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Novel 2-indenyl *ansa*-zirconocenes for the polymerization of α-olefins

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Abstract

A new synthetic route to C-2 bridged indenyl metallocenes utilizing the anion of 1-indanone has been developed. Two new *ansa*-zirconocene complexes **1a** and **1b** were synthesized and examined as precursors for the polymerization of α-olefins. These metallocenes were shown to be active for the polymerization of ethylene and for the oligiomerization of propylene when activated with excess methylaluminoxane (MAO). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2-Indenyl; Metallocene; Zirconium; Olefin polymerization

1. Introduction

Brintzinger and Kaminsky first reported the polymerization of α-olefins using an *ansa*-metallocene co-catalyst in 1985 [1]. Since that time, an extraordinary amount of effort has been devoted to the synthesis of metallocene catalyst precursors that exhibit improved reactivity and stereospecificity [2]. Many of these studies are based on the indenyl ring system. Most of the *ansa*-metallocenes incorporating an indenyl moiety are bridged at the C-1 position of the indenyl ring for both synthetic convenience and for stereospecificity concerns. To date, there have not been any reports relating to the polymerization characteristics of *ansa*-metallocenes bridged by a single carbon unit at the 2-position.

There have been several previous studies in the area of 2-indenyl metallocene complexes. Halterman and Ramsey [3] along with Ellis et al. [4] have prepared indenyl and tetrahydroindenyl metallocenes with biaryl bridging components at the 2-position of the indenyl moiety as epoxidation catalysts. Jordan and co-workers [5] have serendipitously prepared dimethylsilylene(η^5-1-indenyl)(η^3-2- indenyl)hafnium bisdimethylamide through an interesting [1,5]-silyl shift. Nantz et al. [6] have reported the synthesis of a series of ethylene bis(2-indenyl) titanocene complexes that were also examined as epoxidation catalysts. Baker et al. [7] have recently reported the synthesis of a series of [1-(9-fluorenyl)-2-(2-indenyl) naphthalene]zirconium dichloride complexes. These were reported as the first examples of a C(sp^2)–C(sp^2) bridge at the 2-position. Very recently, Schaverien et al. [8] have prepared a family of chiral ethylene-bridged bis(2-indenyl) zirconocenes and shown them to be active for the polymerization of ethylene and propylene as well as for the co-polymerization of ethylene–propylene and ethylene–1-hexene.

In the present study, two new *ansa*-zirconocenes (**1a**, **1b**), bridged at the 2-position of the indenyl moiety by an isopropylidene group (Fig. 1) have been synthesized, and evaluated as catalyst precursors for the polymerization of ethylene and propylene.

2. Results and discussion

2.1. Synthesis of pre-catalysts

The synthetic route is based on the reaction of the 1-indanone anion with 6,6-dimethylfulvene (Scheme 1). Adamczyk et al. [9] have successfully used the 1-indanone anion to produce 2-alkylindenes where the alkyl group was methyl, ethyl or propyl. They found that the yield-limiting step was the initial addition of the desired alkyl group, with yield decreasing as the size of the alkyl group increased. In Adamczyk's study, reduc-

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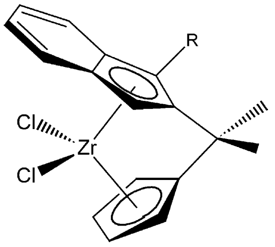


1a R = H
1b R = Me

Fig. 1. 2-Indenyl-*ansa*-zirconocenes.

tion of the ketones to the alcohols and subsequent dehydration reactions all proceeded in greater than 80% yield.

In our synthetic procedure, reaction of the 1-indanone anion with a threefold excess of 6,6-dimethylfulvene at −78 °C resulted in the ketone **2** in 43% conversion (59% yield based on recovery of unreacted starting material). Allowing the anion to warm to above −40 °C resulted in O-alkylation. Purification was achieved via vacuum distillation. By reducing the equivalents of 6,6-dimethylfulvene, percent conversion to **2** decreases while yield increases (1:2 excess: 37% conversion, 72% yield; 1:1 no excess: 24% conversion, 84% yield).

