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Novel C_1 symmetric zirconocenes containing substituted fluorenyl moieties for the polymerization of olefins

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Abstract

The synthesis and polymerization behavior of four new asymmetric *ansa*-metallocenes containing a 2,7-disubstituted fluorenyl moiety and an indenyl moiety is reported. Three of the four catalysts, dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-bis-(2,4,6-trimethylphenyl)-η^5-9-fluorenyl]zirconium (**11**), dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-bis-(2,6-dimethylphenyl)-η^5-9-fluorenyl]zirconium (**12**), and dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-bis-(2-methylphenyl)-η^5-9-fluorenyl] zirconium (**13**) were highly active for the polymerization of both ethylene and propylene when activated with excess methylaluminoxane (MAO). Dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-dibenzyl-η^5-9-fluorenyl]zirconium (**14**) was poorly active for the polymerization of ethylene and was therefore not evaluated as a propylene catalyst. The activities for propylene polymerizations with catalysts **11**–**13** increased as the size of the substituents around the ligand framework increased, following the trend **11** > **12** > **13**. Molecular weights of the polypropylenes decreased as the temperature was increased. The molecular weight data follows the same trend (**11** > **12** > **13**) as the activity data, wherein the largest substituents gave rise to the highest molecular weights.

Keywords: Zirconocenes; Asymmetric metallocenes; Polypropylene; Olefin polymerization

1. Introduction

A major focus of our research program has been the design and synthesis of novel asymmetric C_1 catalyst precursors for the polymerization of ethylene and propylene. Both Thomas et al. [1] and Rieger et al. [2] have studied several mixed ring indenyl–fluorenyl metallocenes with specific attention focused on the effects of substituents on the indenyl moiety. More recently, Thomas has investigated the effects of changing the fluorenyl moiety to its partially or fully saturated tetrahydrofluorenyl and octahydrofluorenyl analogs, respectively [1c,1d]. In that study, the authors found that these modifications could both increase the activity of the catalytic species and also increase the overall stability of the catalyst precursor. Unfortunately, the molecular weight of the polymer produced using tetrahydrofluorenyl- and octahydrofluorenyl-containing zirconocenes was very low.

In an effort to increase the molecular weight of polymers produced using indenyl–fluorenyl C_1 symmetric zirconocenes, we have investigated the effect of varying the bridging moiety to create a more sterically biased ligand environment [3]. The introduction of a sterically crowded environment around the metal center did increase the molecular weight of polymer produced slightly, presumably by inhibiting the chain termination mechanism of the growing polymer chain. However, the overall molecular weights obtained for the polymers were still relatively low.

In the present study, further attempts to increase the molecular weight of polymers obtained using C_1 symmetric zirconocenes were probed. Alt et al. [4] have shown that in bridged C_s symmetric zirconocenes, a 2,7-bis(mesityl)fluorenyl moiety or other related 2,7-disubstituted fluorenyl moieties can dramatically increase

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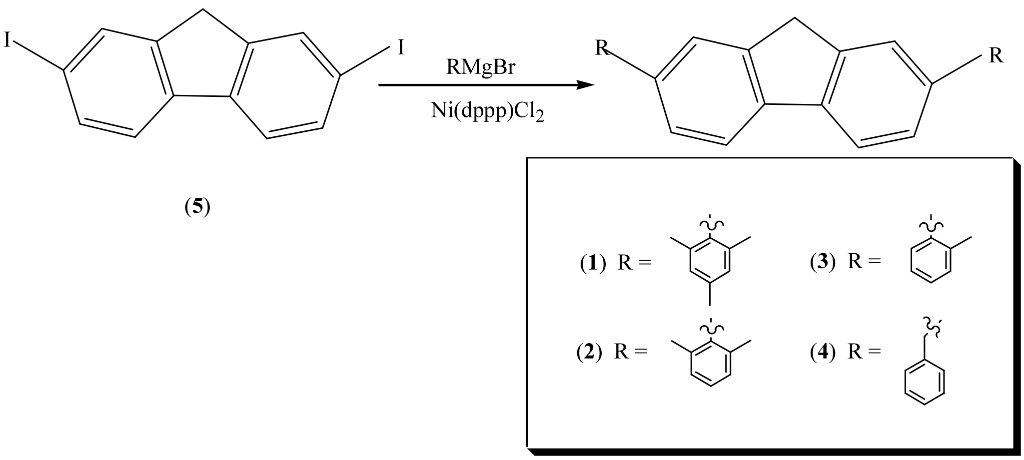


