

Mixed Ligand Metallocenes as Catalysts for Elastomeric Polypropylene

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A new synthesis of unbridged mixed ring zirconocenes was developed and a series of mixed ligand zirconocenes with substituted 2-arylindenyl and 1-methyl-2-arylindenyl ligands have been prepared. When activated with methylaluminoxane, the mixed ligand complexes catalyze the polymerization of propylene to give elastomeric polypropylene. The propylene polymerization behavior of the mixed ligand catalysts was compared to that of their bis(indenyl) analogues to determine the relative contribution of each ligand to the activity and stereospecificity of the catalyst. The effects of 2-arylindenyl and 1-methyl-2-arylindenyl ligands on the stereospecificity of the catalysts are essentially additive; the stereospecificity of the mixed ring complex is intermediate to that of the bis(2-aryllindene) analogues. However, the effect of 1-methyl substitution on catalyst productivity is not additive; the productivities exhibited by bis(2-arylindenyl)ZrCl₂/MAO and (1-methyl-2-arylindenyl)(2-arylindenyl)ZrCl₂/MAO derived catalysts are similar and substantially higher than those of the bis(1-methyl-2-phenylindenyl)ZrCl₂/MAO catalysts.

Introduction

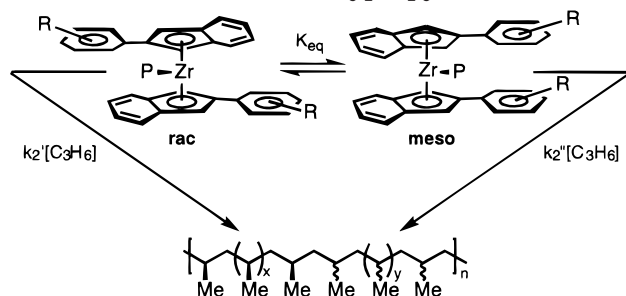
Natta's discovery of thermoplastic elastomeric polypropylene in the late 1950s¹ prompted both industrial and academic interest in producing and studying this material. To explain the intriguing elastomeric properties, Natta proposed that the material had a stereoblock microstructure, consisting of alternating segments of isotactic and atactic sequences, which resulted from a dynamic mechanism in which the catalyst active site altered its stereospecificity several times during the formation of the polymer chain.² Unfortunately, the heterogeneous nature of the catalysts frustrated efforts to investigate the mechanism and optimize these polymerization reactions. Nevertheless, a number of industrial efforts have made substantial progress for the synthesis of elastomeric polypropylenes with a wide range of structures and mechanical properties.^{3–18}

Furthermore, Chien and Collins have shown that homogeneous catalysts with well-defined structures are also capable of producing elastomeric polypropylene.^{19–25}

Recently, our group reported a new strategy for producing elastomeric polypropylene.^{26–31} The approach is based on a fluxional bis(2-arylindenyl)zirconium homogeneous catalyst system that can isomerize between stereospecific chiral and aspecific achiral geometries during the course of the polymerization (Scheme 1). Investigations of these systems have shown that the

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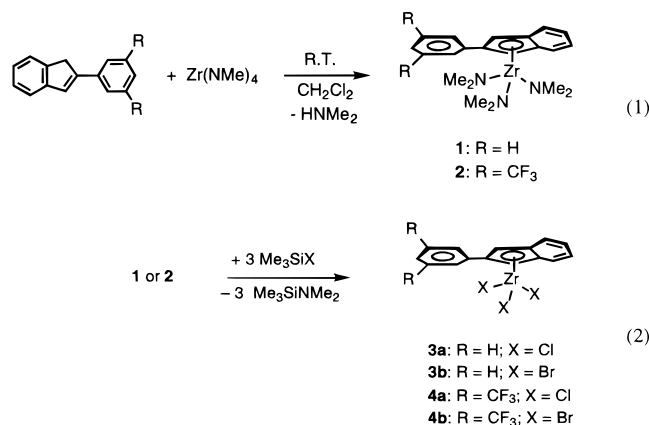
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Scheme 1. Proposed Mechanism for Formation of Elastomeric Polypropylene

productivity and stereospecificity of the catalysts (and thus, the physical and mechanical properties of the resulting polymers) can be significantly influenced by utilizing different substituents in the 1- and 3',5'-positions of the 2-phenylindenyl ligand.^{27,30} To further investigate the effects of ligand substituents on catalyst behavior and produce a family of catalysts capable of accessing a broader range of polypropylene structures, we now report a new route to unbridged mixed ring zirconocenes and describe the polymerization behavior of mixed ring 2-arylindeindenyl zirconocenes.

Results

Synthesis of Mixed Ligand Bis(2-arylindeindenyl)-zirconium Complexes. The reaction of 2-arylindeindenyls with zirconium tetrakis(dimethylamide) eliminates 1 equiv of dimethylamine to produce 2-arylindeindenylzirconium tris(dimethylamide) (**1** and **2**) (eq 1).³² The complexes may be isolated by crystallization from hexane or used without purification. Reaction of **1** or **2** with 3 equiv of trimethylsilylhalide in methylene chloride results in the elimination of trimethylsilyl(dimethyl)amide and the formation of the corresponding 2-arylindeindenylzirconium trihalide (**3** and **4**) (eq 2).^{33,34}



The identity of the halide substituent appears to influence the properties of half-sandwich complexes **3** and **4** in solution. The trichloride complexes **3a** and **4a** appear to exist primarily as oligomers as indicated by broad NMR resonances and low solubilities in most

solvents. However, the tribromide complexes **3b** and **4b** exhibit sharp ¹H NMR resonances, which are consistent with a monomeric structure. Thus, relatively soluble tribromides **3b** and **4b** were recrystallized from toluene in good yield, while trichloride **3a** and **4a** could only be purified by successive diethyl ether, toluene, and pentane washes and were isolated in lower yields.

NMR analysis of **4** revealed residual signals from Me₃-Si and NMe₂-containing impurities which could not be removed by recrystallization. Nevertheless, the impurities did not have a detrimental effect on the subsequent transformations of **4**, and the complexes were used without further purification.

Mixed ring zirconocene dihalide complexes were easily prepared by reaction of half-sandwich zirconium trihalides **3** and **4** with the corresponding lithium 2-arylindeindenyl in toluene. When optimized, the mixed ring complexes were obtained in good yield (50–80%). To identify the effect of the halogen ligands, bis(indenyl) complexes (2PhInd)₂ZrBr₂ (**5b**) (2PhInd = 2-phenylindenyl) and (BArf)₂ZrBr₂ (**10b**) (BArf = 2-(3',5'-bistrifluoromethylphenyl)indenyl) were prepared from the half-sandwich tribromides **3b** and **4b**, respectively. The preparation of dichloride analogues **5a** and **10a** has been previously described.^{26,27}

All previously characterized bis(2-arylindeindenyl)zirconium dichloride precatalysts exhibit C_{2v} symmetry in solution (as judged by ¹H NMR spectroscopy), which is consistent with rapid rotation of the indenyl ligands.^{26–29} Similarly, 3',5'-substituted mixed ligand catalysts exhibited C_s symmetry in solution, and the ring rotation could not be substantially slowed even at low temperatures (–80 °C). Introduction of a 1-Me substituent on one of the ligands further decreased the symmetry of complexes **8,9** and **12,13** to C₁ and made the two cyclopentadienyl-type protons on the second ligand diastereotopic. A characteristic doublet–doublet–singlet (*J* ≈ 2.5 Hz) pattern in the cyclopentadienyl proton region was observed for the 1-Me-substituted mixed ligand complexes.

