

Novel C_1 symmetric zirconocenes containing substituted indenyl moieties for the stereoregular polymerization of propylene

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Abstract

The synthesis and polymerization behavior of four new asymmetric *ansa*-metallocenes containing a fluorenyl moiety and a substituted indenyl moiety is reported. The zirconocenes diphenylsilylene-(η^5 -9-fluorenyl)-[η^5 -1-(3-*t*-butyl)indenyl]-zirconium dichloride (**4**), dimethylsilylene-(η^5 -9-fluorenyl)-[η^5 -1-(3-*t*-butyl)indenyl]-zirconium dichloride (**5**), ethylene-1-(η^5 -9-fluorenyl)-2-[η^5 -1-(3-*t*-butyl)indenyl]-zirconium dichloride (**6**), and diphenylsilylene-(η^5 -9-fluorenyl)-[η^5 -1-(2-methyl-4-phenyl)indenyl]-zirconium dichloride (**8**) were all found to be highly active for the polymerization of both ethylene and propylene when activated with excess methylaluminoxane. Compound **8** was found to produce highly isotactic polypropylene with an [mmmm] value of 83%.

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1. Introduction

The use of Ziegler–Natta type metallocenes in the production of highly isotactic polypropylene has attracted a great deal of interest both academically and in industrial settings. Chiral metallocene catalysts possessing C_2 symmetry have been widely studied in order to optimize and to better understand their ability to catalyze the stereoregular polymerization of propylene [1–3]. Spaleck et al. [4] have shown that substitution at the 2- and 4-positions of the indenyl moiety are necessary to achieve high M_w and high isotacticity in propylene polymerizations using C_2 symmetric catalysts. To date, the best metallocene catalyst, reported by Spaleck et al., for the production of isotactic polypropylene is dimethylsilylene-bis[2-methyl-4-naphthylindenyl]zirconium dichloride which produces *i*-PP with M_w of 920 000 Daltons and [mmmm] = 99%.

Recently, research efforts have increased in the area of C_1 symmetric metallocenes. Unlike C_2 symmetric

metallocenes, C_1 symmetric metallocenes possess no direct relationship between the catalyst geometry and the resulting polymer microstructure. C_1 symmetric catalysts have been shown to produce polyolefins with a wide variety of microstructures ranging from atactic [5] to syndiotactic [6] to stereoblock [7] to hemiisotactic [8] to isotactic [9] depending on the electronic and steric environment around the metal center.

For example, Razavi et al. [9a] demonstrated that by replacing a methyl group with a *tert*-butyl group at the 3-position of the cyclopentadienyl moiety of the C_1 symmetric isopropylidene(3-methylcyclopentadienyl)(fluorenyl)zirconium dichloride, a highly isotactic polypropylene could be produced whereas the methyl substituted parent system produced hemiisotactic polypropylene. This observation was attributed to the fact that the larger *tert*-butyl group better prevented the polymer chain from occupying one of the two coordination sites. This in turn led to stereoselective monomer coordination at one site, and a chain stationary insertion mechanism was proposed.

To date, there have been only a few reports on the use of C_1 symmetric metallocenes for the production of isotactic polypropylene, especially when compared to the large number of C_2 symmetric species that have been

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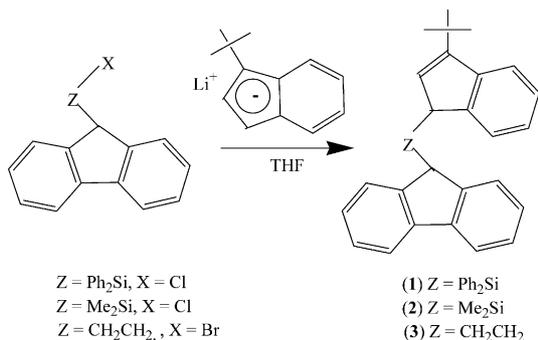
studied. Most of the asymmetric catalyst systems known have been employed to produce hemiisotactic or stereo-block polypropylenes. However in 1994, Rieger et al. [9b] published the synthesis of several new ethylene bridged *ansa*-zirconocenes containing both an indenyl and a fluorenyl moiety. The unsubstituted derivative ethylene-1-(9-fluorenyl)-2-(1-indenyl) zirconium dichloride was shown to produce moderate isotacticity (64%) in propylene polymerizations. Since that time both Thomas et al. [10] and Rieger et al. [11] have synthesized several highly active catalysts of this type for the formation of highly isotactic polypropylene by placing substituents at key locations around the ligand framework. Both Thomas and Rieger have shown the 2- and 4-positions of the indenyl moiety to be important in producing highly isotactic polypropylene with C_1 symmetric catalysts [10,11].