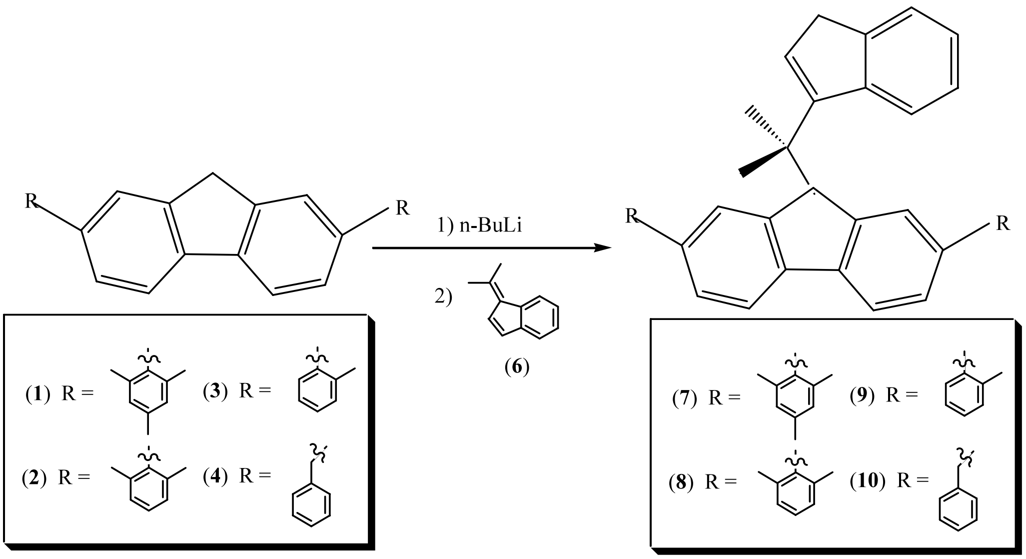
polymer molecular weight. Based on the work of Thomas et al. [1c,1d] it was therefore of interest to study whether a similar effect could be obtained by replacing the fluorenyl moiety in C_1 symmetric zirconocenes with a 2,7-disubstituted fluorenyl analog.

2. Results and discussion

2.1. Synthesis of organic ligands

2,7-Bis(mesityl)fluorene (**1**) and several new 2,7-disubstituted fluorenes **2**–**4** were synthesized by reaction of 2,7-diiodofluorene (**5**) [5] with the Grignard salt of an aryl or benzylic bromide in the presence of a catalytic amount of [1,3-bis(diphenylphosphino)propane]-dichloronickel(II) (Ni(dppp)Cl$_2$) following a modified version of the procedure developed by Alt et al. [4]. The reactions proceeded in good yield, ranging from 70 to 81%. Depending on the steric and electronic nature of the organic bromide, varying reaction times were necessary to achieve optimal yields. Formation of 2,7-bis(mesityl)fluorene (**1**) and 2,7-bis(2,6-dimethylphenyl)fluorene (**2**) required refluxing the reaction mixture overnight to ensure completion. In contrast, 2,7-bis(2-methylphenyl)fluorene (**3**) and 2,7-dibenzylfluorene (**4**) were formed after only 30 min of heating at reflux.

Several new *ansa*-ligands were synthesized by modification of a general literature procedure for making isopropylidene-bridged ligands [6]. Initially, reaction of **1**–**4** with one equivalent of butyllithium, followed by subsequent reaction with 2,3-benz-6,6-dimethylfulvene (**6**) gave the corresponding ligands (**7**–**10**) in good yields. Crystallization from pentane or acetone produced **7**–**10** in elementally pure form.



2.2. Synthesis of zirconocenes

Synthesis of zirconocenes **11**–**14** was accomplished by double deprotonation of ligands **7**–**10** in Et_2O with two equivalents of *n*-butyllithium to initially produce the corresponding dilithium salts. The dilithium salts were then reacted with one equivalent of $ZrCl_4$ in an Et_2O solution to produce the desired zirconocenes. Overall yields ranged from ca. 13–21%. A rapid workup of **11**–**14** was necessary due to the high sensitivity of these compounds to air and moisture. Furthermore, once **11**–**14** were isolated as solids, exposure to solvent resulted in almost immediate decomposition of the zirconocenes. Hence, polymerizations were run by directly adding the solid metallocenes to an MAO–toluene solution. This allowed for the rapid generation of the active cationic species which limited the amount of decomposition observed.

