1.480	1.430
μ(Mo Kα), cm^{-1}	65.8	74.4	79.6	66.9
temp, K	173(2)	243(2)	173(2)	173(2)
diffractometer	Siemens P4/CCD			
radiation	Mo Kα ($\lambda = 0.71073$ Å)			
$R(F)$, %[a]	3.74	9.85	4.10	4.55
$R(wF^2)$, %[a]	12.80	24.86	19.26	14.08

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$.

Table 2. Comparison of Structural Parameters for **2**, **3**, **5**, and **6**

parameter	**2**	**3**	**5**	**6**
Zr−Cl (Å)[a]	2.419(1)	2.443(4)	2.437(3)	2.421(5)
Cl−Zr−Cl (deg)	96.8(1)	97.86(3)	98.00(11)	99.44(3)
Zr−CR[b] (Å)	2.243(4)	2.230(4)	2.251(6)	2.256(5)
Zr−C(Cp) min (Å)	2.478(3)	2.463(3)	2.484(10)	2.466(2)
Zr−C(Cp) max (Å)	2.640(4)	2.650(3)	2.663(9)	2.665(2)
CR−Zr−CR′ (deg)	128.5(3)	128.7(4)	128.4(6)	127.5
PL−PL′ (deg)[c]	59.2	59.9	59.8	61.3
θ[d]	131.4	141.2(8)	139.3(9)	139.4
Φ[e](calcd)[f]	44.4 (50)	35.5 (34)	30.7 (55)	55.9 (67)
	44.8	46.7	41.3	73.0

[a] Averages. [b] CR, centroids of the Zr-bound C_5 rings. [c] PL and PL′, mean planes of the C_5 rings. [d] Average ligand mouth angles. [e] Measured torsion angle between aryl and Cp plane. [f] Estimated with Molecular Simulations Inc. Cerius^2 Version 4.2 software on a Silicon Graphics Indigo^2 work station.

polypropylene with sufficiently low stereoregularity for all of the steric pentad intensities to be measured and fit to the enantiomorphic site control model.[16]

Results and Discussion

X-ray Analyses of 3, 5, 6, and 8. The coordination geometries at Zr determined by X-ray diffraction for **2**, **3**, **5**, and **6** are very similar to each other, with no deviations greater than 2° nor 0.02 Å (rows 1−7 in Table 2, Figures 1−3). Significant structural differences are, however, found in the vicinity of the non-Cp coordination sites, with the ligand mouth angles (θ) subtended between the 5/5 and 5/6 rings in the front of the complexes (Chart 2, **I**, **II**) being about 10° larger for the heterocenes than for **2** and the dihedral angles (Φ) between the phenyl rings and the Cp planes differing from one another (Table 2, entries 8, 9). The measured torsion disagrees considerably even within each otherwise C_2-symmetric heterocene and also rarely agrees with theoretical values. The dihedral angles are therefore consistent with low rotational barriers and with the preferred conformations being influenced by either crystal packing forces or cocrystallized solvent molecules rather than simply following the theoretical trends for α-substituted biphenyls, as discussed by Spaleck and co-workers earlier.[6] Nonbonded

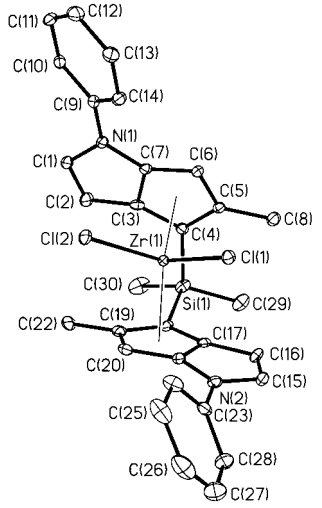

Figure 1. Thermal ellipsoid plot of **3**. H atoms omitted for clarity. Ellipsoids at 30% probability.

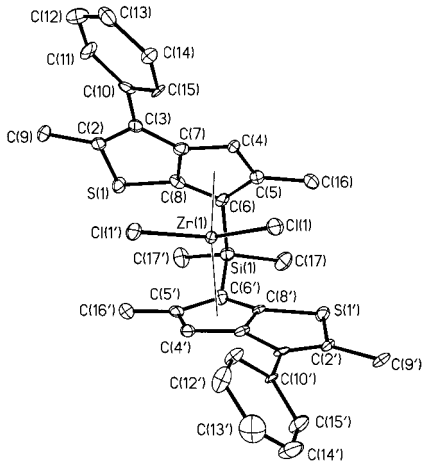

Figure 2. Thermal ellipsoid plot of **5**. H atoms omitted for clarity. Ellipsoids at 30% probability.

contacts between ion pairs and catalyst supports can therefore affect this sensitive structural parameter and possibly influence catalyst performance under different scenarios (vide infra).

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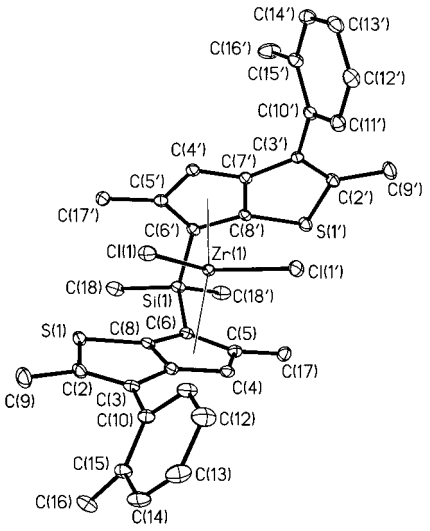
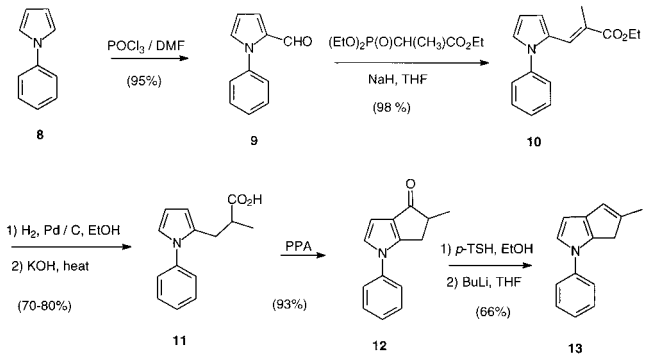
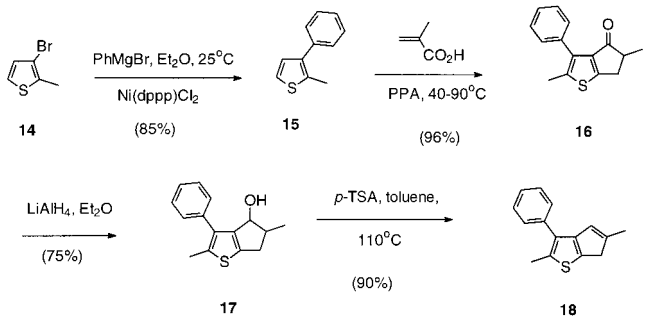


Figure 3. Thermal ellipsoid plot of **6**·CH_2Cl_2. H atoms omitted for clarity. Ellipsoids at 30% probability.

Scheme 1



Scheme 2



Preparation of Cyclopenta[*b*]heterocycles. 5-Methyl-1-phenyl-cyclopenteno[*b*]pyrrole (**13**) was prepared as outlined in Scheme 1, analogous to the previously described procedure[9] for its 2,5-dimethyl analogue but absent the initial methylation. The selectivity of the $POCl_3$/DMF acylation to **9** improved by 30% in the absence of the 2-methyl group. Cyclization of intermediate **11** with PPA proceeded in nearly quantitative yield, and **13** was also isolated in higher yield than for the dimethyl analogue.

The syntheses of the cyclopenta[*b*]thiophenes followed the outline in Scheme 2. **14** was obtained by regioselective 2-lithiation of 3-bromothiophene at −78 °C with lithium diisopropylamide (LDA), followed by methylation with iodomethane.[17] The coupling of PhMgBr and **14** proceeded smoothly in ether at 25 °C with Ni(dppp)Cl_2 as a catalyst.[18] The cyclic ketone **16** was obtained in 98% yield by reaction of the 2,3-disubstituted thiophene **15** with methacrylic acid in 87% super polyphosphoric acid.[19] 2,3-Disubstituted thiophenes are therefore attractive targets for studies of C_2-symmetric metallocene ligand effects. In comparison, a similar Friedel−Crafts alkylation/acylation reaction using 3-phenylthiophene proceeded in only 44% yield.

Silyl Bridges. The dimethylsilyl bridges were introduced in **3**−**7** by deprotonation of the methylcyclopentene methylene carbons with *n*-BuLi and reacting the resulting anions with dichlorodimethylsilane in THF. The dimethylsilyl-bridged mixed ligand for **8** was obtained by reacting the azapentalene anion with dimethylchloro(2-methyl-4-phenyl-1-indene)silane.

Metallocene Syntheses. 3−**7** were prepared from $ZrCl_4$ and their ligand dianions in ether and pentane solvents using standard procedures, and detailed descriptions of these and the other synthetic methods are given in the Experimental Section. In all cases, except for **4**, it was possible to isolate the pure racemic forms by fractional crystallization from different solvents. The pseudo-*meso* form of **8** was isolated by fractional crystallization from dichloromethane. Complexes **5**−**7** with silicon-bridged cyclopenta[*b*]thiopene ligands were unusually stable toward moisture. The zirconocenes could be isolated on open filter funnels, and addition of small amounts of water to NMR solutions of **5** did not decompose the complex.

Propylene Polymerization Catalysis with 2−**7.** The polymerization data and polymer analyses with **2**−**7** activated with methyl alumoxanes (MAO) at 70°C are summarized in Table 3. Polymerization test results on the influences of hydrogen (Table 4), MAO concentration (Table 5), and $B(C_6F_5)_4^-$ with and without hydrogen (Table 6) are also provided.