Very recently, Resconi et al. [12] synthesized methylene-bis(3-*t*-butyl)-1-indenylzirconium dichloride. The authors were able to demonstrate that with a sufficiently bulky group in the 3-position (such as a *tert*-butyl group), one could mimic the effect of substitution at the 2- and 4-positions and therefore catalyze the polymerization of propylene to highly isotactic polypropylene ([*mmmm*] = 98%) of high M_w ($M_w = 780\,000$ Daltons). We wish to report the results of our investigation into the effect that a (3-*t*-butyl)indenyl moiety in C_1 symmetric *ansa*-metallocenes has on the polymerization of propylene to isotactic polypropylene.

2. Results and discussion

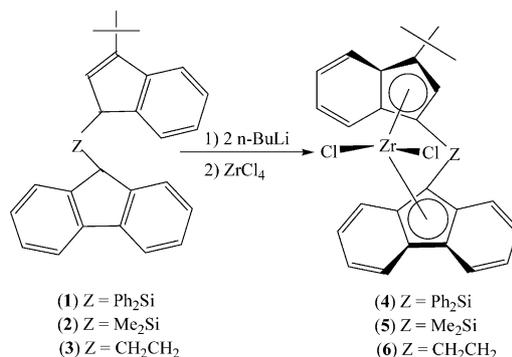
2.1. Synthesis of the *t*-butyl indenyl containing ligands

The synthesis of the ligands was accomplished via a relatively straightforward procedure. Initially, 3-(*t*-butyl)indene was deprotonated with one equivalent of *n*-BuLi to produce 1-(*t*-butyl)indenyllithium. The lithium salt was then reacted with chlorodiphenylsilylfluorene, chlorodimethylsilylfluorene, or bromoethylfluorene to produce the ligands 1–3, respectively in 50–64% yields.



2.2. Synthesis of the *t*-butyl indenyl containing zirconocenes

Synthesis of zirconocenes 4–6 was accomplished by double deprotonation of ligands 1–3 in Et_2O with two equivalents of *n*-BuLi to initially produce the dilithium salts. The dilithium salts were then reacted with one equivalent of ZrCl_4 in an Et_2O solution to produce the desired zirconocenes. The silylene-bridged derivatives, 4 and 5 were incredibly sensitive to air, moisture, and solvents. The work up had to be done very rapidly to prevent decomposition of the complexes. Furthermore, once 4 and 5 were isolated as solids, exposure to solvent would result in almost immediate decomposition of the zirconocenes. This sensitivity is not uncommon for silylene-bridged zirconocenes containing a fluorenyl moiety. There are several reports of similar compounds that possess the same instability [10b,11a,13]. The observed instability is most likely due to ring slippage of the metal–fluorenyl bond from η^5 to η^3 to η^1 and finally to complete dissociation. The ethylene-bridged derivative 6 possessed a much greater stability than its silylene bridged counterparts.



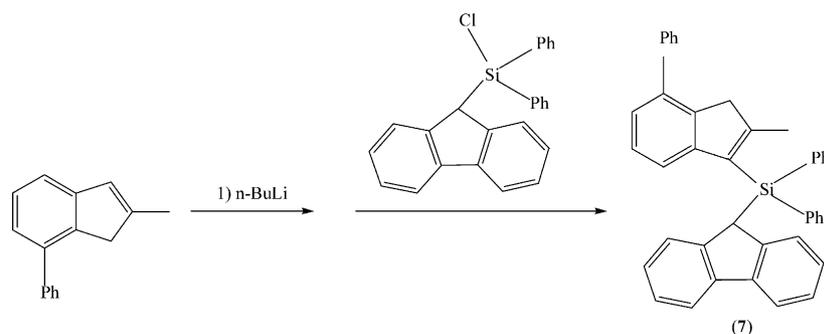
2.3. Synthesis of the 2-methyl-7-phenyl indenyl containing ligand

