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Steric and electronic effects of R in (2-(4-R-C_6H_4)indenyl)$_2ZrCl_2$ catalysts on the synthesis of elastomeric polypropylene

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Abstract

Metallocene catalysts derived from bis(2-arylindenyl)zirconium dichloride catalysts yield elastomeric stereoblock polypropylene. A study of the steric and electronic effects of varying the 4-substituent of bis(2-(4-R-C_6H_4)indenyl)zirconium dichloride [(**1** R=H, **2** R=Me, **3** R=Et, **4** R=*n*Bu, **5** R=*t*Bu, **6** R=$SiMe_3$, **7** R=CF_3, **8** R=Cl)] on propylene polymerization at 25, 50, 75 psig and bulk propylene revealed that the polymerization behavior of these catalysts is not strongly influenced by the nature of the substituent in the 4-position of the 2-aryl substituent. Examinations of the microstructure of the elastomeric polypropylenes produced showed that for catalysts **2**–**8** the isotacticities varied over a small range and were similar to those produced by catalyst **1** ($20\% \leq [mmmm] \leq 44\%$). The catalyst productivities and molecular weights also showed the same trend. Complex **3** was crystallographically characterized and was found to crystallize in exclusively the *meso* conformation.

Keywords: Elastomeric polypropylene; Metallocene; Electronic effects

1. Introduction

Metallocene catalysts derived from bis(2-phenylindenyl)zirconium dichloride catalysts [1] yield elastomeric stereoblock polypropylene [2–10]. The proposed mechanism for stereoblock polymer formation involves interconversion between an aspecific and an isospecific state of the catalysts at a rate slower than the rate of monomer insertion, but faster than the rate of synthesis of a single polymer chain (Fig. 1). The microstructure of polymers produced by these catalysts is sensitive to experimental conditions and to the ligand structure around the metal [1,11]. Specifically, variation of substituents at the 3,5-positions of the phenyl ring in (2-(3,5-R_2-C_6H_3)indenyl)$_2ZrCl_2$ has been shown to have dramatic effects on the tacticity ([mmmm]) of the polymers, as measured by ^{13}C NMR: for (2-(3,5-R_2-C_6H_3)indenyl)$_2ZrCl_2$ [mmmm] = 24% for R=CH_3, whereas [mmmm] = 73% for

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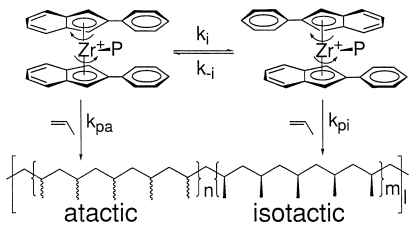

Fig. 1. Proposed mechanism for formation of stereoblock polypropylene.

R=CF_3. In this report, we report investigations of the effects of substituents at the 4-position in (2-(4-R-C_6H_4)indenyl)$_2ZrCl_2$/MAO catalysts. The family of catalysts studied is shown in Fig. 2.

2. Results

Catalysts **2**–**7** were synthesized in a manner analogous to **1** in low to moderate yields [1,11,12]. Crystallization of catalyst **3** from toluene/pentane at 18°C afforded crystals suitable for X-ray analysis. The molecular structure and selected bond distances and angles for **3** are given in Fig. 3. The structure of **3** resembles that of the *meso* rotamer previously reported for

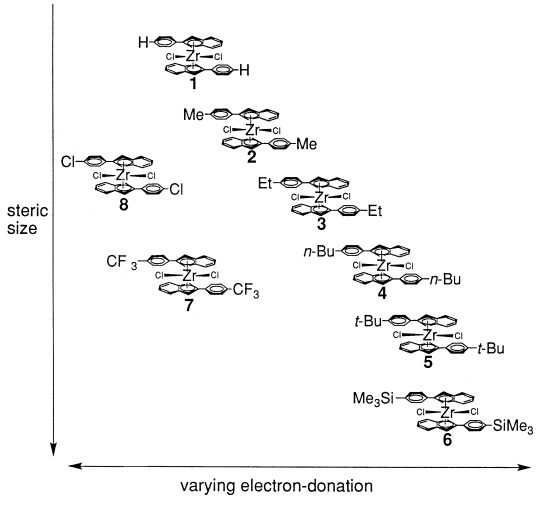

Fig. 2. Variation of substituents for (2-4-R-C_6H_4)indenyl)$_2ZrCl_2$ catalysts.

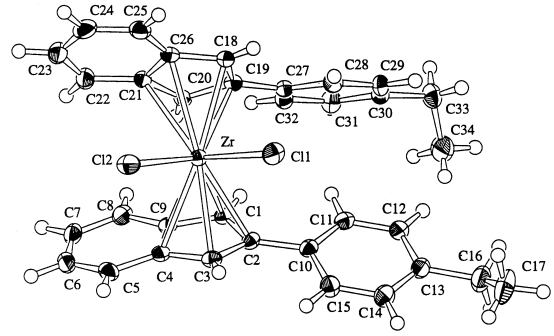

Fig. 3. ORTEP diagram and selected bond distances (°) and bond angles (°) for **3**. Zr–C(1) 2.475(2), Zr–C(2) 2.567(2), Zr–C(3) 2.527(2), Zr–C(4) 2.603(2), Zr–C(9) 2.550(2), Zr–C(18) 2.551(2), Zr–C(19) 2.508(2), Zr–C(20) 2.473(2), Zr–C(21) 2.94(2), Zr–C(26) 2.647(2), Cl(1)–Zr(1)–Cl(2) 97.55(2), C(1)–C(2)–C(3) 107.3(2), C(18)–C(19)–C(20) 108.3 (2).