Catalyst Activities. The activities for **2**−**4** and the most crowded Tp complex (**7**) are on the same order of magnitude, whereas the polymerization rates for **5** and **6** are significantly

Table 3. Liquid Propylene Polymerization Test Results with **2**−**7**[a]

metallocene[b] (mg)	activity[c] (kg PP/ mmol Zr.h)	$10^{-3}M_w$[d] (g/mol)	APP[e] (wt %)	T_m (°C)	*mrrm* (%)	2,1-units[f] (%)
2 (0.4)	518	1184	0.6	156	0.1_9	0.4_9
3 (0.4)	443	145	9.4	146	2.1_0	0.1_6
4 (0.4)	324	198	7.0	155	1.4_3	0.1_0
5 (0.05)	1953	445	0.1	156	0.4_1	0.3_5
6 (0.1)	850	604	0.4	160	0.3_5	0.2_1
7 (0.2)	479	795	0.9	160	0.2_6	0.2_4

[a] Conditions: 1-gal autoclave, 2.2 L of propylene, 10 mL of 10% MAO in toluene, 70 °C, 1 h. [b] *rac, %:* **2**, **5**, **6**, **7** = 100%; **3**, **4** = 50%. [c] Activities of the *rac* isomers. [d] M_w of isotactic fraction. [e] Xylene-soluble fraction. [f] Erythro 2,1-regioerrors determined by ^{13}C NMR.

Table 4. Liquid Propylene Polymerization Test Results with Hydrogen[a]

metallocene (mg)	activity[b] (kg PP/ mmol Zr.h)	$10^{-3}M_w$ (g/mol)	APP[c] (wt %)	T_m (°C)	*mrrm* (%)	2,1-units[d] (%)
2 (0.1)	2123	242	0.4	157	0.1_8	0.4_4
3 (0.4)	886	53	13	147		
5 (0.05)	5004	122	0.2	157	0.4_3	0.2_5
6 (0.1)	3318	182	0.1	160	0.3_7	0.2_1
7 (0.2)	1363	299	0.1	161	0.2_4	0.2_4

[a] Conditions: 1-gal autoclave, 2.2 L of propylene, 55 mmol of H_2 (total added), 5 mL of 10% MAO in toluene, 70 °C, 1 h. [b] *rac* isomer. [c] Xylene-soluble fraction. [d] Erythro 2,1-regioerrors determined by ^{13}C NMR.

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Table 5. Polymerization Results with **5** versus MAO[a]

Al (mL)	yield (g)	Al/Zr	activity (kg/mmol cat.h)	$10^{-3}M_w$ (g/mol)	T_m (°C)
10.0	146	215 000	1953	447	155
5.0	90	107 749	1204	545	154
2.5	64	53 875	856	707	154
1.5	57	32 325	763	786	154

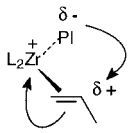
[a] Polymerization conditions: 0.05 mg of **5**, 10 wt % MAO in toluene, 2.2 L of propylene, 70 °C, 1 h, bulk.

Table 6. Results of Liquid Propylene Polymerizations with $[Ph_3C][B(C_6F_5)_4]$-Activated Catalysts[a]

metallocene (mg)	activity (kg PP/ mmol Zr.h)	$10^{-3}M_w$ (g/mol)	APP[d] (wt %)	T_m (°C)	*mrrm* (%)	2,1-units[e] (%)
5 (0.2)	687	564	0.1	157		
5 (0.1)[b]	2101	465	0.1	160	0.3_9	0.1_5
6 (0.2)	553	1165	0.1	162		
6 (0.1)[b]	648	473	0.3	164	0.0_6	0.0_9
6 (0.58)[c]	1422	358	0.2	164		
7 (0.5)[b]	83	555	0.1	166		

[a] Conditions: 1-gal autoclave, 2.2 L of propylene, 1.4 mg of $[Ph_3C][B(C_6F_5)_4]$, 1.0 mmol of Al(*i*-Bu)$_3$, 70 °C, 1 h. [b] 15 mmol of H_2 added to the reactor. [c] 10-gal autoclave, 22 L of propylene, 3.5 mg of $[Ph_3C][B(C_6F_5)_4]$, 12 mmol of Al(*i*-Bu)$_3$, 55 mmol of H_2, 70 °C, 1 h. [d] Xylene-soluble fraction. [e] *erythro*-2,1-regioerrors determined by ^{13}C NMR.

Chart 3



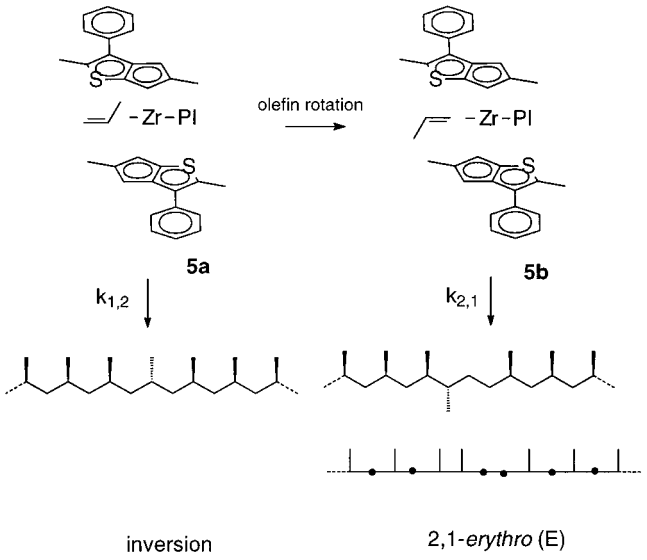
higher (Table 3). The similarity in the activities for **2** and **3** is consistent with earlier results for **2** versus **4**.[9] It is possible that opposing steric and electronic effects are at work, with N electronically deactivating **3** and **4** and the larger mouth angle for the 5/5 systems reactivating them.

5 has the highest activity known for metallocenes, and its 5-fold increase over the Pyr analogue **4** is attributed to greater electron donation by the Tp ligand to Zr and the effect this has on the propagation rate. This is in accord with the electronegativities of S and N, the two catalysts being isostructural, and the Tp complex more than doubling M_w under the same polymerization conditions. Faster insertion reactions with increased ligand electron donation is a consequence of the alkyl ligand being rendered more anionic, which should enhance nucleophilic migration to the olefin already polarized by the Zr cation, i.e., should promote insertion (Chart 3).[20]

A comparison of the electronic contribution to the relative activities of Tp versus Ind catalysts is not possible since they are not structural analogues, their relative basicities are unknown, and the 3.5-fold improvement in activity for **5** versus **2** may be partially steric in origin. An unusual trend for the 5/5 catalysts in Table 3 not found for Ind catalysts is the decreasing activities with increasing ligand bulk.

IPP Molecular Weights. M_w is proportional to the ratio of propagation and termination rates. M_w in Table 3 is lower for all of the heterocenes than for **2**, even in cases where the activities are higher for the former, suggesting faster termination rates for the heterocenes. It can be inferred from the inverse dependence of M_w on MAO and from M_w increasing even as

Chart 4



activity decreases (Table 5) that transfer to Al is an important termination mechanism with **5**. It is logical that less sterically hindered structures have faster bimolecular transfer to Al and transfer to monomer terminations.

The M_w data in Table 3 for the 5/5 systems are consistent with steric inhibition of termination reactions affecting M_w since the heterocene-produced IPP M_w increases in every case as the ligands become more bulky and since this trend occurs regardless of the catalyst activity. M_w for **5** is double that of **4** for these sterically equivalent species and is consistent again with an electronic difference between pyrrole and thiophene resulting in **5** having the higher propagation rate.

Activities and IPP M_w values tend to vary hand-in-hand with metallocenes.[5] The more unusual low activity−high IPP M_w relationship for the Pyr catalyst **4** relative to **3** (Table 3) arises from Me versus H substitutions at the ligands' 5-positions (Chart 1, **3** and **4**). The bulkier 5-Me apparently results in **4** having both lower termination rates and, to a lesser extent, a lower propagation rate. Steric considerations might likewise account for the similar, albeit more extreme, trend for **2** versus **5**.

The effect of hydrogen with five catalysts shows catalyst activation by 2−4-fold with large decreases in M_w but no significant changes in T_m, *mrrm*, nor 2,1-units (Table 4). An electronic effect on hydrogen response for **3** versus **5** is not obvious with the limited data.

Microstructures. The molecular assembly **5a** for a 1,2-insertion with the "wrong" π-face coordinated results in a steric inversion or "error", as depicted in Chart 4 (*R,R,si*: *ent* = *S,S,re*). There is a steric driving force for **5a** to convert to the 2,1-*erythro* preinsertion intermediate **5b** via a 180° propylene rotation.[21] These are the only microstructural defects in the polymers, and accordingly catalyst stereo- and regiospecificities share a common origin with the "wrong" face coordinated. The total of a catalyst's "errors" in stereospecific (enantioselective) IPP polymerizations can therefore be taken as the sum of its polymer's *mrrm* units and 2,1-units, and the ratio of (*mrrm*/2,1-units) is presumably determined by the relative activation energies for the competing reactions in Chart 4 and monomer dissociations. The total enantiofacial "errors" with MAO increase in the order **7** (0.5%) < **6** (0.6%) < **2** (0.7%) < **5** (0.8%) ≪ **4** (1.5%) < **3** (2.3%), and the (*mrrm*/2,1-unit) ratios

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are roughly Pyr = 15, Tp =1.5, and Ind = 0.4. The two Pyr catalysts are about 3 times lower in enantiofacial selectivity and 3 times higher in regiospecificity than the more closely equivalent Ind and Tp catalysts. A stronger effect of 2,1-units than *mrrm* on T_m is seen when comparing the data for **2** (T_m = 156 °C, *mrrm* = 0.2%, 2,1-units = 0.5%) and **4** (T_m = 155 °C, *mrrm* = 1.4%, 2,1-units = 0.1%). This effect on T_m with carbocene catalysts has been noted before.[22]

The difference in steresopecificity between **3** and **4** is attributed to a steric effect on stereoregulation. There is no precedent for an effect on stereoregulation due to methyl substitution at an analogously remote Cp position. However, ϕ is predicted to be 20° higher for **4** compared to **3** due to the 5-methyl group, and the polymerization data show **4** with T_m increased by 9 °C and *mrrm* decreased by 0.7% (Table 3). It can be tentatively argued that with a larger ϕ an *ortho*-carbon of the Ph ring is closer in proximity to the propylene methyl group for the "wrong" preinsertion intermediates such as **5a** (Chart 4), making **4** more stereospecific than **3**, with the caveat that unknown ion-pairing effects on the preferred conformations of the pendant phenyl groups are also likely (vide supra).