Reports by Razavi et al. [14] have suggested that a one atom bridge containing two phenyl substituents is better than a dimethylsilylene- or ethylene- bridge in producing a high molecular weight polymer. It is suggested that the bulk provided by the phenyl groups helps to inhibit backbiting of the growing polymer chain which in turn leads to greater chain lengths. In an effort to study the effect of a diphenylsilylene-bridge on molecular weight, we wanted to study a stable C_1 symmetric zirconocene. Thomas et al. [10b] have shown that dimethylsilylene[(2-methyl-4-phenyl)-1-indenyl]-(9-fluorenyl)zirconium dichloride is a highly stable and active catalyst for the production of highly isotactic polypropylene. We therefore decided to synthesize and

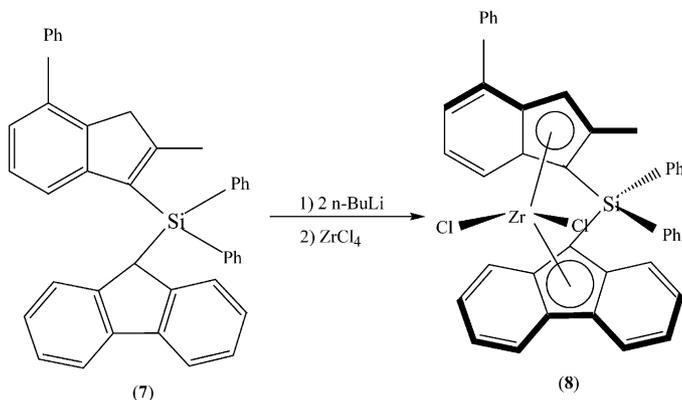
study the diphenylsilylene derivative of the aforementioned compound.

Compound **7** was synthesized in an analogous procedure to the synthesis of **1–3**. Initially, 2-methyl-7-phenylindene was deprotonated with one equivalent of *n*-BuLi. The resulting lithium salt was reacted with chlorodiphenylsilylfluorene to produce ligand **7** in 64% yield.

2.4. Synthesis of the 2-methyl-4-phenyl indenyl containing zirconocenes



Synthesis of **8** was accomplished by the double deprotonation of **7** with two equivalents of *n*-BuLi. The dilithium salt was then reacted with one equivalent of $ZrCl_4$ to produce the desired metallocene. The stability and ease of handling of **8** relative to **4** and **5** was remarkable. Compound **8** was stable in solution for several days and could be manipulated both in and out of solution without significant decomposition.



2.5. Ethylene polymerization

All of the complexes tested were highly active in catalyzing the polymerization of ethylene when activated with MAO (Table 1). The activities obtained ranged from ca. 4×10^6 to 9×10^7 depending on polymerization temperature and catalyst structure. The highest activity overall was obtained with complex **8** which is also the most stable complex. In general, for all of the species tested, the activity was lowest at 0 °C and greatest at 20 °C. There was a slight dip in activities as the polymerization temperature was increased further to

50 °C, which could be attributed to a more facile decomposition of the complex at elevated temperatures.

For complexes **4–6**, 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 for the silylene-bridged catalysts **4** and **5** over the ethylene-bridged catalyst **6**. This follows the general trend that is observed for most metallocene catalysts. Also of interest is that the diphenylsilylene-bridged catalyst **4** produced a higher molecular weight polymer than its dimethylsilylene bridged counterpart **5**. Lastly, **8** does not follow the molecular weight pattern observed for **4–6**. For compound **8**, maximum molecular weight is achieved at 20 °C instead of at 0 °C. This anomaly may be attributable to incomplete activation at lower temperature for **8**.

