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Synthesis of Unbridged Bis(2-R-indenyl)zirconocenes Containing Functional Groups and Investigations in Propylene Polymerization

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Five new indenyl zirconium metallocenes with 2-alkyl and 2-aryl substituents were synthesized and characterized. For the synthesis of the ligand the di-Grignard reagent 1,2-bis(magnesiomethyl)benzene dichloride was explored as a synthon to 2-substituted indenes. This procedure provides access to a variety of functionalized 2-indenylmetallocenes such as bis(2-ferrocenylindene)zirconium dichloride and bis(2-adamantylindenyl)zirconium dichloride. Crystallographic characterization of bis[2-(4-(dimethylamino)phenyl)indenyl] zirconium dichloride revealed an *anti* conformation with a coplanar orientation of the dimethylamino substituent to the aryl ring in the solid state. The polymerization behavior of all five zirconocene dichlorides in liquid propylene was studied in the presence of MAO at various temperatures, and the results were compared to those for the known catalyst system bis-(2-phenylindenyl)zirconium dichloride/MAO (**M1**/MAO). The productivity of the 2-arylindene metallocenes in propylene polymerization was on the order of 100−7000 kg of PP/((mol of Zr) h). In contrast, the (2-adamantylindenyl)metallocenes exhibited very low productivities of 6 kg PP/((mol of Zr) h) in propylene polymerization.

Introduction

Since the discovery that group 4 metallocenes could be activated by methylaluminoxane (MAO) to polymerize propylene, the field of metallocene design has dramatically expanded.[1−3] Group 4 metallocenes have been developed to produce atactic, isotactic, hemiisotactic, syndiotactic, and stereoblock polypropylene.[3]

The synthesis of elastomeric polypropylene using metallocene catalysts was first reported by Chien and co-workers with a stereorigid chiral *ansa*-titanocene.[4−6] Collins has also developed a family of chiral metallocenes for the production of elastomeric polypropylene.[7−9] We have been investigating a class of unbridged bis(2-arylindene)metallocenes for the synthesis of stereoblock elastomeric polypropylenes.[10−17] These catalysts were designed to interconvert between chiral and achiral torsional isomers[18−20] on the time scale of the polymerization reaction in order to produce an isotactic and atactic stereoblock structure (Figure 1). The nature of the substituent in the 2-position of the indenyl ligand is crucial; unbridged bis(indenyl)zirconium dichloride/MAO and a variety of bis(2-alkylindenyl)zirconocenes produce atactic polypropylenes.[14,21−23]

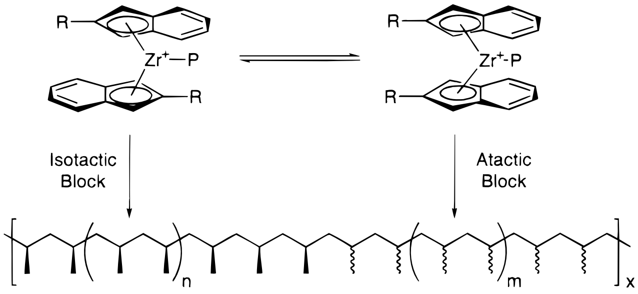

Figure 1. Proposed mechanism for formation of stereoblock polypropylene.

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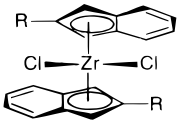
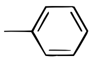
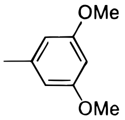
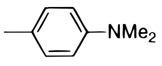
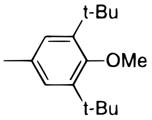
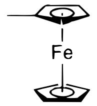
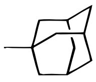
Table 1. Numbering Scheme and Yield of Ligands and Zirconocene Dichlorides



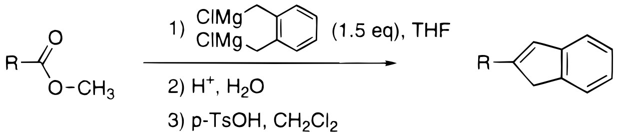
Substituent R:						
Ligand						
L	1	2	3	4	5	6
(Yield)		(45%)	(75%)	(87%)	(68%)	(56%)
Metallocene						
L_2ZrCl_2	M1	M2	M3	M4	M5	M6
(Yield)		(50%)	(10%)	(36%)	(>25%)	(29%)

As part of our investigations on the polymerization behavior of unbridged indenylmetallocenes, we have examined the effects of 1-substitution on the indene,[12] the nature of the metal atom,[13] the ligand aromaticity,[14] and the steric and inductive effect of the aryl substituent[11,15] on the polymerization behavior. We present here a further study of the influence of the 2-substituent with particular regard to aryl substituents containing heteroatoms and sterically demanding substituents such as an adamantyl group. Five new 2-substituted indenylzirconocenes have been synthesized (Table 1: **M2**−**M6**), characterized, evaluated, and compared to bis(2-phenylindenyl)zirconium dichloride (**M1**) in propylene homopolymerization.

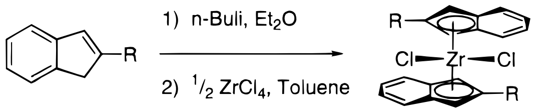
Results

Bis(2-phenylindenyl)zirconium dichloride (**M1**) was synthesized according to a literature procedure.[10,13] This method involves nucleophilic attack of phenylmagnesium bromide on 2-indanone. A major drawback of this method is the susceptibility of 2-indanone to enolization.[23] This is particularly troublesome for most organolithium nucleophiles as well as sterically demanding nucleophiles. In our efforts to prepare 2-ferrocenylindene[24] (**5**) we searched for a complementary approach that would accommodate the introduction of more sterically demanding substituents at the 2-position. We found that this could easily be realized by reaction of the di-Grignard reagent 1,2-di(magnesiomethyl)benzene dichloride, first reported by Lappert et al.,[25] with the corresponding methyl ester of the sterically demanding substituent (Scheme 1). This method has been applied by Ellis et al. for the synthesis of 2,2′-bis(indenyl)biphenyl.[26] As shown below, this method proved a versatile way to synthesize a variety of 2-substituted indenes in reasonable to good yields (Table 1). The starting methyl esters, if not commercially available, were synthesized by nucleophilic attack of the carboxylic acid on iodomethane.[27,28]

Scheme 1. Ligand Synthesis



Scheme 2. Metallocene Synthesis



The synthesis of the zirconocenes **M2**−**M6** from the corresponding indenes **2**−**6** was straightforward, through deprotonation of the ligand with *n*-butyllithium and reaction of the lithium salt of the ligand with zirconium tetrachloride in toluene (Scheme 2, Table 1).