1. The dihedral angle between the planes defined by the indenyl ligands and the aryl rings is larger (15.3° and 15.6°) for **3** than that observed for **1** or the two 3,5-aryl substituted catalysts ($\leq 10°$) [1,11].

The results of solution polymerizations at 25, 50, 75 psig propylene and liquid propylene (bulk) for catalysts **1**–**8** activated with methylaluminoxane (MAO) are summarized in Table 1. All polymerizations were conducted with the same batch of MAO to minimize differences in productivity, as well as fluctuations in molecular weight and tacticity of the polymers produced. Entries 20–22 are duplicate runs of catalyst **5** in liquid propylene to insure reproducibility of the experiment.

As expected, productivity increased with propylene pressure (monomer concentration) for the catalyst series [13]. This trend has also been observed for other propylene polymerization catalysts. From Table 1, it is apparent that all productivities are of the same magnitude for each catalyst at similar monomer pressures.

The data in Table 1 also show an increase in molecular weight with propylene pressure as expected; M_w for a polymer made at a given pressure is similar for catalysts **1**–**8**. Polydispersities are higher than what is predicted for homogeneous Ziegler–Natta catalysts

Table 1
Propylene polymerizations using catalysts **1**–**8** and MAO

Entry	Catalyst (2-(4-R)PhInd)$_2$ZrCl$_2$	Pressure (psig)[a]	Productivity (kgPP/mol Zr/h)	M_w^b (kg/mol)	M_w/M_n	[m] %	[mmmm] %[c]
1	**1**	25	863	220	3.66	66	27
2	(R=H)	50	1780	303	4.34	71	33
3		75	2679	386	4.93	70	33
4		Bulk	2710	496	5.01	70	33
5	**2**	25	842	163	3.29	69	32
6	(R=CH_3)	50	1290	311	3.76	72	39
7		75	1474	410	3.81	73	41
8		Bulk	2001	510	5.76	73	42
9	**3**	25	780	211	3.58	69	31
10	(R=Et)	50	1544	343	4.15	73	37
11		75	2364	406	5.10	72	38
12		bulk	2390	505	4.42	74	39
13	**4**	25	697	217	3.49	67	29
14	(R=*n*Bu)	50	1289	351	4.16	71	37
15		75	2322	408	5.64	73	40
16		Bulk	2440	506	5.41	72	37
17	**5**	25	578	219	3.23	67	29
18	(R=*t*Bu)	50	1174	357	3.66	71	34
19		75	2019	381	4.84	73	40
20		Bulk	2698	439	4.64	71	33
21		Bulk	2356	388	4.77	71	32
22		Bulk	2314	444	4.08	68	28
23	**6**	25	786	173	2.97	68	29
24	(R=TMS)	50	1344	317	3.67	70	33
25		75	2269	413	4.39	71	37
26		Bulk	2510	480	3.83	74	39
27	**7**	25	775	138	2.84	62	21
28	(R=CF_3)	50	1281	190	3.21	66	26
29		75	1704	470	5.30	69	33
30		Bulk	2631	457	4.71	69	30
31	**8**	25	331	102	3.60	60	20
32	(R=Cl)	50	689	149	4.00	66	27
33		75	1141	328	4.70	67	27
34		Bulk	3333	490	4.00	76	44

[a] $[Zr] = 5 \times 10^{-5}$ M, $[Al]/[Zr] = 1000$; 100 ml toluene total volume, 1 h, 20°C (solution runs); 80 ml liquid propylene, 20 ml toluene, 20–40 min, 20°C (bulk runs).
[b] Determined by high-temperature GPC vs. polypropylene standards.
[c] Pentad distribution determined from ^{13}C NMR (300 MHz, tetrachloroethane, 100°C).

($M_w/M_n \approx 2.0$) [13] and follow no observable trend with pressure.

The microstructure of the polypropylenes produced was determined by ^{13}C NMR [13]. [1] We observed an increase in isotactic pentads, [mmmm], in solution polymerizations with increasing monomer concentration (pressure) which has been seen previously with this type of catalyst [1,12]. [2] For a given catalyst, the

[1] Pentad percentages have measured errors of approximately ±2%.

[2] E. Hauptman, R.M. Waymouth, unpublished results.

isotacticity of polymers produced in bulk polymerizations was usually similar to that of the 75 psig solution polymerizations, the only exception being catalyst **8**.

Comparisons of polymer isotacticities for a given pressure revealed that the polymerization behavior of these catalysts is not strongly influenced by the nature of the substituent in the 4-position of the 2-aryl substituent. Catalysts derived from metallocenes **1–6** all yield polymers of similar tacticity, molecular weight and molecular weight distribution. Catalysts derived from the trifluoromethyl and chloro-substituted complexes **7** and **8** yield polymers with lower isotacticities than catalysts **1–6**, especially at lower pressures. Although catalyst **8** produced polymers with the highest [mmmm] content out of all the catalysts studied in liquid propylene, in the solution polymerizations it yielded polymers of lower isotacticity than catalysts **1**–**6**.