2.6. Propylene polymerization

All of the complexes tested were also highly active in catalyzing the polymerization of propylene when activated with MAO (Table 2). The activities obtained ranged from ca. 2×10^5 to 1.7×10^7 depending on polymerization temperature and catalyst structure. The

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
4	0	0.36 ± 0.03	0.4	132	666 000
4	20	1.31 ± 0.05	1.7	130	649 000
4	50	0.86 ± 0.03	1.5	130	477 000
5	0	0.45 ± 0.02	0.5	128	590 000
5	20	1.39 ± 0.11	1.8	127	524 000
5	50	1.15 ± 0.17	2.0	127	218 000
6	0	0.81 ± 0.06	0.9	130	350 000
6	20	6.73 ± 0.51	8.7	131	327 000
6	50	4.81 ± 0.44	8.4	130	298 000
8	0	0.99 ± 0.02	1.1	131	462 000
8	20	6.96 ± 0.36	9.0	129	586 000
8	50	4.18 ± 0.22	7.3	129	174 000

^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).

highest activity was obtained with the ethylene-bridged catalyst **6** at 50 °C. For similar catalyst systems, it has been demonstrated that ethylene-bridged species are usually more active than the silylene-bridged counterparts. This is the trend observed for our systems as well.

The silylene-bridged species **4** and **5** were so unstable in the presence of propylene that visible decomposition was immediately evident at polymerization temperatures greater than 0 °C. The pink color normally attributable to an active cationic species turned yellow almost immediately and no polymer was obtained. At 0 °C, decomposition was also observed but it occurred over a ca. 10 min time period, which allowed the catalyst to produce some isolable polymer. The activity measurements obtained for **4** and **5** are therefore in question since the polymerization was allowed to proceed for 1 h at which time the catalyst had presumably been inactive for about 50 min.

Compound **8** was stable at all polymerization temperatures despite the fact that it contained a silylene bridge. This is attributable to the added stability gained by placing substituents at the 2- and 4-positions of the

indenyl moiety as has been previously demonstrated by Thomas et al. [10b]. The activities obtained for **8** were in the 10⁶ range as the activity increased as the polymerization temperature increased reaching a maximum activity of 2.9 × 10⁶ at 50 °C.

The highest molecular weights were obtained using catalyst **4**. A diphenylsilylene bridge afforded a two-fold increase in molecular weight over the dimethylsilylene analog **5**. A molecular weight of 104 000 Daltons was obtained using **4**, which is among the highest M_w polypropylene produced using a C₁ catalyst of this type. Unfortunately, the instability of **4** hinders its usefulness in an industrial setting. Catalyst **8** also exhibited a two-fold increase in molecular weight (40 800 Daltons) over the previously published dimethylsilylene[(2-Me-4-Ph)-1-indenyl]-(9-fluorenyl)zirconium dichloride analog which gave polypropylene with molecular weights of ~ 20 000 Daltons [10b].

The isotacticity of the polypropylenes produced was moderate. There was an increase in stereoregularity using **4–6** reaching a maximum of 82% versus the unsubstituted ethylene-1-(9-fluorenyl)-2-(1-indenyl) zir-

Table 2
Polymerization of propylene with zirconocene complexes activated with MAO^a

Catalyst	Temperature (°C)	Yield (g) ^b	10 ⁻⁶ A ^c	M _w	[mmmm] (%)
4	0	0.25 ± 0.02	0.22	104 000	72
5	0	0.17 ± 0.02	0.15	56 300	69
6	0	1.35 ± 0.07	1.2	n.d.	82
6	20	4.24 ± 0.25	5.1	24 700	79
6	50	6.64 ± 0.32	17.0	6600	75
8	0	0.45 ± 0.04	0.4	45 000	80
8	20	0.83 ± 0.05	1.0	40 800	83
8	70	0.42 ± 0.03	2.9	6800	83

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

^b Yields are averages of duplicate runs.

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

conium dichloride, which exhibited an *mmmm* pentad of 64% [8b]. For **4** and **5** the *mmmm* pentad was 72 and 69%, respectively. Although these values are respectable, they do not approach the 95–98% obtained by Resconi with his bis-[3-(*t*-butyl)indenyl]zirconium dichloride catalysts [12]. The best overall stereoregularity was obtained with the ethylene-bridged species **6**. The maximum isotacticity was obtained at 0 °C. The stereoregularity steadily decreased to 79% at 20 °C and finally to 75% at 50 °C. Both Rieger et al. [9b,11] and Thomas et al. [10] have observed the general trend of decreased stereoregularity at elevated temperatures in similar ethylene-bridged systems.