Elemental characterization of **2** (a high-boiling oil) does not confirm C-alkylation, so the cyclopentadienyl moiety was converted to a dimethylfulvene ligand via reaction with acetone and pyrrolidine [10] to give a derivative **7** in 94% yield. Compound **7** (Fig. 2) was characterized via elemental analysis, X-ray crystal structure and mass spectrometry. The X-ray structure

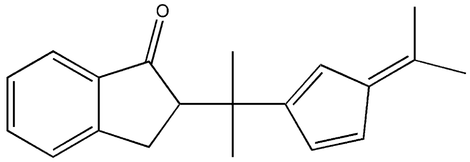
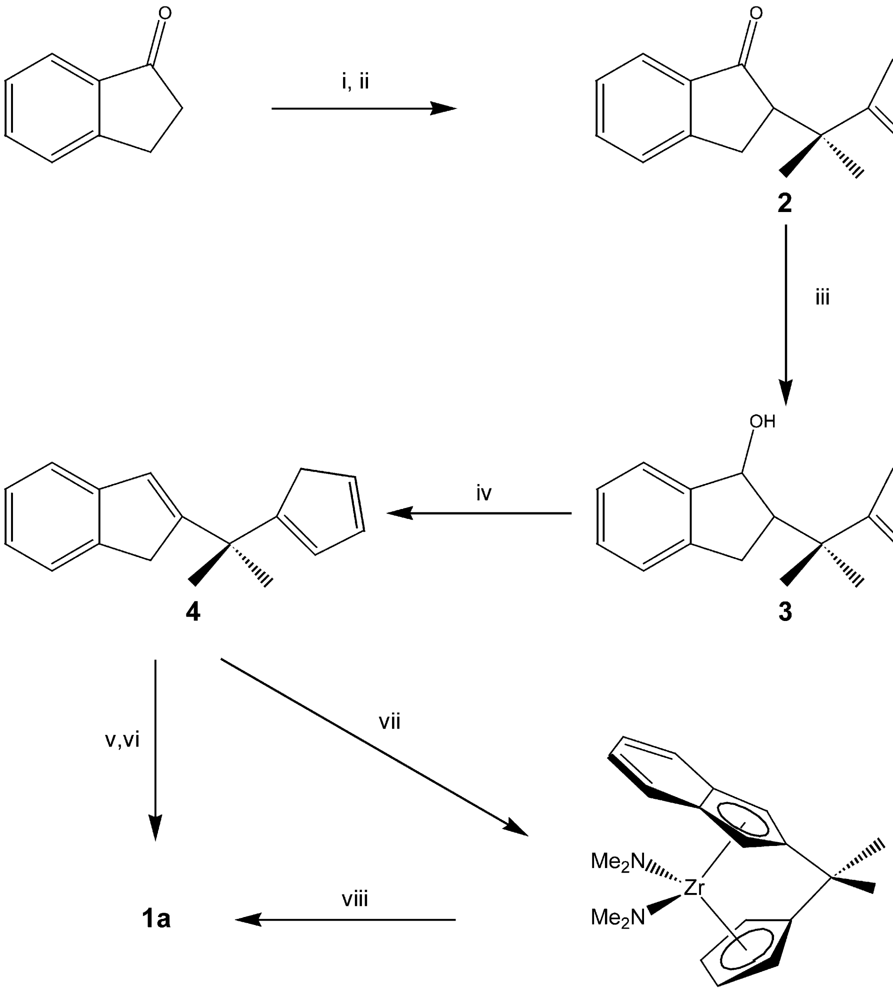


Fig. 2. Derivative **7**.



Scheme 1. (i) LDA, THF, −78 °C; (ii) 6,6-dimethylfulvene; (iii) $NaBH_4$, THF–MeOH; (iv) *p*-toluenesulfonic acid, benzene; (v) 2 butyllithium, diethyl ether; (vi) $ZrCl_4$; (vii) $Zr(NMe_2)_4$, toluene; (viii) 10 Me_3Si–Cl.

confirmed the presence of the bridge at the 2-position instead of O-alkylation.

The ketone **2** was then reduced with $NaBH_4$ to yield the alcohol (**3**) in nearly quantitative yield. Stronger reducing agents such as lithium aluminum hydride apparently reduced one of the double bonds on the cyclopentadienyl moiety to give the dihydro species with none of the desired product being isolated [11]. The alcohol **3** was then dehydrated using catalytic *p*-toluenesulfonic acid in benzene to give the desired ligand (**4**) in only 17% yield.