The stereospecificities for the Tp series are similar to those of **2**, follow the trend for increasingly large aryl groups at the 4-indenyl position,[6] and are in the order *p*-Xyl (99.5%) ≈ *o*-Tol (99.4%) > Ph (99.2%), with the slightly higher stereospecificity of **6** and **7** relative to **5** in accord once again with the 12° lower ϕ for **5** than for **6** and **7** and the preferred conformation proposal of Spaleck et al.[6] *On the other hand, the higher stereospecifcity for **5** as compared with that for **4** suggests an unprecedented electronic effect because there are no structural differences between the two to account for this. The differences in regioregulation between the Pyr and Tp series may also be an electronic effect.* It has been suggested that the higher *mrrm* placements and the lower 2,1-*erythro* (*E*) units in the Pyr catalysts may reflect a more highly unsymmetrical metal−propylene bonding since olefins coordinate to d^0 metal complexes in an unsymmetrical fashion with buildup of positive charge at C2. As this effect is enhanced, as might be the case with stronger metal−olefin adducts, then there should be a stronger electronic preference for 1,2-insertion and hence a lower 2,1-insertion tendency.[23,24]

The slightly higher IPP T_m and enantioface selectivities obtained with thiophene catalysts using $Ph_3CB(C_6F_5)_4$/TIBAL as an activator (Table 6) compared with MAO (Table 3) are consistent with anions having an influence on stereoregulation despite their being present as olefin-separated ion pairs required for chain growth.[25] The IPP melting points increased to as high as 166 °C with **6** under commercial polymerization conditions. The reason for this effect is unproven, but the results are consistent with cation/anion contacts with MAO^- and $B(C_6F_5)_4^-$ influencing ϕ differently and hence affecting the catalyst's stereospecificities and activities. The same phenomenon has been previously noted for *rac*-Me_2Si(2-Me-4-(1-naphthyl)-Ind)$_2ZrCl_2$ at very low polymerization temperatures.[7c]

Low Site Control Stereoregulation. Propylene polymerizations were conducted with pseudo-*meso*-**8** (Figure 4) in order to test the theory that an *ortho*-carbon of the pendant Ph makes contact with the propylene methyl and influences stereoselectivity.

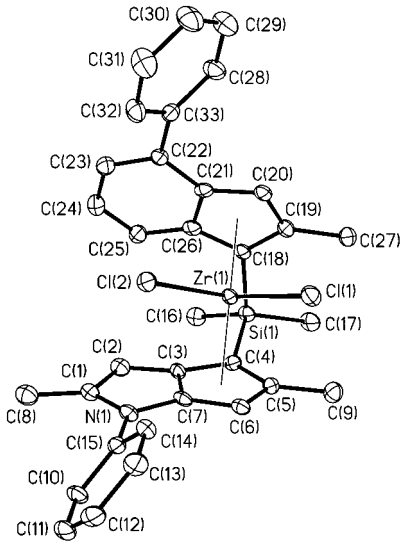
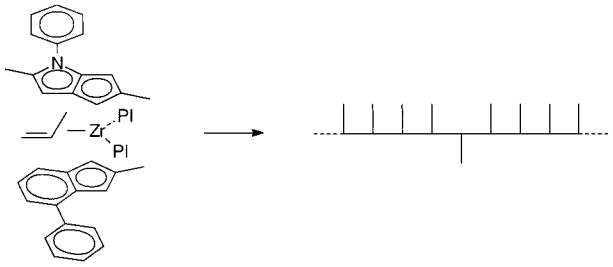


Figure 4. Thermal ellipsoid plot of **8**·0.5CH_2Cl_2. H atoms omitted for clarity. Ellipsoids at 30% probability.

Chart 5



There is a strong steric driving force for the chain to return to the uncrowded side of *meso* structures, where it has no preferred chiral chain orientation and has no influence on stereoselectivity.[8] Insertions are infrequent or do not occur at all while the chain is at the highly crowded sides of C_1 species, even in bulk propylene.[9b] The complete regiospecificity of **8** is consistent with the chain being on the less crowded side of the catalyst during insertion since propylene rotation (Chart 4) is inhibited for this arrangement.[8] Further, it is unlikely that stereoregulation occurs with the chain-orientated mechanism while the chain resides at the crowded side of **8** since this would lead to hemi-isotactic (hit-PP) or an atactic/hemi-isotactic mixed microstructure in the event of some intervening back-skip reactions. It is reasoned that if **8** obeys the site-controlled model rather than the hit-PP models,[11,26] this would be evidence for stereocontrol from the differences in the energies of the contacts between the propylene methyl and the two phenyl rings sandwiching the monomer. The proposed stereoselective 1,2-insertion assembly for **8** and the enantiomorphic site control microstructure for IPP are displayed in Chart 5 with the selection of an *S*,*si* assembly on the basis that **2** is about 1% more stereospecific than **4**.

The polymerization data with **8**, the ^{13}C NMR spectrum for the 68% *m* polymer methyl region, and the fit of the pentads to the enantiomorphic site pentad intensity equations[27] are displayed in Figure 5. This is the first time all steric pentads have been fit to the enantiomorphic site model. It is also the first

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(23) We thank an anonymous reviewer for pointing this out.

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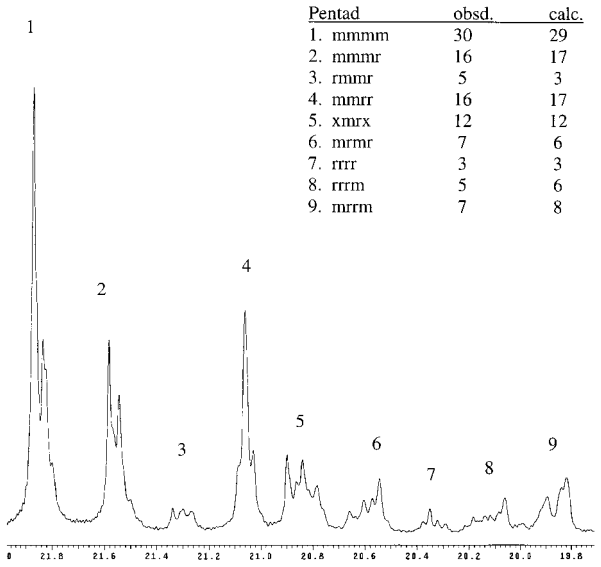

Figure 5. ^{13}C NMR spectrum of the methyl pentad region of isotactic polypropylene produced with an activity of 138 kg g-cat^{-1} h^{-1} in bulk for 1 h at 50 °C by pseudo-*meso* **8**, and the fit of the pentad intensities to the enantiomorphic site model.

instance we are aware of with stereoregulation for a catalyst with all the stereodirecting groups on the same side. The modest degree of site control stereoregulation for **8** is consistent with the small differences in stereoselectivities for **2** and **4**. In light of these results and the failure of both the hit-PP model and a mixed hit-PP/APP model, the hypothesis of the influence of an *ortho*-carbon on the pendant phenyls contacting the monomer methyl group to give some degree of stereocontrol seems reasonable.

Experimental Section

General Procedures. All manipulations with air-sensitive materials were performed under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmospheres drybox (except polymerizations, which were conducted using argon as the inert gas). THF, ether, and toluene were distilled from sodium/benzophenone, pentane was distilled from sodium/benzophenone/triglyme, and dichloromethane was distilled from CaH_2 and stored over 4-Å molecular sieves. Mass spectra of organic intermediates were measured with a Hewlett-Packard 6890 series gas chromatograph equipped with a 5973 mass-selective detector (EI, 70 eV). Mass spectra of zirconocenes were measured on a Hewlett-Packard quadrupole 5889B series, using a direct insetion probe (DIP) in electron impact (EI) mode. Scan parameters were set from mass 100 to 800. Samples were prepared under a nitrogen atmosphere, inserted in the DIP, and heated from 30 to 300 °C at 20 °C/min. The source and quadrupole were heated at 300 and 150 °C, respectively. NMR spectra of organic and organometallic compounds were recorded on a Varian Unity-300 NMR spectrometer at ambient probe temperature. ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$. Melting points are uncorrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. *rac*-{(2-Me-4-Ph-1-indenyl)$_2$SiMe$_2$}ZrCl$_2$ (**2**) was purchased from Boulder Scientific Co. {(2,5-Me$_2$-1-Ph-cyclopento[3,2-*b*]pyrrol-4-yl)$_2$SiMe$_2$}ZrCl$_2$ (**4**) and {(2,5-Me$_2$-1-Ph-cyclopento[3,2-*b*]pyrrol-4-yl)(2-Me-4-Ph-inden-1-yl)SiMe$_2$}-ZrCl$_2$ (**8**) were prepared by literature methods.[9] Super PPA[28] was (typically) prepared by stirring 164.3 g of P_2O_5 in 975.7 g of commercial polyphosphoric acid (Aldrich Chemical Co.) at 140 °C until all P_2O_5 dissolved.

1-Phenylpyrrole-2-carbaldehyde (9). $POCl_3$ (107.3 g, 0.70 mol) was added dropwise to 76 mL of DMF (71.7 g, 0.98 mol) and stirred for 10 min. The temperature was lowered to 0 °C, and a solution of 1-phenylpyrrole (100 g, 0.70 mol) in 100 mL of dichloromethane was added slowly. The viscous solution was slowly warmed to 50 °C and stirring continued for 1 h. After being cooled to room temperature, the flask was opened to the air and charged with 750 g of crushed ice. A 20 wt % solution of NaOH (885 mL) was added cautiously, and the mixture was immediately heated to 85−90 °C and stirred for 10 min. The solvent was distilled off in the process. The flask was placed in an ice bath and cooled to room temperature, and the reaction mixture was extracted with dichloromethane (2 × 200 mL). The combined organic fractions were washed with water and dried ($MgSO_4$). Evaporation of the solvent yielded 114 g of product as an orange oil containing ca. 10% of the 1-phenylpyrrole-3-carbaldehyde isomer. The product was used without further purification. ^1H NMR ($CDCl_3$): δ 9.5 (s, 1H), 7.4 (m, 3H), 7.3 (m, 2H), 7.1 (dd, 1H), 7.0 (t, 1H), 6.35 (dd, 1H). ^{13}C NMR ($CDCl_3$): δ 178.1, 138.1, 131.9, 130.4, 128.4, 127.5, 125.4, 121.3, 110.3. EIMS: *m*/*z* (relative intensity) 171 (M^+, 100), 154 (7), 142 (8), 115 (50), 93 (42), 77 (16).