Crystallization of bis[2-(4-(dimethylamino)phenyl)-indenyl]zirconium dichloride (**M3**) from methylene chloride/pentane at room temperature gave crystals suitable for X-ray structural analysis. **M3** crystallizes in a *anti* conformation (Figure 2), and shows many similarities to the structure of *rac*-bis(2-phenylindenyl)zirconium dichloride[29] (***rac*-M1**).[10] The dihedral angle between the Cp and the attached phenyl plane is small (11.16°); the Cp−Zr−Cp angle is 133°, so that the dihedral angle between the two phenyl planes is 24.68°. The dimethylamino group is tilted by a very small angle (3.0−4.6°) relative to the phenyl plane. Only one rotamer of the

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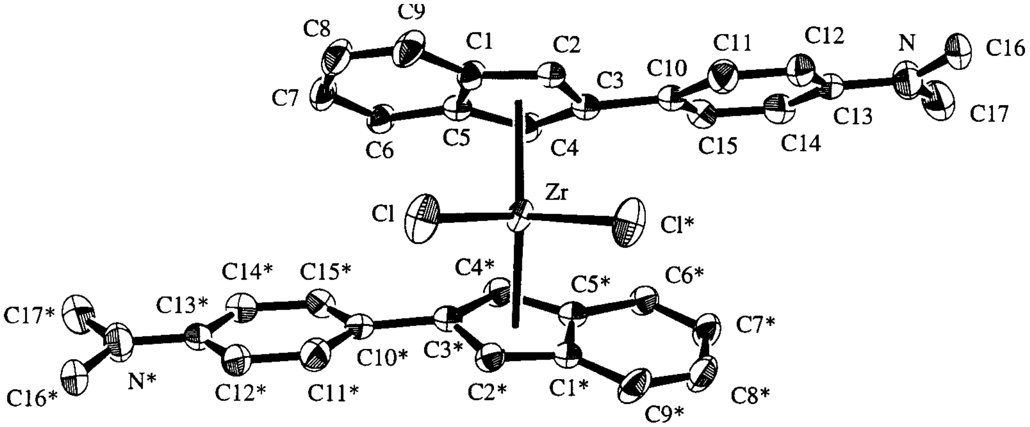

Figure 2. Perspective drawing of **M3** with atom-numbering scheme.

Table 2. Selected Bond Lengths (Å)[a] of M3

Zr−C1	2.614(3)	C13−N	1.385(4)
Zr−C2	2.556(4)	N−C16	1.439(5)
Zr−C3	2.562(3)	N−C17	1.446(6)
Zr−C4	2.451(3)	Zr−Cl	2.4252(9)
Zr−C5	2.517(3)	C3−C10	1.473(4)
av	2.54		

[a] Numbering scheme according to Figure 2.

Table 3. Selected Bond Angles[a] and Dihedral Angles (deg) between Least-Squares Planes[b] for M3 and *rac*-M1

M3		*rac*-M1[10]	
Cl−Zr−Cl*	96.70(5)	Cl−Zr−Cl*	95.44(4)
cp−Zr−cp′	133[c]	cp−Zr−cp′	131[c]
C16−N−C17	118.8(3)		
plane 1−plane 2	11.16	plane 1−plane 2	11.54
		plane 1*−plane 2*	13.53
plane 2−plane 2*	24.7	plane 2−plane 2*	23.9

[a] Numbering scheme according to ORTEP of **M3** and ***rac*-M1**,[10] respectively (Figure 2). [b] Legend: plane 1 = C1−C5, plane 1* = C1*-C5*, plane 2 = C10−C15, plane 2* = C10*-C15*. [c] The angle given is that between the centroids of the five-membered rings of the indenyl ligands (cp = plane 1, cp′ = plane 1*) and the zirconium atom.

two possible *anti* conformations was found in the crystal, in contrast to **M1**, where *anti* and *syn* rotamers are present in the unit cell.[10,30] Table 2 contains selected bond lengths of **M3**; Table 3 gives selected bond angles and the dihedral angles between the cyclopentadienyl and the phenyl planes.

The UV/vis absorption spectra of **M1**−**M6** were measured in methylene chloride (Figure 3). A general feature present in all spectra is the absorption at 280−290 nm. While **M1**−**M4** show a distinctive peak, **M3** and **M5** exhibit the highest extinction coefficient (approximately ϵ_{max} = 40 000 L/(mol cm). Most conspicuous is the difference of the spectra of dimethylamino-substituted **M3** relative to the other spectra with its intense absorption at 330 nm (ϵ_{max} = 37 980 L/(mol cm)) and 430 nm (ϵ_{max} = 16 916 L/(mol cm)). The spectrum of **M4** has a similar pattern with a less intense peak at 380 nm and a shoulder near 320 nm.

At room temperature, the ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of each zirconocene dichloride **M1**−**M6** exhibit time-averaged C_2 symmetry consistent with rapid rotation of the indenyl ligands around the indenylzirconium vector. **M1** is known to show no coalescence for the cyclopentadienyl protons down to −100 °C.[13] Although the Cp proton peaks begin to broaden below −60 °C, no decoalescence was observed for **M2**−**M4** down to a temperature of −110 °C (500 MHz, methylene chloride-d_2). At room temperature the Cp protons of the adamantyl-substituted **M6** appear as a sharp single resonance at 5.86 ppm. This resonance begins to broaden below −60 °C and disappears at −100 °C, indicating the onset of decoalescence near this temperature.

Propylene polymerizations were carried out in the presence of the zirconocene dichlorides **M1**−**M6** and MAO (Zr:Al = 1:(1000 ± 150)) in toluene solution in liquid propylene at several temperatures (Table 4). Catalysts derived from metallocenes **M1** and **M4** exhibit roughly comparable productivities; catalysts derived from **M2**, **M3**, and **M5** are 3−6 times less productive.[31] Due to the very low productivity of **M6** (6−7 kg of PP/((mol of Zr) h), 20 °C), its polymerization behavior was not investigated at different temperatures.

The weight-average molecular weights (M_w) of the produced polypropylenes are in the range of M_w = 100 000−860 000. All catalysts show a trend of lower M_w with increasing polymerization temperature. The molecular weight distributions of the polymers produced from these catalysts are broad; the polymer derived from **M3** exhibited a very broad polydispersity (M_w/M_n = 10.3) at 40 °C.[32]

The isotacticity of the produced polymers was investigated by ^{13}C NMR spectroscopy and is reported in terms of the mole fractions of isotactic pentads ([*mmmm*]).[33−35] The nature of the substituent in the

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(30) The preliminary X-ray structure of **M4** indicates that it also crystallizes in the *rac* conformation with both enantiomers in the unit cell. Unfortunately, disorder in the crystal structure prevents a more detailed comparison of the structures.