The surprisingly low yield of **4** from alcohol **3** is apparently due primarily to a competing side reaction. At elevated temperatures, **3** undergoes a ring-closure reaction that results in a ring-fused compound (**8**) (Fig. 3). This process is probably thermally initiated since attempted distillation of the alcohol **3** results almost entirely in conversion to compound **8**. However, separation of ligand **4** and compound **8** was achieved cleanly via chromatography.

The compound **1a** could be formed via two different routes. The first route was through the di-lithium salt of **4**. However, **1a** produced by this route proved difficult to purify and resulted in a low yield of **1a**. Much of the material recovered was insoluble in CH_2Cl_2 and was presumed to be polymeric. Therefore, the $Zr(NMe_2)_4$ route developed by Jordan et al. [12] followed by reaction with excess Me_3SiCl was used to successfully isolate **1a** in 30% yield. When isolated, **1a** was found to be very air- and moisture-sensitive.

Alkylation at the C-1 position of the indenyl moiety was also possible (Scheme 2). Treatment of **2** with two equivalents of methylmagnesium bromide resulted in the alcohol (**5**) in 73% yield. Using a single equivalent of methylmagnesium bromide resulted in only starting material, presumably due to initial preferential reaction with the acidic proton on the cyclopentadienyl moiety of **2**. Dehydration was again accomplished using catalytic *p*-toluenesulfonic acid in benzene to give the desired ligand **6** in 26% yield [13]. The corresponding zirconocene **1b** was formed in 32% yield via reaction with $Zr(NMe_2)_4$ followed by reaction with Me_3SiCl. Attempts to obtain an analytical sample of elemental purity of **1b** were unsuccessful due to decomposition during purification.

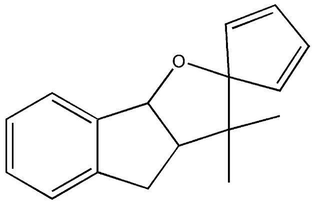


Fig. 3. Dehydration side-product **8**.

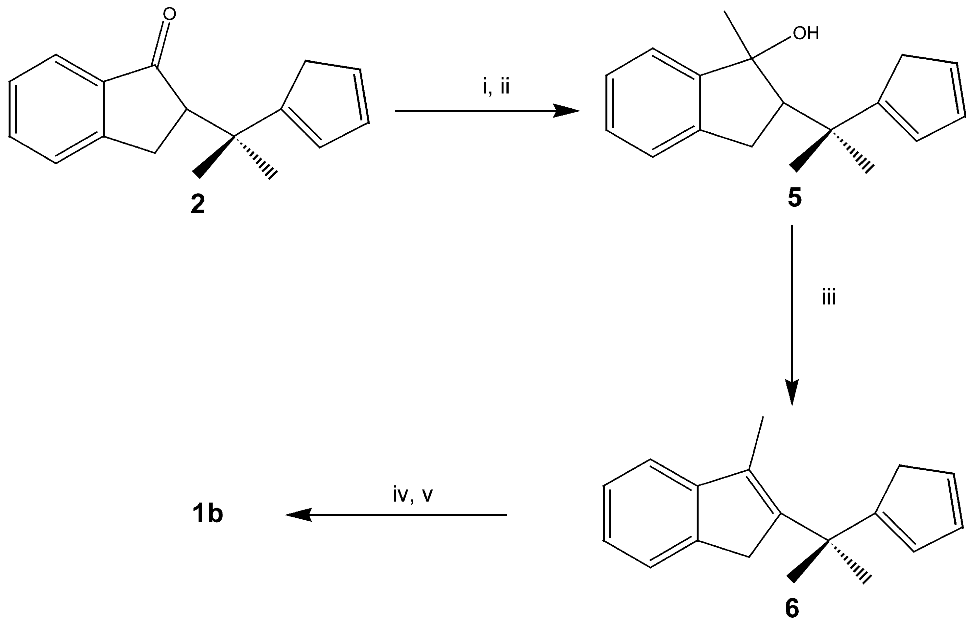
2.2. Polymerization

Both **1a** and **1b** proved to be active pre-catalysts for the polymerization of ethylene and propylene in the presence of methylaluminoxane (MAO) (Tables 1 and 2). Due to solubility factors, the compounds **1a** and **1b** were pre-activated with MAO before being exposed to the desired monomer.

