Propylene Polymerization with 1,2′-Bridged Bis(indenyl)zirconium Dichlorides

Maik Finze, Sarah E. Reybuck, and Robert M. Waymouth*

Department of Chemistry, Stanford University, Stanford, California 94305

Received July 23, 2003; Revised Manuscript Received September 4, 2003

ABSTRACT: A series of C_1 symmetric, 1,2′-bridged bis(indenyl)zirconium dichlorides were prepared to study the effect of ligand substitution, symmetry, and bridge identity on the stereoselectivity of propylene polymerization. Unsubstituted [1-(1-indenyl)-2-(2-indenyl)ethane]zirconium dichloride, Et(2-Ind)(1-Ind)-$ZrCl_2$ (**1**), was synthesized, and its propylene polymerization behavior was compared to three 2-phenyl-substituted complexes with different bridges: [2-(2-indenyl)-1-(2-phenyl-1-indenyl)ethane]zirconium dichloride, Et(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**2**), [(2-indenyl)-(2-phenyl-1-indenyl)dimethylsilyl] zirconium dichloride, Me_2Si(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**3**), and [(2-indenyl)-(2-phenyl-1-indenyl)methane]zirconium dichloride, CH_2(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**4**). The polymerization activity, polypropylene molecular weight, and microstructure were dependent upon the identity of the bridge and the substitution patterns on the metallocenes. Metallocenes **1**, **2**, **3**, and **4** are characterized by a gauche orientation of the indenyl ligands, in contrast to the anti or syn orientation of 1,1′-bridged *ansa*-bis(indenyl)metallocenes. The gauche metallocene **3** yields a polypropylene of intermediate isotacticity ([mmmm] = 58%) when compared to the C_2 symmetric *anti*-Me_2Si(2-phenyl-1-indenyl)$_2ZrCl_2$ ([mmmm] = 86%) and the C_s symmetric *syn*-Me_2Si(2-phenyl-1-indenyl)$_2ZrCl_2$ ([mmmm] = 7%). The gauche metallocene **2** yielded the most highly isotactic polypropylene ([mmmm] = 74%). Analysis of the sequence distributions of the polypropylenes derived from metallocenes **1**−**4** reveals a predominance of [mrrm] stereoerrors. The high stereoselectivity of the bridged metallocenes **1**−**4** implies that gauche conformations may be responsible for some of the higher tacticity fractions observed in polypropylenes derived from the unbridged 2-arylindene metallocenes.

Introduction

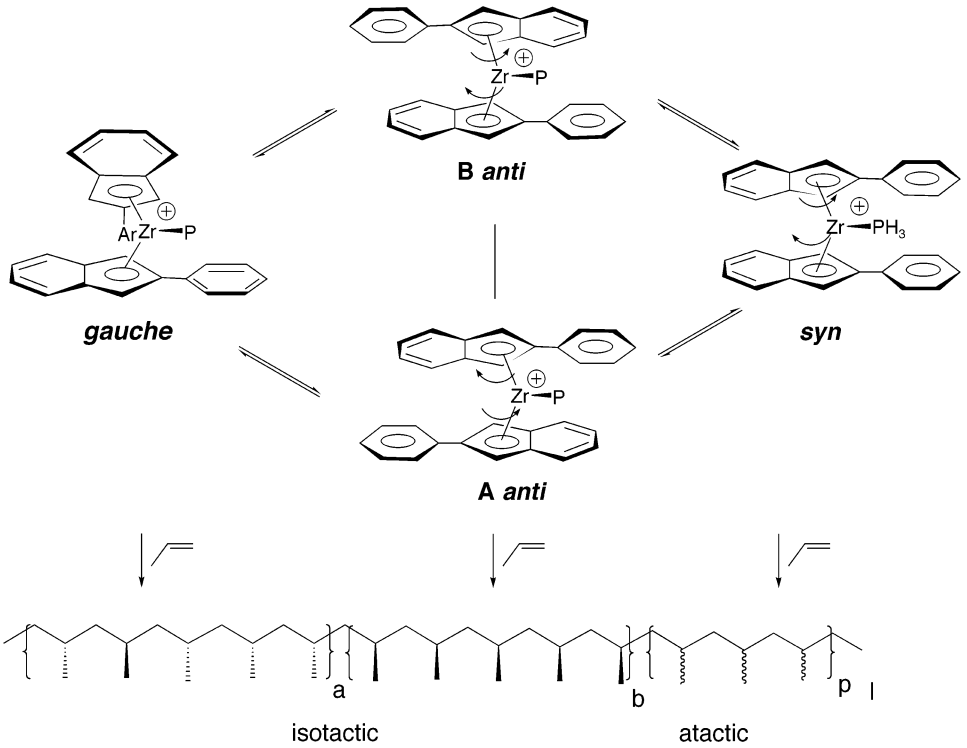
The physical properties of polypropylenes are strongly dependent upon the microstructure of the polymer chain.[1] Considerable effort has focused on establishing the relationship between the stereoselectivity of metallocene catalysts and their symmetry and ligand substitution pattern.[2,3] Metallocene-based catalyst systems give access to different polypropylene microstructures through manipulation of the ligand environment around the metal.[2] Isotactic,[4−6] syndiotactic,[7−9] hemiisotactic,[10] and stereoblock[11−21] microstructures have been prepared through modification of metallocene symmetry and ligand substitution pattern. Among the more well-studied bridged systems, metallocenes with anti-oriented C_2 symmetric ligand environments possess homotopic coordination sites and typically yield isotactic microstructures. The achiral, syn-oriented C_s symmetric metallocenes have heterotopic coordination sites and afford atactic polypropylenes.[2] Metallocenes with C_1 symmetry also possess heterotopic coordination sites and can generate a range of polypropylene microstructures including atactic, isotactic, syndiotactic, or stereoblock polypropylenes.[8,14−20,22−24] The rich stereoselectivity of many C_1 symmetric metallocenes is due to the presence of both stereoselective and nonstereoselective coordination sites. The probability of olefin insertion at one or both of these sites is a sensitive function of both the ligand substitution pattern and the polymerization conditions.[15,16,25,26]

Unbridged indenyl metallocenes also yield an array of polypropylene microstructures as a consequence of a conformationally dynamic ligand environment that can generate several conformations with different stereoselectivities.[27−32] We have recently investigated a class of coordination compounds that exhibit multisite polymerization behavior in an effort to prepare novel polymer architectures not readily accessible from single-site catalysts.[27] The polymerization behavior of these systems is more complicated than that of the more conformationally constrained bridged catalysts but provides access to new types of polymer architectures. Conformationally dynamic metallocenes based on unbridged 2-arylindene ligands generate interesting polypropylenes with intermediate tacticities and crystallinities. Some of these low-tacticity polypropylenes have elastomeric properties and yet retain the high melting temperatures of more crystalline isotactic polypropylenes.[13,28,29,33−50] The interconversion of the metallocenes between stereoselective and nonstereoselective conformations at a rate comparable to chain propagation has been proposed as a possible mechanism for generating stereoblock polypropylene microstructures (Scheme 1). We have proposed that the anti rotamer generates isotactic sequences and the syn-oriented conformation is responsible for the observed atactic sequences,[27] although others have questioned the role of the syn isomers as a source of atactic stereosequences.[28,29,32,50,51] Recently, the "T-shaped", gauche conformation has been suggested as a source of short atactic sequences in these stereoblock polypropylenes (Scheme 1).[50]

To assess the role of the different rotational isomers on the polymerization behavior of these conformationally dynamic systems, it is imperative to have a basic understanding of the stereoselectivity of the different conformations accessible to unbridged indenyl metallocenes.[42,48] To that end, we have investigated the polymerization behavior of bridged syn and anti model complexes to establish the chemical competence and stereoselectivity of these conformations in propylene polymerization.[2,42,48] As little is known about the polymerization behavior of gauche-oriented bis(indenyl)

10.1021/ma0303972 CCC: $25.00
Published on Web 11/18/2003

Scheme 1. Proposed Mechanism for Propylene Polymerization by $(2PhInd)_2ZrCl_2$



metallocenes,[52−54] we report here the synthesis and polymerization behavior of this novel class of metallocene catalysts.