(31) The presence of some of the free ligand in the sample of metallocene **M3** may have resulted in an underestimation of the productivity of this catalyst.

(32) The broad molecular weight distributions appear to be a general trend for unbridged 2-arylindene catalysts that yield polymers of intermediate isotacticity. For the polymers reported here, the GPC traces are monomodal for all catalysts except **M2**, which shows a shoulder on the high-molecular-weight end of the distribution. The origin of these broad molecular weight distributions is not clear but is the subject of ongoing investigations.

(33) For random (atactic) polypropylene, [*mmmm*] = 6%; for pure isotactic polypropylene, [*mmmm*] = 100%.

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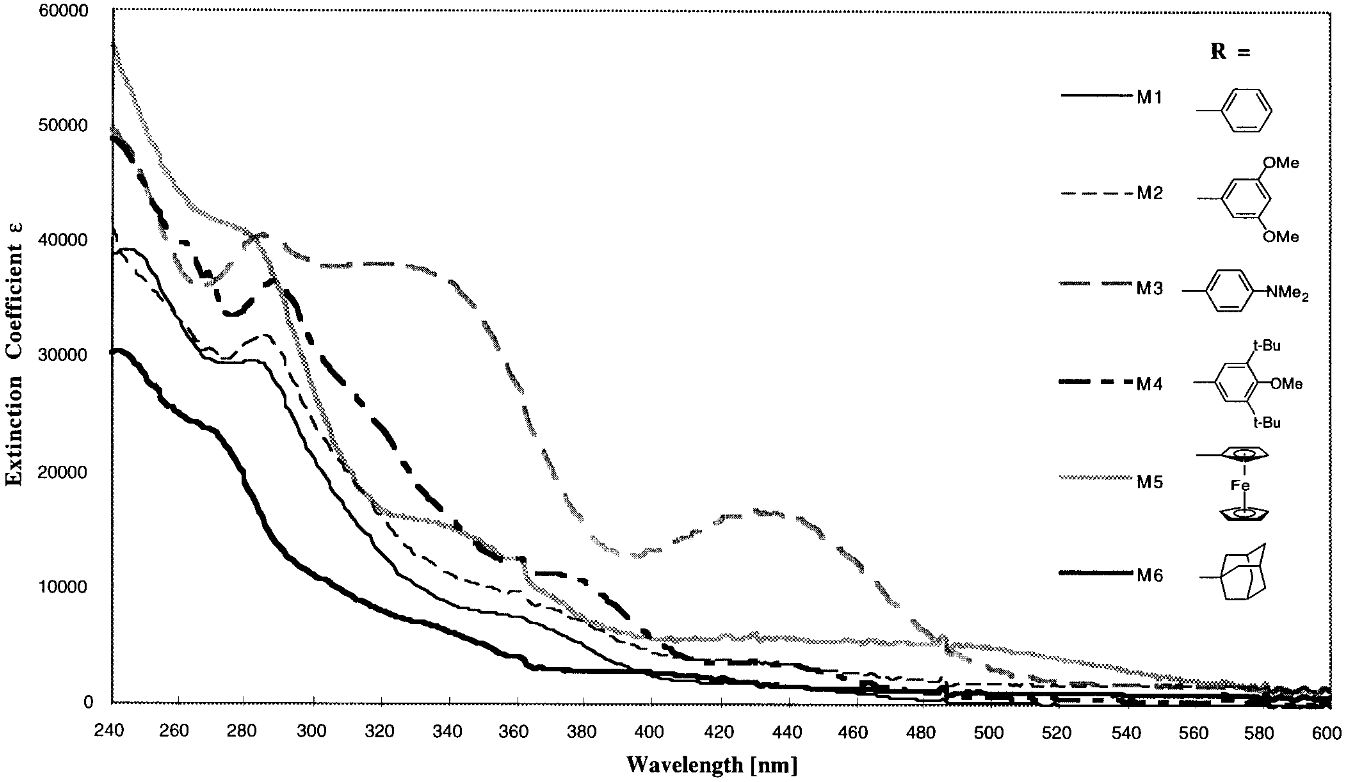

Figure 3. UV/vis absorption spectra of **M1**–**M6**.

Table 4. Summary of Polymerization Behavior of M1–M6

entry	catalyst	temp (°C)	productivity (kg of PP/((mol of Zr) h)	[*mmmm*][d] (%)	[*m*] (%)	IR index	$10^3 M_w$[e]	M_w/M_n
1	**M1**	0	1850	38	72	0.41	461	2.8
2		0	3639	39	74	0.37	651	2.9
3		20	2496	39	73	0.34	539	4.7
4		20	2508	39	73	0.35	518	3.3
5		40	4165	29	67	0.30	169	3.4
6		40	4104	30	69	0.31	157	3.3
7	**M2**	0	188	75	90	0.80	691	8.7
8		0	139	75	89	0.84	514	5.9
9		20	441	71	87	0.77	423	8.5
10		20	362	70	87	0.74	509	7.4
11		40	689	62	83	0.70	199	12.0
12		40	538	61	82	0.62	189	8.0
13	**M3**[a]	0	311	44	76	0.56	372	4.0
14		0	295	43	74	0.45	368	3.7
15		20	332	53	79	0.55	243	5.9
16		20	359	51	79	0.45	209	5.2
17		40	883	53	77	0.60	140	10.6
18		40	604	48	74	0.53	108	10.4
19	**M4**	0	668	84	95	0.83	451	3.9
20		0	3180	85	95	0.78	718	3.3
21		20	2578	77	93	0.74	731	3.3
22		20	2643	76	92	0.72	661	3.0
23		40	6600	73	91	0.77	418	4.6
24		40	7158	72	91	0.79	462	3.7
25	**M5**[b]	0	763	37	79	0.40	451	4.5
26		0	667	37	80	0.40	521	2.9
27		20	885	40	76	0.34	278	3.0
28		20	783	38	75	0.32	264	3.2
29		40	607	37	73	0.37	107	2.6
30		40	476	38	74	0.36	106	2.7
31	**M6**	20	6	20	54	*c*	*c*	*c*
32		20	7	21	55	*c*	*c*	*c*

[a] The metallocene fraction contained 0.415 mol of ligand/mol of metallocene. [b] The metallocene fraction contained 0.585 mol of CH_2Cl_2/mol of metallocene. [c] Not enough material for investigation. [d] Determined by ^{13}C NMR. [e] Determined by GPC versus polypropylene standards.