In general, pre-catalyst **1b** showed slightly greater activity compared with **1a** for both ethylene and propylene over the polymerization temperatures examined. This could possibly be due to the mild electron donating effect of the methyl substituent at the C-1 position of the indenyl moiety. An electron donating group could help stabilize the cationic active species formed between **1b** and MAO. This has been found to be true with methyl substituents on cyclopentadienyl rings in other metallocenes [14].

The polypropylene that was produced by both pre-catalysts **1a** and **1b** was consistently low molecular weight atactic oligiomers of approximately 30 repeat units over the range of temperatures examined. The polyethylene was also of low molecular weight ($0.7–1.7 \times 10^4$) in comparison to most metallocene linear polyethylene ($4–11 \times 10^4$) [15]. The low molecular weight may be due to the relatively open geometry of these systems which could lead to a high rate of chain termination versus monomer insertion. Previously reported X-ray crystal structures [16] of the related isopropylidene-(cyclopentadienyl)$_2$ZrCl$_2$ show that the cyclopentadienyl rings are drawn back from the metal, opening up the coordination site. This suggests the possibility that the metal center in these systems is also opened up, allowing for more rapid β-hydride elimination. The ^{1}H-NMR spectra of the polypropylene produced indicates vinylic end groups, suggesting β-hydride elimination as a chain termination step. However, inverse gated ^{13}C-NMR spectra of the polyethylene obtained shows a 1:2.8 ratio of vinylic carbon end groups to methyl carbon end groups, which suggests that β-hydride elimination accounts for about 35% of chain termination events. The majority of chain termination steps are presumably due to chain transfer to free trimethylaluminum present in the MAO.

Our group has previously synthesized the analogous C-1 bridged isopropylidene(1-indenyl)(cyclopentadienyl)ZrCl$_2$ (**9**) [17]. The polymerization characteristics of **9**, **1a** and **1b** are quite similar. The activities [18] for ethylene at 25 °C are 0.94×10^6, 1.71×10^6, and 2.46×10^6, respectively. The activities for propylene at 0 °C are 2.7×10^5, 2.0×10^5, and 4.6×10^5, respectively. The similarity in activity suggests that the bridge position has little effect on the electronic environment of the active species. The methyl substituted **1b** has slightly greater activities than either **9** or **1a**, and is due to the more stable active site as previously mentioned.



Scheme 2. (i) 2 CH_3MgBr, diethyl ether; (ii) H_3O^+; (iii) p-toluenesulfonic

Table 1
Propylene polymerizations

Complex	Temperature (°C)	Yield (g) [a]	Activity [b] (10^{-5})	M_n [c]
1a	0	0.23 ± 0.01	2.0	1000
1a	25	0.33 ± 0.06	4.0	1000
1a	50	0.41 ± 0.02	10.4	1000
1b	0	0.52 ± 0.07	4.6	1000
1b	25	1.09 ± 0.10	13.1	1000
1b	50	1.31 ± 0.10	33.5	1000

Conditions: 50 ml toluene, 25 μM Zr, 1 h, 1:4000 Zr:MAO.

[a] Yields are averages of duplicate runs.

[b] g polymer/(mol Zr[monomer]h).

[c] ^{1}H-NMR end-group analysis.

In summary, we have demonstrated a new route to 2-indenyl isopropylidene bridged zirconocenes. A side product in the synthesis of ligand **4** was identified as a new ring-fused spiro compound **8**. Two novel pre-catalysts, **1a** and **1b**, were shown to be active for the polymerization of ethylene and propylene in the presence of MAO. The polymers produced were shown to be of low molecular weight and, in the case of propylene, atactic.