3. Experimental

All reactions were carried out under an inert Ar atmosphere using standard Schlenk techniques. The Ar was purified by drying with phosphorus pentoxide, calcium chloride and molecular sieves, and deoxygenated with BTS catalyst. Toluene, hexane, Et₂O, and pentane were distilled from Na/K alloy under Ar. Methylene chloride was distilled under Ar from CaH₂. Tetrahydrofuran (THF) was dried initially over sodium wire, distilled from sodium/benzophenone under Ar, and finally distilled from Na/K alloy under Ar.

Methylaluminoxane was purchased from Akzo Nobel. Celite was purchased from Fisher Scientific. Chlorodiphenylsilylfluorene [15], chlorodimethylsilylfluorene [15], bromoethylfluorene [10a], 3-(*t*-butylindene) [12], and 2-methyl-7-phenylindene [3a] were synthesized by literature procedures. All other reagents were purchased from Aldrich and were used without further purification. ¹H-NMR spectra were recorded on a Varian XL-200 spectrometer using Me₄Si 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.

3.1. (9-Fluorenyl)-1-[(3-*t*-butyl)indenyl]diphenylsilane (**1**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 0.60 g (3.52 mmol) of 3-(*t*-butyl)indene. The solid was dissolved in 25 ml of dry Et₂O and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (2.2 ml, 3.52 mmol) was added dropwise via syringe producing a yellow solution. The solution was allowed to warm to r.t. and was stirred for 4 h. Next, 1.35 g (3.52 mmol) of chlorodiphenylsilylfluorene were dissolved in 20 ml of dry Et₂O and transferred slowly to the indenyl lithium solution via cannula. The resulting solution was stirred overnight

producing a yellow suspension, which was hydrolyzed with a saturated NH₄Br (aq.) solution. The mixture was separated and the aqueous layer was extracted with 2 × 25 ml of CH₂Cl₂. The organic layers were combined, dried over anhydr. MgSO₄, filtered, and the solvent removed yielding a yellow oil. The oil was dissolved in a minimal amount of pentane and cooled to –20 °C to produce a white precipitate. Recrystallization from toluene gave 1.17 g (64.4%) of **1** as white crystals, m.p. 206–207 °C. Anal. Found: C, 87.80; H, 6.74 C₃₈H₃₄Si. Anal. Calc.: C, 87.98; H, 6.61%. ¹H-NMR (CDCl₃): δ 7.71–6.80 (m, 26H, aromatic H); 6.39 (d, 1H, sp²-H); 4.80 (s, 1H, Flu-C₅-sp³); 4.41 (d, 1H, Ind-C₅-sp³); 1.10 (s, 9H, C(CH₃)₃).

3.2. (9-Fluorenyl)-1-[(3-*t*-butyl)indenyl]dimethylsilane (**2**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 1.20 g (7.05 mmol) of 3-(*t*-butyl)indene. The solid was dissolved in 50 ml of dry Et₂O and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (4.4 ml, 7.05 mmol) was added dropwise via syringe producing a yellow solution. The solution was allowed to warm to r.t. and was stirred for 4 h. Next, 1.83 g (7.05 mmol) of chlorodimethylsilylfluorene were dissolved in 25 ml of dry Et₂O and transferred slowly to the indenyl lithium solution via cannula. The resulting solution was stirred overnight producing a yellow suspension, which was hydrolyzed with a saturated NH₄Br (aq.) solution. The mixture was separated and the aqueous layer was extracted with 2 × 25 ml of CH₂Cl₂. The organic layers were combined, dried over anhydr. MgSO₄, filtered, and the solvent removed yielding a yellow oil. The oil was dissolved in a minimal amount of pentane and cooled to –20 °C to produce a white precipitate. Recrystallization from hexane gave 1.51 g (55%) of **2** as white crystals, m.p. 123–124 °C. Anal. Found: C, 85.49; H, 7.56 C₂₈H₃₀Si. Anal. Calc.: C, 85.22; H, 7.66%. ¹H-NMR (CDCl₃): δ 7.93 (d, 2H, aromatic H); 7.66–7.02 (m, 10H, aromatic H); 5.84 (d, 1H, sp²-H); 4.08 (s, 1H, Flu-C₅-sp³); 3.37 (d, 1H, Ind-C₅-sp³); 1.31 (s, 9H, C(CH₃)₃); –0.14 (s, 3H, CH₃SiCH₃); –0.51 (s, 3H, CH₃SiCH₃).