2-position has a dramatic influence on the isotacticity of the polymer. Metallocene **M6** is the least stereospecific of the unbridged catalysts investigated but produced so little polymer that the properties of these materials could not be fully investigated. Metallocene **M5** exhibits behavior very similar to that of **M1** at 0 and 20 °C but appears to exhibit less of a loss in stereospecificity at 40 °C than does **M1**. The 3,5-aryl-substituted metallocenes **M2** and **M4** produce a polymer with a significantly higher isotactic pentad content (70–

80%). They also show the most obvious trend of lower isotacticity with rising polymerization temperature. The trends in the IR index (A_{998}/A_{973}), a measure of the isotactic helical content,[36−38] tracks the results obtained from ^{13}C NMR.

Discussion

Polymerization catalysts derived from bis(2-arylindenyl)zirconium dihalides are known to produce elastomeric polypropylene in the presence of MAO. The elastomeric properties of these materials have been interpreted in terms of a stereoblock microstructure of alternating atactic and isotactic diasterosequences.[10−17] A full exploration of the steric and electronic effects on propylene polymerization performance requires access to a wide variety of ligand substitution patterns. In this paper, we report a synthetic procedure utilizing the di-Grignard reagent 1,2-di(magnesiomethyl)benzene dichloride[25,26] as a precursor to a family of 2-substituted indenes. The variety of commercially available methyl ester and carboxylic acids provides access to a wide range of new indene ligands. Metallocenes **M2**−**M4** contain ligands with electron-donating substituents on the 2-aryl substituents and varying steric demand. **M5** contains a electron-poor aryl substituent with high steric demand. **M6** was synthesized to study the effect of a bulky substituent without aromaticity.

The solid-state structure of the (dimethylamino)-phenyl-substituted metallocene **M3** reveals a closely coplanar arrangement of the dimethylamino group and the planes defined by the aryl and the indene groups. The dihedral angles between the indenyl and the phenyl planes are on the order of 10−12°, and the small torsional angles (C12−C13−N−C16 = −4.6° and C14−C13−N−C17 = 3.0°) of the dimethylamino group are indicative of some conjugation of the nitrogen lone pair into the 2-arylindene ligand. The bond length between the N-atom of the dimethylamino group and the C-atom of the phenyl ring (1.385 Å) is between the bond lengths found for the directly substituted bis[2-(dimethylamino)-indenyl]zirconium dichloride (1.354 Å)[39−41] and their bridged *ansa* analogues (1.397−1.406 Å)[39,41] and is indicative of some double-bond character. The extended conjugation engendered by the *p*-dimethylamino group is further indicated by the UV absorption spectra of metallocene **M3**, which exhibit absorption bands at 430 and 317 nm.

The polymerization behavior of (2-arylindene)metallocenes **M2**−**M6** reveals that all but **M6** are competent propylene polymerization catalysts. It is becoming quite clear that a variety of functional groups can be introduced into appropriate positions of metallocene ligands without significant loss in activity.[39,42−44] In the present instance, introduction of methoxy or dimethylamino groups onto the 2-aryl substituent does not dramatically inhibit polymerization, although the productivity of the bis-3,5-dimethoxy-substituted **M2** is approximately 10 times less productive than the *p*-methoxy-substituted **M4**. This difference might well be accounted for by the shielding effect of the adjacent *tert*-butyl groups.

We had previously observed that the introduction of a variety of substituents at the 4-positions of the 2-aryl substituent had little influence on the stereospecificity of unbridged (2-arylindenyl)metallocenes.[15] The behavior of metallocene **M3** suggests that this may not be general for substituents with strong π-donor abilities such as the dimethylamino group. For example, while the isotacticity of **M3** is approximately equal to that of **M1** at a polymerization temperature of 0 °C, **M3** exhibits a higher stereospecificity at both 20 and 40 °C ([$mmmm$] = 53% relative to 39%). We had no means of predicting the stereospecificity of the ferrocenyl-substituted metallocene **M5**. It is less productive but produces a polymer with a tacticity similar to that produced by the prototype metallocene **M1**.

We had also previously observed that introduction of trifluoromethyl groups at the 3′,5′-positions of the 2-aryl substituent lead to much higher isotacticities while the 3′,5′-dimethylphenyl-substituted metallocene behaved very similarly to the (2-phenylindenyl)metallocene **M1**.[11,13] The observation that both the dimethoxy-substituted **M2** and the di-*tert*-butyl-substituted **M4** yield more highly tactic polymers ([$mmmm$] from 70 to 85%) suggests that the influence of substituents at this position is largely steric in origin. That is, substituents larger than methyl in the 3,5-positions lead to higher tacticities for these unbridged 2-arylindene metallocenes.

The very low productivity observed for the 2-adamantyl-substituted **M6** (6 kg of PP/((mol of Zr) h)) can be contrasted to that reported[14] for the bis(2-cyclohexylindenyl)zirconium dichloride metallocene (2340 kg of PP/((mol of Zr) h)) and suggests that the rigid and sterically demanding adamantyl substituent inhibits polymerization. The stereospecificities of 2-adamantyl (**M6**, [$mmmm$] = 20%) and 2-cyclohexyl ([$mmmm$] = 15%)[14,23] are only slightly different under comparable polymerization conditions.

We have previously proposed a mechanism (Figure 1) involving the interconversion of isospecific and aspecific forms of the catalysts by means of torsional isomerism[18−20] of the indenyl ligands.[10] To obtain a stereoblock structure in the polymer chain by this mechanism, the forms of the active catalyst must be close in energy and the rate of interconversion must be slower than insertion of the olefin but faster than the time it takes to construct a single polymer chain.[45] Changing the nature of the ligands is likely to alter several factors at once and renders predictions of the polymerization behavior of a given metallocene very difficult. Nevertheless, the studies reported here, in

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[36] For highly isotactic polypropylene the IR index approaches unity.

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[40] Luttikhedde et al. report a structure with two different C−N bond lengths for the same compound.[41]

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conjunction with our other observations on the ligand effects of unbridged indenylmetallocenes,[10-17] are beginning to illuminate some of the basic structure/activity relationships for this class of metallocene catalysts.

Conclusions

A short and effective route to 2-substituted indenes and their corresponding zirconocenes was developed. Sterically demanding as well as functionalized aryl substituents are easily introduced into the 2-position of the indenyl ligand using a di-Grignard reagent as a synthon.

Propylene polymerization studies reveal that methoxy and dimethylamino substituents on the 2-arylindene ligand do not dramatically inhibit the polymerization activity and may exert some electronic influence on the polymerization behavior of the metallocene catalysts. Bis(2-ferrocenylindenyl)metallocenes are competent propylene polymerization catalysts and produce polymers similar to that of the parent bis(2-phenylindenyl)zirconocene.