3. Experimental

All air-sensitive manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo Nobel and used as received. All other reagents were purchased from Aldrich and used without further purification. Diiso-

Table 2
Ethylene polymerizations

Complex	Temperature (°C)	Yield (g) [a]	Activity [b] (10^{-5})	M_w (10^{-3}) [c]	M_w/M_n [c]	T_m (°C) [d]
1a	0	0.14 ± 0.02	5.3	10.7	2.8	121.9
1a	25	0.40 ± 0.12	17.1	8.0	3.3	118.7
1a	50	1.61 ± 0.30	93.5	6.8	3.7	116.3
1b	0	0.11 ± 0.01	4.1	17.8	3.3	129.8
1b	25	0.57 ± 0.15	24.6	11.0	4.3	123.9
1b	50	2.78 ± 0.33	162.0	7.9	3.3	117.5

Conditions: 50 ml toluene, 25 μM Zr, 30 min, 1:4000 Zr:MAO.

[a] Yields are averages of duplicate runs.

[b] g polymer/(mol Zr[monomer]h).

[c] GPC, 1,2,4-trichlorobenzene at 135 °C.

[d] DSC.

propylamine was distilled from Na_2CO_3 under argon. Acetone was distilled from K_2CO_3 under argon. Et_2O, THF, and pentane were distilled from Na–K alloy under argon. Dichloromethane was distilled from CaH_2 under argon. 6,6-Dimethylfulvene was prepared according to literature procedures [10]. $Zr(NMe_2)_4$ was prepared according to literature procedures [12]. ^{1}H-NMR spectra were recorded on a Bruker AC-200 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, and mass spectra were performed by the Mass Spectrometry Center, University of Massachusetts, Amherst, MA.

*3.1. 2-(Cyclopentadienyl)-2-(2-indan-1-one)propane (**2**)*

Diisopropylamine (14.0 ml, 0.100 mol) was dissolved in 100 ml of THF and cooled to 0 °C. *n*-Butyllithium, 1.6 M in hexanes (62.5 ml, 0.100 mol), was added dropwise to give a light-yellow solution, which was stirred at room temperature (r.t.) for 2 h. The reaction mixture was cooled to −78 °C and indan-1-one (11.83 g, 0.090 mol) dissolved in 50 ml THF was added dropwise. The resulting light-brown solution was stirred for 2 h at −78 °C. 6,6-Dimethylfulvene (28.67 g, 0.270 mol) dissolved in 50 ml THF was added dropwise to give a yellow-tan solution. The reaction was stirred for 1 h at −78 °C and then allowed to slowly warm to r.t. with stirring overnight. The resulting deep red solution was hydrolyzed with NH_4Cl (aq) and extracted in Et_2O. The extracts were collected, dried ($MgSO_4$) and filtered, and the solvents were removed to give an orange oil. Vacuum distillation (149–151 °C @ 0.05 mmHg) yielded 9.11g (42%) of compound **2** as a viscous orange oil. ^{1}H-NMR ($CDCl_3$): δ 7.73–7.33 (m, 4H), 6.60–5.99 (m, 3H), 2.96 (m, 5H), 1.48 (s, 3H), 1.16 (s, 3H). HRMS (EI) *m*/*z* calc. for $C_{17}H_{18}O$: 238.1358. Found: 238.1368%. Anal. Calc. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.38; H, 7.62.

*3.2. 2-(Cyclopentadienyl)-2-(2-indan-1-ol)propane (**3**)*

Compound **2** (2.83 g, 11.9 mmol) was dissolved in 80 ml THF and 40 ml methanol. The solution was cooled to 0 °C and $NaBH_4$ (0.68 g, 17.9 mmol) was added in portions. The reaction was stirred for 20 h at r.t. The resulting bright yellow solution was hydrolyzed with NH_4Cl (aq) and extracted in Et_2O. The extracts were collected, dried ($MgSO_4$) and filtered, and the solvents were removed to give 2.82 g (99%) of crude **3** as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 7.35–7.25 (m, 4H), 6.70–6.18 (m, 3H), 4.99 (t, 1H), 3.50, 3.48 (d, 1H), 3.21–2.74 (m, 4H), 2.49–2.34 (m, 1H), 1.46 (s, 3H), 1.39 (s, 3H).