The synthesis and polymerization behavior of a series of 1,2′-bridged bis(indenyl)zirconium dichlorides are described: [1-(1-indenyl)-2-(2-indenyl)ethane]zirconium dichloride, Et(2-Ind)(1-Ind)$ZrCl_2$ (**1**), [2-(2-indenyl)-1-(2-phenyl-1-indenyl)ethane]zirconium dichloride, Et(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**2**), [(2-indenyl)-(2-phenyl-1-indenyl)dimethylsilyl] zirconium dichloride, Me_2Si(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**3**), and [(2-indenyl)-(2-phenyl-1-indenyl)methane]zirconium dichloride, CH_2(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**4**). The polymerization behavior of these metallocenes illuminates the role of ligand substituents and bridge type on stereospecificity as well as productivity for this class of metallocenes and provides some insight into the polymerization behavior of gauche rotamers of unbridged, conformationally dynamic bis-(2-arylindenyl)metallocene systems.[13,28,29,33−50]

Results and Discussion

The syntheses of the ethylene- and methylene-bridged 1,2′-bis(indenyl) ligands are shown in Scheme 2. Depending on the identity of R^1, indene or 2-phenylindene was deprotonated with *n*-butyllithium and reacted with either methyl 3-bromopropionate or methyl bromoacetate. The preparation of 3-(2-phenyl-1-indenyl)propionic acid methyl ester proceeded in low yield due to the formation of methyl acrylate via competing dehydrohalogenation. An alternative route using a mixed organocyanocuprate was investigated but led to similar low yields (Scheme 3).[55−57] Condensation of the ester with a di-Grignard solution of α,α′-dichloro-*o*-xylylene in THF[45] followed by dehydration of the purified 2-indanol derivative with *p*-toluenesulfonic acid in toluene yielded the ligand precursors **11**−**13**. For the synthesis of the dimethylsilyl-bridged ligand, (2-indenyl)-(2-phenyl-3-indenyl)dimethylsilane (**14**), a patent literature procedure was used, giving 60% isolated yield (Scheme 4).[53]

The four ligand precursors were metalated by reacting the lithium salts with a suspension of zirconium tetrachloride in diethyl ether at 0 °C (Scheme 5). The synthesis of **1** has been previously reported.[54] The best yields for the metalation were obtained for the phenyl-substituted derivatives. Complex **2** was also prepared in toluene instead of diethyl ether, but yields in this case were on the order of 3% of analytically pure metallocene. The solubility of these metallocenes decreases from the silicon-bridged complex **3** to the single carbon-bridged analogue **4**.

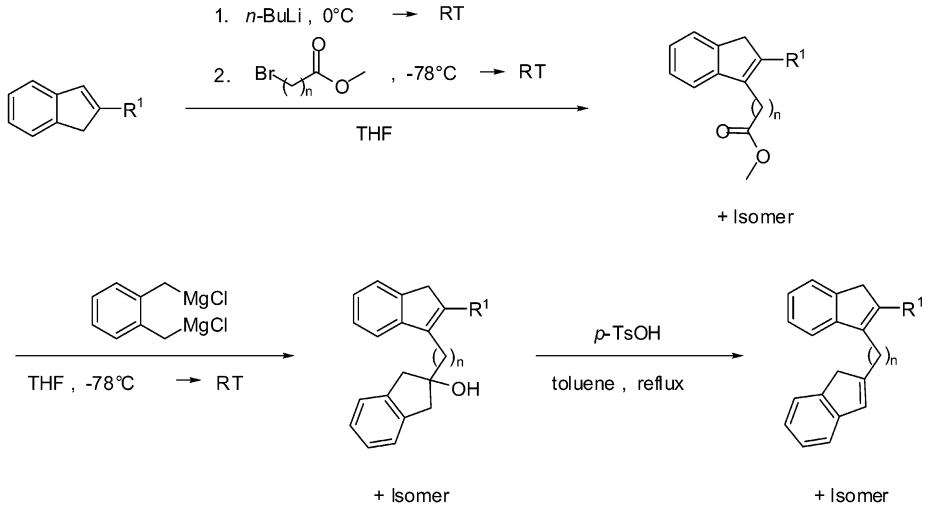
Propylene polymerizations for metallocenes **1**−**4** activated with Akzo-modified methylaluminoxane (MMAO) were performed in liquid propylene. While the single carbon-bridged complex **4** produces an amorphous, extremely sticky material, complexes **2** and **3** gave powdery solids. The polypropylene produced with complex **1** was rubbery.

The productivities obtained from the polymerizations in 100 mL of liquid propylene are shown in Table 1. The unsubstituted complex **1** gave the highest productivity among the four metallocenes while the 2-phenyl-substituted complex **2** gave the lowest. Among the 2-phenyl-substituted carbon-bridged metallocenes, the productivity decreased upon going from a one-carbon (**4**) to a two-carbon (**2**) bridge.

Polypropylene molecular weights were sensitive to both bridge type and ligand substitution. For the carbon-bridged metallocenes, the methylene-bridged system **4** showed the lowest molecular weights and the ethylene-bridged system **2** showed the highest. Substitution of a phenyl group in the 2-position resulted in a higher molecular weight for metallocene **2** compared to the unsubstituted **1**. The molecular weight distributions were narrow for all four metallocenes.

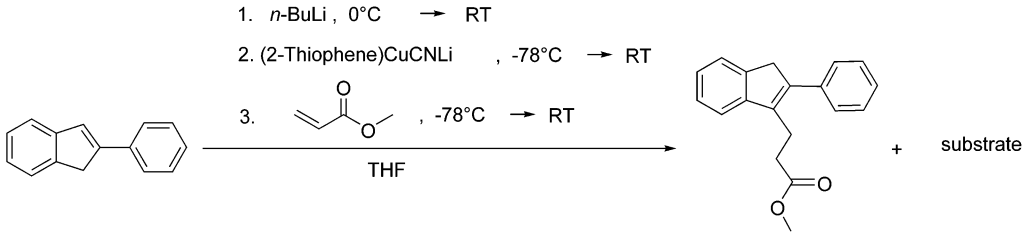
The microstructure of the polypropylenes was investigated by analysis of stereosequence pentad distributions determined by ^{13}C NMR spectroscopy (Table 2). Metallocenes **1**−**4** all yield polypropylenes of intermedi-

Scheme 2. Synthesis of Ethylene- and Methylene-Bridged 1,2-Bis(indenyl) Ligands

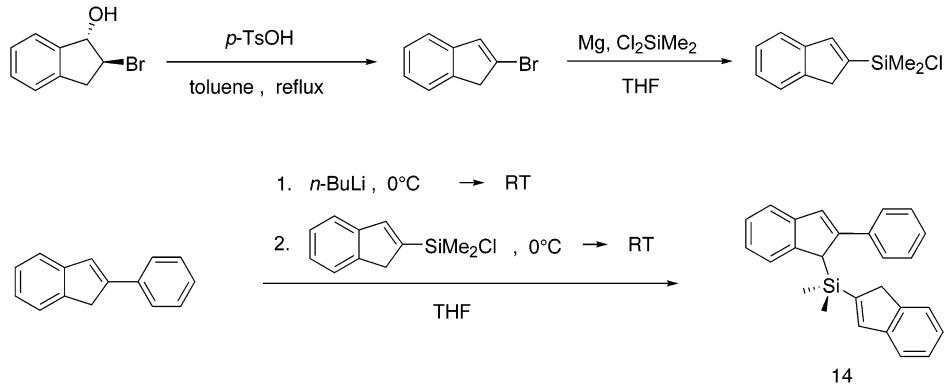


		Yield			
R^1	n	ester	2-indanol	Ligand	overall
H	2	52% (**5**)	78% (**8**)	70% (**11**)	28%
Ph	1	91% (**6**)	58% (**9**)	92% (**12**)	49%
Ph	2	24% (**7**)	78% (**10**)	85% (**13**)	16%

Scheme 3. Alternative Route for the Preparation of 3-(2-Phenyl-1-indenyl)propionic Acid Methyl Ester



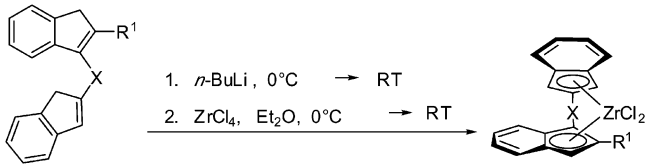
Scheme 4. Synthesis of Dimethylsilyl-Bridged Ligand



ate tacticities, with values for the isotactic pentads ranging from [mmmm] = 27% for **4** to [mmmm] = 74% for **2.** Analysis of the pentad distributions obtained by ^{13}C NMR shows that the major stereoerrors for all four catalyst systems are single random misinsertions into the growing polymer chain as indicated by the pentads [mmmr], [mmrr], and [mrrm], which are the strongest pentads apart from [mmmm].

The stereoselectivity of these metallocenes is sensitive to both the nature of the ligand substitution pattern and the nature of the bridging group. For the series of 1,2′-bridged metallocenes, the effect of substitution by a 2-phenyl group was analyzed by comparison between **1** and **2**. The effect of bridge type on polymerization was

Scheme 5. Ligand Metalation



+ Isomer

Metallocene	X	R^1	Yield
1	CH_2CH_2	H	13%
2	CH_2CH_2	Ph	25%
3	$SiMe_2$	Ph	40%
4	CH_2	Ph	42%

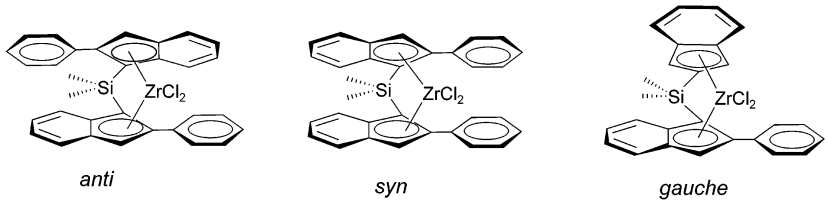


Figure 1. Anti, syn, and gauche isomers.