Ethyl (2*Z*)-2-Methyl-3-[1-phenylpyrrol-2-yl]prop-2-enoate (10). A solution of triethyl 2-phosphonopropionate (153 mL, 0.714 mol) in 75 mL of THF was added slowly to a mixture of sodium hydride (24.3 g, 1.0 mol) in 60 mL of THF at 0 °C. The slurry was warmed to room temperature and stirred for 1 h. The temperature was lowered to −10 °C, and a solution of **9** (113 g, 0.665 mol) in 200 mL of THF was added dropwise. The reaction mixture was warmed to room temperature over 30 min, resulting in a thick precipitate. A saturated aqueous solution of NH_4Cl (100 mL) was added cautiously, giving a two-phase solution. THF was distilled off, and the crude product was extracted with ether (2 × 200 mL). The ether extract was washed with brine solution and dried ($MgSO_4$). The solvent was evaporated, and the crude product was washed with hexane to give the product as a white crystalline solid. Yield: 89% (151 g). ^1H NMR ($CDCl_3$): δ 7.4 (m, 4H), 7.3 (m, 2H), 7.0 (dd, 1H), 6.7 (dd, 1H), 6.4 (t, 1H), 4.1 (q, 2H), 2.2 (s, 3H), 1.2 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 168.6, 139.0, 129.4, 129.0, 127.3, 126.1, 126.0, 124.8, 122.8, 114.1, 109.9, 60.2, 14.1. EIMS: *m*/*z* (relative intensity) 255 (M^+, 50), 226 (5), 210 (23), 182 (100), 167 (47), 154 (12), 115 (7), 77 (18). Mp: 73 °C.

Ethyl 2-Methyl-3-[1-phenylpyrrol-2-yl]propanoate (20). A mixture of **10** (55 g, 0.22 mol) and 10% Pd/C (2.3 g) in 300 mL of dichloromethane was stirred under 80 psig of hydrogen for 4 h. After the catalyst was filtered off and washed with dichloromethane, solvent was removed on a rotary evaporator to give the product. Yield: 54 g (97%). ^1H NMR ($CDCl_3$): δ 7.4 (m, 3H), 7.2 (m, 2H), 6.7 (m, 1H), 6.1 (m, 1H), 6.0 (m, 2H), 4.0 (q, 2H), 2.9 (m, 1H), 2.5 (m, 2H), 1.2 (t, 3H), 1.0 (d, 3H). ^{13}C NMR ($CDCl_3$): δ 175.6, 128.9, 127.0, 126.0, 121.8, 107.8, 60.0, 39.3, 30.3, 16.7, 13.9. EIMS: *m*/*z* (relative intensity) 257 (M^+, 9), 216 (7), 184 (6), 146 (100), 77 (16).

2-Methyl-3-[1-phenylpyrrol-2-yl]propanoic Acid (11). The ester **20** (42.1 g, 0.164 mol) was treated with 78 mL of Claisen's reagent and heated to 90−95 °C. After being stirred for 1 h, the solution was poured onto crushed ice and acidified to pH 1−2 with 6 N HCl. The precipitated free acid was extracted with ether (2 × 200 mL), washed with brine solution, and dried ($MgSO_4$). Ether was removed from the product by rotary evaporation. Yield: 27.9 g (75%). ^1H NMR ($CDCl_3$): δ 7.2−7.6 (m, 5H), 6.7 (d, 1H), 6.2 (t, 1H), 6.1 (d, 1H), 3.0 (m, 1H), 2.6 (m, 2H), 1.1 (d, 3H).

5-Methyl-1-phenyl-5,6-dihydrocyclopenta[1,2-*b*]pyrrol-4-one (12). A solution of **11** (43 g, 0.188 mol) in 75 mL of dichloroethane was added dropwise to 1000 g of super PPA at 100 °C. After being stirred for 5 h, the mixture was cooled to 60 °C and poured slowly onto crushed ice. The product was extracted with 30% (v/v) dichloromethane in hexane (2 × 200 mL). The combined organic fractions were washed with a saturated aqueous solution of $NaHCO_3$ and dried ($MgSO_4$). Solvents were removed on a rotary evaporator, leaving the product as a tan solid. Yield: 37 g (93%). ^1H NMR ($CDCl_3$): δ 7.5 (m, 2H), 7.4 (m, 3H), 7.1 (d 1H), 6.4 (d, 1H), 3.3 (dd, 1H), 3.0 (m, 1H), 2.6 (dd, 1H), 1.3 (d, 3H). ^{13}C NMR ($CDCl_3$): δ 199.6, 156.6, 138.8, 129.8, 129.2, 127.9, 127.2, 122.0, 104.1, 47.5, 30.8, 17.1. EIMS: *m*/*z* (relative

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intensity) 211 (M^+, 100), 196 (55), 182 (33), 167 (27), 154 (12), 120 (23), 105 (38), 77 (46). Mp: 120 °C.

Tosyl Hydrazone of 5-Methyl-1-phenyl-5,6-dihydrocyclopenta-[1,2-*b*]pyrrol-4-one (21). The ketone **12** (36 g, 0.171 mol), *p*-toluenesulfonhydrazide (33 g, 0.177 mol), and *p*-toluenesulfonic acid monohydrate (6.6 g, 0.035 mol) were stirred in 220 mL of ethanol at 70 °C for 16 h. After the solution was cooled to room temperature and left to stand for several hours, the precipitated product was collected on a filter funnel, washed with ether, and dried under vacuum. Solvents were evaporated from the filtrate, and additional product was obtained by trituration of the residue with toluene. A tan solid was recovered. Yield: 58.9 g (91%). ^{1}H NMR ($CDCl_3$): δ 7.9 (d, 2H), 7.1−7.6 (m, 7H), 7.1 (d, 1H), 6.7 (d, 1H), 3.5 (m, 1H), 3.2 (dd, 1H), 2.6 (dd, 1H) 2.4 (s, 3H), 1.3 (d, 3H). ^{13}C NMR ($CDCl_3$): δ 162.2, 147.0, 143.5, 138.9, 135.5, 129.7, 129.2, 128.1, 126.9, 126.3, 121.8, 121.4, 105.5, 42.8, 32.4, 21.5, 19.7. Mp: 186 °C (dec).

5-Methyl-1-phenyl-4-hydrocyclopenta[2,1-*b*]pyrrole (13). To a solution of the tosylhydrazone **21** (32.5 g, 0.086 mol) in THF (200 mL) was added 76 mL of *n*-butyllithium in hexanes (2.5 M, 0.189 mol) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 16 h. A saturated aqueous solution of NH_4-Cl (20 mL) was added dropwise, and the organic solvents were distilled off. Water (100 mL) was added, and the mixture was extracted with ether (2 × 100 mL). The combined ether fractions were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The brown oily residue was stirred vigorously with hexane (150 mL) for 1 h. The insoluble products were removed by filtration, and the hexane was evaporated, giving the product as a light yellow oil. Yield: 12 g (72%). Two isomers were recovered. ^{1}H NMR ($CDCl_3$): δ 7.5 (m, 4H), 7.3 (m, 1H), 7.1 (d, 1H), 7.0 (d, 1H), 6.6 (s, 1H), 6.4 (s, 1H) 6.3 (d, 1H), 6.2 (d, 1H), 3.3 (s, 1H), 3.1 (s, 1H), 2.2 (s, 3H), 2.17 (s, 3H). EIMS: *m*/*z* (relative intensity) 195 (M^+, 100), 180 (28), 167 (7), 152 (10), 139 (2), 127 (3), 116 (3), 91 (12), 77 (8).

(5-Me-1-Ph-4-hydrocyclopenta[3,2-*b*]pyrrol-4-yl)SiMe$_2$Cl (22). A solution of **13** (11.2 g, 0.057 mol) in 100 mL of ether was treated with 28 mL of *n*-butyllithium in hexanes (2.5 M, 0.070 mol) at −10 °C and stirred at room temperature for 16 h. Pentane (50 mL) was added to the reaction mixture, the precipitated lithium salt was allowed to settle, and the liquid was removed with a filter stick. The precipitate was redissolved in ether (150 mL) and cooled to −78 °C, and dichlorodimethylsilane (10.5 mL, 0.086 mol) was added by syringe. The reaction mixture was warmed to room temperature and then refluxed for 2 h. After the mixture was cooled and filtered, volatiles were removed from the filtrate in vacuo (100 mTorr, 40 °C), giving the product as a colorless oil. Yield: 12.7 g (77%). ^{1}H NMR (CD_2Cl_2): δ 7.5 (m, 4H), 7.3 (m, 1H), 7.0 (d, 1H), 6.6 (s, 1H), 6.3 (d, 1H), 3.3 (s, 1H), 2.3 (s, 3H), 0.5 (s, 3H) 0.1 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 144.9, 129.9, 125.5, 121.1, 120.6, 117.9, 106.2, 45.0, 18.0, 0.95, −1.25.

(5-Me-1-Ph-4-hydrocyclopenta[3,2-*b*]pyrrol-4-yl)$_2$SiMe$_2$ (23). A solution of **13** (4.7 g, 24 mmol) in 60 mL of ether was treated with 11.2 mL of *n*-butyllithium in hexanes (2.5 M, 28 mmol) and stirred for 16 h. Pentane (50 mL) was added, and the slurry was filtered through a closed frit funnel. The tan lithium salt was redissolved in 50 mL of THF, cooled to −78 °C, and treated with chlorosilane **22** (6.7 g, 24 mmol) dissolved in 50 mL of THF. The dark brown solution was slowly warmed to 50 °C and stirred for 16 h. Volatiles were removed in vacuo, and the residue was extracted with dichloromethane to remove LiCl. Evaporation of the solvent gave the product as a white solid. Yield: 8.5 g (81%). Two isomers were recovered. ^{1}H NMR (CD_2Cl_2): δ 7.5 (m, 8H), 7.25 (m, 2H), 7.05 (d, 1H), 6.95 (d, 1H), 6.6 (s, 2H), 6.5 (d, 1H), 6.3 (d, 1H), 3.45 (s, 2H), 2.3 (s, 3H), 2.2 (s, 3H), −0.20 (s, 3H), −0.22 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 146.3, 146.2, 141.3, 140.7, 130.3, 129.9, 125.2, 120.9, 120.2, 120.1, 117.0, 106.4, 106.2, 42.8, 42.5, 18.3, 18.25, −6.9, −7.2. EIMS: *m*/*z* (relative intensity) 446 (M^+, 18), 252 (100), 237 (8), 224 (7), 194 (7), 165 (3).