*3.3. 2-(Cyclopentadienyl)-2-(2-indenyl)propane (**4**)*

To a solution of crude **3** (8.51 g, 35.4 mmol) in 200 ml of benzene was added *p*-toluenesulfonic acid (0.67 g, 3.5 mmol). The flask was equipped with a Dean–Stark trap and refluxed for 2 h, at which time the mixture turned from yellow to dark brown. The reaction mixture was cooled to r.t., washed with 50 ml of $NaHCO_3$ (aq) and 50 ml of water. The organics were collected, dried ($MgSO_4$), and filtered, and the solvents were removed to give a brown oil. The crude oil was chromatagraphed (SiO_2, 1:20 Et_2O–hexanes), followed by vacuum distillation (129–131 °C @ 0.05 mmHg) with the product **4** (1.34 g, 17%) distilling first as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 7.50–7.05 (m, 4H), 6.58–5.98 (m, 4H), 3.25 (s, 2H), 2.99 (d, 1H), 2.86 (d, 1H), 1.50 (s, 6H). HRMS (EI) *m*/*z* calc. for $C_{17}H_{18}$: 222.1409. Found: 222.1449%. Anal. Calc. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.41; H, 8.56.

*3.4. 2-(Cyclopentadienyl)-2-(2-(1-methyl-indan-1-ol))propane (**5**)*

Compound **2** (4.42 g, 18.5 mmol) was dissolved in 150 ml Et_2O and cooled to −78 °C. CH_3MgBr, 3.0 M in Et_2O (13.7 ml, 41.0 mmol), was added dropwise and the reaction was stirred for 30 min at −78 °C. The reaction mixture was allowed to warm to r.t. and stir for 1.5 h after which it was hydrolyzed with NH_4Cl (aq) and extracted in Et_2O. The extracts were collected, dried ($MgSO_4$) and filtered, and the solvents were removed to give a yellow oil. The oil was chromatagraphed (SiO_2, pentane) to give **5** (3.44 g, 73%). ^{1}H-NMR ($CDCl_3$): δ 7.30–7.04 (m, 4H), 5.88–5.24 (m, 3H), 3.25 (bs, 1H), 3.14–2.50 (m, 3H), 1.83 (t, 1H), 1.50 (s, 3H), 0.94 (s, 3H), 0.54 (s, 3H).

*3.5. 2-(Cyclopentadienyl)-2-(2-(1-methyl-indenyl))propane (**6**)*

Following the procedure described for **4**, compound **5** (4.42 g, 17.4 mmol) and *p*-toluenesulfonic acid (0.33 g, 1.7 mmol gave **6** (1.07 g, 26%) as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 7.40–7.02 (m, 4H), 6.38–6.01 (m, 3H), 3.37, 3.36 (d, 2H), 2.93 (d) 2.77 (d, 2H), 1.80 (t, 3H), 1.42, 1.41 (d, 6H). MS (EI) *m*/*z* calc. for $C_{18}H_{20}$: 236. Found: 236%. Anal. Calc. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 90.83; H, 8.28.

*3.6. Isopropylidene(cyclopentadienyl)(2-indenyl)$ZrCl_2$ (**1a**)*

Compound **1a** was synthesized via two routes: Method A: Ligand **4** (1.79, 8.1 mmol) was dissolved in 25 ml of Et_2O and the reaction was cooled to 0 °C. *n*-Butyllithium, 1.6 M in hexanes (10.1 ml, 16.2 mmol), was added dropwise to give a yellow solution, which was stirred at r.t. for 4 h. The solvent was removed via reduced pressure and the resulting yellow powder was washed with 30 ml of pentane and dried via reduced pressure. Fresh Et_2O (25 ml) was added and the reaction was cooled to 0 °C. $ZrCl_4$ (1.88 g, 8.1 mmol) was added as a solid and the reaction mixture was stirred overnight at r.t. The solvent was removed via reduced pressure and the resulting reddish–brown oil was extracted with 30 ml of CH_2Cl_2. The extract was concentrated and the product allowed to crystallize overnight at −20 °C. Removal of excess solvent resulted in 0.23 g (7%) of **1** as a yellow powder.