Table 1. Propylene Polymerization Conditions and Results[a]

catalyst precursor	press. (psig)	[metallocene] (10^{-5} mol/L)	productivity (kg/(mol h))	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Et(2-Ind)(1-Ind)$ZrCl_2$ (**1**)	130	1.2	16 200	32 400	15 000	2.2
Et(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**2**)	130	1.2	5 700	165 000	74 900	2.2
Me_2Si(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**3**)	129	2.5	13 100	108 000	48 500	2.2
CH_2(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**4**)	132	2.5	6 500	9 000	4 200	2.2

[a] Polymerization conditions: $n_{MAO}/n_{Zr} = 1000/1$, temperature = 20 °C, time = 20 min.

Table 2. Pentad Distributions for Polypropylene from 1,2-Bridged Bis(indenyl)zirconium Dichlorides

catalyst precursor	mmmm	mmmr	rmmr	mmrr	mrmm+ rmrr	mrmr	rrrr	rrrm	mrrm
Et(2-Ind)(1-Ind)$ZrCl_2$ (**1**)	45	17	3	17	4	2	1	2	9
Et(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**2**)	74	9	2	6	2	1	1	2	3
Me_2Si(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**3**)	58	14	2	12	4	2	1	2	5
CH_2(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**4**)	27	17	4	16	11	7	4	5	9

Table 3. DSC Results for Polypropylene Samples

catalyst precursor	T_m (°C)	ΔH_f (J/g)	crystallinity (%)	mmmm (%)
Et(2-Ind)(1-Ind)$ZrCl_2$ (**1**)	68 (43)[a]	26	13	45
Et(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**2**)	128	67	61	74
Me_2Si(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**3**)	96	41	20	58
Me(2-Ind)(2-Ph-1-Ind)$ZrCl_2$ (**4**)	43	4	2	27

[a] DSC spectrum shows two peaks.

analyzed by synthesis and comparison of polymerization by the 2-phenyl-substituted complexes **2**, **3**, and **4**, metallocenes with ethylene, dimethylsilyl, and methylene bridges, respectively.

Comparison of polymerization results for the 2-phenyl-substituted, bridged metallocenes (**2**−**4**) in Tables 1 and 2 reveals that the nature of the bridging group has a significant influence on the polymer microstructure and properties. The bridging group can influence both the steric properties of metallocenes and their electronic properties; recent studies reveal that the electronic effects of ansa-bridges can be significant.[58] For the 2-phenyl-substituted systems, the stereoselectivity (as measured by the isotactic pentads [mmmm]) depends on the bridge and increases in the order CH_2 < Me_2Si < CH_2CH_2 (**4** < **3** < **2**). The lower stereoselectivity of **4** is likely a consequence of the wider coordination gap observed for methylene-bridged metallocenes compared to the ethylene- or dimethylsilyl-bridged systems.[58] The higher stereoselectivity of the ethylene-bridged metallocene **2** relative to the silicon-bridged metallocene **3** is intriguing. For bis(indenyl)zirconocenes, the influence of the bridge on the stereoselectivity generally follows the trend H_2C < Me_2C < C_2H_4 < Me_2Si.[2] For the C_1 symmetric metallocenes **2** and **3**, it is possible that the higher stereoselectivity of **2** is a consequence of a higher probability of insertion at the stereoselective site due to a higher degree of site epimerization (also called "backskip")[16,21,26] for the ethylene-bridged metallocene relative to the silicon-bridged metallocene, but further studies are necessary to support this hypothesis. The molecular weights of the polypropylenes derived from the 2-phenyl-substituted systems increase in the order CH_2 < Me_2Si < CH_2CH_2 (**4** < **3** < **2**), whereas the productivity follows the trend **2** < **4** < **3**.

The substitution pattern of the indenyl ligands also influences the polymerization behavior. Comparison of metallocenes **1** and **2** reveals that introduction of a 2-phenyl substituent lowers productivity but improves stereoselectivity and increases the molecular weights. The origin of the higher stereoselectivity is not clear but could be a consequence of the slightly higher stereoselectivities generally observed upon introduction of a 2-substituent on 1,1′-bridged bis(indenyl)zirconocenes.[2] Alternatively, a greater degree of site isomerization may explain this observation for the more sterically encumbered phenyl-substituted metallocene **2**.[16,21,26]

The effect of different ligand orientations around the metal coordination site can be analyzed by comparison of metallocenes with the same ligands, but with different bridge placement. Propylene polymerizations with 1,1′-dimethylsilyl-bridged complexes *anti*- and *syn*-dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride have been previously reported by our group.[42] A comparison between polymerization with the 1,1′-bridged syn and anti isomers and 1,2′-bridged gauche isomer (Figure 1) is presented in Table 4. The [mmmm] for the gauche isomer (58%) is intermediate between the isotactic value of 87% for the chiral anti isomer and the atactic value of 7% for C_s symmetric syn isomer. Higher productivity is obtained with the gauche isomer. The molecular weight of the polymers obtained from metallocene **3** is lower than for the anti isomer but similar to that from syn.

The melting points and degrees of crystallinity of the polymers derived from metallocenes **1**−**4** correlate with their degrees of isotacticity. The percent crystallinity was calculated from ΔH_f of the polymer samples using a theoretical number of 209 J/g for 100% crystallinity (Table 3).[35] For metallocenes **1**−**4**, the melting points

Table 4. Comparison of Polypropylene from 3 with Syn and Anti Isomers

catalyst precursor	productivity (kg/(mol h))	mmmm (%)	T_m (°C)	M_w ($\times 10^{-3}$)	M_w/M_n	ΔH_f (J/g)	crystallinity (%)
Me_2Si(2-Ind)(2-Ph-1-Ind)$ZrCl_2$	13100	58	97	108	2.2	41	20
anti-Me_2Si(2-Ph-1-Ind)$_2ZrCl_2$	2400	87	139	410	3.1	70	33
syn-Me_2Si(2-Ph-1-Ind)$_2ZrCl_2$	4000	7		150	2.1		

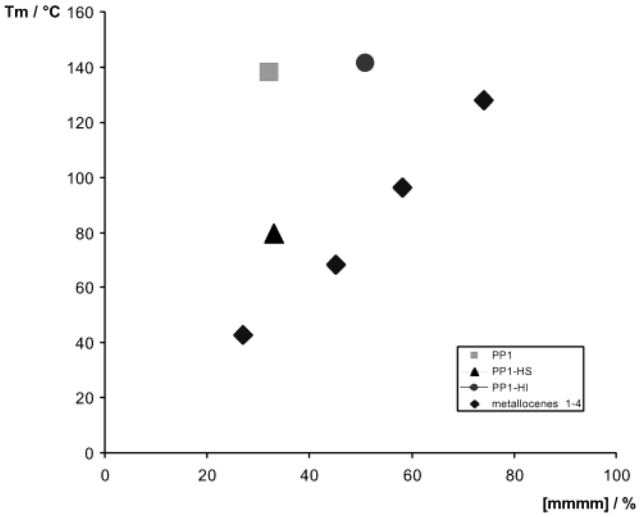


Figure 2. T_m (°C) vs [mmmm] for polypropylenes from **1-4**, PP1, PP1-HS, and PP1-HI.

and heats of fusion increased with increasing [mmmm] and vary from low (**4**; T_m = 43.1 °C, ΔH_f = 4.5 J/g) to high tacticity (**2**; T_m = 128.4 °C, ΔH_f = 67.2 J/g). This trend follows that reported by Resconi for a variety of low-tacticity polypropylenes (Figure 2)[2] and is consistent with a random distribution of stereoerrors, as indicated by the pentad distributions. The tensile properties of these materials have not been investigated, but the tacticities and crystallinities of these polypropylenes fall in the range of elastomeric and plastomeric polypropylenes prepared by other C_1 symmetric metallocene catalysts.[12,14,15,20,25,59]

The stereoselectivity of the gauche metallocenes **1**−**4** provides additional insight into the possible role that such conformations may play in contributing to the stereoselectivity of conformationally dynamic bis(2-arylindenyl)metallocenes such as bis(2-phenylindenyl)-zirconocene dichloride, (2PhInd)$_2ZrCl_2$ (Scheme 1).[60] We have proposed that the isotactic/atactic stereoblock microstructure produced from unbridged 2-arylindene metallocenes is a consequence of the interconversion of several conformations that can enchain propylene with different stereoselectivities. Structural,[13] mechanistic,[42,48] and theoretical studies[30,61−63] support the hypothesis that both syn and anti conformations are viable candidates for the generation of atactic and isotactic sequences, respectively, although recent studies have questioned whether it is necessary to invoke the syn conformations as a source of the atactic stereosequences.[28,29,50,51] The possible role of the gauche conformations was addressed theoretically by Brintzinger,[30] whose calculations predict that such conformations are ∼6−7 kcal higher in energy than the syn or anti rotamers and were in fact proposed as a possible transition state for interconversion of the syn/anti conformations. Busico[50] has suggested that the gauche isomers are nonstereoselective and may be responsible for short atactic sequences in otherwise highly tactic fractions of polypropylenes obtained from the (2PhInd)$_2ZrCl_2$/PhNMe$_2$HB(C$_6$F$_5$)$_4$/TIBA catalyst systems (TIBA = triisobutylaluminum). The results of this study indicate that gauche conformations can be quite highly stereoselective, and thus are unlikely to generate atactic sequences, but rather may be responsible for some of the isotactic-enriched sequences observed in stereoblock polypropylenes obtained with bis(2-arylindene)metallocenes.