In general, the chemical shifts of the cyclopentadienyl protons of the mixed ligand complexes fell between those of the parent bis(indenyl) complexes. This was particularly evident for ligands having substantially different electronic properties and chemical shifts. For example, the chemical shift of the cyclopentadienyl protons of (2PhInd)₂ZrCl₂ (**5a**) and (BArf)₂ZrCl₂ (**10a**) appear at δ 6.41 and 5.69, respectively. The corresponding resonances of mixed ring complex **6a** appear at δ 6.23 and 5.87; thus, the cyclopentadienyl protons of the 2-PhInd and BArf ligands are shifted 0.18 ppm upfield and 0.18 downfield, respectively, from their analogous resonances of **5a** and **10a**.

Dimethyl-substituted **7** has been characterized by X-ray diffraction (Figure 1). Unlike **5a**, in which both the syn- and anti-rotamers are present in the asymmetric unit cell,²⁶ **7** adopts only the syn-like structure in the solid state, similar to that observed for (DMPInd)₂ZrCl₂ (**14**) (DMPInd = 2-(3',5'-dimethylphenyl)indenyl).²⁷ Aside from the difference in halogen bond lengths, mixed ligand **7** is essentially isostructural to the syn-rotamer of both **5a** and **14**. For example, the dihedral angles between the phenyl and indenyl rings of **7** are 13° for

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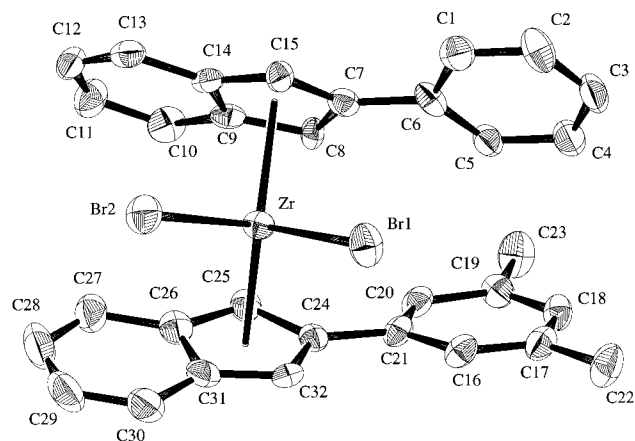


Figure 1. X-ray crystal structure of the mixed ring indenylmetallocene **7**.

Ph–Ind and 11° for DMP–Ind) compared to 10° and 12° for *syn*-**5a**.

Polymerization Studies: Effect of Halide Ligands. The nature of the halogen atom of (2-ArInd)₂ZrCl₂ does not appear to influence the stereospecificity, measured by isotactic pentad content ([mmmm]), or productivities of the catalysts produced by reaction with MAO (Table 1, entries 1–6). The stereospecificities of the dichloride **10a**/MAO ([mmmm] = 67%) and the dibromide **10b**/MAO ([mmmm] = 69%) are identical within experimental error (ca. 2%). The productivities for the dichloride and dibromide derivatives are also quite similar, as both unsubstituted **5a** and **5b**/MAO showed productivities of 2500 kg/(mol Zr·h). Catalysts derived from trifluoromethyl-substituted **10a** and **10b**/MAO differ only slightly, having productivities of 3000 and 2700 kg/(mol Zr·h), respectively. However, the molecular weight distributions of the polymers produced by dichloride complexes **5a**, **6a**, and **10a**/MAO are slightly broader than those produced by the analogous dibromide catalysts.

Polymerization Studies: 3',5'-Substituted Mixed Ligand Complexes. All mixed ligand zirconocenes in combination with MAO were active propylene polymerization catalysts (Table 1). The isotacticity of the polymers produced by the 3',5'-substituted mixed ligand complexes ranged from 21% for DMPInd/2PhInd-ligated **7**/MAO to 54% for DMPInd/Barf-substituted **11**/MAO (Table 1, entries 7, 8). In general, the isospecificities of the mixed ligand catalysts fell between the extremes defined by their respective bis(indenyl) analogues. This behavior was particularly evident when the bis(indenyl) complexes had widely different isospecificities. For example, (DMPInd)₂ZrCl₂ (**14**)/MAO produces a polymer with a relatively low isotacticity ([mmmm] = 23%), while (Barf)₂ZrX₂ (**10**)/MAO derived catalysts are highly isospecific ([mmmm] = 67–69%, Table 1, entries 9 and 5,6). The corresponding mixed ligand catalyst **11**/MAO shows an intermediate isospecificity of [mmmm] = 54% (Table 1, entry 7). Similarly, the isotacticity of polymers produced by mixed ligand **6**/MAO ([mmmm] = 33–35%) falls between those exhibited by its bis(indenyl) analogues (2PhInd)₂ZrX₂ (**5**)/MAO ([mmmm] = 28%) and **10**/MAO ([mmmm] = 67–69%) (Table 1, entries 1–6). The single exception was dimethyl-substituted **7**/MAO, which produced a polymer having essentially the same isotacticity ([mmmm] = 21%) as that of its homo ligand

analogue **14**/MAO ([mmmm] = 23%) (Table 1, entries 8,9, and 1,2, respectively).

The productivities and molecular weights of polymers produced by 3',5'-substituted mixed ligand catalysts were similar to those generally observed for bis(2-arylindenyl)zirconium catalysts. The productivities ranged from 1140 kg/(mol Zr·h) for **6b**/MAO to 2180 kg/(mol Zr·h) for **11**/MAO.

Polymerization Studies: Effect of 1-Me Substitution. The productivity trends for **9**, **12**, **13**/MAO were consistent with our previous observation that 1-methyl substitution lowers propylene polymerization productivity of catalysts of this type (Table 1, entries 6, 7, 11, 12).³⁰ Surprisingly, the productivity of 2PhInd/1Me2PhInd **8**/MAO (1Me2PhInd = 1-methyl-2-phenylindenyl) was somewhat higher than that found for unsubstituted bis(2-phenylindenyl)zirconium dichloride **5a**/MAO. Isotactic pentad contents of mixed ligand catalysts ranged from 14% for **8**/MAO to 47% for **13**/MAO and fell into the limits set by their corresponding bis(indenyl) analogues *meso*-(1Me2PhInd)₂ZrCl₂ (*meso*-**15**)/MAO (11%) at the lower end and (Barf)₂ZrCl₂/MAO (**10a**, 68%) at the higher end (Table 1, entries 14, 11,12, and 5,6). Molecular weights (from 217 000 to 293 000) and molecular weight distributions (*M_w*/*M_n* = 3–7) observed for **8**, **9**, **12**, **13**/MAO are also in the range typically observed for unbridged bis(2-arylindenyl) catalysts.