3.3. 1-(9-Fluorenyl)-2-[(3-*t*-butyl)indenyl]ethane (**3**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 1.87 g (11.0 mmol) of 3-(*t*-butyl)indene. The solid was dissolved in 80 ml of dry THF and the solution was cooled to 0 °C. A 1.6 M solution of *n*-BuLi in hexane (6.9 ml, 11.0 mmol) was added dropwise via syringe producing an orange solution. The solution was allowed to warm to r.t. and was stirred for 4 h. Next, 3.0 g (11.0 mmol) of bromoethylfluorene were added as a solid. The resulting solution

was stirred overnight and was hydrolyzed with a saturated NH_4Br (aq.) solution. The mixture was separated and the aqueous layer was extracted with 2×25 ml of Et_2O . The organic layers were combined, dried over anhydr. MgSO_4 , filtered, and the solvent removed yielding a yellow oil. The oil was dissolved in a minimal amount of EtOH and cooled to -20°C to produce 2.0 g (50%) of **3** as a yellow precipitate which melted upon warming to r.t. Anal. Found: C, 92.24; H, 7.58 $\text{C}_{28}\text{H}_{28}$. Anal. Calc.: C, 92.26; H, 7.74%. $^1\text{H-NMR}$ (CDCl_3): δ 7.85 (d, 2H, aromatic H); 7.54–7.03 (m, 10H, aromatic H); 6.06 (d, 1H, $\text{sp}^2\text{-H}$); 3.96 (t, 1H, $\text{Flu-C}_5\text{-sp}^3$); 3.24 (m, 1H, $\text{Ind-C}_5\text{-sp}^3$); 2.42–1.55 (m, 4H, CH_2CH_2 bridge); 1.33 (s, 9H, $\text{C}(\text{CH}_3)_3$).

3.4. Diphenylsilylene-(η^5 -9-fluorenyl)-[η^5 -1-(3-*t*-butyl)indenyl]-zirconium dichloride (**4**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 0.237 g (0.46 mmol) of **1**. The solid was dissolved in 20 ml of dry Et_2O and the solution was cooled to 0°C . A 1.6 M solution of *n*-BuLi in hexane (0.571 ml, 0.92 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 0.106 g (0.46 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 red–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 0.083 g (26.8%) of **4**. MS (EI) Calc. for $\text{C}_{38}\text{H}_{32}\text{Cl}_2\text{SiZr}$: 677; Found: 677. $^1\text{H-NMR}$ (CDCl_3): δ 7.78–6.82 (m, 22H, aromatic H); 6.31 (s, 1H, Ind-C_5); 1.17 (s, 9H, $\text{C}(\text{CH}_3)_3$).

3.5. Dimethylsilylene-(η^5 -9-fluorenyl)-[η^5 -1-(3-*t*-butyl)indenyl]-zirconium dichloride (**5**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 1.24 g (3.16 mmol) of **2**. The solid was dissolved in 50 ml of dry Et_2O and the solution was cooled to 0°C . A 1.6 M solution of *n*-BuLi in hexane (3.95 ml, 6.32 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 0.736 g (3.16 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 red–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 0.399 g (22.8%) of **5**. MS (EI) Calc. for $\text{C}_{28}\text{H}_{28}\text{Cl}_2\text{SiZr}$: 554; Found: 554. $^1\text{H-NMR}$ (CDCl_3): δ 8.01–6.82 (m, 12H, aromatic H); 5.72 (s, 1H, Ind-C_5); 1.50 (s, 3H, CH_3SiCH_3); 1.36 (s, 9H, $\text{C}(\text{CH}_3)_3$); 1.24 (s, 3H, CH_3SiCH_3).

3.6. Ethylene-1-(η^5 -9-fluorenyl)-2-[η^5 -1-(3-*t*-butyl)indenyl]-zirconium dichloride (**6**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 0.509 g (1.4 mmol) of **3**. The solid was dissolved in 20 ml of dry Et_2O and the solution was cooled to 0°C . A 1.6 M solution of *n*-BuLi in hexane (1.75 ml, 2.8 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 0.326 g (1.4 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 red–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 0.114 g (15.6%) of **6**. Anal. Found: C, 62.21; H, 5.23. Anal. Calc.: C, 64.10; H, 5.00%. MS (EI) Calc. for $\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{Zr}$: 524; Found: 524. $^1\text{H-NMR}$ (CDCl_3): δ 7.95–7.03 (m, 12H, aromatic H); 6.36 (s, 1H, Ind-C_5); 4.66–3.82 (m, 4H, bridge); 1.27 (s, 9H, $\text{C}(\text{CH}_3)_3$).