The polypropylenes obtained from *gauche*-**3** are of intermediate and higher isotacticity than the elastomeric polypropylene PP1 obtained from the unbridged (2PhInd)$_2ZrCl_2$ activated with MAO in liquid propylene at 20 °C (Table 5).[35] Comparison of the polypropylene obtained from **3** with the heptane-insoluble fraction of PP1 (PP1-HI) is instructive as both have similar degrees of isotacticity ([mmmm] = 58% vs 51%). While the percentages of isotactic pentads for the two polymers are similar, closer inspection of the pentad distributions reveals significant differences in the types and amounts of stereoerrors. The stereoerrors in polypropylenes obtained from **3** are revealed in the [mmmr], [mmrr], and [mrrm] pentads and are consistent with isolated [mrrm] stereosequence errors typical of enantiomorphic site control (type A, Figure 3).[2] In contrast, stereoerrors in PP1-HI derived from (2PhInd)$_2ZrCl_2$ are revealed predominantly in [mmmr], [mmrr], [mmrm(+rmrr)], and [mrmr] pentads (types A, B, and C, Figure 3). Thus, the two polypropylenes have both different types and different sequences of stereoerrors. As previously discussed by us and others,[28,29,49−51] polypropylenes derived from (2PhInd)$_2ZrCl_2$ generate a range of stereoerrors, including those of types A, B, and C. Stereoerrors of type A are consistent with enantiomorphic site control errors and are expected for any conformation that is not completely stereoselective. Stereoerrors of type B have been proposed to arise from a conformational interconversion between two stereoselective anti conformations A and B (Scheme 1),[28,29,49−51] and stereoerrors of type C are consistent with atactic stereosequences. These differences in sequence distributions as measured by NMR spectroscopy are also manifested in the thermal properties of these two polypropylenes: the highest melting point observed for the polypropylene derived from **3** is 97 °C, whereas PP1-HI exhibits a melting point as high as 141 °C. These higher melting points, combined with the pentad distributions, indicate that not only the types of errors but also the sequence distribution of these errors are different in the two samples: PP1-HI contains longer isotactic sequences than the polypropylene derived from **3** even though the average isotacticity (as measured by [mmmm]) is the same.[27]

While the presence of isolated r stereoerrors (from [mrmm] pentads) is observed even in the heptane-insoluble fraction of PP1 (Table 5), both we[35] and Busico's group[50] have observed more highly tactic fractions in polypropylenes prepared either in the presence of hydrogen[35] or in the presence of the catalyst system (2PhInd)$_2ZrCl_2$/PhNMe$_2$HB(C$_6$F$_5$)$_4$/TIBA.[50] The origin of these highly isotactic fractions has been proposed to arise from a fraction of the catalyst sites that are "locked" into stereoselective conformations by interac-

Table 5. Comparison of Molecular Weights and Stereosequence Distributions

catalyst precursor	fract	wt %	prod[a]	M_w ($\times 10^{-3}$)	M_w/M_n	mmmm	mmmr	rmmr	mmrr	rmrr+ mmrm	mrmr	rrrr	mrrr	mrrm	T_m (°C)	ΔH_f (J/g)
3			13100	108	2.2	58	14	2	12	4	2	1	2	5	96.7	41.3
$(2PhInd)_2ZrCl_2$	PP1	100	2756	455	2.7	32	15	4	10	18	9	2	5	5	138.1	24
	PP1-ES	36		339	2.5	18	16	6	12	22	11	3	8	5		
	PP1-HS	43		367	2.4	33	16	5	11	17	8	2	5	4	79.7	11.0
	PP1-HI	21		598	3.1	51	13	3	7	13	6	1	4	4	141.6	65

[a] Kilograms of polypropylene per mole Zr per hour.

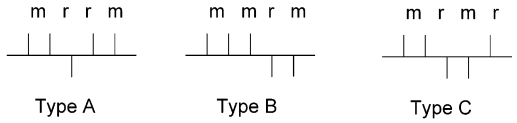


Figure 3. Types of polypropylene stereoerrors.

tion of the metallocenes with the anionic cocatalyst.[50] The results of this study suggest that the gauche isomers are competent candidates for these "locked" conformations, as some of the bridged gauche isomers (notably **2**) are capable of generating quite highly tactic polypropylenes. The nature of these "locked" conformations and the role of various counterions in stabilizing these species are, as yet, not well established but underscore the important role that counterions can have on the behavior of these conformationally dynamic catalysts.[21,35,64]

Experimental Section

General Considerations. All experiments involving air- and moisture-sensitive compounds were carried out under dry nitrogen using Schlenk line techniques or a Vacuum Atmospheres drybox. Toluene and pentane were passed over columns of activated alumina and supported copper (Q5) catalyst before use. Tetrahydrofuran (THF), diethyl ether, and methylene chloride were passed over alumina columns before use. *n*-Butyllithium was obtained as a 1.6 M or 2.5 M solution in hexane from Aldrich. Zirconium(IV) chloride was purchased from Fluka or Strem and used without further purification. 2-Bromoindene was prepared following a literature procedure.[65,66] Chloro-2-indenylsilane was prepared following a patent procedure.[53] All other chemicals were purchased from Aldrich and, if not noted otherwise, used without further purification. Flash chromatography was performed using Merck silica gel 60 with a particle size of 0.040−0.063 mm (230−400 mesh ASTM).

Chloroform-*d* and 1,1,2,2-tetrachloroethane-d_2 were dried over calcium hydride. The ^{1}H NMR data were referenced against tetramethylsilane (TMS) at 0 ppm in chloroform-*d* and against 1,1,2,2-tetrachloroethane at 5.95 ppm in 1,1,2,2-tetrachloroethane-d_2. The ^{13}C{^{1}H} NMR spectra were referenced against chloroform-*d* at 77.12 ppm and against 1,1,2,2-tetrachloroethane-d_2 at 74.00 ppm.

^{1}H and ^{13}C{^{1}H} NMR spectroscopy were performed on a Varian Gemini 400 MHz (100 MHz resolution for ^{13}C{^{1}H} NMR) or a Varian Inova 500 MHz (125 MHz resolution for ^{13}C NMR) spectrometer. Elemental analyses were obtained from E&R Microanalytical Laboratory. Gas chromatography was performed on a Hewlett-Packard 6890 series GC/MS spectrometer.

Ligand and Metallocene Preparation. General Procedure for the Synthesis of Methyl Ester-Substituted Indenes and 2-Phenylindenes from the Corresponding Bromomethyl Esters. *n*-Butyllithium (1.05 equiv) was added dropwise to a stirred solution of the indene derivative in THF (approximately 0.1 M). The reaction mixture was warmed to room temperature and stirred for approximately 4 h. The bromoester (1 equiv) was added at −78 °C over 10−30 min depending on the indene derivative. The reaction mixture was then warmed to ambient temperature and stirred overnight. After quenching the reaction with water, volatiles were removed under reduced pressure, and the crude product was taken up into diethyl ether and water. The organic layer was separated, and the aqueous phase was washed two times with diethyl ether. After drying the combined organic layers with magnesium sulfate, the solvent was removed in vacuo. The crude product was purified by flash chromatography using a mixture of hexanes and diethyl ether as eluant.

3-(1-Indenyl)propionic Acid Methyl Ester (5). The substance was prepared according to the general procedure. Substrates: technical grade indene (90+%) 6.0 g and methyl 3-bromopropionate 8.0 g (46.5 mmol). Yield: 4.84 g of a yellow oil (23.9 mmol, 52% based upon methyl 3-bromopropionate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95−2.03 (m, 1H), 2.14−2.33 (m, 3H), 3.54 (td, J = 4.8 and 2.6 Hz, 1H), 3.63 (s, 3H), 6.45 (dd, J = 5.6 and 1.8 Hz, 1H), 6,82 (dd, J = 5.5 and 1.5 Hz, 1H), 7,19 (td, J = 7.4 and 1.1 Hz, 1H), 7.26 (td, J = 7.3 and 0.9 Hz, 1H), 7.35 (d, J = 7.3 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 26.2, 30.9, 49.3, 51.7, 121.3, 123.0, 125.1, 126.9, 131.9, 138.2, 144.5, 146.7, 174.1.