Discussion

Synthesis. In general, L₂ZrCl₂ complexes (L = cyclopentadienyl or indenyl-type ligand) are easily made from the corresponding alkali cyclopentadienide or indenide and zirconium tetrachloride. However, due to the difficulties in preparing the intermediate half-sandwich zirconium complexes (LZrCl₃), very few mixed ring zirconocenes (L'L''ZrCl₂) have been prepared. Apparently, the high reactivity of alkali cyclopentadienides and trimethylsilylcyclopentadienes, combined with the relative solubility of LZrCl₃ compared to ZrCl₄, precludes single substitution for all but sterically demanding ligands.^{35–37} Alternatively, routes involving free radical chlorination of commercially available Cp₂ZrCl₂ were needed to prepare Cp₂ZrCl₃.^{38,39}

Recently, Morris and co-workers reported that the reaction of indenyltrialkyltin with ZrCl₄ generated IndZrCl₃ in good yields.⁴⁰ While we found that **3a** could be successfully produced by the tin-mediated synthesis, we have found the following method to be much more convenient and efficient to prepare 2-arylindenyl half-sandwich complexes. The reaction of 2-arylindenes with zirconium tetrakis(dimethylamide) allows the introduction of only a single ligand, presumably due to steric constraints (eq 1).³² The half-sandwich trihalide complex can then be prepared simply by the addition of 3 equiv

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Table 1. Propylene Polymerization with Fluxional Homogeneous Catalysts ($L^1L^2ZrX_2$)^a

entry no.	catalyst	ligand 1	ligand 2	X	prod ^b	[mmmm] ^c	[m] ^c	M_w ^d	MWD
1	5a	2PhInd	2PhInd	Cl	2480	28	67	459	3.7
2	5b	2PhInd	2PhInd	Br	2490	28	67	393	3.2
3	6a	2PhInd	BArf	Cl	1440	35	72	348	3.3
4	6b	2PhInd	BArf	Br	1140	33	73	306	2.8
5	10a	BArf	BArf	Cl	3000	69	88	505	5.7
6	10b	BArf	BArf	Br	2740	67	88	538	5.2
7	11	BArf	DMPInd	Br	2180	54	81	249	4.4
8	7	2PhInd	DMPInd	Br	1470	21	64	313	2.9
9	14	DMPInd	DMPInd	Cl	780	23	65	240	3.0
10	12	BArf	1Me2PInd	Cl	1810	24	65	262	3.7
11	13	BArf	1MeBarf	Cl	1030	47	78	270	6.5
12	8	2PhInd	1Me2PInd	Cl	2800	14	59	293	3.8
13	9	2PhInd	1MeBarf	Cl	1350	31	67	217	4.4
14	meso-15	1Me2PInd	1Me2PInd	Cl	140	11		69	8.6
15	rac-15	1Me2PInd	1Me2PInd	Cl	250	16		56	15.3

^a Polymerization conditions: 100 mL propylene/20 mL toluene, 20 °C, $[Zr] = 5 \times 10^{-5}$ M, $[Al]/[Zr] = 1000$. ^b kg/(mol Zr·h). ^c (%). ^d ($\times 1000$).

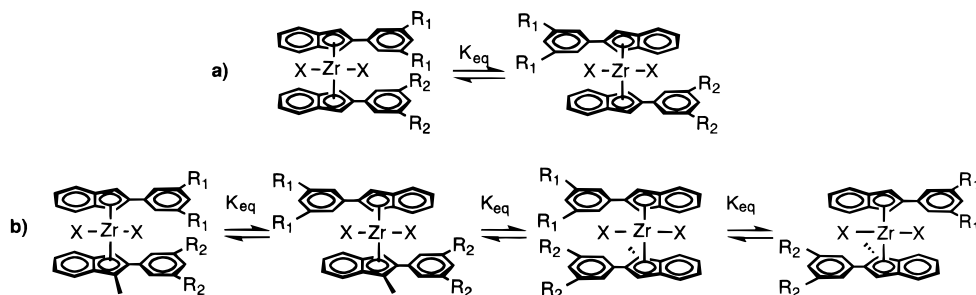
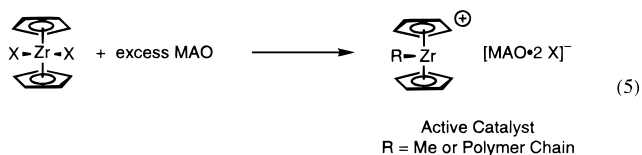
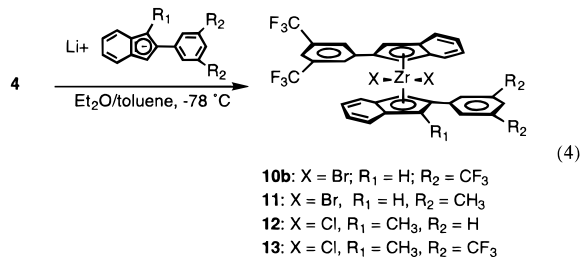
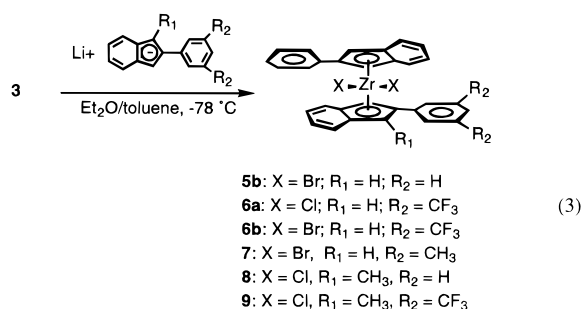


Figure 2. (a) Syn- and anti-rotamers of a 3',5'-substituted mixed 2-aryindenyl catalyst. (b) Rotamers that result from 1-Me- and 3',5'-substituted mixed 2-aryindenyl catalyst.

of the desired trimethylsilyl halide (eq 2).^{33,34} The half-sandwich tribromides are more easily isolable due to their enhanced solubility relative to the trichlorides.

Structure. The proposed polymerization mechanism by which the bis(2-aryindenyl) catalysts produce stereoblock polypropylene involves an equilibrium between the syn- and anti-rotameric forms of the active catalyst. Rappé has calculated that π -stacking interactions between ligands stabilize both rotameric forms of bis(2-aryindenyl)zirconium dichloride complexes in the solid state.⁴¹ Favorable π -stacking interactions might be anticipated to result from increased electrostatic attractions between the differently substituted phenyl rings of mixed ring complexes **6**, **7**, and **11**. However, the chemical shifts in the solution NMR provide no evidence for such intramolecular interactions in solution. Complexes **6**, **7**, and **11** all exhibit C_{2v} symmetry in solution (consistent with rapid rotation of the indenyl ligands), even at low temperatures (-80 °C). In the solid state, mixed ligand complex **7** adopts a syn-like structure similar to that observed for its homoleptic analogue **14**.

Polymerization Behavior: Effect of Halide Ligands. During the preparation of zirconium half-sandwich trihalides, we discovered that the half-sandwich tribromides **3b** and **4b** could be isolated in higher yield than analogous trichlorides **3a** and **4a**. Since much recent work has shown that polymerization occurs at the zirconium cationic species, the active site derived from either halogen complex should be similar (eq 5).⁴² However, several researchers have noted that the identity of the anion can have an effect on the properties (including stereospecificity and productivity) of the catalyst^{43–48} particularly for strongly coordinating anions.⁴⁹ Thus it is possible that the nature of anion might



influence the stereospecificity and activity of the catalyst. To test for possible contributions from the bromide ligands, we prepared bis(indenyl) dibromides **5b** and

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10b for comparison. We also prepared both dihalide derivatives of mixed ligand **6**. The identity of the halogen atom did not affect the stereospecificity or productivity of the catalysts.

Polymerization Studies: Mixed Ligand Complexes. Fluxional 2-arylindenyl catalysts were designed to interconvert between the achiral, aspecific syn and chiral, isospecific anti geometries during the formation of a polymer chain to produce a stereoblock structure (Scheme 1). The overall similarity of the resulting polymer properties suggests that the mixed and homo ligand 2-arylindenyl catalysts operate by a similar mechanism (Figure 2a). We have shown that the isospecificity of bis(2-arylindenyl) catalysts is strongly dependent on the nature of the 3',5'-substituents.²⁷ We now find that mixed ligand complexes have an isospecificity intermediate to that of their bis(indenyl) analogues. However, the isospecificity of the mixed ligand complex is not the weighted average of the homoleptic congeners. For example, BArf/DMPInd-ligated **11** has a much higher isospecificity ([mmmm] = 54%) than BArf/2PhInd-substituted **6**/MAO ([mmmm] = 33–35%), despite the fact that bis(indenyl) complexes (DMPInd)₂ZrCl₂ (**11**/MAO) and (2PhInd)₂ZrCl₂ (**5**/MAO) are quite similar ([mmmm] = 23 and 28, respectively). This may be indicative of some subtle steric or electronic effects between ligands for the 2-arylindenyl catalysts. Nevertheless, as the properties of the mixed ring complexes consistently fall between those of their bis(indenyl) analogues, we conclude that the effects of each ligand on the attributes of the catalysts are primarily additive.