3. Discussion

The activities and stereospecificity of metallocene catalysts depend on steric and electronic environment provided by the cyclopentadienyl ligands [13–15]. In the bridged zirconocene systems electronic effects have been probed by introducing substituents on the indenyl rings sufficiently far away from the catalyst active site such that their steric influence could largely be discounted. For the unbridged catalysts, it is more difficult to divorce steric factors from electronic factors. The substituent R could influence not only monomer coordination and the conformation of the growing polymer chain, but also the rate of rotation of the indenyl rings and the equilibrium constant between the *rac*-like and *meso*-like rotamers. Electronic and steric changes might also affect ion-pairing between the active metal cation and the co-catalyst anion, which may influence ligand rotation and chain propagation rates.

The data in Table 1 show that steric and electronic effects at the 4-position of the aryl ring have little effect on productivities and molecular weights for catalysts **1**–**8**. For example, comparable amounts of polymer are produced by catalysts **5** and **8**, which have the most and least electron-donating substituents, respectively [3] [16,17]. Catalysts **1**–**8** also produced polymers of similar molecular weights. For bridged catalysts, a slight enhancement in M_w is observed with increasing steric size and electron-donating capability of the substituent on the ligand; this effect has been interpreted to be due to the increased electron density at the metal, which discourages conformations that lead to β-H elimination [14,15]. Our results show no such trend.

The nature of the substituent in the 4-position appears to have little effect on polymer microstructure. Catalysts **1**–**8** differ little in [mmmm] over the four monomer concentrations despite the large differences in the steric and electronic demands of the R-substituent. This suggests either that the 4-substituent is not correctly positioned to influence monomer insertion, or that the changes in steric bulk of the substituents is not sufficient to affect the rate of interconversion or the equilibrium between *rac* and *meso* rotamers.

Electronic effects are likewise difficult to interpret in these unbridged systems, in that we observe opposite trends for trifluoromethyl substituted 2-arylindene catalysts depending on whether the trifluoromethyl substituent is substituted in the 3,5- or 4-position of the 2-aryl ring: catalysts derived from 2-(3,5-$(CF_3)_2$-C_6H_3)indenyl)$_2ZrCl_2$ yield polypropylenes with tacticities as high as [mmmm] = 74% [11], whereas catalysts derived from 2-(4-$CF_3C_6H_4$) indenyl)$_2ZrCl_2$ **7** yield polymers with [mmmm] $\leq$ 33%.

[3] Some indication of the variation in steric and electronic properties in the 4-substituent can be taken from Es, the steric Taft parameter, which changes from 1.24 (for R=H) to −1.54 (for R=*t*Bu), and σp, the para Hammett parameter which changes from 0.54 (for R=Cl) to −0.20 (for R=*t*Bu).

4. Conclusions

The results of this study indicate that the polymerization behavior of bis(2-arylindenyl)zirconium dichloride catalyst family is relatively insensitive to substitution at the 4-position. This observation stands in contrast to our previous results, which show that substitution at the 3,5-position of the 2-aryl substituent can have significant effects on the polymerization behavior of 2-arylindene metallocenes. The insensitivity of the catalyst to the 4-substitutent suggests that this position may be utilized as a point of attachment of the complex to a surface as an entry into heterogeneous polymerization systems that produce elastomeric polypropylene.

5. Experimental

5.1. General procedures

All experiments involving air-sensitive compounds were performed under nitrogen in a Vacuum Atmospheres or Braun drybox or under argon using standard Schlenk line techniques. Hydrocarbon solvents, diethyl ether, tetrahydrofuran, and benzene-d_6 were distilled from sodium/benzophenone ketyl. Methylene chloride was distilled from calcium hydride. Deuterated solvents were obtained from Cambridge Isotope Labs.

Butyllithium and 4-substituted aryl Grignards were obtained from Aldrich and used as received. 2-indanone was obtained from Aldrich or Acros and depending on appearance, used as received or purified by sublimation. $ZrCl_4$ was obtained from Fluka and used as received. $ZrCl_4(THF)_2$ was prepared according to literature procedures.

^1H spectra were recorded on Varian Gemini 200, XL-400, or Varian Unity Plus 500 spectrometers while ^{13}C NMR were recorded at 100 or 125 MHz on a Varian XL-400 or Varian Unity Plus 500 spectrometer. Elemental Analyses were performed by Desert Analytics or E + R Microanalytics Laboratory.

5.2. Polymer analysis

Solution ^{13}C NMR spectra were run at 75 MHz on a Varian Anova-300 NMR spectrometer equipped with a 10 mm broad-band probe. Samples were run as solutions in $C_2D_2Cl_4/C_2H_2Cl_4$ at 100°C. Qualitative spectra were acquired with $\approx 500-1000$ transients with no delay between pulses. Decoupling was always on during acquisition, so the nuclear Overhauser enhancement was present. High-temperature GPC measurements of polymers were performed at Amoco Chemical using a Watts 150C GPC at 100°C in dichlorobenzene and referenced to polypropylene standards.