3-(2-Phenylindenyl)acetic Acid Methyl Ester and 1-(2-Phenylindenyl)acetic Acid Methyl Ester (6). The substance was prepared according to the general procedure yielding a mixture of both possible isomers. The ratio of isomers was 76% 3-(2-phenylindenyl)acetic acid methyl ester and 14% 1-(2-phenylindenyl)acetic acid methyl ester as measured by GC/MS and ^{1}H NMR. Substrates: 2-phenylindene 4.0 g (20.4 mmol) and methyl bromoacetate 3.12 g (20.4 mmol). Yield: 4.897 g of a yellow oil (18.5 mmol, 91%). A clean sample of the major isomer was obtained by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 4H), 3.79 (s, 3H), 7.26 (td, J = 7.4 and 1.1 Hz, 1H), 7.35−7.39 (m, 2H), 7.43−7.58 (m, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 32.7, 41.7, 52.3, 119.7, 123.7, 125.2, 126.7, 127.6, 128.4, 128.7, 131.3, 136.7, 142.4, 144.5, 145.6, 171.8. The peaks of the minor isomer were assigned by comparison of the clean spectra of the major isomer and the spectra of the mixed fractions. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (dd, J = 17.6 and 10.4 Hz, 1H), 2.91 (dd, J = 17.6 and 3.6 Hz, 1H), 3.72 (s, 3H), 4.42 (dd, J = 10.4 and 3.6 Hz, 1H), 7.09 (s, 1H), 7.23 (td, J = 7.4 and 1.2 Hz, 1H), 7.31−7.71 (m, 8H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 36.7, 45.5, 51.9, 121.4, 123.5, 125.3, 127.0, 127.3, 127.4, 127.8, 129.0, 134.9, 143.8, 147.2, 150.0, 173.3.

3-(2-Phenyl-1-indenyl)propionic Acid Methyl Ester (7). The substance was prepared according to the general procedure and an alternative route (see below). Substrates: 2-phenylindene 5 g (25.5 mmol) and methyl 3-bromopropionate 4.26 g (25.5 mmol). Yield: 1.67 g of a pale yellow solid (6.0 mmol, 24%). Recovered 2-phenylindene: 2.04 g (10.6 mmol, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76 (dd, J = 16.3, 10.5, and 5.8 Hz, 1H), 1.89 (dd, J = 16.3, 10.7, and 5.5 Hz, 1H), 2.13−2.19 (m 1H), 2.41−2.50 (m, 1H), 3.47 (s, 3H), 4.09 (t, J = 4.9 Hz, 1H), 7.09 (s, 1H), 7.20 (td, J = 7.3 and 1.1 Hz, 1H), 7.26−7.31 (m, 2H), 7.36−7.45 (m, 4H), 7.52−7.55 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 25.7, 28.4, 47.8, 51.5, 121.3, 123.3, 125.1, 126.9, 127.2, 127.7, 128.7, 128.9, 135.3, 144.5, 146.4, 149.9, 174.0.

3-(2-Phenyl-1-indenyl)propionic Acid Methyl Ester—Alternative Route. The compound was prepared according to a literature procedure.[55,56] *n*-Butyllithium, 3.16 mL (5.05 mmol, 1.6 M in hexane), was added dropwise to a stirred solution of 2-phenylindene, 1.0 g (5.05 mmol), in 30 mL of THF. The mixture was brought to room temperature and stirred for an additional 2 h. Meanwhile, in a second Schlenk flask, freshly distilled thiophene, 0.41 mL (5.05 mmol), was depro-

tonated with *n*-butyllithium, 3.16 mL (5.05 mmol, 1.6 M in hexane), at 0 °C in 5 mL of THF. After stirring for 30 min at room temperature, the mixture was cooled to −78 °C and added to a suspension of copper(I) cyanide in 6 mL of THF. The reaction mixture was stirred for 20 min at −78 °C, warmed to 0 °C, and stirred for a further 30 min to give a tan solution. The deprotonated 2-phenylindene solution was cooled to −78 °C and added to the copper reaction mixture. After stirring for 10 min, the mixture was brought to 0 °C and stirred for 1.5 h. Freshly distilled methyl acrylate was diluted in 6 mL of THF and cannula transferred to the copper(I) complex at −78 °C. After warming to room temperature and stirring for 2 h, the reaction mixture was added to diethyl ether and an aqueous solution of sodium thiosulfate. Flash chromatography in hexanes with 1−5% diethyl ether gave two fractions: one containing 2-phenylindene and the other containing product. Yield: 147 mg of a pale yellow solid (0.53 mmol, 10%). Recovered 2-phenylindene: 0.211 mg (1.10 mmol, 21%). The ^{1}H and ^{13}C {^{1}H} NMR spectra show the same peaks obtained with the general procedure for the preparation of methyl ester-substituted 2-phenylindenes.

General Procedure for the Synthesis of Indenyl- and 2-Phenylindenyl-2-indanol Derivatives from the Corresponding Methyl Ester-Substituted Indenes and 2-Phenylindenes. The synthesis followed a slightly modified literature procedure for the preparation of 2-substituted indenes.[45] Magnesium powder (6.0 equiv, 50 mesh) was dried in a 500 mL three-necked round-bottomed flask by heating to 110 °C under vacuum (10−20 mTorr) overnight. The solid was flushed with dry nitrogen and cooled to ambient temperature. Dry THF (10 mL) and 0.25 equiv of 1,2-dibromoethane were added. After approximately 2 min, gas evolution occurred. The flask was cooled to room temperature, and all volatiles were removed in vacuo. A small amount of THF was added to the activated magnesium. Sublimed α,α′-dichloro-*o*-xylylene (1.5 equiv) was dissolved in THF to give a 0.1 M solution and transferred to the addition funnel. Over 4−6 h, depending on the scale, the α,α′-dichloro-*o*-xylylene solution was added to the magnesium suspension dropwise. The reaction mixture was stirred overnight. After settling of the excess magnesium turnings, the mixture was cannula transferred to a Schlenk frit and filtered, leaving a pale yellow solution. The methyl ester-substituted indene (1.0 equiv) was dissolved in THF, yielding a 0.1 M solution that was then transferred to a dropping funnel. Over a period of 3−5 h, depending on the scale, the ester solution was added to the di-Grignard solution at −78 °C. The mixture was warmed to room temperature and stirred overnight. After quenching the reaction mixture with water (3 equiv), the solvents were removed under reduced pressure. Diethyl ether was added, and the mixture was neutralized with 1 M HCl. The ether phase was separated, and the aqueous phase was extracted two more times with diethyl ether. After drying the combined organic phases with anhydrous magnesium sulfate and filtering off all solids, the solvent was removed using a rotary evaporator. The crude product was purified by flash chromatography using a mixture of hexanes and diethyl ether.

2-[2-(1-Indenyl)ethyl]-2-indanol and 2-[2-(3-Indenyl)-ethyl]-2-indanol (8). The synthesis followed the described general route to yield an inseparable mixture of both isomers. The obtained ratio of isomers was 64% 2-[2-(1-indenyl)ethyl]-2-indanol and 36% 2-[2-(3-indenyl)ethyl]-2-indanol, measured by ^{1}H NMR. Substrate: 3-(1-Indenyl)propionic acid methyl ester 4.84 g (23.9 mmol). Yield: 5.16 g of a pale yellow solid (18.7 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63−1.88 (m, 4H, major isomer, 1H, minor isomer), 2.14−2.22 (m, 1H, major isomer, 2H minor isomer), 2.77−2.82 (m, 2H, minor isomer), 2.89 (d, J = 16.2 Hz, 1H, major isomer), 2.91 (d, J = 16.2 Hz, 1H, major isomer), 2.99 (d, J = 16.2 Hz, 1H, major isomer), 3.02 (d, J = 16.2 Hz, 1H, major isomer), 3.04 (d, J = 16.2 Hz, 2H, minor isomer), 3.16 (d, J = 16.2 Hz, 2H, minor isomer), 3.35 (d, J = 1.9 Hz, 2H, minor isomer), 3.54 (m, 1H, major isomer), 6.25 (t, J = 1.6 Hz, 1H, minor isomer), 6.54 (dd, J = 5.5 and 1.8 Hz, major isomer), 6.83 (dd, J = 5.5 and 1.8 Hz, major isomer), 7.14−7.48 (m, 8H arom. both isomers). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.1, 26.3, 37.5, 37.9, 39.0, 46.9, 47.2, 50.3, 82.5, 119.1, 121.2, 123.0, 124.7, 124.9, 125.3, 125.4, 126.2, 126.7, 126.8, 126.9, 127.8, 131.4, 139.1, 141.3, 141.4, 144.5, 144.6, 147.6.