{Me$_2$Si(5-Me-1-Ph-cyclopento[3,2-*b*]pyrrol-4-yl)$_2$}ZrCl$_2$ (3). A solution of **23** (4.0 g, 9.0 mmol) in 100 mL of ether was cooled to −78 °C, treated with 8.0 mL of butyllithium in hexanes (2.5 M, 20 mmol), and warmed to room temperature. After the solution was stirred overnight, the pressure was reduced to evaporate the solvents. The residue was washed with pentane (40 mL) and dried in vacuo to a free-flowing tan powder. $ZrCl_4$ (2.09 g, 9.0 mmol) was added to the flask, and the contents were stirred overnight in a mixture of pentane (75 mL) and ether (1.5 mL). The solids were collected on a closed frit funnel, washed with pentane, and dried under vacuum, giving an orange solid (5.9 g). A portion of the crude product (5.65 g) was stirred in dichloromethane (75 mL) and filtered. The filtrate was concentrated to a small volume, and pentane was added to precipitate the complex. Yield: 4.1 g (79%, 50/50 *rac/meso*). Crystals of the *rac* isomer were obtained by slow evaporation of a dichloromethane/toluene solution of the *rac/meso* complex. ^{1}H NMR (CD_2Cl_2): δ 7.3−7.5 (m, 8H, *rac* and *meso*), 7.38 (d, J = 3.5 Hz, 2H, *rac*), 7.15−7.25 (m, 2H, *rac* and *meso*), 7.12 (d, J = 3.5 Hz, 2H, *meso*), 6.45 (s, 2H, *rac*), 6.4 (s, 2H, *meso*), 6.32 (d, J = 3.5 Hz, 2H, *rac*), 6.2 (d, J = 3.5 Hz, 2H, *meso*), 2.4 (s, 6H, *meso*), 2.2 (s, 6H, *rac*), 1.125 (s, 3H, *meso*), 1.118 (s, 3H, meso), 1.10 (s, 6H, *rac*). Anal. Calcd for $C_{30}H_{28}Cl_2N_2SiZr$: C, 59.38; H, 4.65. Found: C, 59.78; H, 4.74.

3-Bromo-2-methylthiophene (14). To a solution containing 62.0 g (610 mmol, 88 mL) of diisopropylamine dissolved in 150 mL of THF was added 210 mL of *n*-butyllithium in hexanes (2.5 M, 610 mmol) while the temperature was maintained at 0 °C. After addition was complete, stirring continued for an additional 30 min. The flask containing lithium diisopropylamide (LDA) was cooled to −78 °C, and then a solution containing 100 g (610 mmol) of 3-bromothiophene dissolved in THF (60 mL) was added dropwise. After addition was complete, the solution was warmed to 0 °C (ice bath) and stirred an additional 30 min. The temperature of the reaction slurry was lowered to −78 °C, and a solution containing 86.5 g (610 mmol) of iodomethane dissolved in 40 mL of THF was added in one portion. The reaction mixture was stirred an additional 30 min at −78 °C and then warmed to room temperature and stirred for 1 h. The organic layer was collected with ether, washed with water, dried over magnesium sulfate, and filtered, and then solvents were removed in vacuo. A light orange oil was recovered. Yield: 89.8 g (74.8%), 90.7% by GC. ^{1}H NMR ($CDCl_3$): δ 7.1 (d, 1H), 6.9 (d, 1H) 2.4 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 134.6, 130.3, 123.3, 109.8, 14.8. EIMS: *m*/*z* (relative intensity) 176, 178 (M^+, 57), 97 (100), 81 (4), 69 (12), 53 (14).

2-Methyl-3-phenylthiophene (15). To a slurry containing **14** (89.8 g, 460 mmol) and 1 g of [bis(diphenylphosphino)propane)]dichloronickel (Ni(dppp)Cl_2) in 200 mL ether was added 152 mL of phenylmagnesium bromide in ether (3 M, 456 mmol) dropwise. After addition was complete, the reaction flask was stirred for 1 h, and the reaction was quenched with water. The organic fraction was extracted with dichloromethane, washed with water, and dried over magnesium sulfate, and then the solvents were removed in vacuo. A dark orange oil was recovered. Yield: 77.13 g (84.7%), 87.2% by GC. ^{1}H NMR (ppm, $CDHCl_2$): δ 7.3−7.6 (m, 5H), 7.1−7.25 (m, 2H), 2.6 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 139.1, 137.2, 134.6, 129.6, 129.2, 129.1, 128.9, 128.8, 127.7, 127.5, 127.1, 122.0, 14.4. EIMS: *m*/*z* (relative intensity) 176 (6), 175 (18), 174 (100), 173 (98), 172 (6), 171 (14), 158 (2), 147 (9), 141 (15), 135 (4), 129 (18) 115 (15).

2,5-Dimethyl-3-phenyl-5,6-dihydrocyclopenta[1,2-*b*]thiophen-4-one (16). A solution containing **15** (124.7 g, 542 mmol), methacrylic acid (61.7 g, 715 mmol), and 200 mL of dichloromethane was added slowly to 1000 g of super PPA with stirring at 70 °C. The flask and contents were refluxed for 10 h, with an additional 208 g of methacrylic acid in 250 mL of dichloromethane added in 60- or 75-g portions during the reaction. After being stirred for 10 h, the reaction mixture was poured onto ice. The organic layer was collected with 20% (v/v) dichloromethane in hexane and washed with water, a saturated solution of sodium hydrogen carbonate, and then water again. The organic layer was dried over magnesium sulfate and filtered, and then solvents were removed in vacuo, leaving a dark brown oil. Yield: 202.9 g (81.7% by GC, 95.6%), used in subsequent steps without additional purification. *Note:* Two isomers of **16** were recovered in a ratio of 3:1. ^{1}H NMR (CD_2Cl_2): δ 7.05−7.4 (m, 5H), 2.6−3.0 (m, 2H), 2.3 (s, 3H), 1.7−1.85 (m, 1H), 1.1 (d, 3H). ^{13}C NMR (CD_2Cl_2): δ 199.9, 167.6, 152.1, 136.5, 134.6, 130.4, 129.6, 139.4−127.1, 46.5, 33.8, 17.1, 17.0, 16.2. EIMS: *m*/*z* (relative intensity) 242 (100), 227 (54), 214 (10), 213 (17), 199 (38), 185 (21), 184 (11), 165 (14), 152 (8), 139 (4), 128 (5), 115 (12).

2,5-Dimethyl-3-phenyl-4,5,6-trihydrocyclopenta[1,2-*b*]thiophen-

4-ol (17). A 1.0 M solution of lithium aluminum hydride in ether (300 mmol, 300 mL) was added dropwise at 0 °C to 202 g of **16** dissolved in 300 mL of THF. After addition was complete, the temperature of the reaction flask was raised to room temperature, and then the solution was stirred an additional 2 h. The reaction was quenched with water, the organic layer was collected with ether, washed with water, dried over magnesium sulfate, and filtered, and then the solvents were removed in vacuo. Multiple isomers of the product were recovered. An additional 16 g of material was recovered by repeated washing of the lithium prill. The product was recovered as a yellow solid Yield: 139.1 (75%), 78.5% by GC, used in subsequent steps without additional purification. ^{1}H NMR (CD_2Cl_2): δ 7.2−7.8 (m, 4H), 4.9 (0.5H), 4.8 (0.5H), 2.6−3.2 (m, 3H), 2.4−2.6 (m, 3H), 1.1−1.3 (m, 3H). ^{13}C NMR (CD_2Cl_2): δ 146.8, 140.2, 136.4, 129.5, 129−127, 80.8, 74.4, 73.7, 49.0, 43.9, 35.7, 35.4, 35.2, 19.4, 15.3, 15.27, 14.7. EIMS: *m*/*z* (relative intensity) 244 (100), 229 (48), 211 (26), 201 (21), 188 (10) 187 (12), 185 (15), 184 (14), 178 (16), 171 (13), 167 (12), 165 (16), 153 (11), 152 (13), 115 (17).

2,5-Dimethyl-3-phenyl-4,5,6-trihydrocyclopenta[1,2-*b*]thiophen-4-ol (17). A 1.0 M solution of lithium aluminum hydride in ether (300 mmol, 300 mL) was added dropwise at 0 °C to 202 g of **16** dissolved in 300 mL of THF. After addition was complete, the temperature of the reaction flask was raised to room temperature, and then the solution was stirred an additional 2 h. The reaction was quenched with water, the organic layer was collected with ether, washed with water, dried over magnesium sulfate, and filtered, and then the solvents were removed in vacuo. Multiple isomers of the product were recovered. An additional 16 g of material was recovered by repeated washing of the lithium prill. The product was recovered as a yellow solid Yield: 139.1 (75%), 78.5% by GC, used in subsequent steps without additional purification. ^{1}H NMR (CD_2Cl_2): δ 7.2−7.8 (m, 4H), 4.9 (0.5H), 4.8 (0.5H), 2.6−3.2 (m, 3H), 2.4−2.6 (m, 3H), 1.1−1.3 (m, 3H). ^{13}C NMR (CD_2Cl_2): δ 146.8, 140.2, 136.4, 129.5, 129−127, 80.8, 74.4, 73.7, 49.0, 43.9, 35.7, 35.4, 35.2, 19.4, 15.3, 15.27, 14.7. EIMS: *m*/*z* (relative intensity) 244 (100), 229 (48), 211 (26), 201 (21), 188 (10) 187 (12), 185 (15), 184 (14), 178 (16), 171 (13), 167 (12), 165 (16), 153 (11), 152 (13), 115 (17).