2.3. Ethylene polymerization

Compounds **11**–**13** were highly active in catalyzing the polymerization of ethylene when activated with MAO (Table 1). Interestingly, **14** was poorly active in catalyzing the polymerization of ethylene when activated with MAO, giving only traces of polyethylene at all of the polymerization temperatures probed. The poor activity exhibited by **14** could be attributable to coordination of the pendant benzyl groups to the active metal center. Benzylic coordination could block previously vacant coordination sites on the metal center, which could in turn inhibit monomer coordination and lead to decreased polymerization activity.

The activities obtained using **11**–**13** ranged from ca. 3×10^{7} to 1×10^{8} depending on polymerization temperature and catalyst structure. The highest activity overall was obtained with complex **13** at 50 °C, which is also the least sterically hindered complex. In general, for all of the species tested, the activity was lowest at 0 °C and greatest at 50 °C.

For complexes **11**–**13**, the maximum molecular weights were obtained at low temperatures. Molecular weights of the polymers decreased as the polymerization temperature was increased. In general, the highest molecular weights were obtained with the most hindered complexes following the general trend, **11** > **12** > **13**. Furthermore, **11**–**13** all exhibited greater activity and produced polyethylene of higher molecular weights than the unsubstituted derivative, 2-fluorenyl-2-indenyl propane zirconium dichloride synthesized by Alt et al. which exhibited an activity of 1.7×10^{7} and produced polyethylene with M_w of 100,000 Da [6]. This trend supports our hypothesis that the added steric bulk around the metal center should increase the resulting polymer molecular weight by decreasing accessibility of the growing polymer to chain termination steps.

2.4. Propylene polymerization

Due to its poor activity in ethylene polymerizations, **14** was not evaluated as a potential propylene catalyst. However, **11**–**13** were shown to be highly active in catalyzing the polymerization of propylene when acti-

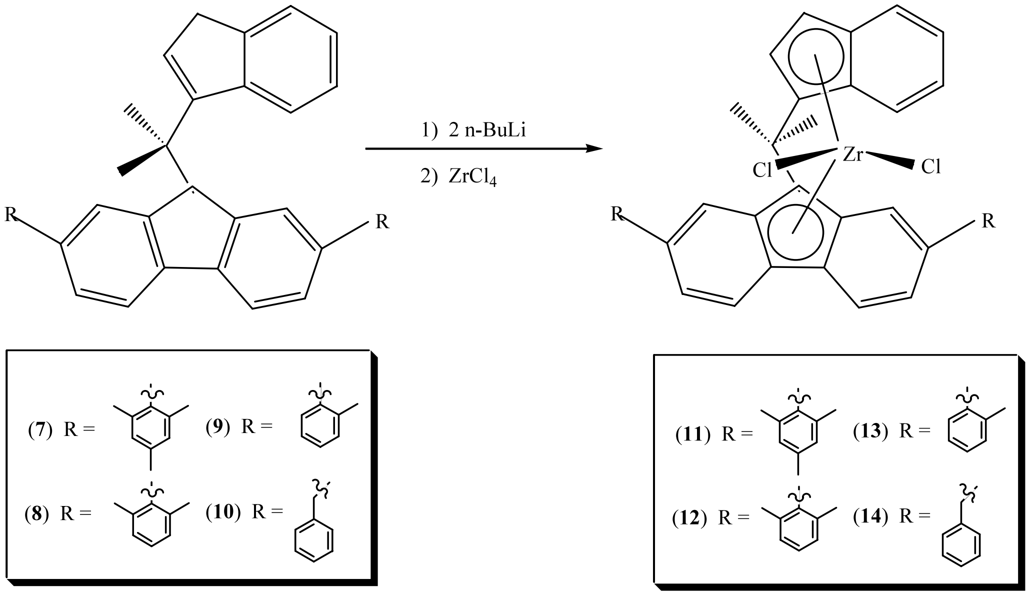


Table 1
Polymerization of ethylene with zirconocene complexes activated with MAO [a]

Catalyst	Temperature (°C)	Yield (g) [b]	10^{-7} A [c]	Tm (°C)	M_w
11	0	0.51±0.05	5.7	135	750,000
11	20	0.49±0.05	6.3	135	681,000
11	50	0.50±0.06	8.8	134	452,000
12	0	0.28±0.02	3.1	134	697,000
12	20	0.46±0.04	5.9	136	611,000
12	50	0.48±0.03	8.4	136	359,000
13	0	0.56±0.08	6.2	133	584,000
13	20	0.66±0.11	8.5	135	422,000
13	50	0.56±0.06	9.8	134	325,000
14	0	Trace	–	–	–
14	20	Trace	–	–	–
14	50	Trace	–	–	–

[a] Polymerization conditions: [Zr] = 5 μM; Al/Zr = 4000:1; reaction time = 5 min.