1-Substituted **8,9** and **12,13** are completely devoid of symmetry elements, which leads to a greater number of possible rotamers and thus further complicates the interpretation of the behavior of these catalysts (Figure 2b). Furthermore, the 1-Me substituent is very close to the active site and should thus have a much larger steric influence on the behavior of the catalyst than the relatively distant 3',5'-substituents. Nevertheless, as was observed for 3',5'-substitution, the stereospecificities and polymer molecular weights and molecular weight distributions of the 1-Me-substituted mixed ring catalysts consistently fall between the two extremes set by their bis(indenyl) analogues. However, the contributions of 1-Me-substituted ligands on the productivities and molecular weights of mixed ring complexes are not strictly additive. For example, the productivities and molecular weights of both *rac*- and *meso*-**15** are an order of magnitude lower and the molecular weight distributions much higher (indicating decreased rate of rotamer interconversion) than those of bis(2-arylindenyl) catalysts without 1-Me substituents as well as

mixed ligand complexes **8,9** and **12,13**.³⁰ Thus, a single 1-Me substituent does not significantly affect the behavior of the catalyst.

Conclusions

We have developed a new and convenient route to generate mixed ligand zirconium complexes and have examined the polymerization behavior of several fluxional, mixed ligand 2-arylindenyl complexes having substituents in the 1- and/or 3',5'-positions. While the effects of the substituents on the dynamic behavior are complex, it is clear that the mixed ligand catalysts generally have properties intermediate to those observed for their bis(indenyl) analogues.

Experimental Section

General Considerations. All organometallic reactions were conducted using standard Schlenk and drybox techniques. Elemental analyses were performed by E&R Microanalytical Laboratory and Desert Analytics. Unless otherwise specified all reagents were purchased from commercial suppliers and used without further purification. 1-Methyl-2-phenylindene, 2-(3',5'-bis(trifluoromethyl)phenyl)indene, 2-(3',5'-dimethylphenyl)indene, bis(2-phenylindenyl)zirconium dichloride (**5a**), bis((3',5'-bistrifluoromethylphenyl)indenyl)zirconium dichloride (**10a**), and *rac*-bis(1-methyl-2-phenylindenyl)zirconium dichloride were prepared according to literature procedures.^{27,28,30} Hexane, pentane, and methylene chloride were distilled from calcium hydride under nitrogen. Tetrahydrofuran was distilled from sodium/benzophenone under nitrogen. Toluene was passed through two purification columns packed with activated alumina and supported copper catalyst and collected under argon. Methylene dichloride-*d*₂ and chloroform-*d*₃ were vacuum transferred from calcium hydride. Benzene-*d*₆ was vacuum transferred from sodium/benzophenone.

(2-(3',5'-Bis(trifluoromethyl)phenyl)indenyl)zirconium Tris(dimethylamide) (2). A 250 mL Schlenk flask was charged with 2-(3',5'-bis(trifluoromethyl)phenyl)indene (0.356 g, 1.08 mmol), zirconium tetrakis(dimethylamide) (0.283 g, 1.07 mmol), and toluene (25 mL). The yellow mixture was stirred at room temperature for 100 min and then evaporated to dryness. The off-white residue was dissolved in hexane (25 mL) and filtered by cannula. The yellow solution was concentrated to a volume of 10 mL and stored at -20 °C for 16 h and then -50 °C for 2 days. Decantation of the solvent by cannula and drying in vacuo afforded 2-(3',5'-bis(trifluoromethyl)phenyl)indenylzirconium tris(dimethylamide) as yellow crystals (0.477 g, 81%). ¹H NMR (C₆D₆, 400 MHz, 296 K): δ 2.50 (s, 18 H), 6.14 (s, 2 H), 6.92 (dd, 2 H), 7.45 (dd, 2 H), 7.67 (s, 1 H), 7.91 (s, 2 H).

2-Phenylindenylzirconium Trichloride (3a). A 100 mL Schlenk tube was charged with 2-phenylindene (0.460 g, 2.40 mmol), zirconium tetrakis(dimethylamide) (0.506 g, 1.89 mmol), and toluene (15 mL). The yellow solution was stirred for 3 h at room temperature and then evaporated to dryness. The residue was extracted with hexane (10 mL), filtered by cannula, and then evaporated to dryness to give (2-PhInd)Zr-(NMe₂)₃ (**1**). The residue was dissolved in methylene chloride (10 mL), and the light yellow solution was cooled to 0 °C. Chlorotrimethylsilane (0.80 mL, 6.3 mmol) was added by syringe. The solution immediately became colorless and then gradually turned bright yellow. The solution was warmed to 20 °C, stirred for 1 h, and then evaporated to dryness. The orange foam was dissolved in toluene (20 mL) and stirred. Within 10 min a bright yellow powder began to precipitate. The slurry was stirred for 12 h, and the mixture was filtered by cannula. The bright yellow powder was washed with toluene (5 mL) and dried in vacuo (two crops, 0.137 g, 41%). ¹H NMR

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(C₆D₆, sparingly soluble, 400 MHz, 296 K): δ 6.60 (s, 2 H), 6.90 (dd, J = 3, 3 Hz, 2 H), 7.06 (d, J = 7 Hz, 1 H), 7.12 (observed), 7.22 (dd, J = 3, 3 Hz, 2 H), 7.51 (d, J = 7 Hz, 2 H). ¹H NMR (CD₂Cl₂, 400 MHz, 296 K), a mixture of monomer and oligomers: δ 6.87 (sharp s, 2 H), 7.19 (sharp dd), 7.30 (broad s), 7.40 (broad m), 7.46 (broad m), 7.60 (sharp dd), 7.70–7.90 (broad m). Anal. Calcd for C₁₅H₁₁Cl₃Zr: C, 46.34; H, 2.85. Found: C, 46.00; H, 2.82.

2-Phenylindenylzirconium Tribromide (3b). A 250 mL Schlenk flask was charged with 2-phenylindene (0.700 g, 3.59 mmol), zirconium tetrakis(dimethylamide) (0.930 g, 3.51 mmol), and ether (100 mL). The yellow solution was stirred for 16 h at room temperature and then evaporated to dryness to give (2-PhInd)Zr(NMe₂)₃ (**1**). Powdery **1** was dissolved in toluene (120 mL), and bromotrimethylsilane (1.6 mL, 12 mmol) was added by syringe. The yellow solution was stirred for 16 h. An orange precipitate had formed. The mixture was stirred for an additional 20 h. The yellow solution was filtered by cannula into a 500 mL Schlenk flask, concentrated to a volume of 100 mL, and stored at –20 °C for 2 days to afford (2-PhInd)-ZrBr₃·0.3 toluene (**3b**) as yellow blocks (two crops, 1.51 g, 78%). ¹H NMR (C₆D₆, 400 MHz, 296 K): δ 6.71 (s, 2 H), 6.87 (dd, J = 3, 3 Hz, 2 H), 7.06 (d, J = 7 Hz, 1 H), 7.11 (dd, J = 7, 7 Hz, 2 H), 7.23 (dd, J = 3, 3 Hz, 2 H), 7.54 (d, J = 7 Hz, 2 H). ¹³C NMR (CD₂Cl₂, 100 MHz, 296 K): δ 103.13, 126.85, 127.46, 128.51, 129.03, 129.31, 129.54, 130.04, 130.60. Anal. Calcd for C₁₅H₁₁Br₃Zr: C, 34.50; H, 2.12. Found: C, 34.21; H, 2.21.