2,5-Dimethyl-3-phenyl-6-hydrocyclopenta[1,2-*b*]thiophene (18). To a solution containing 28 g (114.3 mmol) of **17** dissolved in 100 mL of toluene was added a 1-g portion of *p*-toluenesulfonic acid (*p*-TSA), and the mixture was refluxed for 30 min. The reaction mixture was quenched with water, and the organic layer was separated. The organic layer was washed with bicarbonate and water and dried ($MgSO_4$), and then the solvents were removed in vacuo. A dark red oil was recovered (two isomers). Yield: 26.6 g (90%), 87% by GC. ^{1}H NMR (CD_2Cl_2): δ 6.8−7.6 (m, 5H), 6.1−6.3 (2s, 1H), 3.1, 2.9 (s, 2H), 2.3 (m, 3H), 1.9 (m, 3H). ^{13}C NMR (CD_2Cl_2): δ 150.6, 146.9, 145.9, 145.6, 141.0, 137.0, 136.8, 135.8, 134.3, 131.3, 129.5, 129.1, 128.8, 127.1, 126.9, 123.5, 122.4, 41.0, 40.8, 17.2, 17.1, 15.1, 15.0. EIMS: *m*/*z* (relative intensity) 227 (20), 226 (100), 225 (34), 211 (34), 210 (17), 209 (10), 193 (19), 178 (28).

(2,5-Me$_2$-3-Ph-6-hydrocyclopenta[2,3-*b*]thiophen-6-yl)$_2$SiMe$_2$ (24). To a solution containing 22.6 g (100 mmol) of **18** dissolved in THF (80 mL) was added a 2.5 M solution of *n*-butyllithium in hexane (100 mmol, 40 mL) at room temperature. The contents of the flask were stirred for an additional 5 h. In a separate flask was added 6.45 g (50 mmol) of dichlorodimethylsilane dissolved in THF (40 mL). The temperature was lowered to −78 °C, and then the THF solution containing the anion prepared above was added dropwise. After addition was complete, the flask and contents were allowed to warm to room temperature and stirred for 6 h. The reaction mixture was poured onto water, and then the organic fraction was collected with dichloromethane, dried over magnesium sulfate, and concentrated in vacuo. The solids were recrystallized from ether, collected on a medium glass frit filter, and dried in vacuo, producing an off-white powder: Yield: 11.33 g (45%), 99% by GC. ^{1}H NMR (CD_2Cl_2): δ 7.2−7.6 (m, 10H), 6.2, 6.5, 6.55 (s, 2H), 3.85, 4.08 (s, 2H), 2.5 (s, 6H), 2.1−2.4 (m, 6H), −0.2, −0.55, −0.75 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 136.9, 135.7, 129.5−122.44, 123.4−121.7, 68.2, 40.8, 40.7, 18.1, 17.7, 15.0, −202, −2.5. EIMS: *m*/*z* (relative intensity) 509.1 (9) 508 (22) 283 (100), 255 (10), 241 (6), 210 (6), 178 (18), 152 (3).

{Me$_2$Si(2,5-Me$_2$-3-Ph-cyclopento[2,3-*b*]thiophen-6-yl)$_2$}ZrCl$_2$ (5). To a solution containing 1.82 g (3.6 mmol) of **24** slurried in 100 mL of diethyl ether was added a 2.5 M solution of *n*-butyllithium in hexane (2.9 mL, 7.2 mmol) dropwise at room temperature. Stirring was continued for 5 h, and then 0.83 g (3.6 mmol) of zirconium tetrachloride was added slowly as a dry powder. The reaction mixture was stirred an additional 3 h, and then the solution was filtered. The solids collected in this fashion were washed with ether, and then the solvents were removed in vacuo, leaving 770 mg of a 3:5 *rac*/*meso* mixture. The solids remaining on the filter were then slurried in dichloromethane and filtered, and the solvents were removed from the solution in vacuo. A 350 mg amount of pure *rac* isomer was recovered. Yield: 1.12 g (47%). ^{1}H NMR (CD_2Cl_2): δ 7.25−7.6 (m, 10H, *rac*), 6.58 (s, 2H, *rac*), 2.55 (s, 3H, *rac*), 2.3 (s, 3H, *rac*), 1.05 (s, 6H, *rac*). ^{13}C NMR (CD_2Cl_2): δ 168.8, 147.6, 145.3, 135.5, 135.4, 129.95, 129.47, 128.2, 119.0, 85, 19.9, 16.0, 0.0. EIMS: *m*/*z* 669 ($M^{\bullet+}$ + 1 of theo).

2-Methyl-3-(2-methylphenyl)thiophene (25). An ether solution of *o*-tolylmagnesium bromide (350 mL, 2.0 M, 0.7 mol) was added slowly to a mixture of 3-bromo-2-methylthiophene, **14** (123 g, 0.7 mol), and 1.2 g of Ni(dppp)Cl$_2$ in 50 mL of ether. After the mixture was stirred overnight, water (200 mL) was added slowly to the reaction mixture at room temperature. The organic layer was separated, washed with brine solution (100 mL), and dried ($MgSO_4$). Solvents were removed in vacuo. Yield: 136 g, used without further purification. ^{1}H NMR ($CDCl_3$): δ 7.2−7.4 (m, 4H), 7.18 (t, 1H), 6.98 (t, 1H), 2.35 (d, 3H), 2.27 (d, 3H). EIMS: *m*/*z* (relative intensity) 188 ([M^+], 100), 173 (62), 155 (34), 141 (9), 128 (33), 115 (15).

2,5-Dimethyl-3-(2-mehylphenyl)-5,6-dihydrocyclopenta[1,2-*b*]-thiophen-4-one (26). A solution of **25** (80 g, 0.43mol) and methacrylic acid (44 g, 0.51mol) in 100 mL of dichloroethane was added dropwise to 1000 g of super PPA at 80 °C and stirred for 5 h. The dark red mixture was poured onto crushed ice (1000 g) and stirred until the PPA was completely decomposed. The product was extracted with 30% (v/v) dichloromethane in hexane (2 × 400 mL). The combined organic fractions were washed with a saturated aqueous solution of $NaHCO_3$ and dried ($MgSO_4$). Solvents were removed on a rotary evaporator, leaving 74 g of product, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 7.1−7.3 (m, 3H), 7.0 (d, 1H) 2.7−3.0 (m, 2H), 2.25 (s, 3H), 2.18 (m, 1H), 2.05 (s, 3H), 1.2 (d, 3H). ^{13}C NMR ($CDCl_3$): δ 199.6, 167.3, 152.2, 136.6, 135.9, 133.4, 130.2, 129.7, 128.1, 125.8, 46.1, 46.0, 32.8, 19.5, 16.9, 15.4. EIMS: *m*/*z* (relative intensity) 256 ([M^+], 85), 241 (100), 227 (6), 213 (35), 199 (22), 184 (7), 165 (15), 152 (9), 128 (11).

2,5-Dimethyl-3-(2-methylphenyl)-6-hydrocyclopenta[1,2-*b*]thiophene (27). A solution of **26** (74 g, 0.286 mol) in 200 mL of THF was treated with 145 mL of $LiAlH_4$ in THF (1.0 M, 0.145 mol) at 0 °C. After the solution was stirred at room temperature for 3 h, water was added cautiously (50 mL), and the resulting slurry was filtered. THF was evaporated from the filtrate, and the solid filter cake was washed with dichloromethane (3 × 150 mL). The dichloromethane wash and filtrate residue were combined, washed with water (50 mL), dried ($MgSO_4$), and evaporated to a brown liquid (67.2 g). The crude product was redissolved in 250 mL of toluene and stirred with 2.0 g of *p*-TSA at 70 °C for 1.5 h. After cooling, the toluene solution was washed with water (50 mL), $NaHCO_3$ solution (50 mL), and brine solution (50 mL) and dried ($MgSO_4$). Solvents were removed on a rotary evaporator, leaving a brown oil. Distillation (120 °C, ∼0.05 Torr) gave a light yellow liquid. Yield: 47 g (68%). Two isomers were recovered. ^{1}H NMR ($CDCl_3$): δ 7.1−7.3 (m, 4H), 6.7 (m, 1H), 6.4 (m, 1H), 3.6 (s, 2H), 3.2 (ss, 2H), 2.6 (s, 3H), 2.55 (s, 3H), 2.47 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 146.2, 145.2, 137.0, 136.4, 134.2, 133.7. 130.2, 130.0, 129.5, 127.5, 127.4, 125.7, 123.4, 122.4, 40.1, 19.9, 17.1, 14.4. EIMS: *m*/*z* (relative intensity) 240 ([M^+], 100), 225 (65), 210 (10), 192 (20), 178 (8), 165 (15), 149 (5), 128 (5).

Analytical Data for the Lithium Salt of 27 Prepared by Reaction with *n*-Butyllithium. ^{1}H NMR (THF-d_8): δ 7.2 (m, 2H), 7.1 (m, 2H), 5.5 (d, 1H), 5.22 (d, 1H), 2.19 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (THF-d_8): δ 140.3, 137.9, 131.2, 130.5, 126.8, 125.7, 124.1, 120.1, 117.2, 92.4, 91.9, 20.6, 16.4, 15.2.

(2,5-Me$_2$-3-(2-MePh)-6-hydrocyclopenta[2,3-*b*]thiophen-6-yl)$_2$Si-Me$_2$ (28). A solution of **27** (36.9 g, 0.154 mol) in 150 mL of THF was

cooled to −78 °C and treated with 62 mL of *n*-butyllithium in hexanes (2.5 M, 0.155 mol). After being stirred for 16 h at room temperature, the solution was added dropwise to a solution of dichlorodimethylsilane (9.94 g, 0.077 mol) in 70 mL of THF with stirring at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 days. A saturated aqueous solution of NH_4Cl was added slowly (10 mL), and most of the THF was removed on a rotary evaporator. The residue was partitioned with ether (500 mL) and water (150 mL). The water layer was separated and re-extracted with fresh ether (100 mL), and the combined ether fractions were dried ($MgSO_4$). Evaporation of solvent yielded 41 g of product as an off-white solid (91% purity by GC). An 18.7 g amount of crude product was chromatographed on silica (5% CH_2Cl_2/hexane), giving 13.3 g of the target as a mixture of isomers. EIMS: *m*/*z* (relative intensity) 536 ([M^+], 22), 297 (100), 281 (6), 223 (5), 192 (12), 165 (6). The proton NMR spectrum showed a complex mixture of isomers.

Analytical Data for the Lithium Salt of 28 Prepared by Reaction with *n*-Butyllithium. ^{1}H NMR (THF-d_8): δ 7.08−7.18 (m, 8H), 5.43 (s, 2H), 2.28 (d, 3H), 2.21 (d, 3H), 1.19 (s, 3H), 0.89 (d, 3H), 0.63 (s, 3H).