5.3. Preparation of 2-(4-methyl-C_6H_4)indene

A 3-neck 500-ml round-bottomed flask fitted with a condenser and an addition funnel was charged with 2.66 g (0.11 mol) of Mg turnings and 20 ml of anhydrous Et_2O. Slow addition of a solution of 15.0 g (0.09 mol) of 4-bromotoluene in Et_2O (100 ml), followed by refluxing for 30 min, gave an orange solution of the aryl Grignard reagent. The solution was cooled to room temperature, filtered over a plug of Celite, and the solvent was removed in vacuo from the filtrate. Toluene (40 ml) was added, and the solution cooled to 0°C, whereupon a solution of 2-indanone (9.27 g, 0.07 mol) in toluene (70 ml) was added dropwise to give an orange slurry. This mixture was warmed to room temperature and stirred for an additional 3 h. After cooling to 0°C, it was quenched with 150 ml of water. Hexane (150 ml) was added, and the reaction mixture neutralized with 5 M HCl. The organic layer was separated, and the aqueous layer was extracted with two 50-ml portions of hexane. The combined organic layers were washed with two 50-ml portions of

brine and dried over anhydrous magnesium sulfate. After filtration over Celite, the solvent was removed in vacuo yielding 2-(4-methyl)phenylindanol as a solid.

Under argon, this alcohol and *p*-toluenesulfonic acid monohydrate (200 mg) were dissolved in benzene (200 ml), and the solution was heated to reflux for 2 h. After cooling to room temperature, the solvent was removed in vacuo and the product, 2-(4-methyl-C_6H_4)indene, was recrystallized from Et_2O/hexane. Yield: 7.17 g (50%). ^{1}H NMR ($CDCl_3$, 23°C, 400 MHz): δ 7.56 (d, $J = 8$ Hz, 2H); 7.49 (d, $J = 8$ Hz, 1H); 7.41 (d, $J = 7$ Hz, 1H); 7.36–7.14 (overlapping signals integrating for 5H); 3.80 (s, 2H, CH_2); 2.40 (s, 3H, CH_3). ^{13}C{H} NMR ($CDCl_3$, 23°C, 100 MHz): δ 146.5 (s), 145.5 (s), 143.0 (s), 137.4 (s), 133.2 (s), 129.4 (s); 126.6 (s), 125.64 (s), 125.57 (s), 124.5 (s), 123.6 (s), 120.8 (s), 39.0 (s, CH_2), 21.3 (s, CH_3). C, H analysis: Anal. Found (Calcd.): C, 93.25 (93.16); H, 7.00 (6.84).

5.4. Preparation of 2-(4-ethyl-C_6H_4)indene

Synthesis similar to 2-(4-methyl-C_6H_4)indene. Recrystallized the yellow solid obtained from ether to give white crystals, which were rinsed with hexanes and then dried. Yield = 32%. ^{1}H NMR ($CDCl_3$, 20°C, 200 MHz): δ 7.56 (d, $J = 8.2$, 2H); 7.46 (d, $J = 7.2$, 1H) 7.38 (d, $J = 7.2$, 1H), 7.25-7.16 (overlapping signals, 5H), 3.77 (s, 2H, CH_2), 2.63 (q, $J = 7.2$, CH_2CH_3), 1.26 (t, $J = 7.6$, CH_2CH_3). ^{13}C{H} NMR ($CDCl_3$, 19°C, 100 MHz): δ 146.48, 145.53, 143.81, 143.04, 133.47, 128.17, 126.55, 125.67, 125.63, 124.50, 123.60, 120.78, 38.99, 28.63, 15.54. C, H analysis: Anal. Found (Calcd): C, 92.68 (92.68), H, 7.35 (7.31).

5.5. Preparation of 2-(4-n-butyl-C_6H_4)indene

Synthesis of this ligand was similar to that of 2-(4-methyl-C_6H_4)indene. Yield = 28%. ^{1}H NMR ($CDCl_3$, 20°C, 200 MHz): δ 7.55 (d, $J = 8.2$, 2H); 7.46 (d, $J = 8.2$, 1H), 7.39 (d, $J = 6.8$, 1H), 7.25–7.16 (overlapping signals, 5H), 3.78 (s, 2H, CH_2), 2.63 (t, $J = 7.4$, CH_2-$CH_2CH_2CH_3$), 1.58 (m, 2H, CH_2CH_2-CH_2CH_3), 1.58 (m, 2H, CH_2CH_2-CH_2CH_3), 0.94 (t, 3H, CH_2CH_2-CH_2CH3). ^{13}C{H} NMR ($CDCl_3$, 19°C 100 MHz): δ 146.50, 145.55, 143.04, 142.50, 133.41, 128.73, 126.55, 125.63, 125.54, 125.23, 124.49, 123.59, 120.77, 38.99, 35.38, 33.57, 22.35, 13.97. C, H analysis: Anal. Found (Calcd): C, 91.31 (91.88), H, 8.08 (8.12).