2-(3',5'-Bis(trifluoromethyl)phenyl)indenylzirconium Trichloride (4a). A 100 mL Schlenk tube was charged with Zr(NMe₂)₄ (1.260 g, 4.713 mmol), 1-methyl-2-(3',5'-bis(trifluoromethyl)phenyl)indene (1.505 g, 4.58 mmol), and toluene (30 mL). The green-brown solution was stirred at room temperature under slightly reduced pressure for 2.5 h and then was evaporated to dryness. The green-brown solid was extracted with pentane (30 mL) and filtered through a cannula fitted with a double layer of filter paper. The resulting pentane solution was concentrated to a volume of 8 mL and stored at –50 °C overnight. The resulting green-brown crystals (**2**) were isolated, dried in vacuo, and redissolved in CH₂Cl₂ (20 mL). The solution was cooled to 0 °C and chlorotrimethylsilane (2 mL, 15.8 mmol) was added by syringe. The turbid yellow solution was allowed to warm to room temperature, stirred for 1 h, and then concentrated to a volume of 1 mL. The solution was diluted with toluene (30 mL), and the resulting suspension was stirred for 24 h to afford a lemon yellow powdery solid (1.390 g). ¹H NMR spectroscopic analysis revealed that the desired (Barf)ZrCl₃ (**4a**) was contaminated by what appeared to be residual Me₃SiNMe₂. As the attempted removal of these impurities resulted in severely reduced yield and the impurities had little or no detrimental effect on the subsequent reactions of the complex, the powder was used without further purification. ¹H NMR (CDCl₃, 400 MHz, 296 K): δ 8.19–8.17 (br, 1 H), 8.10 (br, 2 H), 7.99 (br, 1 H), 7.83 (br, 1 H), 7.77 (br, 1 H), 7.61 (br, 2 H), 7.53 (appears as poorly resolved dd, 2 H), 7.44–7.38 (br, 1 H), 7.30 (br, 2 H), 7.20 (m, 1 H), 7.03 (br, 2 H), 6.95 (s, 1 H), 6.83 (br, 1 H), 2.45 (br, 6 H), 0.41 (s, 9 H). Broad peaks in the aromatic region appear to indicate the presence of dimerized or oligomerized forms of (Barf)ZrCl₃.

2-(3',5'-Bis(trifluoromethyl)phenyl)indenylzirconium Tribromide (4b). A 100 mL Schlenk tube was charged with **2** (0.385 g, 0.70 mmol) and CH₂Cl₂ (20 mL). The yellow solution was cooled to 0 °C, and bromotrimethylsilane was added by syringe. The solution turned bright yellow and was stirred at 0 °C for 30 min. The mixture was warmed to room temperature, stirred for an additional 2 h, and then evaporated to dryness. The yellow powder was extracted with toluene (25 mL) and filtered by cannula. The yellow solution was stored at –20 °C for 10 h. The solution was filtered by cannula, and the resulting bright yellow powder was dried in vacuo (0.350 g). ¹H NMR spectroscopic analysis revealed that the desired

(Barf)ZrBr₃ (**4b**) was contaminated by what appeared to be residual Me₃SiNMe₂ and Me₃SiBr. As the attempted removal of these impurities resulted in severely reduced yield and the impurities had little or no detrimental effect on the subsequent reactions of the complex, the powder was used without further purification. The yield calculated for **2b**·0.5Me₃SiNMe₂·0.5Me₃SiBr was 63%. ¹H NMR (C₆D₆, 400 MHz, 296 K): δ 6.34 (s, 2 H), 6.93 (m, 2 H), 7.33 (m, 2 H), 7.65 (s, 1 H), 7.97 (s, 2 H). Broad peaks in the aromatic region appear to indicate the presence of dimerized or oligomerized forms of (Barf)ZrBr₃.

(2-Phenylindenyl)(2-(3,5-bis(trifluoromethyl)phenyl)indenyl)zirconium Dichloride (6a). A 50 mL Schlenk tube was charged with 2-(3,5-bis(trifluoromethyl)phenyl)indene (0.113 g, 0.344 mmol) and ether (10 mL). The solution was cooled to –78 °C, and butyllithium (2 M in hexane, 0.19 mL, 0.38 mmol) was added by syringe. The mixture was warmed to room temperature and stirred for 10 min. The green-orange solution was cooled to –78 °C, and the slurry was transferred by cannula to a 100 mL Schlenk tube containing **3a** (0.123 g, 0.316 mmol) in toluene (25 mL) at 0 °C. The green slurry was allowed to warm to room temperature, and after stirring for 6 h, the solution was orange. The mixture was stirred for an additional 16 h and then was evaporated to dryness. The orange powder was extracted with toluene (25 mL) and filtered through Celite. The Celite was washed with toluene (10 mL). The combined filtrates were concentrated to a volume of 5 mL, and the solution was stored at –20 °C for 16 h to give a yellow-orange powder. Recrystallization from ether (8 mL) afforded **6a** as yellow microcrystals (0.092 g, 42%). ¹H NMR (C₆D₆, 400 MHz, 296 K): δ 5.87 (s, 2 H), 6.23 (s, 2 H), 6.88 (m, 4 H), 7.06 (dd, 2 H, J = 3, 3 Hz), 7.08–7.15 (m, 3 H), 7.24 (dd, 2 H, J = 3, 3 Hz), 7.29 (m, 2 H), 7.62 (br s, 2 H), 7.67 (br s, 1 H). Anal. Calcd for C₃₂H₂₀Cl₂F₆Zr: C, 56.47; H, 2.96. Found: C, 56.46; H, 2.86.

(2-Phenylindenyl)(2-(3,5-bis(trifluoromethyl)phenyl)indenyl)zirconium Dibromide (6b). A 50 mL Schlenk tube was charged with 2-(3,5-bis(trifluoromethyl)phenyl)indene (0.175 g, 0.53 mmol) and ether (10 mL). The solution was cooled to –78 °C, and butyllithium (1.6 M in hexane, 0.34 mL, 0.54 mmol) was added by syringe. The mixture was warmed to room temperature and stirred for 10 min. The green-orange solution was cooled to –78 °C, and the slurry was transferred by cannula to a 100 mL Schlenk tube containing **3b** (0.270 g, 0.517 mmol) in toluene (15 mL) at –78 °C. The orange slurry was stirred at –78 °C for 20 min and then allowed to warm to room temperature and was stirred for 16 h. The orange solution was evaporated to dryness. The orange powder was extracted with toluene (15 mL) and filtered through Celite. The Celite was washed with toluene until the filtrates were colorless. The combined filtrates were evaporated to dryness. Recrystallization from ether (8 mL) afforded **6b** as orange needles (three crops, 0.153 g, 39%). ¹H NMR (CD₂Cl₂, 400 MHz, 296 K): δ 6.53 (s, 2 H), 6.64 (s, 2 H), 7.21 (dd, J = 3, 3 Hz, 2 H), 7.28 (dd, J = 3, 3 Hz, 2 H), 7.35 (dd, J = 3, 3 Hz, 2 H), 7.45 (m, 3 H), 7.55 (m, 4 H), 7.82 (br s, 2 H), 7.85 (br s, 1 H). ¹³C NMR (CD₂Cl₂, 100 MHz, 296 K): δ 104.06, 104.39, 122.16 (septuplet, J_{C-F} = 4 Hz), 123.70 (q, J_{C-F} = 271 Hz), 125.97, 126.05, 126.86, 127.04, 127.14, 127.08, 127.32, 127.48, 129.31, 129.54, 131.89 (q, J_{C-F} = 33 Hz), 132.18, 133.26, 133.72, 136.19. Anal. Calcd for C₃₂H₂₀Br₂F₆Zr: C, 49.95; H, 2.62. Found: C, 49.82; H, 2.66.