3.7. (9-Fluorenyl)-1-[2-methyl-4-phenyl]indenyl]diphenylsilane (**7**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 1.0 g (4.85 mmol) of 2-methyl-7-phenyl indene. The solid was dissolved in 50 ml of dry Et_2O and the solution was cooled to 0°C . A 1.6 M solution of *n*-BuLi in hexane (3.0 ml, 4.85 mmol) was added dropwise via syringe producing a yellow solution. The solution was allowed to warm to r.t. and was stirred for 4 h. Next, 1.89 g (4.85 mmol) of chlorodiphenylsilylfluorene was dissolved in 25 ml of dry Et_2O and transferred slowly to the indenyl lithium solution via cannula. The resulting solution was stirred overnight producing a yellow suspension, which was hydrolyzed with a saturated NH_4Br (aq.) solution. The mixture was separated and the aqueous layer was extracted with 2×25 ml of CH_2Cl_2 . The organic layers were combined, dried over anhydr. MgSO_4 , filtered, and the solvent removed yielding a yellow oil. The oil was

dissolved in a minimal amount of pentane and cooled to $-20\text{ }^{\circ}\text{C}$ to produce a white precipitate. Recrystallization from toluene gave 1.70 g (64%) of **7** as white crystals, m.p. $193\text{--}195\text{ }^{\circ}\text{C}$. Anal. Found: C, 89.39; H, 5.88 $\text{C}_{41}\text{H}_{32}\text{Si}$. Anal. Calc.: C, 89.08; H, 5.84%. $^1\text{H-NMR}$ (CDCl_3): δ 8.05 (d, 1H, aromatic H); 7.83 (t, 1H, aromatic H); 7.55–6.71 (m, 24H, aromatic H); 6.29 (s, 1H, $\text{sp}^2\text{-H}$); 4.98 (s, 1H, Flu- $\text{C}_5\text{-sp}^3$); 4.55 (s, 1H, Ind- $\text{C}_5\text{-sp}^3$); 1.99 (s, 3H, CH_3).

3.8. Diphenylsilylene-(η^5 -9-fluorenyl)-[η^5 -1-(2-methyl-4-phenyl)indenyl]-zirconium dichloride (**8**)

To an Ar purged Schlenk tube equipped with a magnetic stir bar was added 0.400 g (0.73 mmol) of **7**. The solid was dissolved in 20 ml of dry Et_2O and the solution was cooled to $0\text{ }^{\circ}\text{C}$. A 1.6 M solution of *n*-BuLi in hexane (0.91 ml, 1.45 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 $0\text{ }^{\circ}\text{C}$ and 0.169 g (0.73 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 red–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 $-20\text{ }^{\circ}\text{C}$ produced an orange solid. The solid was filtered and dried in vacuo to give 0.105 g (20.3%) of **8**. Anal. Found: C, 68.80; H, 4.16. Anal. Calc.: C, 69.08; H, 4.24. $^1\text{H-NMR}$ (CDCl_3): δ 8.34–6.65 (m, 26H, aromatic H); 6.86 (s, 1H, Ind- C_5); 2.08 (s, 3H, CH_3).

3.9. Polymerization procedure

A 250 ml glass pressure bottle was sealed under an Ar 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 methylaluminoxane (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 in toluene 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 MeOH, filtered, and dried in a vacuum oven at $70\text{ }^{\circ}\text{C}$.

3.10. Polymer analyses

Polymer melting points were determined by using a Dupont Thermal Analyst DSC system at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$. $^{13}\text{C-NMR}$ spectra were determined at $135\text{ }^{\circ}\text{C}$ in 1,2,4-trichlorobenzene with C_6D_6 on an AMX

500 spectrometer. Molecular weights were determined by high temperature GPC in 1,2,4-trichlorobenzene at $135\text{ }^{\circ}\text{C}$.

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