[b] Yields are averages of duplicate runs.

[c] Activity = g of PE/(mol Zr)(conc. of monomer)(h).

vated with MAO (Table 2). The activities obtained ranged from ca. 2.3×10^6 to 9.6×10^6, depending on polymerization temperature and catalyst structure. The highest activity was obtained with **11** at 50 °C. The activities of the catalysts also increased as the size of the substituents increased, following the trend **11** > **12** > **13**, which is further illustrated in Table 2.

The highest molecular weight polypropylenes were also obtained using catalyst **11**. A molecular weight of 189,000 was obtained at 50 °C using **11**, which is among the highest M_w polypropylene produced using a C_1 catalyst of this type [1]. Molecular weights decreased as the temperature was increased. The molecular weight data follows the same trend (**11** > **12** > **13**) as the activity data, wherein the largest substituents give rise to the highest molecular weights.

3. Conclusion

In summary, we have synthesized four new C_1 symmetric metallocenes and have studied their ability to catalyze the polymerization of ethylene and propylene. Three of the four catalysts, **11**–**13**, were active for the polymerization of both ethylene and propylene. Compound **14** was poorly active for the polymerization of ethylene and was therefore not evaluated as a propylene catalyst.

In general, for the polymerization of propylene, the most sterically hindered catalysts are more active and produce polymers of higher molecular weights than do their less hindered counterparts, as is evidenced by the direct trend as one goes from 2,4,6-trimethylphenyl to 2,6-dimethylphenyl to 2-methylphenyl to no substituents, respectively.

Table 2
Polymerization of propylene with zirconocene complexes activated with MAO [a]

Catalyst	Temperature (°C)	Yield (g) [b]	10^{-6} A [c]	M_w
11	20	3.41±0.22	8.2	189,000
11	50	1.88±0.29	9.6	156,000
12	20	2.66±0.29	6.4	163,000
12	50	1.00±0.17	5.1	132,000
13	20	1.41±0.13	3.4	98,000
13	50	0.45±0.34	2.3	58,000

[a] Polymerization conditions: [Zr] = 25 μM; Al/Zr = 4000:1; reaction time = 30 min.

[b] Yields are averages of duplicate runs.

[c] Activity = g of PP/(mol of Zr)(conc. of monomer)(h).

4. Experimental

All reactions were carried out under an inert argon atmosphere using standard Schlenk techniques. The argon was purified by drying with phosphorus pentoxide, calcium chloride and molecular sieves, and deoxygenated with BTS catalyst. Toluene, hexane, diethyl ether, and pentane were distilled from Na/K alloy under argon. Methylene chloride was distilled under argon from calcium hydride. Tetrahydrofuran (THF) was dried initially over sodium wire, distilled from sodium/benzophenone under argon, and finally distilled from Na/K alloy under argon.

Methylaluminoxane was purchased from Akzo Nobel. Celite was purchased from Fisher Scientific. 2,3-Benz-6,6-dimethylfulvene (**6**) [7] and 2,7-diiodofluorene (**5**) [5] were synthesized via literature procedures. All other reagents were purchased from Aldrich and were used without further purification. ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer using Me_4Si as an internal standard. Mass spectrometry was performed by the Mass Spectrometry Center, University of Massachusetts, Amherst. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

*4.1. 2,7-Bis-(2,6-dimethylphenyl)fluorene (**2**)*

An argon purged 250 ml three neck flask was equipped with an addition funnel, gas inlet valve, magnetic stir bar, and a reflux condenser attached to a mercury overpressure valve. Magnesium turnings (1.2 g, 49 mmol) were suspended in 50 ml of dry Et_2O. Next, 0.25 ml of 1,2-dibromoethane was added to the flask. The solution began to turn cloudy and 9.07 g (49 mmol) of 2-bromo-*m*-xylene was slowly added to the reaction flask via the addition funnel. The suspension was heated at reflux overnight.