Experimental Section

General Considerations. All experiments involving air-sensitive compounds were performed under nitrogen in a Vacuum Atmospheres drybox or under argon using standard Schlenk line techniques. Toluene was passed over a column of activated alumina and a supported copper (Q5) catalyst and then degassed and stored under argon. All other solvents were distilled from appropriate drying agents under a nitrogen atmosphere and stored in Strauss flasks under an argon atmosphere, unless otherwise indicated. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone. Methylene chloride and chloroform were distilled from calcium hydride. Pentane and hexanes were distilled from lithium aluminum hydride. Acetone was dried and distilled over calcium sulfate (Drierite). Dry methylene chloride-d_2 was bought in 0.5 mL ampules from Cambridge Isotope Laboratories; chloroform-d_3 was refluxed over calcium hydride, vacuum-transferred, and stored under nitrogen. Organolithium reagents were transferred to Strauss flasks and stored at 4 °C under an argon atmosphere. All other chemicals and reagents were bought from Aldrich or Alfa Aesar and used without further purification unless specified otherwise.

Methyl esters were prepared by a slightly modified literature procedure.[27]

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz or Varian Gemini 400 MHz spectrometer, UV/vis spectra were recorded on a HP 845X UV/vis spectrometer. Elemental analyses were performed by E + R Microanalytical Laboratory.

Polymer Analysis. Solution ^{13}C NMR spectra were run at 75 MHz on a Varian Inova 300 MHz spectrometer equipped with a 10 mm broad-band probe. Samples were run as solutions in 1,1,2,2-tetrachloroethane containing about 0.5 mL of 1,1,2,2-tetrachloroethane-d_2 at 100 °C and 500−2000 transients were collected per sample. IR spectra were obtained from polypropylene films on a Perkin-Elmer 1600 series FTIR. High-temperature GPC measurements of polymers were perfomed at Amoco Chemical using a Waters 150C GPC at 100 °C in 1,2,4-trichlorobenzene and referenced to polypropylene standards.

Ferrocenecarboxylic Acid. Lithioferrocene was prepared according to a literature procedure.[46] A Schlenk tube was charged with 4.00 g (21.07 mmol) of ferrocene and 0.30 g (2.67 mmol) potassium *tert*-butoxide, evacuated, and purged with argon three times. THF (200 mL) was added and the mixture stirred at room temperature until all solids were completely dissolved. After the reaction mixture was cooled to −78 °C, 24.8 mL (42.15 mmol) of *tert*-butyllithium (1.7 M in pentane) was added dropwise over a period of 15 min, with the temperature maintained below −70 °C. The mixture was stirred at −78 °C for 60 min and then poured into a slurry of dry ice (excess) and diethyl ether (not purified). The mixture was warmed to room temperature and extracted with 0.75 M sodium hydroxide solution (2 × 100 mL, 50 mL). The combined aqueous layers were carefully neutralized with dilute hydrochloric acid (pH >4), and the resulting orange solid was extracted with diethyl ether until the organic phase remained colorless. The combined organic layers were filtered (to remove traces of ferrocenedicarboxylic acid) and dried over magnesium sulfate. The dried ether solution was concentrated, hexanes was added, and the solution was again concentrated until the acid precipitated. The orange solid was collected by filtration. The concentration−filtering procedure was repeated several times. Yield: 4.72 g (20.52 mmol, 97%). ^{1}H NMR (DMSO-d_6): δ 4.20 (s, 5H), 4.30 (t, J = 1.9 Hz, 2H), 4.69 (t, J = 1.9 Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 69.51, 69.90, 71.07, 172.18.

Methyl Ferrocenylcarboxylate. Substrate: ferrocenecarboxylic acid (vide supra), 4.688 g (20.38 mmol). Reaction conditions: 20 h reflux; flash chromatography on silica gel with 10% ether in hexanes, then recrystallization from hexanes. Yield: 4.511 g of an orange solid (18.48 mmol, 90%). ^{1}H NMR (CDCl$_3$): δ 3.78 (s, 3H), 4.18 (s, 5H), 4.37 (t, J = 1.8 Hz, 2H), 4.78 (t, J = 1.8 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 51.57, 69.70, 70.06, 71.25, 172.22.

Methyl 1-Adamantanylcarboxylate. Substrate: 1-adamantanecarboxylic acid, 3.619 g (19.87 mmol). Reaction conditions: 20 h reflux; isolation and purification of the ester by recrystallyzation from hexanes. Yield: 3.058 g of colorless crystals (15.74 mmol, 79%). ^{1}H NMR (CDCl$_3$): δ 1.65−1.73 (m, 6H), 1.86 (d, J = 3.0 Hz, 6H), 1.99 (s br, 3H), 3.62 (s, 3H). ^{13}C NMR (CDCl$_3$): δ 27.94, 36.51, 40.71, 51.59.

Methyl 3,5-Di-*tert*-butyl-4-methoxybenzoate. In contrast to the general procedure, 5.584 g (40 mmol) potassium carbonate and 6.3 mL (100 mmol) iodomethane were reacted with 2.554 g (10 mmol) of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid. Also, the reaction mixture was heated only to 45 °C for 30 h. Flash chromatography of the crude product on silica gel with 7.5% ether in hexanes and then recrystallization from hexanes at −20 °C gave the product. Yield: 2.213 g (7.95 mmol, 80%). ^{1}H NMR (CDCl$_3$): δ 1.42 (s, 18H), 3.68 (s, 3H), 3.87 (s, 3H), 7.93 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 31.91, 35.86, 51.93, 64.40, 124.35, 128.24, 144.01, 163.84, 167.45.

General Procedure for the Synthesis of Indenyl Ligands from the Corresponding Methyl Esters. The di-Grignard reagent of *o*-xylylene dichloride was prepared with reference to the literature procedure.[26,47] Magnesium powder (50 mesh, 1.167 g, 48.00 mmol) was dried in a 500 mL three-necked, round-bottomed flask equipped with a pressue-equalizing addition funnel by heating to 120 °C under vacuum (10−20 mTorr) overnight. After the mixture was cooled to room temperature, the apparatus was repressurized with argon. THF (10 mL) and 0.25 mL (3.00 mmol) of 1,2-dibromoethane were added, and the mixture was heated with a heat gun. The heating was stopped 1 min after gas evolution occurred. All volatiles were removed in vacuo. After the apparatus was purged with argon, 10 mL of THF was added and 2.101 g (12.00 mmol) of *o*-xylylene dichloride (purified by Kugelrohr distillation prior to use) was dissolved in 125 mL of THF in the addition funnel while purging the apparatus was purged with argon. The solution in the addition funnel was added