2-(2-Phenyl-3-indenylmethyl)-2-indanol (9). The synthesis followed the described general route except that the flash chromatography was followed by a recrystallization from diethyl ether at −40 °C. Substrates: 3-(2-phenylindenyl)acetic acid methyl ester and 1-(2-phenylindenyl)acetic acid methyl ester 4.70 g (17.8 mmol). Yield: 3.49 g of an off-white solid (10.3 mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78 (s, 1H), 2.80 (d, J = 16.0 Hz, 2H), 2.97 (d, J = 16.0 Hz, 2H), 3.29 (s, 2H), 3.78 (s, 2H), 7.02−7.09 (m, 4H), 7.20−7.42 (m, 5H), 7.46−7.52 (m, 3H), 7.56 (d, J = 7.6 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 34.9, 42.9, 46.7, 84.1, 120.7, 123.6, 125.0, 126.5, 126.6, 127.3, 128.5, 128.9, 135.5, 138.1, 141.4, 142.7, 144.9, 147.2.

2-[2-(2-Phenyl-3-indenyl)ethyl]-2-indanol and 2-[2-(2-Phenyl-1-indenyl)ethyl]-2-indanol (10). The compounds were synthesized according to the general procedure. Three fractions were collected from the flash chromatography: the first containing pure 2-[2-(2-phenyl-3-indenyl)ethyl]-2-indanol and the third only 2-[2-(2-phenyl-1-indenyl)ethyl]-2-indanol, with the middle fraction being a mixture of both isomers. The ratio of the isomers was 66% 2-[2-(2-phenyl-3-indenyl)ethyl]-2-indanol and 34% 2-[2-(2-phenyl-1-indenyl)ethyl]-2-indanol, measured by ^{1}H NMR. Substrate: 3-(2-phenyl-1-indenyl)-propionic acid methyl ester 4.84 g (23.9 mmol). Yield: 5.16 g of a yellow solid (18.7 mmol, 78%). 2-[2-(2-Phenyl-3-indenyl)-ethyl]-2-indanol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (s, 1H), 2.13−2.17 (m, 2H), 2.95−2.99 (m, 2H), 3.00 (d, J = 16.2 Hz, 2H), 3.13 (d, J = 16.2 Hz, 2H), 3.74 (s, 2H), 7.12−7.52 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 39.6, 41.6, 47.1, 82.3, 119.5, 123.7, 124.8, 125.2, 126.7, 126.9, 130.1, 131.0, 131.7, 137.6, 138.9, 140.7, 141.1, 143.9, 146.5. 2-[2-(2-Phenyl-1-indenyl)ethyl]-2-indanol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13−1.23 (m, 1H), 1.27−1.35 (m, 1H), 1.36 (s, 1H), 2.04−2.13 (m, 1H), 2.28−2.37 (m,1H), 2.64 (d, J = 16.5 Hz, 1H), 2.70 (d, J = 16.5 Hz, 1H), 2.75 (s, 2H), 4.11 (t, J = 4.6 Hz, 1H), 7.05−7.13 (m, 4H), 7.21 (td, J = 7.4 and 1.1 Hz, 1H), 7.26−7.32 (m, 3H), 7.38−7.43 (m, 3H), 7.50 (d, J = 7.3 Hz, 1H), 7.54−7.56 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 25.6, 34.3, 46.6, 47.1, 48.7, 82.3, 121.2, 123.1, 125.0, 125.1, 126.6, 126.9, 127.0, 127.5, 127.7, 128.9, 135.6, 141.3, 144.7, 147.4, 150.6.

General Procedure for the Ligand Synthesis from the Corresponding Indenyl- and 2-Phenylindenyl-2-indanol Derivatives. *p*-Toluenesulfonic acid monohydrate (0.15 equiv) and the 2-indanol substrate (1.0 equiv) were suspended in reagent grade toluene to give a 0.1 M suspension. The mixture was refluxed for 2 h and then cooled to room temperature. Distilled water was added until the solid went into solution. The toluene phase was separated and the aqueous layer washed twice with diethyl ether. The combined organic layers were dried with anhydrous magnesium sulfate and the solvents removed under reduced pressure. Depending on the ligand, purification was performed by flash chromatography, recrystallization, or a combination of both methods.

1-(1-Indenyl)-2-(2-indenyl)ethane and 1-(3-Indenyl)-2-(2-indenyl)ethane (11). The compounds were synthesized by the described general route. A mixture of both isomers was obtained after flash chromatography with hexanes. Separation of the major isomer, 1-(1-indenyl)-2-(2-indenyl)ethane, was achieved by recrystallization from a solution in hexanes at −40 °C. The ratio of isomers was 70% 1-(1-indenyl)-2-(2-indenyl)-ethane and 30% 3-(1-indenyl)-2-(2-indenyl)ethane, measured by ^{1}H NMR. Substrates: 2-[2-(1-indenyl)ethyl]-2-indanol and 2-[2-(3-indenyl)ethyl]-2-indanol 5.16 g (18.7 mmol). Yield: 3.19 g of a pale yellow solid (12.4 mmol, 66%). 1-(1-Indenyl)-2-(2-indenyl)-ethane: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83−1.90 (m, 1H), 2.21−2.28 (m, 1H), 2.46−2.59 (m, 2H), 3.30 (s, 2H), 3.54−3.57 (m, 1H), 6.54 (s, 1H), 6.58 (dd, J = 5.7 and 1.7 Hz, 1H), 6.84 (dd, J = 5.7 and 1.5 Hz, 1H), 7.10 (t, J = 7.3 Hz, 1H), 7.19−7.28 (m, 5H), 7.37 (d, J = 7.3 Hz, 1H), 7.44 (d, J = 7.3 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 28.9, 30.8, 41.2, 50.1, 120.0, 121.2, 122.9, 123.5, 123.8, 124.9, 126.4, 126.5,

126.7, 131.3, 138.9, 143.1, 144.4, 145.6, 147.5, 150.3. 3-(1-Indenyl)-2-(2-indenyl)ethane: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (s, 4H), 3.32 (s, 2H), 3.37 (s, 2H), 6.22 (s, 1H), 6.57 (s, 1H). All aromatic peaks cannot be assigned because they are covered by the aromatic peaks of the major isomer.

(2-Indenyl)-(2-phenyl-3-indenyl)methane (12). By following the general route for the ligand preparation, only the 3-substituted isomer was obtained. After flash chromatography, an additional recrystallization step from hexanes at −40 °C led to the product. Substrate: 2-(2-phenyl-3-indenylmethyl)-2-indanol 2.50 g (7.4 mmol). Yield: 2.18 g of a pale yellow solid (6.8 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (s, 2H), 3.86 (s, 2H), 3.89 (s, 2H), 6.58 (s, 1H), 7.09−7.14 (m, 1H), 7.17−7.43 (m, 6H), 7.46−7.52 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 28.7, 41.2, 41.6, 119.9, 120.2, 123.4, 123.9, 124.8, 126.3, 126.5, 127.1, 127.8, 128.0, 128.5, 136.3, 137.1, 142.2, 142.5, 143.2, 145.4, 146.5, 147.6.

2-(2-Indenyl)-1-(2-phenyl-3-indenyl)ethane and 2-(2-Indenyl)-1-(2-phenyl-1-indenyl)ethane (13). The synthesis yielded a mixture of both isomers. Cleaning of the crude product was achieved by recrystallization from a 90:10 mixture of hexanes and diethyl ether at −40 °C. The ratio of isomers was 53% 2-(2-indenyl)-1-(2-phenyl-3-indenyl)ethane and 47% and 2-(2-indenyl)-1-(2-phenyl-1-indenyl)ethane, measured by ^{1}H NMR. Substrates: 2-[2-(2-phenyl-3-indenyl)ethyl]-2-indanol and 2-[2-(2-phenyl-1-indenyl)ethyl]-2-indanol 2.51 g (7.0 mmol). Yield: 2.0 g of an off-white solid (with an additional flash chromatography with hexanes, a white solid was obtained that shows no differences in the spectra) (6 mmol, 85%). Since a separation of isomers was not necessary for the metallocene preparation, only mixed spectra were obtained: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98−2.03 (m, 1H, minor isomer), 2.09−2.20 (m, 2H, minor isomer), 2.34−2.42 (m, 1H, minor isomer), 2.85−2.89 (m, 2H, major isomer), 3.04−3.09 (m, 2H, major isomer), 3.08 (s, 2H, minor isomer), 3.33 (s, 2H, major isomer), 3.77 (s, 2H, major isomer), 4.14 (t, J = 4.5 Hz, 1H, minor isomer), 6.35 (s, 1H, minor isomer), 6.57 (s, 1H, major isomer), 7.01−7.57 (m, 14H, major isomer; 14H, minor isomer). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 25.6, 25.8, 29.9, 30.4, 41.0, 41.1, 41.5, 48.6, 119.3, 119.8, 120.0, 121.1, 123.1, 123.3, 123.4, 123.5, 123.6, 123.7, 124.8, 124.9, 126.0, 126.1, 126.3, 126.4, 126.5, 126.8, 126.9, 127.3, 127.5, 128.0, 128.5, 128.7, 128.8, 135.6, 137.4, 138.5, 141.2, 142.8, 142.9, 143.1, 144.5, 145.4, 146.2, 147.3, 149.8, 150.2, 150.4, 151.0.