To a second argon purged 250 ml round bottom flask was added 10.0 g (24 mmol) of **5**, 0.20 g (0.4 mmol) of $Ni(dppp)Cl_2$, and 50 ml of dry Et_2O under constant stirring. Using a filter cannula, the Grignard solution was transferred dropwise into the flask. Upon completion of the addition, the suspension was heated at reflux overnight. The suspension was cooled of to 0 °C and was slowly hydrolyzed with 3 M HCl. Washing with saturated $NaHCO_3$ followed by extraction with Et_2O produced a yellow solution, which was dried with anhyd. $MgSO_4$, filtered, and the solvent removed. Crystallization from ethyl acetate afforded 6.28 g (70%) of **2** as white crystals, m.p. 258–259 °C. Anal. Found: C, 92.43; H, 7.03 $C_{29}H_{26}$. Calc.: C, 93.00; H, 7.00%. ^{1}H-NMR ($CDCl_3$): δ 7.89–7.13 (m, 12H, aromatic H); 3.99 (s, 2H, C_5–sp^3); 2.13 (s, 12H, CH_3).

*4.2. 2,7-Bis-(2-methylphenyl)fluorene (**3**)*

An argon purged 250 ml three neck flask was equipped with an addition funnel, gas inlet valve, magnetic stir bar, and a reflux condenser attached to a mercury overpressure valve. Magnesium turnings (1.2 g, 49 mmol) were suspended in 50 ml of dry Et_2O. Next, 0.25 ml of 1,2-dibromoethane was added to the flask. The solution began to turn cloudy and 5.9 ml (49 mmol) of 2-bromotoluene was slowly added to the reaction flask via the addition funnel. The suspension was heated at reflux for 2 h as all of the magnesium had been consumed.

To a second argon purged 250 ml round bottom flask was added 10.0 g (24 mmol) of **5**, 0.20 g (0.4 mmol) of $Ni(dppp)Cl_2$, and 50 ml of dry Et_2O under constant stirring. Using a filter cannula, the Grignard solution was transferred dropwise into the flask. Upon completion of the addition, the suspension was heated at reflux for 30 min. The suspension was cooled of to 0 °C and was slowly hydrolyzed with 3 M HCl. Washing with saturated $NaHCO_3$ followed by extraction with Et_2O produced a yellow solution, which was dried with anhyd. $MgSO_4$, filtered, and the solvent removed. Crystallization from toluene produced 6.74 g (81%) of **3** as white crystals, m.p. 165–166 °C. Anal. Found: C, 93.52; H, 6.56 $C_{27}H_{22}$. Calc.: C, 93.60; H, 6.40%. ^{1}H-NMR ($CDCl_3$): δ 7.84 (d, 2H, aromatic H); 7.50 (s, 2H, aromatic H); 7.37–7.24 (m, 4H, aromatic H); 3.99 (s, 2H, C_5–sp^3); 2.32 (s, 6H, CH_3).

*4.3. 2,7-Dibenzylfluorene (**4**)*

An argon purged 250 ml three neck flask was equipped with an addition funnel, gas inlet valve, magnetic stir bar, and a reflux condenser attached to a mercury overpressure valve. Magnesium turnings (1.2 g, 49 mmol) were suspended in 50 ml of dry Et_2O. Next, 0.25 ml of 1,2-dibromoethane was added to the flask. The solution began to turn cloudy and 5.9 ml (49 mmol) of benzyl bromide was slowly added to the reaction flask via the addition funnel. The suspension was heated at reflux for 2 h.

To a second argon purged 250 ml round bottom flask was added 10.0 g (24 mmol) of **5**, 0.20 g (0.4 mmol) of $Ni(dppp)Cl_2$, and 50 ml of dry Et_2O under constant stirring. Using a filter cannula, the Grignard solution was transferred dropwise into the flask. Upon completion of the addition, the suspension was heated at reflux for 30 min. The suspension was cooled of to 0 °C and was slowly hydrolyzed with 3 M HCl. Washing with saturated $NaHCO_3$ followed by extraction with Et_2O produced a yellow solution, which was dried with anhyd. $MgSO_4$, filtered, and the solvent removed. Crystallization from toluene afforded 5.98 g (72%) of **4** as white crystals, m.p. 122–124 °C. Anal. Found: C, 93.52; H, 6.66 $C_{27}H_{22}$. Calc.: C, 93.60; H, 6.40%. ^{1}H-NMR ($CDCl_3$): δ 7.64 (d, 2H, aromatic H); 7.31–7.17 (m, 14H, aromatic H); 4.04 (s, 4H, C_6-α-CH_2); 3.78 (s, 2H, C_5–sp^3).