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dropwise over a period of 3−4 h, and the reaction mixture was stirred vigorously for 15 h at room temperature. The magnesium was filtered off using a Schlenk frit under argon to yield a pale green solution. The receiving flask was equipped with a pressure-equalizing addition funnel, and the apparatus was purged with a vigorous argon flow for 15 min. The methyl ester (8 mmol) was dissolved in 65 mL of THF in the addition funnel and added to the di-Grignard solution at −78 °C over approximately 60 min, with the temperature consistently maintained below −70 °C during the addition. The reaction mixture was warmed to 0 °C over 1−2 h, and 80 mL of distilled water was added through the addition funnel over 15−30 min. After the reaction mixture was warmed to room temperature, the THF was removed completely from the reaction mixture. The remaining suspension was acidified to pH 1 and extracted with methylene chloride. The combined organic layers were dried over magnesium sulfate and stirred with 0.300 mg (1.57 mmol) of *p*-toluenesulfonic acid hydrate for 1 h at room temperature. After extraction with distilled water and drying over magnesium sulfate, the crude product was transferred to silica gel and purified by flash chromatography.

2-Ferrocenylindene (5). Substrate: Methyl ferrocenylcarboxylate, 3.851 g (15.78 mmol). Flash chromatography on silica gel with hexanes. Yield: 3.229 g of amber crystals (10.76 mmol, 68%). ^{1}H NMR (CD$_2$Cl$_2$): δ 3.67 (s, 2H), 4.09 (s, 5H), 4.33 (t, J = 1.8 Hz, 2H), 4.58 (t, J = 1.8 Hz, 2H), 6.82 (s, 1H), 7.12 (td, J = 7.3 Hz, J = 1.2 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.43 (d, J = 7.3 Hz, 1H). ^{13}C NMR (CD$_2$Cl$_2$): δ 40.16, 66.80, 69.44, 69.76, 81.23, 120.09, 123.79, 123.96, 124.00, 126.82, 143.11, 146.39, 147.80.

2-(3,5-Dimethoxyphenyl)indene (2). Substrate: Methyl 3,5-dimethoxybenzoate, 1.568 g (8.00 mmol). Flash chromatography on silica gel with 5% ether in hexanes. Yield: 0.899 g of brilliant white needlelike crystals (3.56 mmol, 45%). ^{1}H NMR (CD$_2$Cl$_2$): δ 3.78 (s, 2H), 3.83 (s, 6H), 6.40 (t, J = 2.2 Hz, 1H), 6.80 (d, J = 2.3 Hz, 2H), 7.18 (td, J = 7.4 Hz, J = 1.2 Hz, 1H), 7.25 (s, 1H), 7.26 (t, J = 7.0 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.48 (d, J = 7.3 Hz, 1H). ^{13}C NMR (CD$_2$Cl$_2$): δ 39.48, 55.68, 99.81, 104.14, 121.30, 123.98, 125.22, 126.90, 127.35, 129.57, 138.42, 143.57, 146.76, 161.39.

2-[4-(Dimethylamino)phenyl]indene (3). Substrate: Methyl 4-(dimethylamino)benzoate, 1.707 g (9.33 mmol). Flash chromatography on silica gel with 50% methylene chloride in hexanes. Yield: 1.638 g of a pearl-colored solid (6.96 mmol, 75%). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.98 (s, 6H), 3.75 (s, 2H), 6.73 (dt, J = 9.0 Hz, J = 2.5 Hz, 2H), 7.02 (d, J = 0.5 Hz, 1H), 7.10 (td, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.22 (tt, J = 7.5 Hz, J = 0.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.53 (dt, J = 9.0 Hz, J = 2.5 Hz, 2H). ^{13}C NMR (CD$_2$Cl$_2$): δ 39.72, 40.56, 112.58, 120.39, 122.69, 123.77, 124.08, 124.48, 126.78, 126.92, 143.17, 146.52, 147.44, 150.55.

2-(3,5-Di-*tert*-butyl-4-methoxyphenyl)indene (4). Substrate: Methyl 3,5-di-*tert*-butyl-4-methoxybenzoate, 2.245 g (8.06 mmol). Flash chromatography on silica gel with hexanes. Yield: 2.346 g of white oil (7.01 mmol, 87%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.47 (s, 18H), 3.71 (s, 3H), 3.79 (s, 2H), 7.14 (s, 1H), 7.15 (td, J = 7.0 Hz, J = 0.8 Hz), 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.54 (s, 2H). ^{13}C NMR (CD$_2$Cl$_2$): δ 32.18, 36.09, 39.47, 64.65, 120.88, 123.89, 124.41, 124.68, 125.36, 126.87, 130.67, 143.53, 144.24, 146.05, 147.55, 159.94.

2-(1-Adamantanyl)indene (6). Substrate: Methyl 1-adamantanylcarboxylate, 1.603 g (8.25 mmol). In contrast to the general procedure, after the removal of the THF the reaction mixture was not extracted with methylene chloride but with diethyl ether. After drying with magnesium sulfate, the ether was removed in vacuo. Toluene and 0.300 g (1.5 mmol) of *p*-toluenesulfonic acid were added, and the mixture was heated to 110 °C for 120 min with a Dean−Stark trap to remove the produced water. After it was cooled to room temperature, the reaction mixture was washed with water, the separated organic layer was dried over magnesium sulfate, and the toluene was removed. The crude product was purified by flash chromatography on silica gel with hexanes. Yield: 1.164 g of brilliant white solid (4.65 mmol, 56%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.75 (dt br, J = 11.5 Hz, J = 3.0 Hz, 3H),1.79 (dr br, J = 12 Hz, J = 3.0 Hz, 3H), 1.86 (d, J = 3 Hz, 6H), 2.05 (s br, 3H), 3.72 (t, J = 0.8 Hz, 2H), 6.49 (sx, J = 0.5 Hz, 1H), 7.07 (td, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.19 (td, J = 7.5 Hz, J = 0.5 Hz, 1H), 7.26 (d, J = 7.0 Hz, 1H), 7.38 (dq, J = 7.5 Hz, J = 0.8 Hz, 1H). ^{13}C NMR (CD$_2$Cl$_2$): δ 29.19, 35.79, 37.04, 37.25, 43.14, 120.31, 123.15, 123.76, 123.79, 126.43, 143.36, 145.92, 161.29.