(2-Indenyl)-(2-phenyl-3-indenyl)dimethylsilane (14). *n*-Butyllithium, 10.9 mL (17.4 mmol, 1.6 M in hexane), was added to a stirred solution of 2-phenylindene, 3.17 g (16.5 mmol), in 180 mL of THF at 0 °C over 20 min. The reaction mixture was warmed to room temperature, stirred for 5 h, and transferred to a dropping funnel over a flask containing a solution of chloro-2-indenylsilane, 3.63 g (17.4 mmol), in 50 mL of THF. The lithium salt solution was added dropwise over a period of 2 h. After stirring at room temperature overnight, the reaction was quenched with 50 mL of distilled water. THF was removed under reduced pressure, and diethyl ether and brine were added to the crude product. After separating the ether layer, the aqueous phase was washed two times with diethyl ether. After the combined organic layers were dried with anhydrous magnesium sulfate, the volatiles were removed in vacuo. The crude product was purified by flash chromatography using hexane as solvent. Two fractions were collected. The first was a 3:1 mixture of the product and 2-phenylindene. The second fraction contained the pure ligand. Yield: 3.75 g of a yellow oil, which crystallizes upon standing to give an off-white solid (9.9 mmol, 60%) and 2.05 g from the mixed fraction (4.8 mmol, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.10 (s, 3H), 0.02 (s, 3H), 2.81 (dd, J = 23.1 and 1.7 Hz, 1H), 3.14 (dd, J = 23.0 and 1.8 Hz, 1H), 4.26 (s, 1H), 6.84−6.86 (m, 1H), 7.05 (s, 1H), 7.09−7.47 (m, 13H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ −4.3, −2.6, 42.8, 46.0, 121.0, 121.1, 123.3, 123.6, 124.9, 125.3, 125.5, 126.2, 127.3, 128.4, 137.4, 142.7, 144.5, 145.2, 145.3, 147.0, 149.8.

General Procedure for Metallocene Synthesis from the Corresponding Bridged Ligands. The ligand (1 equiv) was suspended or dissolved, depending on the solubility of the ligand, in diethyl ether (0.1 M) in a Schlenk flask under nitrogen. After adding *n*-butyllithium (2.05 equiv, 1.6 or 2.5 M solution in hexane) dropwise at 0 °C over 20−30 min, the reaction was warmed to room temperature, stirred an additional 6−9 h, cooled again to 0 °C, and transferred by cannula to a suspension of zirconium(IV) chloride (1.05 equiv) in diethyl ether at 0 °C. The reaction mixture immediately turned a bright color. The mixture was warmed to room temperature and stirred overnight. After all volatiles were removed in vacuo, and dry methylene chloride was added. The suspension was cannula transferred to a Schlenk frit with Celite and filtered to give a bright colored solution. All zirconocenes were purified by recrystallization from dry methylene chloride or methylene chloride layered with pentane.

[1-(1-Indenyl)-2-(2-indenyl)ethane]zirconium Dichloride (1). The compound was synthesized by the described general route. An orange solution in methylene chloride was obtained after the filtration. The substance was purified by recrystallization from a concentrated methylene chloride solution layered with pentane at −40 °C, followed by a second recrystallization from a concentrated methylene chloride solution at −40 °C. The compound decomposes quickly even in the glovebox. Substrate: 1-(1-indenyl)-2-(2-indenyl)ethane, 858 mg (3.32 mmol). Yield: 182 mg of a yellow solid (0.44 mmol, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39−3.55 (m, 3H), 3.69−3.77 (m, 1H), 6.13 (d, J = 2.5 Hz, 1H), 6.37 (d, J = 2.7 Hz, 1H), 6.53 (d, J = 3.4 Hz, 1H), 6.78 (d, J = 3.4 Hz, 1H), 7.13−7.36 (m, 5H), 7.47−7.55 (m, 2H), 7.65−7.68 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 28.0, 31.6, 99.6, 104.7, 112.1, 114.6, 121.7, 121.8, 123.4, 125.2, 125.3, 126.0, 126.1, 126.9, 127.0, 128.0, 129.3, 130.4, 140.7, 145.5. Anal. Calcd for $C_{20}H_{16}Cl_2Zr$: C, 57.40; H, 3.85. Found: C, 57.25; H, 4.07.

[2-(2-Indenyl)-1-(2-phenyl-1-indenyl)ethane]zirconium (2). The compound was synthesized according to the general route. A yellow solution in methylene chloride was obtained after the filtration. The crude product was dissolved in methylene chloride, concentrated, and layered with about the same volume of dry pentane. The flask was transferred to a −40 °C freezer for 4 days. The yellow solid obtained by cannula filtration still showed impurities. The recrystallization was repeated to give the analytically pure product. Substrate: 2-(2-indenyl)-1-(2-phenyl-3-indenyl)ethane and 2-(2-indenyl)-1-(2-phenyl-1-indenyl)ethane 810 mg (2.42 mmol). Yield: 302 mg of a yellow solid (0.61 mmol, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19−3.34 (m, 2H), 3.77−3.93 (m, 2H), 5.72 (d, J = 2.5 Hz, 1H), 6.16 (d, J = 2.5 Hz, 1H), 6.88 (s, 1H), 7.13−7.32 (m, 5H), 7.41−7.50 (m, 3H), 7.54−7.58 (m, 2H), 7.65−7.68 (m, 1H), 7.84−7.87 (m, 2H). ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_4): δ 27.0, 30.6, 100.9, 103.9, 112.7, 117.1, 122.2, 125.1, 125.2, 125.5, 125.7, 125.8, 126.3, 127.0, 127.1, 127.3, 128.6, 128.8, 128.9, 129.2, 129.5, 132.5, 134.5, 141.2. Anal. Calcd for $C_{26}H_{20}Cl_2Zr$: C, 63.14; H, 4.08. Found: C, 63.23; H, 4.05.

[(2-Indenyl)-(2-phenyl-1-indenyl)dimethylsilane]zirconium Dichloride (3). The compound was synthesized according to the general route. A yellow solution in methylene chloride was obtained after the filtration. The crude product was dissolved in methylene chloride, concentrated, and layered with about the same volume of dry pentane. The flask was transferred to a −40 °C freezer for 4 days. After filtration, the mother liquor was concentrated and layered with dry pentane. After 4 days in the freezer at −40 °C a second crop was filtered off. Substrate: (2-Indenyl)-(2-phenyl-3-indenyl)dimethylsilane, 1.318 g (3.62 mmol). Yield: 759 mg of a yellow solid (1.45 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.55 (s, 3H), 1.1 (s, 3H), 5.66 (dd, J = 2.5, 0.9 Hz, 1H), 6.12 (dd, J = 2.5, 0.9 Hz, 1H), 7.06 (d, J = 0.7 Hz, 1H), 7.14−7.22 (m, 2H), 7.28−7.38 (m, 2H), 7.40−7.58 (m, 5H) 7.59−7.72 (m, 4H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ −1.0, 1.6, 87.6, 104.6, 108.5, 112.2, 120.8, 125.1, 125.4, 125.6, 126.3, 126.6, 127.1, 127.2, 127.5, 128.3, 128.7, 129.1, 130.9, 131.4, 132.5, 134.6, 135.9, 140.7. Anal. Calcd for $C_{26}H_{22}Cl_2SiZr$: C, 59.52; H, 4.23. Found: C, 59.40; H, 4.28.

[(2-Indenyl)-(2-phenyl-1-indenyl)methane]zirconium Dichloride (4). The compound was synthesized according to

the described general route. A yellow solution in methylene chloride was obtained after the filtration and was concentrated until a precipitate formed. The flask was transferred to a −40 °C freezer. The first crop was filtered off after 4 days, and a second crop crystallized from 5 mL of methylene chloride layered with 6 mL dry pentane at −40 °C. The combined crops were recrystallized from methylene chloride at −40 °C to give the product. Substrate: (2-indenyl)-(2-phenyl-3-indenyl)-methane, 1.01 g (3.14 mmol). Yield: 638 mg of a yellow solid (1.33 mmol, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.54 (d, J = 13.7 Hz, 1H), 5.05 (d, J = 13.7 Hz, 1H), 5.08 (dd, J = 2.1 and 0.7 Hz, 1H), 5.83 (dd, J = 2.1 and 0.7 Hz, 1H), 6.95 (s, 1H), 7.16−7.63 (m, 11H), 7.87−7.90 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 25.6, 88.0, 97.8, 98.2, 100.4, 111.0, 112.6, 121.7, 122.5, 124.9, 125.2, 125.8, 126.3, 126.4, 126.8, 126.9, 127.2, 128.4, 128.7, 129.4, 129.8, 132.3, 133.5. Anal. Calcd for $C_{25}H_{18}Cl_2Zr$: C, 62.51; H, 3.78. Found: C, 60.71; H, 3.78.