*4.4. 9-[1-(Inden-3-yl)-1-methylethyl]-2,7-bis(2,4,6-trimethylphenyl)-fluorene (**7**)*

To an argon purged Schlenk tube was added 1.0 g (2.5 mmol) of **1** and 30 ml of dry Et_2O. The solution was cooled to 0 °C and 1.56 ml of a 1.6 M solution of butyllithium in hexane (2.5 mmol) was added dropwise. The solution was warmed to room temperature (r.t.) and stirred for 4 h. Next, the solution was cooled to 0 °C and 0.39 g (2.5 mmol) of 2,3-benz-6,6-dimethylfulvene (**6**) was added. Upon completion of the addition, the solution was warmed to r.t. and stirred overnight. After hydrolysis with aqueous NH_4Cl, the organic layer was separated. The aqueous layer was extracted with 2 × 10 ml of Et_2O and the organic layers were combined. The resulting organic solution was then dried with $MgSO_4$, filtered, and the solvent removed. The resulting yellow foam was triturated with pentane and crystallized from acetone resulting in 0.92 g (66%) of **7** as a light yellow solid, m.p. 203–205 °C. Anal. Found: C, 92.16; H, 7.47 $C_{43}H_{42}$. Calc.: C, 92.42; H, 7.58%. HRMS (EI) Calc. for $C_{43}H_{42}$: 558.329 Found: 558.330. ^{1}H-NMR ($CDCl_3$): δ 7.95–6.91 (m, 14H, aromatic H); 6.10 (s, 1H, C_5–Ind-sp^2); 4.85 (s, 1H, C_5-Fluorene); 3.28 (s, 2H, C_5–Ind-sp^3); 2.33 (s, 6H, *o*-CH_3); 2.10 (s, 6H, *o*-CH_3); 1.93 (s, 6H, *p*-CH_3); 1.22 (bs, 6H, CH_3–C–CH_3).

*4.5. 2,7-Bis(2,4,-dimethylphenyl)-9-[1-(inden-3-yl)-1-methylethyl]fluorene (**8**)*

To an argon purged Schlenk tube was added 0.94 g (2.5 mmol) of **2** and 30 ml of dry Et_2O. The solution was cooled to 0 °C and 1.56 ml of a 1.6 M solution of butyllithium in hexane (2.5 mmol) was added dropwise. The solution was warmed to r.t. and stirred for 4 h. Next, the solution was cooled to 0 °C and 0.39 g (2.5 mmol) of 2,3-benz-6,6-dimethylfulvene (**6**) was added. Upon completion of the addition, the solution was warmed to r.t. and stirred overnight. After hydrolysis with aqueous NH_4Cl, the organic layer was separated. The aqueous layer was extracted with 2 × 10 ml of Et_2O and the organic layers were combined. The resulting organic solution was then dried with $MgSO_4$, filtered, and the solvent removed. The resulting yellow foam was triturated with pentane and crystallized from acetone resulting in 0.82 g (62%) of **8** as a light yellow solid, m.p. 207–209 °C. Anal. Found: C, 92.88; H, 7.28 $C_{41}H_{38}$. Calc.: C, 92.78; H, 7.22%. ^{1}H-NMR ($CDCl_3$): δ 7.92–6.89 (m, 16H, aromatic H); 6.10 (s, 1H, C_5–Ind-sp^2); 4.86 (s, 1H, C_5-Fluorene); 3.27 (s, 2H, C_5–Ind-sp^3); 2.13 (s, 6H, C_6-CH_3); 1.96 (s, 6H, C_6-CH_3); 1.25 (bs, 6H, CH_3–C–CH_3).

*4.6. 9-[1-(Inden-3-yl)-1-methylethyl]-2,7-bis-(2-tolyl)fluorene (**9**)*

To an argon purged Schlenk tube was added 1.0 g (2.9 mmol) of **3** and 30 ml of dry Et_2O. The solution was cooled to 0 °C and 1.8 ml of a 1.6 M solution of butyllithium in hexane (2.9 mmol) was added dropwise. The solution was warmed to r.t. and stirred for 4 h. Next, the solution was cooled to 0 °C and 0.45 g (2.9 mmol) of 2,3-benz-6,6-dimethylfulvene (**6**) was added. Upon completion of the addition, the solution was warmed to r.t. and stirred overnight. After hydrolysis with aqueous NH_4Cl, the organic layer was separated. The aqueous layer was extracted with 2 × 10 ml of Et_2O and the organic layers were combined. The resulting organic solution was then dried with $MgSO_4$, filtered, and the solvent removed. The resulting yellow foam was triturated with pentane and crystallized from acetone resulting in 0.86 g (60%) of **9** as a light yellow solid, m.p. 144–145 °C. Anal. Found: C, 92.92; H, 6.93 $C_{39}H_{34}$. Calc.: C, 93.18; H, 6.82%. ^{1}H-NMR ($CDCl_3$): δ 7.82–7.17 (m, 18H, aromatic H); 6.18 (s, 1H, C_5–Ind-sp^2); 4.86 (s, 1H, C_5-Fluorene); 3.36 (s, 2H, C_5–Ind-sp^3); 2.26 (s, 6H, *o*-CH_3); 1.29 (bs, 6H, CH_3–C–CH_3).