5.6. Preparation of 2-(4-tert-butyl-C_6H_4)indene

Synthesis of this ligand was similar to that of 2-(4-methyl-C_6H_4)indene. Compound was recrystallized from diethyl ether/hexane at −18°C. Yield = 68%. ^{1}H NMR ($CDCl_3$, 23°C, 400 MHz): δ 7.59 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 7$ Hz, 1H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 7$ Hz, 1H), 7.28 (dd, $J = 7$ Hz, 1H), 7.20 (s, 1H), 7.18 (dd, $J = 7$ Hz, 1H), 3.79 (s, 2H), 1.36 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 23°C, 100 MHz): δ 150.7 (s), 146.4 (s), 145.6 (s), 143.1 (s), 133.2 (s), 126.6 (dd, $J_{C-H} = 159$ Hz, $^2J_{C-H} = 7$ Hz), 125.8 (d, $J_{C-H} = 163$ Hz), 125.6 (dd, $J_{C-H} = 157$ Hz, $^2J_{C-H} = 7$ Hz), 125.4 (dd, $J_{C-H} = 158$ Hz, $^2J_{C-H} = 7$ Hz), 124.5 (dd, $J_{C-H} = 159$ Hz, $^2J_{C-H} = 7$ Hz), 123.6 (dd, $J_{C-H} = 158$ Hz, $^2J_{C-H} = 8$ Hz), 120.8 (dd, $J_{C-H} = 159$ Hz, $^2J_{C-H} = 8$ Hz), 39.0 (td, $J_{C-H} = 128$ Hz, $^2J_{C-H} = 6$ Hz, CH_2), 34.6 (s, $C(CH_3)_3$), 31.3.(brq, $J_{C-H} = 126$ Hz, $C(CH_3)_3$). Anal. found (calcd.): C, 91.40 (91.88); H, 7.98 (8.12).

5.7. Preparation of 2-(4-trimethylsilyl-C_6H_4)indene

A 3-neck round-bottom flask fitted with an addition funnel was charged with 1,4-dibromobenzene (35.9 g, 0.152 mol) under an N_2 atmosphere. After adding 150 ml of THF and cooling to −78°C, *n*-butyllithium (100 ml, 0.16 mol, 1.05 equivalents) was added dropwise to the reaction over 40 min to form a pale cream-colored solution. After stirring for an additional

10 min, trimethylchlorosilane (18.16 g, 0.167 mol, 1.10 equivalents) was added over 15 min to yield an olive-drab solution. The reaction was warmed to −20°C and quenched with 25 ml MeOH. After washing with distilled water (3 × 50 ml) and drying over $MgSO_4$, the crude product was isolated by removing the solvent in vacuo. Pure compound was obtained by distillation (second fraction, 50–56°C/0.2 mmHg). Yield = 18.1 g (86% based on 2-indanone).

The indanol was formed and dehydrated in a manner analogous to the other ligand syntheses to yield 18 g of the crude indene. The product was further purified by recrystallization from hexanes to yield 4.9 g (23.5%). ^{1}H NMR ($CDCl_3$, 23°C, 300 MHz): δ 7.62 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 7$ Hz, 2H), 7.40 (d, $J = 7$ Hz, 1H), 7.28 (dd, $2J = 7$ Hz, 1H), 7.25 (s, 1H), 7.18 (dd, $2J = 7$ Hz, 1H), 3.79 (s, 2H), 0.287 (s, 9H, $Si(CH_3)_3$). ^{13}C{H} NMR ($CDCl_3$, 19°C, 100 MHz): δ 146.43, 145.35, 143.18, 139.87, 136.29, 133.71, 126.74, 126.61, 124.90, 124.78, 123.66, 121.00, 38.90, −1.14. C, H analysis: Anal. Found (Calcd): C, 82.03 (81.77), H, 7.69 (7.62).

5.8. Preparation of 2-(4-trifluoromethyl-C_6H_4)indene

Synthesis of this ligand was similar to that of 2-(4-methyl-C_6H_4)indene. **Caution: Fluorinated phenyl Grignards can be explosive when concentrated** [18]. Compound was recrystallized from diethyl ether at −18°C (5.59 g, 65%). ^{1}H NMR ($CDCl_3$, 23°C, 400 MHz): d AB pattern centered at 7.68 ppm and integrating for 4H, 7.51 (d, $J = 7$ Hz, 1H), 7.45 (d, $J = 7$ Hz, 1H), 7.35 (s, 1H), 7.32 (dd, $2J = 7$ Hz, 1H), 7.25 (dd, $2J = 7$ Hz, 1H), 3.81 (s, 2H). ^{13}C NMR ($CDCl_3$, 23°C, 100 MHz): δ 144.8 (s), 144.7 (s), 143.2 (s), 139.3 (s), one quaternary carbon is either masked by the aromatic region, or is coincidental with the signal at 139.3 (somewhat broad), 128.8 (d, $J_{C-H} = 168$ Hz), 126.8 (dd, $J_{C-H} = 168$ Hz, $J_{C-H} = 7$ Hz), 125.7 (dd, $J_{C-H} = 161$ Hz, $J_{C-H} = 7$ Hz), 125.6 (d, J_{C-H} = ca. 160 Hz), 125.5 (d, J_{C-H} = ca. 160 Hz), 124.2 (q, $J_{C-F} = 272$ Hz, CF_3), 123.8 (dd, J_{C-H} = ca. 160 Hz, $J_{C-H} = 9$ Hz), 121.5 (dd, $J_{C-H} = 160$ Hz, $J_{C-H} = 9$ Hz), 38.9 (td, $J_{C-H} = 129$ Hz, $^2J_{C-H} = 7$ Hz, CH_2). C, H analysis: Anal. Found (Calcd.): C, 74.05 (73.84); H, 4.15 (4.26).