(2-Phenylindenyl)(2-(3,5-dimethylphenyl)indenyl)zirconium Dibromide (7). A 50 mL Schlenk tube was charged with 2-(3,5-dimethylphenyl)indene (0.315 g, 1.43 mmol) and ether (10 mL). The solution was cooled to –78 °C, and butyllithium (1.6 M in hexane, 0.94 mL, 1.5 mmol) was added by syringe. The mixture was warmed to room temperature and stirred for 1 h. The yellow-orange solution was cooled to –78 °C, and the slurry was transferred by cannula to a 100 mL Schlenk tube containing **1** (0.700 g, 1.34 mmol) in toluene (15 mL) at –78 °C. The orange slurry was stirred at –78 °C for

20 min and then allowed to warm to room temperature and was stirred for 16 h. The orange solution was evaporated to dryness. The orange powder was extracted with toluene and filtered through Celite. The Celite was washed with toluene until the filtrates were colorless. The combined filtrates were evaporated to dryness. Recrystallization from methylene chloride (8 mL)/ether (8 mL) afforded **7** as orange blocks (three crops, 0.56 g, 63%). ^1H NMR (C_6D_6 , 400 MHz, 296 K): δ 2.21 (s, 6 H), 6.51 (s, 2 H), 6.52 (s, 2 H), 6.80 (br s, 1 H), 6.91 (m, 4 H), 7.0–7.2 (m, partially obscured by solvent resonance), 7.43 (m, 2 H). ^{13}C NMR (CD_2Cl_2 , 100 MHz, 296 K): δ 21.57, 104.59, 104.65, 125.06, 125.72, 125.74, 126.86, 126.90, 127.11, 127.14, 127.22, 129.12, 129.23, 130.89, 132.85, 132.89, 133.37, 133.63, 139.06. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Br}_2\text{Zr}$: C, 58.10; H, 3.96. Found: C, 58.05; H, 3.91.

(2-Phenylindenyl)(1-methyl-2-phenylindenyl)zirconium Dichloride (8). Butyllithium (2.5 M in hexanes, 0.43 mL, 1.08 mmol) was added by syringe to a solution of 1-methyl-2-phenylindene (0.212 g, 1.029 mmol) in diethyl ether (25 mL) at -78°C . The light yellow solution was allowed to warm to room temperature, stirred for an additional 30 min, and then evaporated to dryness. The white powdery solid was combined with **3a** (0.400 g, 1.029 mmol) and toluene (50 mL). The resulting suspension was stirred for 24 h at room temperature and gradually became a turbid yellow solution. The mixture was filtered through a glass frit packed with Celite and then evaporated to dryness. The resulting yellow solid was recrystallized from CH_2Cl_2 (10 mL) layered with pentane (30 mL) at -50°C to afford **8** (0.181 g, 31%). ^1H NMR (C_6D_6 , 400 MHz, 296 K): δ 7.41 (d, 2 H, $J = 11.2$ Hz), 7.30 (d, 2 H, $J = 10.8$ Hz), 7.24–6.80 (m, 13 H), 6.73 (d, 1 H, $J = 11.2$ Hz), 6.50 (d, 1 H, $J = 3.2$ Hz), 6.26 (d, 1 H, $J = 3.3$ Hz), 5.98 (s, 1 H), 2.42 (s, 3 H). ^{13}C NMR (CDCl_3 , 125 MHz, 296 K): δ 133.75 (C), 133.10 (C), 132.38 (C), 131.41 (C), 129.54 (C), 129.06 (C–H), 128.90 (C–H), 128.70 (C–H), 128.67 (C–H), 128.14 (C–H), 126.95 (C), 126.72 (C–H), 126.58 (C–H), 126.56 (C–H), 126.43 (C–H), 126.26 (C–H), 125.58 (C–H), 125.05 (C), 124.90 (CH), 124.56 (C), 124.35 (C–H), 123.68 (C–H), 121.43 (C), 104.34 (C–H, Cp), 100.70 (C–H, Cp), 99.00 (C–H, Cp), 12.54 (CH_3). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{Zr}$: C, 66.65; H, 4.33. Found: C, 66.92; H, 4.36.

(2-Phenylindenyl)(1-methyl-2-(3',5'-bis(trifluoromethyl)phenyl)indenyl)zirconium Dichloride (9). Butyllithium (2.5 M in hexanes, 0.43 mL, 1.08 mmol) was added by syringe to a pale yellow solution of 1-methyl-2-(3',5'-bis(trifluoromethyl)phenyl)indene (0.352 g, 1.029 mmol) in diethyl ether (20 mL) at -78°C . The yellow solution was allowed to warm to room temperature, stirred for an additional 30 min, and then evaporated to dryness. The resulting pale yellow solid was washed with pentane (20 mL) and then combined with **3a** (0.400 g, 1.029 mmol) and toluene (50 mL). The suspension was stirred for 24 h at room temperature and gradually became a turbid yellow solution. The mixture was filtered through a glass frit packed with Celite and then evaporated to dryness. The yellow solid was recrystallized from CH_2Cl_2 layered with pentane at -50°C to afford **9**·1/6· CH_2Cl_2 (0.245 g, 34%). ^1H NMR (C_6D_6 , 400 MHz, 296 K): δ 7.67 (s, br, 1 H), 7.64 (s, br, 2 H), 7.30–6.78 (m, 13 H), 6.43 (d, 1 H, $J = 2.4$ Hz), 6.19 (d, 1 H, $J = 2.4$ Hz), 5.59 (s, 1 H), 5.32 (s, 1/3 H, CH_2Cl_2), 2.24 (s, 3 H). ^{13}C NMR (CDCl_3 , 125 MHz, 296 K): δ 135.91 (C–H), 133.59 (C), 132.58 (C), 131.47 (C–CF₃), $^2J_{\text{CF}} = 33$ Hz), 130.76 (C), 130.51 (C), 129.02 (C–H), 128.98 (C–H), 128.80 (C–H), 126.87 (C–H), 126.81 (C–H), 126.77 (C–H), 126.62 (C–H), 126.52 (C–H), 126.25 (C–H), 126.21 (C), 125.34 (C–H), 125.05 (C), 124.09 (C–H), 123.86 (C), 123.23 (CF₃, $J_{\text{CF}} = 273$ Hz), 123.17 (C), 121.24 (C–H, br), 119.25 (C), 102.70 (C–H, Cp), 101.76 (C–H, Cp), 99.30 (C–H, Cp), 12.12 (CH_3). Anal. Calcd for $\text{C}_{33}\text{H}_{22}\text{F}_6\text{ZrCl}_2$ ·1/6· CH_2Cl_2 : C, 55.86; H, 3.37. Found: C, 56.20; H, 3.18. After having been stored for 3–4 weeks in the drybox in a clear vial the yellow compound turned

greenish in color. No changes in the ^1H NMR spectrum were detected upon the color change.