Polymerizations. Polymerization Procedures. Toluene and liquid propylene were passed over towers containing activated alumina and supported copper (Q5) prior to use. Methylaluminoxane (MMAO, type 4) was obtained from Akzo Nobel as a toluene solution (6.9% v/v) and was dried in vacuo to remove solvent and residual trimethylaluminum prior to use. Polymerizations were carried out in a 300 mL stainless steel Parr reactor equipped with a mechanical stirrer. Temperature was maintained at 20 °C via an ethylene glycol/water cooling loop.

Preparation of Activated Catalysts for Propylene Polymerizations. A metallocene stock solution was prepared by dissolving around 7 mg of the metallocene in 10 mL of toluene in a glovebox. Methylaluminoxane (1000:1 [Al]:[Zr]) was dissolved in toluene and stirred for 10 min. The desired amount of the metallocene stock solution was added to the MMAO solution to give a total volume of 10 mL.

Propylene Polymerization in Liquid Propylene. The reactor was flushed three times with 100 psig of propylene gas. Liquid propylene (100 mL) was then condensed into a sight glass and transferred to the reactor. The activated metallocene solution was injected into the reactor under 200 psig of argon to start the reaction. Polymerizations were allowed to proceed for 20 min and then quenched with 10 mL of methanol injected under argon pressure. The reactor was vented, and the polymers were collected and precipitated into acidified methanol (5% HCl). After stirring overnight, the polymers were washed with methanol and water and dried in a vacuum oven at 40 °C.

Polymer Analysis. ^{13}C NMR spectra were recorded using a Varian Inova 300 MHz (75 MHz resolution for ^{13}C NMR) equipped with a 10 mm broad-band probe. Samples (200 mg) were run in a 90:10 v/v 1,1,2,2-tetrachloroethane/1,1,2,2-tetrachloroethane-d_2 solution at 100 °C. High-temperature GPC was performed at BP-Amoco on a Waters 150C GPC at 139 °C in 1,2,4-trichlorobenzene with two Polymer Laboratories PL GEL Mixed-B columns at a flow rate of 1 mL/min. Polypropylene standards were used. DSC traces were acquired on a Perkin-Elmer DSC 7. Polypropylene samples were annealed at 200 °C for 15 min and then cooled to room temperature with a rate of 10 °C/min. The samples were allowed to age at ambient temperature for 9 h. The samples were then heated to 200 °C with a rate of 20 °C/min.

Acknowledgment. This work was supported by the NSF under Grants CHE-9910240 and CHE-0305436. An Althouse Family Stanford Graduate Fellowship to S.E.R. and a DAAD Fellowship to M.F. are gratefully acknowledged.

References and Notes

(1) Phillips, R. A.; Wolkowicz, M. D. *Polypropylene Handbook: Polymerization, Characterization, Properties, Processing, Applications*; Hanser/Gardner Publications: Cincinnati, OH, 1996; pp 113−176.
(2) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.
(3) Scheirs, J.; Kaminsky, W. *Metallocene-Based Polyolefins: Preparation, Properties, and Technology*; John Wiley & Sons Ltd.: Chichester, 2000; Vol. 2.
(4) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355−6364.
(5) Wild, F.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63−67.
(6) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507−508.
(7) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.
(8) Leino, R.; Gomez, F. J.; Cole, A. P.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 2072−2082.
(9) Gomez, F. J.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 3358−3368.
(10) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48*−*9*, 253−295.
(11) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S. Z.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030−2031.
(12) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G. Y.; Winter, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 8569−8570.
(13) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219.
(14) Miller, S. A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934−945.
(15) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskela, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348−4355.
(16) Nele, M.; Mohammed, M.; Xin, S.; Collins, S.; Dias, M. L.; Pinto, J. C. *Macromolecules* **2001**, *34*, 3830−3841.
(17) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000−1009.
(18) Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061−2068.
(19) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771−3778.
(20) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779−3786.
(21) Mohammed, M.; Nele, M.; Al-Humydi, A.; Xin, S.; Stapleton, R. A.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 7930−7941.
(22) Gomez, F. J.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 3358−3368.
(23) Fan, W.; Leclerc, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 9555−9563.
(24) Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 8619−8625.
(25) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573.
(26) Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1996**, *29*, 4834−4845.
(27) Lin, S.; Waymouth, R. M. *Acc. Chem. Res.* **2002**, *35*, 765−773.
(28) Busico, V.; Cipullo, R.; Kretschmer, W. P.; Talarico, G.; Vacatello, M.; Van Axel Castelli, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 505−508.
(29) Busico, V.; Cipullo, R.; Kretschmer, W.; Talarico, G.; Vacatello, M.; Castelli, V. V. *Macromol. Symp.* **2002**, *189*, 127−141.
(30) Schneider, N.; Schaper, F.; Schmidt, K.; Kirsten, R.; Geyer, A.; Brintzinger, H. H. *Organometallics* **2000**, *19*, 3597−3604.
(31) Knuppel, S.; Faure, J. L.; Erker, G.; Kehr, G.; Nissinen, M.; Frohlich, R. *Organometallics* **2000**, *19*, 1262−1268.
(32) Dreier, T.; Bergander, K.; Wegelius, E.; Frohlich, R.; Erker, G. *Organometallics* **2001**, *20*, 5067−5075.
(33) Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707−2715.
(34) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586−11587.
(35) Hu, Y. R.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908−6916.
(36) Kravchenko, R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 1−6.
(37) Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A: Chem.* **1998**, *136*, 23−33.
(38) Lin, S.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 8283−8290.
(39) Petoff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909−5916.
(40) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174−11182.

(41) Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039−2046.
(42) Petoff, J. L. M.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316−11322.
(43) Petoff, J. L. M.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 7984−7989.
(44) Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 380−388.
(45) Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147−4155.
(46) Lin, S.; Kravchenko, R.; Waymouth, R. M. *J. Mol. Catal. A: Chem.* **2000**, *158*, 423−427.
(47) Lin, S.; Tagge, C. D.; Waymouth, R. M.; Nele, M.; Collins, S.; Pinto, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 11275−11285.
(48) Dankova, M.; Kravchenko, R. L.; Cole, A. P.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 2882−2891.
(49) Wilmes, G. M.; Lin, S.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 5382−5387.
(50) Busico, V.; Castelli, V. V. A.; Aprea, P.; Cipullo, R.; Segre, A.; Talarico, G.; Vacatello, M. *J. Am. Chem. Soc.* **2003**, *125*, 5451−5460.
(51) Busico, V.; Cipullo, R.; Segre, A. L.; Talarico, G.; Vacatello, M.; Castelli, V. V. A. *Macromolecules* **2001**, *34*, 8412−8415.
(52) Christopher, J. N.; Jordan, R. F.; Petersen, J. L.; Young, V. G. *Organometallics* **1997**, *16*, 3044−3050.
(53) Lang, H.; Weiss, T.; Becke, S. Eur. Pat. Appl. 940408, 1999.
(54) Halterman, R. L.; Marin, V. P. *Abstr. Am. Chem. Soc.* **2000**, *219*, 734-INOR.
(55) Lipshutz, B. H.; Kozlowski, J. A.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E. *J. Organomet. Chem.* **1985**, *285*, 437−447.
(56) Lipshutz, B. H.; Ellsworth, E. L.; Behling, J. R.; Campbell, A. L. *Tetrahedron Lett.* **1988**, *29*, 893−896.
(57) Lipshutz, B. H. *Synlett* **1990**, 119−128.
(58) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.
(59) Kukral, J.; Rieger, B. *Macromol. Symp.* **2002**, *177*, 71−86.
(60) Waymouth, R. M.; Wilmes, G.; Finze, M.; Reybuck, S.; Lin, S. *Abstr. Am. Chem. Soc.* **2002**, *224*, U499.
(61) Pietsch, M. A.; Rappe, A. K. *J. Am. Chem. Soc.* **1996**, *118*, 10908−10909.
(62) Cavallo, L.; Guerra, G.; Corradini, P. *Gazz. Chim. Ital.* **1996**, *126*, 463−467.
(63) Maiti, A.; Sierka, M.; Andzelm, J.; Golab, J.; Sauer, J. *J. Phys. Chem. A* **2000**, *104*, 10932−10938.
(64) Wilmes, G. M.; Polse, J. L.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 6766−6772.
(65) McEwen, I.; Ronnqvist, M.; Ahlberg, P. *J. Am. Chem. Soc.* **1993**, *115*, 3989−3996.
(66) Schumann, H.; Karasiak, D. F.; Muhle, S. H.; Halterman, R. L.; Kaminsky, W.; Weingarten, U. *J. Organomet. Chem.* **1999**, *579*, 356−372.

MA0303972