General Procedure for the Synthesis of the Indenylzirconium Dichlorides through the Reaction of the Lithium Salt with Zirconium Tetrachloride. The ligand (1.5 mmol) was dissolved in 30−50 mL of diethyl ether. The solution was cooled to 0 °CC, and 0.6 mL (1.5 mmol) of *n*-butyllithium (2.5 M in hexanes) was added via syringe dropwise. After the addition the cooling bath was removed and the mixture was stirred at ambient temperature for 10 h. All volatiles were removed in vacuo, and the evacuated reaction flask was brought into a nitrogen glovebox. Zirconium tetrachloride (175 mg, 0.75 mmol) was added. Outside the box, 60−100 mL of toluene was added via cannula and the reaction mixture stirred vigorously at room temperature for 3 days. Again, all volatiles were removed in vacuo and 50 mL of methylene chloride was added. The suspension was filtered over Celite through a Schlenk frit under argon. The Celite was washed with methylene chloride until the filtered liquid remained colorless. The resulting clear solution's volume was reduced to one-fourth to one-fifth its original volume, and a layer of pentane, hexanes, or diethyl ether was applied carefully. The layered solution was stored at room temperature or −80 °C for crystallization of the product. After crystallization, the liquid was filtered off via cannula and the remaining solid was dried in vacuo. The filtrate was eventually concentrated to obtain a second crop. Alternately, all volatiles of the filtrate were removed in vacuo, the solid was redissolved in a small amount of methylene chloride, and the solution was filtered via cannula and layered again.

Bis[2-(3,5-dimethoxyphenyl)indenyl]zirconium Dichloride (M2). Ligand: 2-(3,5-dimethoxyphenyl)indene, 524 mg (2.08 mmol). Yield: 336 mg (0.51 mmol, 50%), dark yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.86 (s, 12H), 6.53 (t, J = 2.5 Hz, 2H), 6.62 (s, 4H), 6.73 (d, J = 2.5 Hz, 4H), 7.11−7.15 (m, 4H), 7.18−7.21 (m, 4H). ^{13}C NMR (CD$_2$Cl$_2$): δ 55.82, 101.00, 104.89, 105.41, 125.14, 127.18, 128.78, 132.20, 135.23, 161.62. Anal. Calcd for $C_{34}H_{30}Cl_2O_4Zr$: C, 61.43; H, 4.55. Found: C, 61.18; H, 4.44.

Bis[2-(4-(dimethylamino)phenyl)indenyl]zirconium Dichloride (M3). Ligand: 2-[4-(dimethylamino)phenyl]indene, 512 mg (2.18 mmol). In contrast to the general procedure, the lithium salt was prepared in 60 mL of toluene with 0.78 mL of *n*-butyllithium (2.5 M in hexanes, 1.95 mmol). After the mixture was stirred for 10 h at room temperature, the toluene was removed in vacuo, the evacuated Schlenk tube was brought into a nitrogen glovebox,and 232 mg (1.00 mmol) of zirconium tetrachloride was added. Outside the box, 80 mL of toluene was added via cannula and the reaction mixture stirred at room temperature resulting in a very cloudy brownish orange solution. The toluene was filtered off via cannula, the orange residue was washed with 20 mL of pentane, 80 mL of methylene chloride was added, and this solution was filtered over Celite under argon through a Schlenk frit. The Celite was washed with 60 mL of methylene chloride. The volume of the golden orange filtrate was reduced to one-fourth, during which time a yellow precipitate was produced. The cloudy solution was filtered via cannula but became cloudy after 5 min of standing again. The cloudy solution was stored at room temperature until the yellow precipitate settled to the bottom of the Schlenk tube and a layer of pentane (50 mL) was applied on the clear orange solution. After 7 days of standing at room temperature, orange, needlelike crystals grew from the glass wall into the solution at the original phase border. Unfortunately we were not able to isolate these crystals without some yellow solid on their surface. Yield: 153 mg orange crystals with yellow impurities. Orange crystals were identified as **M3** by X-ray. The mixture of the orange crystals and the yellow solid was identified by ^{1}H NMR as **M3** containing the free ligand **3** in a ratio of 0.415 mol of ligand/mol of **M3**. To 110 mg of the isolated material in a Schlenk tube with a small magnetic stirrbar under argon was added 20 mL of toluene, and the mixture was stirred for 10 min. The solution was filtered off, and again 20 mL of toluene was added. After a second stirring period of 5 min, the solution was filtered off again and the remaining crystals were dried in vacuo. Yield: 64 mg (0.101 mmol, 10%) of orange crystals. ^{1}H NMR ($CDCl_3$): δ 3.07 (s, 12H), 6.53 (s, 4H), 6.77 (d br, $J = 8$ Hz, 4H), 7.04−7.07 (m, 4H), 7.12−7.14 (m, 4H), 7.42−7.46 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 40.35, 102.02, 112.11, 121.10, 124.68, 126.05, 126.47, 127.94, 133.78, 150.53. Anal. Calcd for $C_{34}H_{32}Cl_2N_2Zr$: C, 64.74; H, 5.11. Found: C, 64.55; H, 5.43.

Bis[2-(3,5-*tert*-butyl-4-methoxyphenyl)indenyl]zirconium Dichloride (M4). Ligand: 2-(3,5-*tert*-butyl-4-methoxyphenyl)indene, 655 mg (1.96 mmol). Yield: 293 mg (0.353 mmol, 36%), yellow solid. ^{1}H NMR (CD_2Cl_2): δ 1.56 (s, 36H), 3.82 (s, 6H),), 6.64−6.68 (m, 4H), 6.72 (s, 4H), 6.98−7.01 (m, 4H), 7.63 (s, 4H). ^{13}C NMR (CD_2Cl_2): δ 32.16, 36.13, 64.67, 104.50, 124.32, 125.48, 126.11, 126.40, 127.03, 129.51, 144.65, 160.45. Anal. Calcd for $C_{48}H_{58}Cl_2O_2Zr$: C, 69.54; H, 7.05. Found: C, 69.41; H, 7.24.