5.9. Preparation of 2-(4-chloro-C_6H_4)indene

Synthesis of this ligand was similar to that of 2-(4-methyl-C_6H_4)indene. Compound was recrystallized from diethyl ether at −18°C. Overall yield = 32%. ^{1}H NMR ($CDCl_3$, 20°C, 200 MHz): δ 7.52 (d, $J = 8.5$, 2H); 7.46 (d, $J = 7.3$, 1H), 7.39 (d, $J = 7.6$, 1H), 7.33 (d, $J = 8.6$, 2H), 7.27 (dd, $J = 7.32$, 1H), 7.21–7.18 (overlapping signals (dd and singlet), 3H), 3.76 (s, 2H, CH_2). ^{13}C{H} NMR ($CDCl_3$, 19°C, 100 MHz): δ 145.09, 145.05, 143.00, 134.44, 133.10, 128.80, 127.07, 126.78, 126.70, 124.99, 123.67, 121.09, 38.93. C, H analysis: Anal. Found (Calcd): C 79.47 (79.48), H 4.82 (4.89).

5.10. Preparation of bis(2-(4-methyl-C_6H_4)indenyl)zirconium dichloride (2)

N-Butyllithium (1.6 M in hexanes, 4.2 ml, 6.7 mmol) was added dropwise to a solution of 2-(4-methyl-C_6H_4)indene (1.323 g, 6.4 mmol) in Et_2O (20 ml). The red-orange solution was stirred at ambient temperature for 30 min, after which time the solvent was removed in vacuo. In a drybox, to the resulting solid was added $ZrCl_4$ (0.754 g, 3.2 mmol). The solids were cooled to −78°C and methylene chloride (60 ml) was slowly added. The solution was warmed to room temperature and kept there overnight. The resulting yellow-orange turbid solution was then filtered over a plug of Celite and the Celite was washed with CH_2Cl_2 until the washings were colorless (ca. 60 ml). The product was recrystallized from CH_2Cl_2/hexane at −18°C. Yield: 577 mg (31%). ^{1}H NMR (C_6D_6, 23°C, 400 MHz): δ 7.36 (d, $J = 8$ Hz, 4H); 7.11 (m,

4H); 7.02 (d, $J = 8$ Hz, 4H); 6.92 (m, 4H); 6.43 (s, 4H, Cp–H); 2.17 (s, 6H, CH_3). ^{13}C NMR (CD_2Cl_2, 23°C, 100 MHz): d 139.3 (m, qC), 134.0 (m, qC), 130.5 (qC), 129.9 (dm, $J = 159$ Hz, Ar*C*–H), 127.0 (brs, qC), 127.0 (dd, $J =$ 159 Hz, $J = 7$ Hz, Ar*C*–H), 126.7 (dd, $J = 162$ Hz, $J = 8$ Hz, Ar*C*–H), 125.2 (dd, $J = 172$ Hz, $J = 5$ Hz, Ar*C*–H), 103.4 (dd, $J = 176$ Hz, $J = 7$ Hz, Cp*C*–H), 21.5 (qd, $J = 127$ Hz, $J = 4$ Hz, CH_3). C, H analysis (crystallizes with 1/2 CH_2Cl_2): Anal. Found (Calcd.): C, 63.21 (63.46); H, 4.41 (4.42).

5.11. Preparation of bis(2-(4-ethyl-C_6H_4)indenyl)zirconium dichloride (3)

The corresponding indene (1.00 g, 4.54 mmol) was slurried in dry diethyl ether in a 100 ml Schlenk flask under Ar. The solution was cooled to −78°C and *n*-butyllithium (2.18 ml, 5.45 mmol, 1.2 eq) was added dropwise slowly. The flask was brought to room temperature and stirred for another hour, upon which the orange solution was evaporated to give a reddish solid. This solid was washed with 10 ml dry hexanes and the now off-white solid isolated and dried. After slurrying the lithium salt in 50 ml toluene and cooling to −78°C, a slurry of $ZrCl_4$ (0.528 g, 2.27 mmol) in 20 ml toluene was cannula transferred into the flask. The reaction was warmed to room temperature, during which is turned from yellow to dark brown and became turbid with salts. As the reaction progressed, the insoluble lithium indenyl disappeared. Stirred overnight at room temperature under Ar. Following filtration through a plug of Celite and consequent washing of the Celite with 2 × 5 ml toluene, the solution was concentrated down to 15–20 ml, and then placed in the −78°C freezer for recrystallization. First recrystallization yield = 482 mg (35%). ^{1}H NMR (C_6D_6, 20°C, 400 MHz): δ 7.14 (d, $J = 8.4$ Hz, 4H); 7.08 (d, $J = 8$ Hz, 4H), 6.92 (m, 4H), 6.47 (s, 4H, Cp–H), 2.51 (q, J = 7.6 Hz, CH_2CH_3, 2H), 1.15 (t, $J = 7.6$, CH_2CH_3, 3H). ^{13}C{H} NMR (C_6D_6, 20°C, 100 MHz): δ 151.49, 149.99, 133.46, 131.76, 128.65, 127.59, 127.18, 126.77, 125.8, 103.59, 29.17, 15.82. C, H analysis: Anal. Found (Calcd.): C 67.98 (67.98), H 5.06 (5.03).