Bis(2-(3',5'-bis(trifluoromethyl)phenyl)indenyl)zirconium Dibromide (10b). A 50 mL Schlenk tube was charged with 2-(3',5'-bis(trifluoromethyl)phenyl)indene. The tube was removed from the box and charged with Et_2O (10 mL) and cooled to -40°C . Butyllithium was added dropwise by syringe, and the yellow solution was stirred at -40°C for 15 min. The mixture was allowed to warm to room temperature over 20 min and then was transferred by cannula to a 100 mL Schlenk tube containing **4b** in Et_2O at -40°C . The tube was allowed to warm to room temperature, and the mixture became homogeneous. The orange mixture was stirred at room temperature for 3 h and then was evaporated to dryness. The orange solid was dissolved in toluene (4 mL) and filtered through sintered glass filter paper by cannula into a 50 mL Schlenk tube. Crystallization from toluene at -50°C afforded **10b** as yellow microcrystals in 61% yield (3 crops). ^1H NMR (C_6D_6 , 400 MHz, 296 K): δ 5.78 (s, 4H), 6.87 (dd, 4H, $J = 3, 3.5$ Hz), 7.17 (dd, 4H, $J = 3, 3.5$ Hz), 7.61 (br s, 4H), 7.66 (br s, 2H). Anal. Calcd for $\text{C}_{34}\text{H}_{18}\text{Br}_2\text{F}_{12}\text{Zr}$: C, 45.10; H, 2.00. Found: C, 44.17; H, 1.91. HRMS (EI). m/e calcd for $\text{C}_{34}\text{H}_{18}\text{Br}_2\text{F}_{12}\text{Zr}$: 901.863070 ($^{79}\text{Br}_2^{90}\text{Zr}$); 902.864006 ($^{79}\text{Br}_2^{91}\text{Zr}$); 903.861024 ($^{79}\text{Br}^{81}\text{Br}^{90}\text{Zr}$); 904.861960 ($^{79}\text{Br}^{81}\text{Br}^{91}\text{Zr}$); 905.858978 ($^{81}\text{Br}_2^{90}\text{Zr}$). Found: 901.864656; 902.862248; 903.860369; 904.862783; 905.858306.

(2-(3',5'-Bis(trifluoromethyl)phenyl)indenyl)(2-(3',5'-dimethylphenyl)indenyl)zirconium Dibromide (11). A 50 mL Schlenk tube was charged with 2-(3',5'-dimethylphenyl)indene and Et_2O (10 mL), and the mixture was cooled to -40°C . Butyllithium was added dropwise by syringe, and the orange solution was allowed to warm to room temperature over a period of 20 min. The solution was transferred by cannula to a 100 mL Schlenk tube containing **4b** in Et_2O (20 mL) at -40°C . The mixture immediately turned green. As the mixture was allowed to warm to room temperature (20 min), it turned orange and became homogeneous. The solution was stirred for 1 h at room temperature and then was evaporated to dryness. The orange solid was dissolved in toluene (15 mL) and filtered through sintered glass filter paper by cannula into a 50 mL Schlenk tube. Successive crystallization from toluene afforded **11** as red crystals in 45% yield. As the ^1H NMR spectrum showed that **11** was contaminated with 0.05 equiv of bis(2-(3',5'-dimethylphenyl)indenyl)zirconium dibromide, the fraction was recrystallized. The resulting red crystals (0.035 g, 16%) were still contaminated with 0.02 equiv of bis(2-(3',5'-dimethylphenyl)indenyl)zirconium dibromide (as judged by NMR). However, since further purification would have resulted in a substantial reduction in yield, the impurity was small, and the catalytic behavior of the impurity was known, the effect of the contaminant on the catalytic results of **11** was judged to be insignificant. Thus, the material was used without further purification. ^1H NMR (CD_2Cl_2 , 400 MHz, 296 K): δ 2.38 (s, 6 H), 6.59 (s, 2 H), 6.63 (s, 2 H), 7.06 (s, 1 H), 7.18 (dd, 2 H, $J = 3, 3$ Hz), 7.20 (s, 2 H), 7.29 (m, 4 H), 7.52 (dd, 2 H), 7.84 (br s, 3 H). ^{13}C NMR (CD_2Cl_2 , 100 MHz, 296 K): δ 21.40, 104.30, 104.50, 122.10 (br), 124.92, 125.87, 125.99, 126.90, 127.21, 127.32 (br), 127.42, 131.29, 131.66, 131.91 (q, $J_{\text{CF}} = 33$ Hz), 133.00, 133.81, 136.27, 139.02, 149.48. HRMS (EI). m/e calcd for $\text{C}_{34}\text{H}_{24}\text{Br}_2\text{F}_6\text{Zr}$: 793.919601 ($^{79}\text{Br}_2^{90}\text{Zr}$); 794.920537 ($^{79}\text{Br}_2^{91}\text{Zr}$); 795.917555 ($^{79}\text{Br}^{81}\text{Br}^{90}\text{Zr}$); 796.918491 ($^{79}\text{Br}^{81}\text{Br}^{91}\text{Zr}$); 797.915508 ($^{81}\text{Br}_2^{90}\text{Zr}$). Found: 793.919335; 794.912828; 795.914997; 796.917847; 797.914606.

1-Methyl-2-(3',5'-bis(trifluoromethyl)phenyl)indene and 3-Methyl-2-(3',5'-bis(trifluoromethyl)phenyl)indene (1Me-Barf). A solution of 2-(3',5'-bis(trifluoromethyl)phenyl)indene (1.819 g, 5.54 mmol) in tetrahydrofuran (30 mL) was cooled to -78°C , and butyllithium (2.5 M in hexanes, 2.33 mL, 5.82 mmol) was added dropwise. The resulting orange-brown solution was allowed to warm to room temperature and stirred for an additional 30 min. Iodomethane (1.20 mL, 19 mmol)

was added by syringe; the green reaction mixture was stirred for 20 h at room temperature. Methanol (20 mL) was added to quench excess organometallic reagents, and the mixture was evaporated to dryness. The resulting brown solid was extracted with toluene (30 mL) and filtered through a glass frit packed with Celite. The solution was extracted with H₂O (2 × 10 mL) and saturated NaCl solution (2 × 10 mL), dried over MgSO₄, and then evaporated to dryness. Crystallization from hexanes afforded yellow crystals of 1Me-Barf (1.073 g, 73%). ¹H NMR (CDCl₃, 400 MHz, 296 K): δ 7.87 (s, 2 H), 7.75 (s, 1 H), 7.49 (d, 1 H, *J* = 7.3 Hz), 7.42 (d, 1 H, *J* = 7.5 Hz), 7.37 (t, 1 H, *J* = 7.3 Hz), 7.26 (td, 1 H, *J* = 7.3, 1.1 Hz), 3.78 (s, 2 H), 2.33 (s, 3 H). Anal. Calcd for C₁₈H₁₂F₆: C, 63.16; H, 3.53. Found: C, 63.12; H, 3.62. Repeated crystallization from hexanes gave a mixture of 1Me-Barf and 3Me-Barf (309 mg) in 4:1 ratio. 3Me-Barf was identified from its characteristic pattern in the aliphatic region of the ¹H NMR spectrum: 3.14 (q, 1 H, *J* = 7.0 Hz), 0.87 (d, 3 H, 7.1 Hz). 1Me-Barf and 3Me-Barf form the same product upon deprotonation.