*4.7. 2,7-Dibenzyl-9-[1-(inden-3-yl)-1-methylethyl]fluorene (**10**)*

To an argon purged Schlenk tube was added 1.0 g (2.9 mmol) of **4** and 30 ml of dry Et_2O. The solution was cooled to 0 °C and 1.8 ml of a 1.6 M solution of butyllithium in hexane (2.9 mmol) was added dropwise. The solution was warmed to r.t. and stirred for 4 h. Next, the solution was cooled to 0 °C and 0.45 g (2.9 mmol) of 2,3-benz-6,6-dimethylfulvene (**6**) was added. Upon completion of the addition, the solution was warmed to r.t. and stirred overnight. After hydrolysis with aqueous NH_4Cl, the organic layer was separated. The aqueous layer was extracted with 2 × 10 ml of Et_2O and the organic layers were combined. The resulting organic solution was then dried with $MgSO_4$, filtered, and the solvent removed. The resulting yellow foam was triturated with pentane and crystallized from acetone resulting in 0.92 g (64%) of **10** as a light yellow solid, m.p. 104–106 °C. Anal. Found: C, 93.01; H, 6.89 $C_{39}H_{34}$. Calc.: C, 93.18; H, 6.82%. ^{1}H-NMR ($CDCl_3$): δ 7.94–6.91 (m, 20H, aromatic H); 5.89 (s, 1H, C_5–Ind-sp^2); 4.65 (s, 1H, C_5-Fluorene); 3.91 (s, 4H, benzylic H); 3.06 (s, 2H, C_5–Ind-sp^3); 1.14 (bs, 6H, CH_3–C–CH_3).

*4.8. Dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-bis-(2,4,6-trimethylphenyl)-η^5-9-fluorenyl]zirconium (**11**)*

To an argon purged Schlenk tube equipped with a magnetic stir bar was added 0.500 g (0.89 mmol) of **7**. The solid was dissolved in 25 ml of dry Et_2O and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (1.12 ml, 1.79 mmol) was added dropwise via syringe producing a yellow–orange solution. The solution was allowed to warm to r.t. and was stirred for 8 h. The solution was cooled again to 0 °C and 0.207 g (0.89 mmol) of $ZrCl_4$ was added directly to the dianion solution as a solid. The resulting suspension was stirred overnight at r.t. yielding a bright orange precipitate. Filtration of the Et_2O solution followed by extraction of the residue in CH_2Cl_2 produced a red solution with a white suspension. Filtration of the suspension followed by concentration of the solution to 5 ml and cooling to −20 °C produced an orange solid. The solid was filtered and dried in vacuo to give 0.13 g (19.7%) of **11**. MS (EI) Calc. for $C_{43}H_{40}Cl_2Zr$: 718 Found: 718. ^{1}H-NMR ($CDCl_3$): δ 8.11–6.80 (m, 14H, aromatic H); 6.44 (d, 1H, C_5-Ind); 5.63 (d, 1H, C_5-Ind); 2.35 (s, 6H, C_6-CH_3); 2.08 (s, 6H, C_6-CH_3); 2.04 (s, 6H, C_6-CH_3); 1.26 (s, 3H, bridge CH_3); 0.90 (s, 3H, bridge CH_3).

4.9. Dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-bis-(2,6-dimethylphenyl)-η^5-9-fluorenyl]zirconium (**12**)

To an argon purged Schlenk tube equipped with a magnetic stir bar was added 0.472 g (0.89 mmol) of **8**. The solid was dissolved in 25 ml of dry Et_2O and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (1.12 ml, 1.79 mmol) was added dropwise via syringe producing a yellow–orange solution. The solution was allowed to warm to r.t. and was stirred for 8 h. The solution was cooled again to 0 °C and 0.207 g (0.89 mmol) of $ZrCl_4$ was added directly to the dianion solution as a solid. The resulting suspension was stirred overnight at r.t. yielding a bright orange precipitate. Filtration of the Et_2O solution followed by extraction of the residue in CH_2Cl_2 produced a red solution with a white suspension. Filtration of the suspension followed by concentration of the solution to 5 ml and cooling to −20 °C produced an orange solid. The solid was filtered and dried in vacuo to give 0.082 g (13.4%) of **12**. MS (EI) Calc. for $C_{41}H_{36}Cl_2Zr$: 690 Found: 690. ^{1}H-NMR ($CDCl_3$): δ 8.14–6.89 (m, 16H, aromatic H); 6.46 (d, 1H, C_5-Ind); 5.87 (d, 1H, C_5-Ind); 2.34 (s, 6H, C_6-CH_3); 2.09 (s, 6H, C_6-CH_3); 1.35 (s, 6H, bridge CH_3); 1.04 (s, 3H, bridge CH_3).