5.12. Preparation of bis(2-(4-n-butyl-C_6H_4)indenyl)zirconium dichloride (4)

Synthesis of this complex was similar to that of (**3**). Orange crystals were isolated with yield = 16%. ^{1}H NMR (C_6D_6, 20°C, 400 MHz): δ 7.44 (d, $J = 8.0$ Hz, 4H); 7.13 (d, $J = 8.0$ Hz, 4H), 7.06 (dd, $J = 6.4$, 3.2, 4H), 6.92 (dd, $J = 6.4$, 3.2, 4H), 6.47 (s, 4H, Cp–H), 2.54 (t, $J = 7.6$ Hz, $CH_2CH_2CH_2CH_3$, 2H), 1.57 (m, $CH_2CH_2CH_2CH_3$, 4H), 1.31 (m, $CH_2CH_2CH_2CH_3$, 4H), 0.91 (t, $J = 7.6$, CH_2CH_3, 6H). ^{13}C{H} NMR (C_6D_6, 20°C, 100 MHz): δ 143.48 132.94, 129.03, 127.30, 126.93, 126.59, 126.04, 125.12, 124.8, 103.66, 35.95, 34.01, 22.89, 14.38. Anal. Found (Calcd.): C, 69.09 (69.49); H, 5.81 (5.89).

5.13. Preparation of bis(2-(4-tert-butyl-C_6H_4)indenyl)zirconium dichloride (5)

Synthesis of this compound to similar to that of (**2**). Orange crystals were obtained by recrystallization from toluene. Yield = 61%. ^{1}H NMR (C_6D_6, 23°C, 400 MHz): d AB pattern centered at 7.42 ppm and integrating for 4H, AB pattern centered at 6.96 ppm and integrating for 4H, 6.56 (s, 4H, Cp–H), 1.30 (s, 9H, ^{t}Bu). ^{13}C{H} NMR (C_6D_6, 23°C, 100 MHz): δ 151.7, 132.6, 130.9, 127.2, 126.8, 126.9, 126.6, 125.9, 125.1, 103.5, 34.7, 31.4. Anal. found (calcd.) (crystallizes with 1/2 toluene): C, 71.11 (71.12); H, 6.09 (5.75).

5.14. Preparation of bis(2-(4-trimethylsilyl-C_6H_4)indenyl)zirconium dichloride (6)

Synthesis of this compound is similar to that of (**2**) except that the lithium salt and the catalyst were synthesized in toluene. The product was extracted with CH_2Cl_2 and precipitated

from pentane. Further recrystallizations were done in toluene. Yield = 78%. ^{1}H NMR (C_6D_6, 23°C, 500 MHz): δ 7.55 (d, J = 8.0 Hz, 4H); 7.47 (d, J = 8.0 Hz, 4H), 7.06 (dd, J = 6.5, 3.0, 4H), 6.90 (dd, J = 6.5, 3.0, 4H), 6.53 (s, 4H, Cp–*H*), 0.26 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C{H} NMR (C_6D_6, 23°C, 125 MHz): δ 134.0, 128.3, 127.9, 126.9, 126.6, 125.4, 125.1 124.0, 103.6, 1.38. Anal. found (calcd.): C, 62.60 (62.76); H, 5.72 (5.56).

5.15. Preparation of bis(2-(4-trifluoromethyl-C$_6$H$_4$)indenyl)zirconium dichloride (7)

Synthesis of this compound to similar to that of (**2**). The product was recrystallized from toluene at −18°C. Yield: 471 mg (35%). Note: the compound is extremely insoluble. ^{1}H NMR (C_6D_6, 23°C, 400 MHz): δ 7.36 (d, J = 8 Hz, 4H); 7.12 (dd, J = 6.5 Hz, J = 3.1 Hz, 4H); 7.09 (d, J = 8 Hz, 4H); 6.86 (dd, J = 6.4 Hz, J = 3 Hz, 4H); 6.21 (s, 4H, Cp–H). ^{13}C{H} NMR (CD_2Cl_2, 23°C, 100 MHz): δ 136.7, 132.7, 130.4 (q, J_{C-F} = 33 Hz), 129.2, 127.3, 127.2, 125.9 (m), 125.4, 124.4 (q, J_{C-F} = 272 Hz, *C*F$_3$), 103.7 (Cp *C*–H). C, H analysis: Anal. Found (Calcd.): C, 56.42 (56.47); H, 3.00 (2.96).