(1Me-2-PhInd)(Barf)zirconium Dichloride (12). Butyllithium (2.5 M in hexanes, 0.55 mL, 1.38 mmol) was added by syringe to a solution of 1-methyl-2-phenylindenyl (0.277 g, 1.31 mmol) in diethyl ether (25 mL) at -78 °C. The light yellow solution was allowed to warm to room temperature and stirred for an additional 15 min. The mixture was evaporated to dryness to yield a white powdery solid, which was then combined with **4a** (0.695 g, ca. 1.31 mmol) and toluene (40 mL) at 0 °C. The resulting dark green solution was allowed to warm to room temperature and stirred for 40 h, during which time the solution gradually became lemon yellow. The turbid solution was filtered through a glass frit packed with Celite and then evaporated to dryness. Recrystallization from a CH₂-Cl₂ (5 mL)/pentane (5 mL) solution at -50 °C afforded **12**·1/6·CH₂Cl₂ as orange crystals (0.200 g, 28%). ¹H NMR (CDCl₃, 500 MHz, 296 K): δ 7.84 (s, 2 H, br), 7.82 (s, 1 H, br), 7.52 (t, 2 H, *J* = 7.5 Hz), 7.43 (m, 3 H), 7.36 (m, 2 H), 7.29 (m, 2 H), 7.20 (t, 1 H, *J* = 6.0 Hz), 7.08 (q, 2 H, *J* = 7.0 Hz), 6.68 (d, 1 H, *J* = 2 Hz), 6.38 (d, 1 H, *J* = 2 Hz), 5.99 (s, 1 H), 5.32 (s, 1/3 H, CH₂Cl₂), 2.53 (s, 3 H). ¹³C NMR (CD₂Cl₂, 125 MHz, 296 K): δ 135.48 (C), 133.20 (C), 132.23 (C), 132.20 (C), 131.62 (C-CF₃, ²*J*_{C-F} = 34 Hz), 130.23 (C), 129.03 (CH), 128.61 (CH), 128.44 (C-H), 126.87 (C-H), 126.71 (C-H), 126.70 (C-H), 126.54 (C-H), 126.45 (C-H), 126.24 (C-H), 125.90 (C), 125.17 (C-H), 125.01 (C), 124.43 (C), 124.15 (C-H), 124.13 (C-H), 123.22 (CF₃, *J*_{C-F} = 272 Hz), 121.70 (C-H, br), 102.09 (C-H, Cp), 101.20 (C-H, Cp), 98.51 (C-H, Cp), 12.39 (CH₃). Anal. Calcd for C₃₃H₂₂Cl₂F₆Zr·1/6·CH₂Cl₂: C, 56.20; H, 3.18. Found: C, 56.11; H, 3.09.

(Barf)(1Me-Barf)zirconium Dichloride (13). Butyllithium (2.5 M in hexanes, 0.40 mL, 1.00 mmol) was added by syringe to the solution of 1Me-Barf (0.328 g, 0.958 mmol) in diethyl ether (30 mL) at -78 °C. The light yellow solution was allowed to warm to room temperature and stirred for an additional 2.5 h. The mixture was evaporated to dryness to yield a gray powdery solid, which was washed with pentane, filtered, and then dried in vacuo. The solid was combined with solid **4a** and toluene (50 mL), and the mixture was stirred for 40 h at room temperature. The turbid yellow solution was filtered through a glass frit packed with Celite and then evaporated to dryness. Precipitation from CH₂Cl₂ (10 mL) at -50 °C afforded **13** as a yellow powder (0.100 g, 13%). ¹H NMR (CDCl₃, 500 MHz, 296 K): δ 7.56 (s, 2 H, br), 7.48 (s, 2 H, br), 7.29 (d, 1 H, *J* = 8.5 Hz), 7.08 (m, 2 H), 6.90 (m, 2 H), 6.83 (t, 2 H, *J* = 7.0 Hz), 6.66 (t, 1 H, *J* = 7.5 Hz), 6.00 (d, 1 H, *J* = 2.5 Hz), 5.73 (d, 1 H, *J* = 2.5 Hz), 5.48 (s, 1 H), 2.14 (s, 3 H). ¹⁹F NMR (C₆D₆, 282 MHz, 296 K): δ 63.65 (s, 3F), 63.57 (s, 3F). Anal. Calcd for C₃₄H₂₀Cl₂F₆Zr: C, 50.61; H, 2.43. Found: C, 50.90; H, 2.72.

Representative Polymerization Procedure (7/MAO). In the drybox a 5 mL volumetric flask was charged with **7** (0.0041 g, 0.0062 mmol) and toluene. The solution was stirred until

homogeneous. The yellow solution was added by pipet to a 30 mL jar containing MAO (0.360 g; Akzo Type 4 previously evaporated to dryness) in toluene (15 mL). The mixture turned orange and was aged for 5 min. The solution was transferred by pipet to a 50 mL pressure tube and pressurized to 250 psi with argon. The catalyst solution was injected into a 300 mL stainless steel Parr reactor containing 100 mL of liquid propylene at 16 °C. The temperature immediately climbed to 22 °C, but stabilized at 20 °C within 1 min. The mixture was stirred at 20 °C for 20 min and then quenched with methanol (15 mL). The white polymer was precipitated with acidified methanol and dried in vacuo at 40 °C to constant weight (2.832 g, 1.4 kg/(mol(Zr)·h)). ¹³C NMR (C₂H₂Cl₄/C₂D₂Cl₄ (4/1), 100 MHz, 373 K): [mmmm] 21%.

X-ray Crystallographic Analysis of (2PhInd)(DMPIn-d)ZrBr₂ (7). An orange rectangular crystal of **7** with approximate dimensions of 0.13 × 0.13 × 0.05 mm³, grown from a solution of toluene, 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 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 4627 carefully centered reflections with *I* > 10σ(*I*) in the range 2.81° < 2θ < 52.00° corresponded to a primitive monoclinic cell with dimensions *a* = 13.030(1) Å, *b* = 14.499(1) Å, *β* = 112.164(1)°, *c* = 14.774(1) Å, and *d* = 2584.9(3) Å³. For *Z* = 4 and *fw* = 769.53, the calculated density is 1.98 g/cm³. The intensities of symmetry-equivalent reflections demonstrated a Laue class of 2/*m*. The systematic absence of *h*0*l*, *h*+*l* ≠ 2*n*, and 0*k*0, *k* ≠ 2*n*, uniquely determines the space group to be *P*₂/*n*. Wilson statistics supported a centric space group. The data were collected at a temperature of -112 ± 1 °C using the ω scan technique to a maximum 2θ value of 52.0°.

Data were integrated using the program SAINT with a 1.6 × 1.6 × 0.6° box. A total of 12 337 reflections were collected. A correction for decay was deemed unnecessary. An empirical absorption correction, XPREP, was applied, which resulted in transmission factors ranging from 0.744 to 0.963. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for Mo Kα radiation is 35.93 cm⁻¹. Symmetry-equivalent, non-Friedel reflections were averaged to produce 4740 unique reflections (*R*_{int} = 0.048).

The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.67 and -0.97 e/Å³, respectively. Hydrogen atoms were included at idealized positions, 0.95 Å from their parent atoms. The final cycle of full-matrix least-squares refinement was based on 2492 observed reflections (*I* > 3σ(*I*)) and 316 variable parameters and converged (largest parameter shift was 0.041 times its esd) with unweighted and weighted agreement factors of *R* = 0.037 and *R*_w = 0.045.

The standard deviation of an observation of unit weight was 1.43. The weighting scheme was based on counting statistics and included a factor (*p* = 0.03) to downweight the intense reflections. Plots of Σ_w(|*F*_o| - |*F*_c|)² versus |*F*_o|, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber.⁵⁰ Anomalous dispersion effects were included in *F*_{calc},⁵¹ the values for *Df* and *Df'* were those of Creagh and McAuley.⁵² The values for the mass attenuation

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coefficients were those of Creagh and Hubbel.⁵³ All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.

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Supporting Information Available: Tables of crystal, data collection, positional parameters, bond distances and angles, and polymer NMR data (12 pages). See any current masthead page for ordering and Internet access instructions.

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