Bis(2-ferrocenylindenyl)zirconium Dichloride (M5). Ligand: 2-ferrocenylindene, 1.014 g (3.38 mmol). After the toluene was removed in vacuo, 80 mL of methylene chloride was added and the solution filtered over Celite under argon through a Schlenk frit. The Celite was washed with an additional 20 mL of methylene chloride. All liquid of the filtrate was removed in vacuo, leaving a reddish brown solid, which was a 2:1 mixture of complex to ligand according to the ^{1}H NMR spectrum. To this solid was added 40 mL of methylene chloride, and the solution was filtered via cannula. The filtered, dark red solution was layered with diethyl ether and stored at −45 °C for 2 weeks. The liquid over the dark red-brown precipitate was filtered off and added to the remaining solid from the first filtration. The precipitate was dried in vacuo overnight: 353 mg of dark red-brown solid, identified as **M5** and containing 0.560 mol of methylene chloride/mol of **M5** and 0.275 mol of diethyl ether/mol of **M5** according to ^{1}H NMR (25% yield with regard to the amount of included solvents). The liquid from the filtrate was removed in vacuo, 50 mL of methylene chloride was added, the solution was filtered via cannula, and the filtered solution was layered with 50 mL of toluene and stored at −45 °C for 6 weeks. The remaining solid from the filtration was washed with pentane and dried in vacuo overnight. This solid (reddish brown), yield 88 mg (0.109 mmol, 6.5% with regard to the solvent content), was identified by ^{1}H NMR to contain 0.585 mol of methylene chloride/mol of metallocene.[48] ^{1}H NMR ($CDCl_3$): δ 3.95 (s, 10H),), 4.41 (t, $J = 2.0$ Hz, 4H), 4.55 (t, $J = 2.0$ Hz, 4H), 3.82 (s, 6H), 6.27 (s, 4H), 7.07−7.11 (m, 4H), 7.20−7.23 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 67.31, 69.62, 69.71, 78.82, 102.87, 124.67, 126.02, 126.05, 133.44. HRMS: m/z calcd 763.9506, 762.9520, 761.9487, 760.9474, 759.9473, 758.9504, 757.9470; found 763.9498, 762.9504, 761.9489, 760.9485, 759.9472, 758.9516, 757.9470.

Bis[2-(1-adamantyl)indenyl]zirconium Dichloride (M6). Ligand: 2-(1-adamantyl)indene, 375 mg (1.5 mmol). Yield: 144 mg (0.22 mmol, 29%) of yellow crystals. A second crop was not obtainable because the mother liquor decomposed after the crystals were filtered off. ^{1}H NMR ($CDCl_3$): δ 1.56−1.66 (m br, 24H), 1.90 (s br, 6H), 5.86 (s, 4H), 7.18−7.22 (m, 4H), 7.69−7.23 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 28.56, 36.69, 36.75, 41.80, 101.64, 125.89, 126.60, 156.37. Anal. Calcd for $C_{38}H_{42}Cl_2Zr$: C, 69.06; H, 6.41. Found: C, 68.73; H, 6.20.

Table 5. Summary of Crystallographic Data and Parameters for $C_{34}H_{32}N_2Cl_2Zr$

formula	$C_{34}H_{32}N_2Cl_2Zr$
fw	630.77
temp (K)	178
space group	$I/2a$ (No. 15); monoclinic
cell constants[a,b]	
a (Å)	22.6416(6)
b (Å)	6.8214(1)
c (Å)	18.9410(5)
α (deg)	90.000(1)
β (deg)	104.175(1)
γ (deg)	90.000(1)
V (Å^3)	2836.3(1)
Z	4
abs coeff, μ_{calcd} (cm^{-3})	0.01
F_{000}	1296.00
d_{calcd}[c] (g cm^{-3})	1.48
cryst size (mm)	0.32 × 0.16 × 0.05
radiation (λ, Å)	Mo Kα (0.710 69)
monochromator	highly oriented graphite
diffractometer	Siemens SMART
rflns measd	$0 \le h \le 26$, $-7 \le k \le 7$, $-22 \le l \le 20$
2θ range (deg)	$2.52 \le 2\theta \le 49.40$
scan type	ω
scan width (deg)	0.3
scan speed	10 s frame exposure
no. of rflns collected	6542
no. of unique rflns	2600 ($R_{int} = 0.042$)
no. of rflns with $F_o^2 > 3\sigma(F_o^2)$	1703
no. of variables	177
param to variable ratio	9:62
R (R_w)[d]	0.031 (0.037)
final diff ρ_{max} (e Å^{-3})[e]	+0.39; −0.38

[a] Unit cell parameters and their esd's were derived by a least-squares fitting of 3494 reflections with I > 10σ(I) and 2θ between 2.52 and 49.40°. [b] The esd's of all parameters are given in parentheses. [c] The density of the crystal was not measured. [d] The unweighted and weighted agreement factors in the least-squares refinements were $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w([|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 4F_o^2/s^2(F_o^2)$, $s^2(F_o^2) = S^2(C + R^2B) + (pF_o^2)^2/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz−polarization factor, and p = p factor (0.03). [e] Maximum negative and positive difference peaks.

Polymerizations. Toluene and liquid propylene were passed over towers containing Q5 and alumina prior to use. Methylaluminoxane (MAO type 4) was obtained from Akzo Nobel as a toluene solution and was dried in vacuo to give a white solid before use. Polymerizations were carried out in a 300 mL Parr reactor equipped with a mechanical stirrer. The temperature was maintained with an inside ethylene glycol/water cooling loop (20 °C) and additional outside ice/water bath (0 °C) or an aluminum heating block (40 °C). The reactor bottom was baked in an oven (100 °C) for at least 1 h and assembled while still hot. After evacuation to 30 mTorr and purging with argon three times, leaving the reactor under a argon pressure of 10 psi, liquid propylene (100 mL) was introduced into the reactor and equilibrated to the designated temperature. Catalyst solutions were prepared in the N_2 drybox by dissolving 1000 equiv of MAO (294 mg for 5×10^{-6} mol of metallocene) in toluene. An aliquot of a metallocene solution in toluene was added so that the total volume was 25 mL. The activated catalyst solution was injected under argon pressure. The polymerization was allowed to proceed for 10−60 min and then quenched with 15 mL of methanol injected under argon pressure.

The polymers were collected and precipitated into acidified methanol (5% HCl). After being stirred overnight, the polymers were dried in a vacuum oven at 40 °C.

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(48) Because the remaining solvent in the isolated solid could not be removed in vacuo, elemental analyses were off in carbon about 3%.

X-ray Diffraction Study. Bis[2-(4-(dimethylamino)phenyl)indenyl]zirconium Dichloride (M3). A crystal of $C_{34}H_{32}N_2Cl_2Zr$ with approximate dimensions 0.32 × 0.16 × 0.05 mm^3 grown from a solution of dichloromethane/pentane was mounted on a glass fiber in Paratone oil at −80 °C using an improvised cold stage. All measurements were made on a Siemens SMART[49] diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods[50] and expanded using Fourier techniques.[51] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at idealized positions, 0.95 Å from their parent atoms. All calculations were performed using the teXsan[52] crystallographic software package of Molecular Structure Corp. Crystal data and details of data collection and structure analysis are summarized in Table 5.

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Supporting Information Available: Tables and figures giving additional information on the X-ray crystallographic determination of **M3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990083W

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(49) SMART: Area-Detector Software Package; Siemens Industrial Automation, Inc., Madison, WI, 1995.

(50) Sheldrick, G. SHELXS-86, 1986.

(51) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system; Technical Report of the Crystallography Laboratory; University of Nijmegen, The Netherlands, 1992.

(52) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.