{Me$_2$Si(2,5-Me$_2$-3-(2-MePh)-cyclopento[2,3-*b*]thiophen-6-yl)$_2$}-ZrCl$_2$ (6). A solution of **28** (27.6 g, 51.5 mmol) in 200 mL of ether was cooled to −78 °C and treated with 42 mL of *n*-butyllithium in hexanes (2.5 M, 105 mmol). After the solution was stirred overnight at room temperature, solvents were removed in vacuo, and pentane (150 mL) was added. The yellow slurry was cooled to −78 °C and treated with $ZrCl_4$ (11.7 g, 50.2 mmol). The reaction mixture was warmed to room temperature, stirred for 18 h, and filtered through a closed frit. The yellow solids were washed with pentane (60 mL) and dried under vacuum, giving 33.8 g of crude product. The crude product was stirred in 400 mL of dichloromethane at room temperature and filtered through Celite. Evaporation of the filtrate under reduced pressure gave the product as a 50/50 *rac/meso* mixture (27.9 g, 78.5%). The isomers were separated by dissolving a portion of the *rac/meso* mixture in dichloromethane, adding an equal volume of hexane, and partially evaporating dichloromethane under reduced pressure. In this way, the *meso* isomer was precipitated from the solution and removed by filtration. After a second filtration, solvents were removed from the filtrate, giving the *rac* isomer in ca. 95% purity. ^{1}H NMR (CD_2Cl_2): δ 7.65 (m, 2H, *meso*), 7.60 (m, 2H, *rac*), 7.27 (m, 6H, *meso*), 7.26 (m, 6H, *rac*), 6.33 (s, 2H, *rac*), 6.18 (s, 2H, *meso*), 2.34 (s, 6H, *rac*), 2.32 (s, 6H, *meso*), 2.30 (s, 6H, *rac*), 2.25 (s, 6H, *meso*), 2.09 (s, 6H, *rac*), 2.03 (s, 6H, *meso*), 1.17 (s, 3H, *meso*), 1.13 (s, 3H, *meso*), 1.08 (s, 6H, *rac*). ^{13}C NMR (CD_2Cl_2): δ (*rac* isomer) 148.1, 145.6, 137.3, 134.6, 134.4, 130.8, 130.4, 129.6, 128.2, 126.3, 125.2, 118.5, 19.5, 19.47, 15.2, −0.57. EIMS: *m*/*z* 697 ($M^{\bullet+}$ + 1 of theo).

2-Me-3-(2,5-Me$_2$Ph)thiophene (29). An ether solution of 2,5-dimethylphenylmagnesium bromide (400 mL of a 0.6 M concentration, 0.24 mol) was added slowly to a mixture of 3-bromo-2-methylthiophene, **14** (42.5 g, 0.24 mol), and 1.2 g of Ni(dppp)Cl_2 in 100 mL of ether. After the solution was stirred overnight, water (200 mL) was added cautiously, and the organic layer was separated, washed with brine solution (100 mL), and dried ($MgSO_4$). Evaporation of solvent and starting material yielded 47 g of product, which was used without further purification. EIMS: *m*/*z* (relative intensity) 202 (M^+, 100), 187 (78), 171 (29), 154 (15), 128 (16), 115 (13).

2,5-Dimethyl-3-(2,5-dimethylphenyl)-5,6-dihydrocyclopenta[1,2-*b*]thiophen-4-one (30). A solution of **29** (47 g, 0.23 mol) and methacrylic acid (24 g, 0.28 mol) in 125 mL of dichloroethane was added dropwise to 1000 g of super PPA at 90 °C and stirred for 24 h. The dark red mixture was poured onto crushed ice (1000 g) and stirred until the PPA was completely decomposed. The product was extracted with 25% (v/v) dichloromethane in hexane (2 × 400 mL). The combined organic fractions were washed with a saturated aqueous solution of $NaHCO_3$ and dried ($MgSO_4$). Solvents were removed on a rotary evaporator, leaving 59 g of brown oil. The product was purified by chromatography on silica with 50% (v/v) dichloromethane in hexane. Yield: 26.1 g (42%). ^{1}H NMR ($CDCl_3$): δ 7. (d, 1H), 7.15 (d, 1H), 6.92 (s, 1H), 2.95 (m, 2H), 2.5 (m, 1H), 2.38 (s, 1H), 2.35 (s, 3H), 2.1 (s, 3H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 152.1, 136.2, 135.9, 135,3, 133.5, 133.3, 130.22, 130.20, 130.11, 128.9, 122.5, 46.1, 32.9, 20.8, 19.1, 16.9, 15.4. EIMS: *m*/*z* (relative intensity) 270 (M^+, 86), 255 (100), 241 (6), 227 (37), 213 (25), 198 (11), 179 (10), 141 (7), 128 (15).

2,5-Dimethyl-3-(2,5-dimethylphenyl)-6-hydrocyclopenta[1,2-*b*]-thiophene (31). A solution of **30** (26.1 g, 97 mmol) in 75 mL of THF was treated with 48 mL of $LiAlH_4$ in ether (1.0 M solution, 48 mmol) at 0 °C. After the solution was stirred at room temperature for 5 h, water was added cautiously (10 mL), and the resulting slurry was filtered through a plug of Celite. THF was evaporated from the filtrate, and the filter cake was washed with dichloromethane (3 × 50 mL). The dichloromethane fractions were combined with the filtrate residue and washed with water (50 mL). After drying ($MgSO_4$), the solvent was removed on a rotary evaporator. The product was dissolved in toluene (60 mL) and stirred with 0.4 g of *p*-TSA at 60 °C for 3 h. After cooling, the toluene solution was washed with water (50 mL), $NaHCO_3$ solution (50 mL), and brine solution (50 mL) and dried ($MgSO_4$). Toluene was removed on a rotary evaporator, and the product was purified by distillation (110 °C, ∼0.05 Torr). Yield: 11.5 g (47%). ^{1}H NMR ($CDCl_3$): δ 7.19 (d, 1H), 7.1 (d, 1H), 7.0 (s, 1H), 6.41(s, 1H), 2.93 & 2.90 (ss, 2H, 2 isomers), 2.35 (s, 3H), 2.25 (s, 3H), 2.12 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 146.0, 144.9, 140.1, 136.0, 134.8, 134.1. 133.6, 133.3, 130.4, 129.8, 128.0, 122.1, 39.9, 20.9, 19.1, 16.9, 14.2. EIMS: *m*/*z* (relative intensity) 254 (M^+, 100), 239 (75), 224 (16), 206 (20), 191 (11), 178 (10), 165 (10), 149 (6), 128 (9).

(2,5-Me$_2$-3-(2,5-Me$_2$Ph)-6-hydrocyclopenta[2,3-*b*]thiophen-6-yl)$_2$-SiMe$_2$ (32). A solution of **31** (10.6 g, 41.7 mmol) in 60 mL of THF was cooled to −78 °C and treated with 17 mL of *n*-butyllithium in hexanes (2.5 M solution, 42.5 mmol). After being stirred for 16 h at room temperature, the reaction mixture was added dropwise to a solution of dichlorodimethylsilane (2.69 g, 20.9 mmol) in 30 mL of THF at −78 °C. The cold bath was removed and stirring continued for 18 h at room temperature before the reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL). The reaction product was diluted with ether (250 mL) and washed with water (100 mL). After drying ($MgSO_4$), solvents were removed on a rotary evaporator. The product was purified by chromatography on silica with 5% (v/v) dichloromethane in hexane. Yield: 7.0 g (59%).

Major Isomer of 32. ^{1}H NMR ($CDCl_3$): δ 6.9−7.2 (m, 6H), 6.2 (s, 2H), 3.85 (s, 2H), 2.35(s, 6H), 2.25 (s, 6H), 2.20 (s, 6H), 2.10 (s, 6H), − 0.12 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 149.7, 146.2, 145.9 135.8, 135.6, 134.9, 134.8, 130.8 129.9, 127.8, 123.0, 122.1, 46.2, 20.9, 19.4, 18.0, 14.3, −7.5, −8.9. EIMS: *m*/*z* (relative intensity) 564 (M^+, 25), 311 (100), 282 (6), 253 (4), 237 (5), 206 (12), 189 (5), 165 (3), 128 (3).

{Me$_2$Si(2,5-Me$_2$-3-(2,5-Me$_2$Ph)-cyclopento[2,3-*b*]thiophen-6-yl)$_2$}-ZrCl$_2$ (7). A solution of **32** (2.33 g, 4.1 mmol) in 50 mL of ether was treated with 3.4 mL of *n*-butyllithium in hexanes (2.5 M solution, 8.5 mmol). After the solution was stirred overnight at room temperature, solvents were removed in vacuo, and $ZrCl_4$ (0.96 g, 4.1 mmol) was added. Pentane (60 mL) was added, and the mixture was stirred for 24 h. The solids were collected on a closed frit, washed with pentane, and dried under vacuum. The crude product was stirred in 100 mL of dichloromethane and filtered through Celite. The solvent was removed under reduced pressure, giving the product as yellow solids (2.5 g, 50/50 *rac/meso* mixture). A portion of the product was redissolved in dichloromethane and treated with heptane, giving a light yellow precipitate that was removed by filtration. The filtrate was concentrated under reduced pressure until the solution became cloudy. Upon standing, the *rac* isomer crystallized from the solution and was collected on a closed frit. ^{1}H NMR (CD_2Cl_2): δ 7.43 (s, 2H, *meso*), 7.40 (s, 2H, *rac*), 7.16 (d, 2H, *rac*), 7.15 (d, 2H, *meso*), 7.10 (d, 2H, *rac*), 7.09 (d, 2H, *meso*), 6.32 (s, 2H, *rac*), 6.19 (s, 2H, *meso*), 2.34 (ss, 12H, *meso*), 2.33 (ss, 12H, *rac*), 2.29 (s, 6H, *rac*), 2.25 (s, 6H, *meso*), 2.02 (s, 6H, *rac*), 1.19 (s, 3H, *meso*), 1.15 (s, 3H, *meso*), 1.10 (s, 6H, *rac*). ^{13}C NMR (CD_2Cl_2): δ (*rac* isomer) 148.0, 145.5, 135.7, 134.5, 134.2, 134.1, 131.3, 130.3, 129.9, 128.9, 125.2, 118.5, 21.1, 19.5, 19.3, 15.2, −0.58. EIMS: *m*/*z* 725 ($M^{\bullet+}$ + 1 of theo).