4.10. Dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-bis-(2-methylphenyl)-η^5-9-fluorenyl] zirconium (**13**)

To an argon purged Schlenk tube equipped with a magnetic stir bar was added 0.447 g (0.89 mmol) of **9**. The solid was dissolved in 25 ml of dry Et_2O and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (1.12 ml, 1.79 mmol) was added dropwise via syringe producing a yellow–orange solution. The solution was allowed to warm to r.t. and was stirred for 8 h. The solution was cooled again to 0 °C and 0.207 g (0.89 mmol) of $ZrCl_4$ was added directly to the dianion solution as a solid. The resulting suspension was stirred overnight at r.t. yielding a bright orange precipitate. Filtration of the Et_2O solution followed by extraction of the residue in CH_2Cl_2 produced a red solution with a white suspension. Filtration of the suspension followed by concentration of the solution to 5 ml and cooling to −20 °C produced an orange solid. The solid was filtered and dried in vacuo to give 0.125 g (21.2%) of **13**. MS (EI) Calc. for $C_{39}H_{32}Cl_2Zr$: 662 Found: 662. ^{1}H-NMR ($CDCl_3$): δ 8.13–6.88 (m, 18H, aromatic H); 6.53 (d, 1H, C_5-Ind); 6.04 (d, 1H, C_5-Ind); 2.35 (s, 6H, C_6-CH_3); 2.23 (s, 3H, bridge CH_3); 1.96 (s, 3H, bridge CH_3).

4.11. Dichloro[η^5-1-indenyl(1-methylethylidene)-[2,7-dibenzyl-η^5-9-fluorenyl]zirconium (**14**)

To an argon purged Schlenk tube equipped with a magnetic stir bar was added 0.447 g (0.89 mmol) of **10**. The solid was dissolved in 25 ml of dry Et_2O and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (1.12 ml, 1.79 mmol) was added dropwise via syringe producing a yellow–orange solution. The solution was allowed to warm to r.t. and was stirred for 8 h. The solution was cooled again to 0 °C and 0.207 g (0.89 mmol) of $ZrCl_4$ was added directly to the dianion solution as a solid. The resulting suspension was stirred overnight at r.t. yielding a bright orange precipitate. Filtration of the Et_2O solution followed by extraction of the residue in CH_2Cl_2 produced a red solution with a white suspension. Filtration of the suspension followed by concentration of the solution to 5 ml and cooling to −20 °C produced an orange solid. The solid was filtered and dried in vacuo to give 0.122 g (20.6%) of **14**. MS (EI) Calc. for $C_{39}H_{32}Cl_2Zr$: 662 Found: 662. ^{1}H-NMR ($CDCl_3$): δ 8.05–6.96 (m, 20H, aromatic H); 6.48 (d, 1H, C_5-Ind); 5.61 (d, 1H, C_5-Ind); 3.24 (s, 4H, benzylic H); 2.88 (s, 3H, bridge CH_3); 2.47 (s, 3H, bridge CH_3).

4.12. Polymerization procedure

A 250 ml glass pressure bottle was sealed under an argon atmosphere. Freshly distilled dry toluene (50 ml) was added via syringe, and pressurized with the appropriate monomer (15 psi). A 4000-fold molar excess of MAO was then added to the bottle, which was placed in a water bath at the desired temperature and stirred for 10 min. The zirconium catalyst (2.5 μmol) in an MAO–toluene solution was added and the mixture was stirred magnetically until the desired reaction time was reached. The reaction mixture was subsequently quenched with 2% HCl in methanol, filtered, and dried in a vacuum oven at 70 °C.

4.13. Polymer analysis

Polymer melting points were determined by using a Dupont Thermal Analyst DSC system at a heating rate of 20 °C min^{-1}. Molecular weights were determined by high temperature GPC in 1,2,4-trichlorobenzene at 135 °C.

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