Method B: A flask was charged with $Zr(NMe_2)_4$ (0.58 g, 2.3 mmol) and compound **4** (0.51 g, 2.3 mmol). Toluene (50 ml) was added and the reaction was stirred overnight at 100 °C. The solvent was removed via reduced pressure to give an oily yellow–green powder. Chlorotrimethylsilane (2.9 ml, 23.0 mmol) and toluene (50 ml) were added and the reaction was stirred overnight at r.t. The solvent was removed via reduced pressure and the resulting yellow powder was washed twice with 20 ml of hexane, resulting in 0.26 g (30%) of **1a** as a yellow powder. ^{1}H-NMR ($CDCl_3$): δ 7.57–7.53 (m, 2H), 7.36–7.31 (m, 2H), 6.65 (t, 2H), 5.93 (s, 2H), 5.86 (t, 2H), 1.89 (s, 6H). HRMS (EI) *m/z* calc. for $C_{17}H_{16}ZrCl_2$: 379.9676. Found: 379.9701.

3.7. Isopropylidene(cyclopentadienyl)(2-(1-methylindenyl))$ZrCl_2$ (1b)

A flask was charged with $Zr(NMe_2)_4$ (0.63 g, 2.5 mmol) and compound **6** (0.60 g, 2.5 mmol). Fifty milliliters of toluene was added and the reaction was stirred overnight at 80 °C. The solvent was removed via reduced pressure to give an oily yellow–green powder. Chlorotrimethylsilane (3.2 ml, 25.0 mmol) and toluene (50 ml) were added and the reaction was stirred overnight at r.t. The solvent was removed via reduced pressure and the resulting oily yellow powder was washed first with 30 ml of pentane and then twice with 20 ml of hexane resulting in 0.32 g (32%) of **1b** as a yellow powder. ^{1}H-NMR ($CDCl_3$): δ 7.58–7.44 (m, 2H), 7.39–7.29 (m, 2H), 6.69–6.61 (m, 2H), 5.93 (d, 1H), 5.91–5.85 (m, 2H), 2.44 (s, 3H), 2.06 (s, 3H), 1.94 (s, 3H). HRMS (EI) *m/z* calc. for $C_{18}H_{18}ZrCl_2$: 393.9833. Found: 393.9844.

3.8. 2-{1-Methyl-1-[3-(1-methylethylidene)cyclopenta-1,4-dien-1-yl]ethyl}indan-1-one (7)

Compound **2** (4.51 g, 19.0 mmol) was dissolved in 200 ml of MeOH. Acetone (1.4 ml, 19.0 mmol) followed by pyrrolidine (1.60 g, 19.0 mmol) was added to produce a yellow solution. The reaction was stirred for 3.5 h at r.t. The reaction was quenched with acetic acid (1.10 ml, 19.0 mmol) and extracted with Et_2O. The extracts were collected, dried ($MgSO_4$) and filtered, and the solvents were removed to give a yellow oily solid. Recrystallization from 1:1 acetone–pentane yielded 4.95 g (94%) of **7** as a yellow solid. ^{1}H-NMR ($CDCl_3$): δ 7.73–7.29 (m, 4H), 6.53–6.52 (d, 2H), 6.15 (t, 1H), 3.14–2.76 (m, 3H), 2.16 (s, 6H), 1.52 (s, 3H), 1.14 (s, 3H). MS (EI) *m/z* calc. for $C_{20}H_{22}O$: 278. Found: 278. Anal. Calc. for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.46; H, 7.95%.

3.9. Polymerizations

A 250 ml crown capped glass pressure reactor containing 50 ml of toluene was equilibrated with the appropriate monomer at 15 psi (pressure maintained throughout polymerization) and at the desired temperature. The desired amount of methylaluminoxane (MAO) was added as a solution in toluene via syringe, and the solution was stirred for 5 min. One ml of the appropriate catalyst solution in toluene that had been pre-activated for 5 min was added, and the mixture was stirred until the desired reaction time was reached. The mixture was quenched with 2% HCl in methanol and filtered, or in the case of atactic PP, extracted in hexane, and dried in a vacuum oven at 60 °C.

3.10. Polymer analyses

Melting points were determined by DSC with a Perkin–Elmer DSC-4 system. ^{13}C-NMR spectra of the polypropylene samples were determined on a DPX300 spectrometer in $CDCl_3$ at r.t. ^{13}C-NMR spectra of the polyethylene samples were determined on a Bruker Avance 600 spectrometer in C_6D_6 and 1,2,4-trichlorobenzene at 90 °C. Molecular weights were determined by GPC in 1,2,4-trichlorobenzene at 135 °C for polyethylene and by ^{1}H-NMR using a Bruker AC-200 spectrometer for polypropylene.

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