Pseudo-*meso*-{Me$_2$Si(2,5-Me$_2$-1-Ph-cyclopento[3,2-*b*]pyrrol-4-yl)-(2-Me-4-Ph-inden-1-yl)}ZrCl$_2$ (8). A 50/50 *rac/meso* isomer mixture of {Me$_2$Si(2,5-Me$_2$-1-Ph-cyclopento[3,2-*b*]pyrrol-4-yl)(2-Me-4-Ph-inden-1-yl)}$ZrCl_2$ was dissolved in dichloromethane, concentrated under reduced pressure, and placed in a freezer at −10 °C. After 24 h, the

liquid was poured off from the crystallized pseudo-*meso* isomer **8**. The crystalline product was washed with pentane and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of **8**. ^{1}H NMR (CD_2Cl_2): δ 7.65−7.71 (m, 1H), 7.16−7.64 (m, 11H), 6.89−7.16 (m, 1H), 6.79 (s, 1H), 5.99 (s, 1H), 5.89 (s, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H), 1.29 (s, 3H), 1.17 (s, 3H). Anal. Calcd for $C_{33}H_{31}Cl_2NSiZr$: C, 62.73; H, 4.95. Found: C, 63.65; H, 5.07.

Crystal Structure Determinations. Suitable crystals were selected under an inert atmosphere and sealed in thin-walled capillary tubes. Preliminary unit cell determinations were obtained by harvesting reflections from three orthogonal sets of 15 frames, using −0.3° ω scans. These results were confirmed by refinement of unit cell parameters during integration. Crystallographic information is summarized in Table 1. All structures were solved using direct methods. Non-hydrogen atoms were located by difference Fourier synthesis and were refined anisotropically. Hydrogen atoms were added at calculated positions and treated as isotropic contributions, with thermal parameters defined as 1.2 or 1.5 times that of the parent atom. All software and sources of scattering factors are contained in the SHELXTL program library (version 5.10, G. Sheldrick, Bruker-AXS, Madison, WI.)

The systematic absences in diffraction data for **3**, **5**, **6**, and **8** were consistent with the reported space groups.[29] The *E*-statistics for **3** suggested a noncentrosymmetric space group. The correct absolute structure was unambiguously determined; Flack parameter = 0.08(5). Compound **6**, which was treated as centrosymmetric at all stages of data processing, cocrystallized with one molecule of dichloromethane. The solvent atoms were located in the difference map and refined anisotropically. Compound **8** cocrystallized with half of a molecule of dichloromethane disordered over eight positions in the unit cell. Squeeze/Platon[30] was applied to resolve the disordered solvent. Within the 804.5 Å^3 void space occupied by solvent molecules, a total of 199 electrons was calculated, compared to 168 electrons predicted for the presence of four molecules of dichloromethane. In this treatment, the contribution of the solvent molecules is collective and not as individual atoms. Hence, the atom list does not contain the atoms of the solvent molecules.

Polymerization Procedures. Polymerization grade propylene was purchased from the Matheson Gas Co. and further purified by passing through columns of 3-Å molecular sieves and alumina. Methyl alumoxane (toluene solution, 10% MAO, 4.92% Al) was purchased from Witco Corp. and used as received. Al(*i*-Bu)$_3$ (24.5 wt % solution in heptane) was purchased from Akzo Nobel Chemicals. [CPh_3][$B(C_6F_5)_4$] was received from Asahi Glass Co.

Liquid Propylene Polymerizations. Polymerizations were conducted in a 1- or 10-gal stainless steel autoclave equipped with an air-driven Magnadrive (Autoclave Engineers Co.) stirrer and a steam/water temperature-controlled jacket. The autoclave was swept with dry argon at 90 °C for 1 h prior to polymerization. For MAO-activated catalysts, the zirconocene was dissolved in a 10 wt % toluene solution of MAO, shaken for 10 min, and added to the reactor at 15 °C. Propylene (2.2 L) was added, stirring was initiated (500 rpm), and the reactor and contents were heated to the polymerization temperature within 5−7 min. For [CPh_3][$B(C_6F_5)_4$]-activated catalysts, a toluene solution of the zirconocene and Al(*i*-Bu)$_3$ was added to the reactor at 15 °C, followed by propylene (2.2 or 22 L for 1- and 10-gal reactor, respectively). Stirring was initiated (500 rpm), a toluene solution of [CPh_3][$B(C_6F_5)_4$] was charged to the reactor with 100 mL of propane, and the contents were heated to the polymerization temperature within 5−7 min. In all polymerization tests, carbon monoxide gas was charged to the reactor 1 h after reaching polymerization temperature, and the residual monomer was vented while the reactor was cooled to room temperature. The polymer was removed and dried in a vacuum oven at 50 °C for 1 h before being weighed. Reported activities were calculated from polymer and zirconocene weights.

Polymer Analyses. For polymer NMR analyses, the solution ^{13}C NMR spectra were run at 75.4 MHz on a Varian UNITY-300 NMR spectrometer. The as-polymerized samples were run as 10% (w/v) solutions in *o*-dichlorobenzene-d_4 at 130 °C. All samples were obtained with 100% *rac* isomers, except **3** and **4**, which were 50/50 *rac* and *meso*. The pentads for these latter two samples were calculated with a two-site statistical model and are consistent with the *meso* isomers producing a lower fraction of APP with about 50% *m* placements and no regioirregularities.[27] Chemical shifts are referenced to TMS using a secondary reference, the CH_3 methyl peak of polypropylene at 21.8 ppm. Five thousand transients were accumulated for each spectrum with a 10-s delay between pulses. Decoupling was always on during acquisition, so the nuclear Overhauser enhancement was present. Solution intrinsic viscosity $[\eta]_o$ of polymer samples were determined in Decalin at 135 °C. The intrinsic viscosities were converted to weight-average molecular mass (M_w) by gel permeation chromatography (GPC) using an empirical correlation of M_w and $[\eta]_o$ for metallocene-catalyzed polypropylene homopolymers ($\log [\eta]_o = -3.8996 + (0.7748 \log\{M_w\})$.[31] M_w values for several of the polymer samples were also measured directly by GPC (Waters 150 C instrument, 1,2,4-trichlorobenzene, ToyoSoda GMXHLT mixed-bed columns, polystyrene standards, data reported in terms of polypropylene equivalents). The transition temperature and enthalpy of melting and crystallization of polymer samples were measured using a power compensation mode Perkin-Elmer (PE) DSC-7 and PE PYRIS (revision 3.03) software. A PE Intercooler II (model FC100PEA) was used for cooling. The instrument was calibrated against certified (1) indium with T_{eim} = 156.60 °C; H_f = 28.71 J/g and (2) tin with T_{eim} = 231.88 °C; H_f = 60.46 J/g. The dynamic heating /cooling rate was 20 °C/min. The purge gas was nitrogen flowing at 20 ± 2 cm^3/min. A three-ramp (heat−cool−reheat) procedure was employed with upper and lower temperature limits of 25 and 235 °C, respectively. The isothermal hold time between ramps was 3 min. The results of the second heating are reported.

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Supporting Information Available: X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) For $C_{30}H_{28}Cl_2N_2SiZr$ (**3**): tetragonal, $P4_12_12$, a = 12.7198(2) Å, c = 34.1068(2) Å, V = 5518.25(6) Å^3, Z = 8, FW = 606.75 g mol^{-1}, T = 173(2) K, D_{calc} = 1.461 g cm^{-3}, orange block, GOF = 1.135, μ(Mo Kα) = 65.8 cm^{-1}, λ = 0.71073 Å, Flack = 0.08(5), $R(F)$ = 3.74% for 6582 observed independent reflections (4° ≤ 2θ ≤ 57°). For $C_{39}H_{38}Cl_2S_2SiZr$ (**5**): monoclinic, $P2_1/c$, a = 9.5183(2) Å, b = 35.7383(3) Å, c = 8.8314(2) Å, β = 91.6932(11)°, V = 3002.85(7) Å^3, Z = 4, FW = 668.89 g mol^{-1}, T = 243(2) K, D_{calc} = 1.480 g cm^{-3}, yellow block, GOF = 1.808, μ(Mo Kα) = 74.4 cm^{-1}, λ = 0.71073 Å, $R(F)$ = 9.85% for 4560 observed independent reflections (4° ≤ 2θ ≤ 48°). For $C_{35}H_{36}Cl_4S_2SiZr$ (**6**): triclinic, $P\bar{1}$, a = 11.7096(2) Å, b = 12.6751(2) Å, c = 12.7721(2) Å, α = 96.9974(7)°, β = 106.8513(5)°, γ = 100.2661(3)°, V = 1754.65(3) Å^3, Z = 2, FW = 781.87 g mol^{-1}, T = 173(2) K, D_{calc} = 1.480 g cm^{-3}, yellow block, GOF = 0.959, μ(Mo Kα) = 79.6 cm^{-1}, λ = 0.71073 Å, $R(F)$ = 4.10% for 8065 observed independent reflections (4° ≤ 2θ ≤ 57°). For $C_{33.5}H_{32}Cl_3NSiZr$ (**8**·0.5CH_2Cl_2): monoclinic, $I2/a$, a = 13.7403(2) Å, b = 17.3226(2) Å, c = 26.3308(3) Å, β = 91.6470(2)°, V = 6264.61(8) Å^3, Z = 8, FW = 674.26 g mol^{-1}, T = 173(2) K, D_{calc} = 1.430 g cm^{-3}, yellow blade, GOF = 1.162, μ(Mo Kα) = 66.9 cm^{-1}, λ = 0.71073 Å, $R(F)$ = 4.55% for 5337 observed independent reflections (4° ≤ 2θ ≤ 50°). This compound also crystallized in a second chemically identical form, with the formula $C_{34}H_{33}Cl_4NSiZr$ (**8**·CH_2Cl_2): monoclinic, $P2_1/c$, a = 14.4422(3) Å, b = 16.9027(3) Å, c = 13.2029(2) Å, β = 97.0413(3)°, V = 3198.68(13) Å^3, Z = 4, FW = 716.72 g mol^{-1}, T = 173(2) K, D_{calc} = 1.488 g cm^{-3}, orange plate, GOF = 1.756, μ(Mo Kα) = 74.1 cm^{-1}, λ = 0.71073 Å, $R(F)$ = 8.08% for 4638 observed independent reflections (4° ≤ 2θ ≤ 48°).

(30) Platon, Spek, A. L. *Acta Crystallogr*. **1990**, *A46*, C34.

(31) Phillips, R. A., personal communication.