5.16. Preparation of bis(2-(4-chloro-C$_6$H$_4$)indenyl)zirconium dichloride (8)

The corresponding indene (0.750 g, 3.31 mmol) was slurried in ~10 ml dry tetrahydrofuran in a 50 ml Schlenk flask under Ar. The solution was cooled to −78°C and added dropwise to a slurry of potassium hydride (0.077 g, 4.76 mmol, 1.4 eq) in ~20 ml tetrahydrofuran. The flask was brought to room temperature and stirred for another 2 1/2 h upon which the dark yellow solution was filtered via cannula into a flask containing $ZrCl_4(THF)_2$ (0.620 g, 1.64 mmol, 0.49 eq) in ~30 ml THF at −78°C. Another few milliliters of THF were added to the excess KH to insure complete transfer of the indene salt. The reaction was warmed to room temperature during which is turned to a cloudy straw-yellow and was stirred overnight under Ar. The solvent was removed in vacuo and a few milliliters of pentane were added which were once again removed in vacuo. The yellow solid was then extracted in 15 ml toluene and filtered over a bed of celite. The toluene solution was then concentrated and placed in a −18°C freezer. Due to the low solubility of the compound in toluene, methylene chloride was used in further extractions of the solid left on the frit. The methylene chloride washings were collected, concentrated, and placed in −18°C freezer. The resulting solids were redissolved in toluene and re-filtered to remove any residual salts. Yield = 0.020 g (2%). ^{1}H NMR (C_6D_6, 20°C, 400 MHz): δ 7.12 (overlapping signals consisting of a doublet and a multiplet) (m, 8H), 7.02 (d, J = 8.6, 4H), 6.86 (dd, J = 6.5, 3.0, 4H), 6.17 (s, 4H, Cp–*H*). ^{13}C{H} NMR (C_6D_6, 18°C, 100 MHz): δ 151.51, 134.83, 132.05, 129.21, 128.60, 127.69, 127.20, 126.74, 125.37, 103.07. C, H analysis: Anal. Found (Calc): C 58.63 (58.73), H 3.47 (3.28).

6. General procedure for solution polymerization of propylene

[Zr] = 5×10^{-5} M, [Al]/[Zr] = 1000, Polymerization temp = 20°C, Final volume = 100 ml (75 ml toluene, 25 ml catalyst solution).

6.1. Catalyst solution

In a nitrogen dry box, catalyst stock solution in toluene is prepared in a 25 ml volumetric flask and an aliquot containing 5×10^{-6} mol removed and diluted to 10 ml in a volumetric flask. Methylaluminoxane (Akzo, Type IV) (275 mg) is dissolved in 10 ml toluene. The catalyst solution is added to the MAO solution, producing an orange-gold color almost immediately. This solution is stirred for several minutes and then introduced to a stainless steel, double-ended

injection tube containing 5 ml toluene (final volume 25 ml).

6.2. Polymerization

A 300-ml stainless steel Parr reactor was purged several times with propylene by pressurizing and then venting. The regulator attached to the reactor was set to the desired propylene pressure, the 75 ml toluene (loaded in a stainless steel tube in the box) was injected, and the temperature set to 20°C. This toluene solution was allowed to equilibrate for at least 10 min at the set pressure and temperature. Then the autoclave was vented until the pressure was 10 psig less than the regulator pressure setting. The catalyst solution was injected under propylene pressure and the polymerization temperature kept to 20°C. After 1 h, the polymerization was stopped by injection of 20 ml methanol and the reactor slowly vented. The polymer was precipitated by adding 200 ml acidified methanol (5% HCl/MeOH v/v) and collected by filtration. After drying in the vacuum oven for 18 h, it was weighed and analyzed by ^{13}C NMR.

7. General procedure for liquid propylene polymerization

$[Zr] = 5 \times 10^{-5}$ M′ $[Al]/[Zr] = 1000$, Polymerization temp = 20°C, Final volume = 100 ml (80 ml liquid propylene, 20 ml catalyst solution).

7.1. Catalyst solution

In a nitrogen dry box, catalyst stock solution in toluene is prepared in a 25-ml volumetric flask and an aliquot containing 5×10^{-6} mol removed and diluted in a 10 ml volumetric flask. Methylaluminoxane (Akzo, Type IV) (275 mg) is dissolved in 10 ml toluene. The catalyst solution is added to the MAO solution, producing an orange-gold color almost immediately. This solution is stirred for several minutes and then introduced to a stainless steel, single-ended injection tube (final volume 20 ml). The tube is brought out of the box and pressure with Ar to prevent any air from being introduced.

7.2. Polymerization

A 300-ml stainless steel Parr reactor is dried and evacuated overnight. After filling with Ar and then flushing with gaseous propylene at least three times, 80 ml of liquid propylene is introduced to the reactor. The contents are maintained at 18–19°C using a cooling bath/cooling coil and allowed to remain at that temperature for at least 10 min with stirring (usually $P = 124$–126 psig). A single-ended injection tube containing 20 ml of catalyst/MAO solution in toluene is pressured to 200–250 psig with Ar and the solution injected into the reactor. The temperature is quickly brought to 20°C and kept there through the reaction. The pressure drops initially, then stabilizes around 110–113 psig. The reaction is quenched using 10 ml of MeOH under Ar pressure when the pressure has dropped 2–4 psig (20–40 min depending on the catalyst) and the reactor slowly vented. The polymer is removed and stirred in 5% acidic MeOH for several hours or overnight. It is then dried overnight at 40°C in a vacuum oven and weighed.

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